

Faculté des Sciences et Techniques
Settat

THÈSE DE DOCTORAT

 Pour l'obtention de grade de Docteur en *chimie*

Formation Doctorale: Chimie Appliquée et Environnement

 Spécialité: *Chimie physique et sciences des matériaux*

Sous le thème

 Synthesis, Crystallographic & Vibrational
Studies and Optoelectronic Properties of
Hydroxy-, Fluor- and New Lacunar Apatites,
Studied for Various Applications.

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Soutenue le: 19 Novembre 2020

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Année Universitaire: 2019/2020

Résumé

La thèse académique est composée de plusieurs chapitres, présente les différentes techniques de synthèses et de préparation des isotopes synthétiques et naturels du phosphate d'apatite ainsi les études physico-chimiques pour décrire la structure moléculaire et la distribution atomique, les propriétés vibrationnelles, optiques et électroniques de divers cristaux des phosphates d'apatite lacunaires et ioniques ont été réalisées. Nous avons également réalisés plusieurs applications scientifiques réussies, qui sont l'étude des propriétés de surface, de la composition chimique, de la taille et de la surface des cristaux ainsi que de la durée du processus d'adsorption de la protéine d'albumine sérique bovine en tant qu'application principale. Quant à la deuxième application, elle se reflète dans l'étude de la structure naturelle de la fluorapatite (phosphate brute), et l'élimination des métaux et la matière organiques de l'acide phosphorique résultant, afin de purifier ce dernier de toutes les impuretés nocives, à cause de nombreuses utilisations dans le domaine de l'industrie et de commerce international. Nous avons également consacré la dernière application à l'étude de corrosion du carbone solide en solution chlorhydrique, à différentes concentrations et températures, en utilisant les apatites lacunaires comme bonnes inhibiteurs de corrosion.

Enfin, nous espérons que nos travaux et recherches fourniront des orientations utiles pour les futures études empiriques et théoriques.

Abstract

The academic thesis is composed of several chapters, presents the various techniques of synthesis and preparation of synthetic and natural isotopes of apatite phosphate, as well as physicochemical studies to describe the molecular structure and atomic distribution, vibrational and optical properties and electronics of various lacunar and ionic apatite phosphates crystals, were performed. We have also made several successful scientific applications, which are the study of the surface properties, chemical composition, size and surface of crystals, as well as the duration of the adsorption process of serum albumin protein bovine, as the main application. As for the second application, it is reflected in the study of the natural structure of fluorapatite (raw phosphorus materials), and the removal of metals and organic matter from the resulting phosphoric acid, to purify the latter of all harmful impurities because he has many uses in industry and international trade. We also devoted the last application to the study of the corrosion of solid carbon in hydrochloric solution, at different concentrations and temperatures, using the lacunar apatites, as good inhibitors for corrosion.

Finally, we hope that our work and research will provide useful directions for future empirical and theoretical studies.

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LOUIHI Said

 TITRE: Synthesis, Crystallographic & Vibrational Studies and Optoelectronic
Properties of Hydroxy-, Fluor- and New Lacunar Apatites, Studied for Various
Applications.

 Année : 2019/2020
Initiale Formation doctorale : CAF

Thesis

Presented by: **Mr. Said LOUIHI**

Written and defended for obtaining the DOCTORATE degree in

Physical Chemistry and Materials Sciences

Discipline: ***Chemistry***

Speciality: ***Physical Chemistry and Materials Sciences***

**Synthesis, Crystallographic & Vibrational Studies and
Optoelectronic Properties of Hydroxy-, Fluor- and new
Lacunar Apatites, Studied for Various Applications.**

Defended on 19/11/2020

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Remerciements

*« Je remercie DIEU, le tout puissant, le miséricordieux, qui nous a donné
l'opportunité de mener à bien ce travail ».*

J'adresse mes sincères remerciements à mon encadreur, Monsieur Bouchaib MANOUN directeur de ma thèse. Professeur à la Faculté des Sciences et Techniques de l'Université Hassan 1^{er} SETTAT, directeur de Laboratoire des Sciences des Matériaux des Milieux et de la Modélisation (LS3M) intégré au Laboratoire Rayonnement-Matière et Instrumentation (LRMI), ainsi Professeur Adjoint au Département des Sciences des Matériaux et de Nanotechnologie (SMN) à l'Université Polytechnique Mohammed VI de BEN GUERIR, pour son aide, ses précieux conseils, sa disponibilité permanente, ses encouragements pour l'apprentissage et qui m'a fait partager ses brillantes intuitions. Qu'il soit aussi remercié pour sa gentillesse et pour les nombreux encouragements qu'il m'a prodigué et son meilleur encadrement pour que ce travail soit à la hauteur au long de cette thèse.

Je tiens à exprimer ma profonde gratitude, mes sincères remerciements et ma reconnaissance envers toutes les personnes, professeurs et chercheurs qui ont collaborés à la rédaction et aux réalisations des travaux de recherche.



Monsieur Peter LAZOR ; Professeur au Département des Sciences de la Terre à l'Université d'Uppsala au SUEDE, qui nous a donnés sa confiance à l'accès aux spectromètres Raman à température ambiante et à haute température.



Monsieur Jones ALAMI; Chef du Département des Sciences des Matériaux et de Nanotechnologie (SMN) qui m'a accueilli au sein de son laboratoires, et Monsieur Youssef TAMRAOUI ; Professeur au sein de même département à l'Université Polytechnique Mohammed VI, de BEN GUERIR. Cette thèse est le fruit d'une collaboration de plus de trois années avec lui. C'est à ses côtés que j'ai compris ce que rigueur et précision voulaient dire.

Remerciements



Monsieur Allal BARROUG ; Professeur à la Faculté des Sciences Semlalia, au sien du Laboratoire Physico-Chimie des Matériaux et Environnement (LPCME) de l'Université Cadi Ayyad à MARRAKECH, et Professeur Adjoint au Centre Interface et Application Médicale (CIAM) à l'Université Polytechnique Mohammed VI, de BEN GUERIR. C'est grâce à lui que j'ai pu concilier avec bonheur l'application de la recherche théorique et appliquée pendant cette thèse.



Monsieur Abdellah NIA, Chef de Service du Laboratoire Central de Maroc Chimie (OIS/L/Q) à SAFI, pour m'accorder l'occasion de passer mon stage au sein du laboratoire. Ainsi les responsables du laboratoire Mr. El Mostapha MAGHA et Mr. Jamal BIYA qui ont contribué de près ou de loin au déroulement et à l'élaboration de mon rapport de recherche scientifique, pour leurs soutiens, leurs aides et sont disponibilités durant la période de stage. Qu'ont bien voulu me consacrer une partie de leurs précieux temps pour répondre à toutes mes questions durant toute la période de ma recherche.



Monsieur Mohamed TABYAOUI; Professeur et Vice Doyen chargé des affaires académiques et pédagogiques à la Faculté des Sciences de l'Université Mohammed V de RABAT, qui m'accorder de passer les tests et les analyses de corrosion au sein du Laboratoire des Matériaux, Nanotechnologies et Environnement (LMNE). Ainsi Mr. Abderrahmane ELMELOUKY ; Docteur au sein du Laboratoire de Physique de la Matière Condensée (LPMC), à la faculté des Sciences d'El JADIDA, qui a tout fait pour m'aider pour l'interprétations et l'analyses des résultats des travaux d'impédance électrochimique, qui m'a soutenu et surtout supporté dans tout ce que j'ai entrepris.

Remerciements

Tous mes remerciements aux membres de mon comité de thèse, tout d'abord pour Monsieur Jamal NAJA; Doyen de la Faculté des Sciences et Techniques de l'Université Hassan 1^{er} SETTAT, pour avoir accepté d'être le président de la commission d'examen pour la soutenance de ma thèse.

J'adresse tous mes remerciements à Messieurs Hassan HANNACHE et Said BENMOKHTAR ; Professeurs à la Faculté des Sciences de l'Université Hassan II CASABLANCA, ainsi qu'à Monsieur Abdellah ANOUAR, Professeur à la Faculté des Sciences et Techniques de l'Université Hassan 1^{er} SETTAT, de l'honneur qu'ils m'ont fait en acceptant d'être rapporteurs de cette thèse.

J'exprime ma gratitude à Monsieur Jones ALAMI; Professeur à l'Université Mohammed VI Polytechnique à Benguerir, et à Monsieur Moulay Abderrahim El MHAMMEDI; Professeur à la faculté polydisciplinaire de KOURIBGA de l'Université Sultan Moulay Slimane à BENI MELLAL, qui ont bien voulu être examinateurs.

Enfin, je tiens à remercier tous les membres et les doctorants de Laboratoire des Sciences des Matériaux des Milieux et de la Modélisation. En particulières; les Professeurs : Mr. Nouredine BARKA, Mr. Abdellatif HASNAOUI et Mr. Khalid SBIAAI, et les Docteurs : Mlle. Fatima-Ezzahra MIRINIOUI et Mr. Abdelhadi ELHACHMI, Ainsi les Doctorants : Mme. Rachida HALOUI, Mr. Abdelaziz ELAAMRANI, Mr. Zakaria CHCHIYAI et Mlle. Fatima ELBACHRAOUI.

ملخص عام

الأطروحة تعالج إشكالية المعادن الثقيلة، وخاصة السامة والخطيرة منها على المستوى الإنساني تم البيئي. ذلك بالإبتكار في إنشاء مواد جديدة، عن طريق إدماج العديد من المعادن شديدة السمية وتحويلها في مصفوفات صلبة تعمل على تعطيل هذه السمية، لتكون بذلك نافعة ومستقرة جغرافيا، وإكتشاف التطبيقات الصناعية الجديدة وعمليات التصنيع وإعادة التدوير. لأن تقليل محتوى المعادن في البيئة لايزال أفضل فكرة لجعل هذه العناصر المعدنية قابلة للتحكم والإستعمال، وكذا سهولة تخزينها وإستعادة إستعمالها، شريطة ألا تشكل المواد المستحضرة والمستخدمة أي خطر على الكائنات الحية و علي الطبيعة.

خلال مدة تزيد عن خمس سنوات من البحث المتواصل و بشراكة مع مختلف المختبرات الوطنية و الدولية، قمنا بالعديد من التقنيات لتحضير ودراسة نظائر فوسفات الأباتيت الإصطناعية و الطبيعية، المتكونة بالأساس من العديد من المعادن و كاتيونات أخرى، بما في ذلك تركيب الحالة الصلبة والطرق الكيميائية الرطبة والتوليف الحراري المائي، و كذلك تحضير الأباتيت الطبيعي الغني بالفوسفات بطريقة تعويم الفوسفات الخام. حيث كان برنامج العمل البحثي، يتمحور على الدراسة التجريبية لأتراأستبدال المنفرد، الثنائي و الثلاثي داخل المصفوفات الصلبة لفوسفات الرصاص المجوف وهيدروكسي الفوسفات، وتم ذلك عن طريق دمج كاتيونات الرصاص، الكاديوم، الزنك، السترونشيوم، الكالسيوم ومعادن أخرى في قناة الأباتيت السداسية.

الأطروحة الأكاديمية، تقدم الرسالة العلمية متعددة الفصول: الدراسة الكيميائية الفيزيائية لوصف الهيكل والتركيب الجزيئي والذري، تم الخصائص الاهتزازية، البصرية وإلكترونية لمختلف بلورات فوسفات الأباتيت المجوفة والأيونية الثابتة. كما قمنا بعدة تطبيقات علمية ناجعة، تتمثل في دراسة الخصائص السطحية والتركيب الكيميائي وحجم البلورات ومساحة السطح، وكذلك المدة الزمنية الأزمة في عملية إدمصاص لبروتين الزلال المصل البقري كتطبيق أولي. أما التطبيق الثاني، يتجلى في دراسة هيكل الفلورأباتيت الطبيعي (الفوسفات)، ونزع المعادن والمادة العضوية من حمض الفوسفوريك الناتج عنه، من أجل تنقية و تطهير هذا الأخير من كل الشوائب الضارة، نظرا لإستخداماته الكثيرة في مجال الصناعة. كما خصصنا التطبيق الأخير في دراسة تآكل الكربون الصلب في محلول هيدروكلوريك، بتراكيز و درجات حرارية مختلفة، باستعمال الأباتيتات المجوفة كموانع للتآكل (مثبطات التآكل).

في الاخير نأمل أن توفر أعمالنا وأبحاثنا، إرشادات مفيدة في الدراسات التجريبية والنظرية المستقبلية.

الكلمات المفاتيح

الأباتيت المجوفة - هيدروكسي فوسفات الكالسيوم - الفلورأباتيت الطبيعي - حيود الأشعة السينية - التحليل الطيفي رمان - مطياف الأشعة تحت الحمراء - مطيافية الأشعة فوق البنفسجية والمرئية - عملية إدمصاص - تنقية و تطهير حمض الفوسفوريك - تآكل الكربون الصلب في محلول هيدروكلوريك

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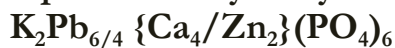


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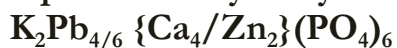


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PROBLEMATIC OF THE THEME

General Introduction

Transition metals are generally defined as metallic elements with a density exceeding 5000kg/m^3 , and depending on their degree of toxicity, cadmium, lead, mercury, and arsenic are very dangerous heavy metals. They occur naturally in our environment and are used massively in industry. Indeed, the industrial wastes discharged containing these toxic metals are transported by the wind and disseminate in soils and aquatic environments, contaminating flora and fauna and reaching man through the food chain. Everyone accepts that these chemicals are acutely toxic to humans and the environment.

These heavy metals are naturally present in the living organism, but generally in very small quantities "in minute traces". They have no known beneficial effect on the cell, but a polluting character with toxic effects for living organisms, even at low concentrations [1]. They are micropollutants of such a nature as to cause nuisance, even when released in very small quantities. Their toxicity develops through bioaccumulation along the food chain.

The four metals in question are used industrially in various applications. In the context of international environmental and chemical policy, there has been increasing reference to heavy metals in recent years. According to the opinion was expressed that meeting the challenge posed by these elements would require international coordination and action. Thus, several international institutions and processes have begun to address heavy metals.

- The Cadmium, which causes hardening of the arteries, is currently not eliminated satisfactorily.
- Mercury is easily fixed in organic matter, as well as in metabolic processes, and is then found in methylated form. Moreover, it is very mobile, since it is volatile at room temperature. Among its harmful effects on the organism, it affects brain functions, as well as the kidneys. It could also be an endocrine disruptor and be responsible for cancers. Mercury is a toxic metal that can cause illness, incapacitation, and death. The international

human rights convention obliges governments to reduce mercury use and emissions in several industries and processes.

- Arsenic has many toxic properties: it decouples the respiratory chain by replacing phosphorus, it has endocrine-disrupting properties, and disrupts cell differentiation and therefore has carcinogenic properties [2].

Lead is the origin of major neurological disorders. In particular, it is the most studied environmental pollutant, and these adverse health effects are well documented. It has long been considered a threat to the health of living things in the community environmentally ore mines and refineries. Children are the most vulnerable and the neurological toxicity of lead can compromise their mental development. Thus, lead poisoning, or lead poisoning, is a public health problem that has been highlighted in developed countries since the 1980s but remains underestimated in developing countries. Several sources of lead exposure are described, including mining activities, pollution from leaded gasoline, industrial emissions, lead-based cosmetics and paint, and many others.

In MOROCCO, in parallel to the common causes of lead exposure, specific causes could be added such as the use of lead-based cooking utensils, the use of remedies and cosmetics containing this element, particularly galena (kohl) the existence of old pipes which can also, under certain conditions, lead to dangerous levels of exposure of drinking water. Our country, as an extractor, importer, and user of heavy metals, subject to international regulations, is required to list the sources of exposure, control the contents of these heavy metals in the environment, as well as in consumer products including drinking water and utensils manufacturing products.

[1]Chiffolleau JF. La contamination métallique. Editions Ifremer. 2004; 39

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Soluble lead in water and aquatic environments has been trapped as lead-apatite, its precipitation and composition are highly dependent on pH and ions in solution in the medium. Currently, processes and methods of depollution for the treatment of wastewater by trapping and absorption of lead are marketed but they are mainly aimed at waters with little pollution, but the retention capacity of the metals used remains low.

The problems and disadvantages of heavy metals (mineral and organic micropollutants) are not limited. The innovation that manifests itself through the creation of new materials, solid matrices trapping these chemical elements, the discovery of new industrial applications, manufacturing and recycling processes, and also how to reduce the metal content in the environment, remains a better help to make these metallic elements controllable, usable and recoverable, provided that their preparation and use do not pose any danger to living beings.

Human activity has changed a lot in recent years. The distribution of chemical elements and their form on the earth's surface has changed, transforming several highly toxic metals incorporated in solid matrices that deactivate this toxicity and are geochemically stable, into soluble or insoluble chemical compounds or elements that manifest their toxicity.

The determination, elimination, and/or reuse of heavy metals, even in trace amounts, is one of the issues that nowadays preoccupy public opinion and environmental sciences, due to their acute and/or chronic toxicity at concentrations exceeding in the majority of cases the thresholds of international and/or national standards. A great deal of attention is thus devoted to heavy metals, in this case, lead, arsenic, mercury, and cadmium. The latter is particularly harmful to man and his environment, even at very low concentrations in the nanogram range. The effects of toxic metals on human health have been seen in the development of diseases such as neurological disorders, nephrotoxicity, bone demineralization, and cancer. To this end, apatites with or without anions, of the chemical formula; $\text{Na}_{1-x}\text{K}_x\{\text{Pb}_{4-y}/\text{Ca}_{5-z}\}\text{M}_{\{y/z\}}(\text{PO}_4)_3\text{Y}_{\{0/1\}}$, can they be materials with high retention capacities of heavy elements, containment matrix of these elements, with Y_1 : OH^- , F^- and M : Sr^{2+} , Fe^{n+} , Ni^{2+} , Cu^{2+} , Zn^{2+} ,

Cd^{2+} , have been synthesized by dry and wet methods, for their great ability to accept various elements in their structural framework. The structural and vibrational characterizations showing that these classes of mixed apatite can contain a wide variety of metal cations while maintaining their unique molecular structure are well studied for the various applications offered by this versatility.

In what follows, in the first point, we will clarify some concepts related to the problem of the theme, and in a second point, we will present the synthesis of previous contributions to the theme presented in five chapters.

Following this introduction on the motivations for our work, this brief is structured as follows:

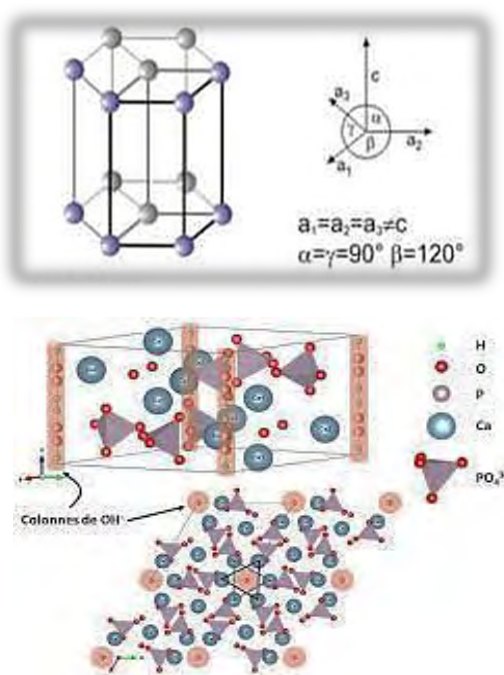
- The introduction of the chapters is structured around two axes: (i) the bibliography on apatitic materials (in particular their modes of synthesis, their properties, and Physico-chemical characterizations as well as the various applications in scientific research and industry, etc.), and (ii) the bibliography on heavy metals (in the particular lead and cadmium).
- The first chapter focused on the different experimental techniques and methods of analysis used for the study of the various synthesized materials.
- The second chapter presents crystallographic (results obtained after structural refinement) and vibrational (infrared and Raman spectroscopies at room temperature and high temperature) studies and optoelectronic properties of the new series of differently substituted lead-based lacunar apatites of the $\text{Na}_{1-x}\text{K}_x\text{Pb}_{(4-y)/2}\{\text{Sr}_y/\text{CaCd}/\text{CaSr}\}(\text{PO}_4)_3$ type.
- The third chapter is devoted to the phenomenon of adsorption of Bovine Serum Albumin Protein (BSA) by synthetic apatites and the structural properties of Hydroxy- and new lacunar apatites of chemical formulae; $\{\text{Ca}_{10/8}/\text{Zn}_2\}(\text{PO}_4)_6(\text{OH})_2$ and $\text{K}_2\text{Pb}_{4/6}\{\text{Ca}_4/\text{Zn}_2\}(\text{PO}_4)_6$. This study examines the impact of synthetic conditions on the Physico-chemical properties and surface reactivity (crystal size and specific surface area) of the prepared materials. The analysis of the interactions of the samples about a selected

model which is the Bovine Serum Albumin (BSA) protein, evaluated under the same experimental conditions.

- The fourth chapter presents the main phosphate mineral in soils, preparations, structural studies, and optoelectronic properties of natural fluorapatite $\text{Ca}_5(\text{PO}_4)_3\text{F}$, from the KHOURIBGA region, as well as the effects and results of demineralization of phosphoric acid, the second most important acid in the world after sulphuric acid. The acid obtained from Maroc Phosphor contains various metallic impurities such as Cd^{2+} , Mg^{2+} , Pb^{2+} , Cu^{2+} , Zn^{2+} , Ni^{2+} , Ba^{2+} , Fe^{3+} , Cr^{3+} , As^{3+} , etc., which are present in the acid. The presence of these impurities leads to severe purification operations. We focus our study on the removal of cadmium from phosphoric acid using new methods of treatment and purification of cadmium-containing liquids.
- The last chapter presents the results of new corrosion inhibitors, $\text{APb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$ ($\text{A} = \text{Na}, \text{K}$), called lacunar apatites. Their corrosion inhibition performance on carbon steel in solution in hydrochloric acid, at different concentrations and different temperatures, was studied by electrochemical impedance spectroscopy. We find it interesting to carry out structural, vibrational, and optical studies, using X-ray diffraction and Raman, infrared, and UV-Vis spectroscopy techniques, for lead-, sodium- and potassium-based strontium-phosphate apatite gap compositions. The results of physical and chemical properties can be analyzed for technical aspects of the structure, surfaces, and interfaces of materials.
- Our brief concludes with a general conclusion on the chapters, in which we outline the importance of the results obtained by the proposed innovations. Such a study allowed us to establish a correlation between the properties and the Physico-chemical characterizations of the apatites studied in the different scientific and industrial applications.

Bibliography of Chapters

Crystalline structures, which can accommodate a wide range of oxidation state elements and stoichiometries, are an important constituent of solid-state chemistry. Materials such as Apatites ($M_5(XO_4)_3Y$), Perovskite (ABO_3), Garnets ($A_3B_2(SiO_4)_3$) and Spinel ($MgAl_2O_4$), as well as compounds of the Nasicon $AM_2(XO_4)_3$ family, are the archetypal structures for large numbers of compounds with diverse chemical compositions within each structure type, widely, each of these types has been extensively studied [1-8]. In particular apatites, these oxide classes can accommodate a wide variety of metal cations while retaining their unique molecular structure and are well studied for various properties afforded by this versatility. Properties can often be tuned or changed by elemental substitution, and materials with the same structural connectivity can be studied for different purposes and various applications.



Based on the ResearchGate platform, social networking service for researchers and scientists from all disciplines. A group of phosphate minerals that includes ten mineral species and has the general formula $X_5(YO_4)_3Z$, where 'X' is generally calcium or lead, 'Y' is phosphorus or arsenic and 'Z' is Chlorine, Fluorine or Hydroxy, whose total publications up to January 2020 are considered to be 33 202 and 45 questions ([McGraw-Hill Dictionary of Scientific and Technical Terms, 4th ed](#)). For this reason, in what follows we are interested in some works and publications that are related to our research topic more precisely to our problematic.

-
- [1] M. T. Anderson, J. T. Vaughey, K. R. Poeppelmeier, Chem. Mater. 1993, 5, 151 – 165.
 - [2] M. T. Anderson, K. B. Greenwood, G. A. Taylor, K. R. Poeppelmeier, Prog. Solid State Chem. 1993, 22, 197 – 233.
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A. Bibliographie on apatites.

A.I. Introduction.

Apatites from a large family of solid compounds, which generally crystallize in a hexagonal system with space group $P6_3/m$ [1]. Historically the name comes from the Greek "απατος" [Aptos] meaning "deception" because apatite is often confused with other minerals. Species described in 1786 by Abraham Gottlob Werner (1749-1817), German geologist of the Freiberg Mining Academy, Fig.1.

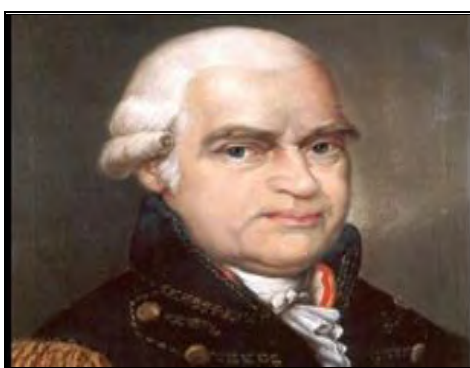


Fig.1: Herr Professor Abraham Gottlob Werner (1749-1817).

These natural and synthetic apatites are characterized by their remarkable chemical and thermal stability, very low solubility in neutral or basic pH and high ion mobility. They have the general chemical formula $M_{10}(XO_4)_6Y_2$ [2-7], as 'M' a cation generally divalent (Ca^{2+} , Sr^{2+} , Pb^{2+} , ...), also monovalent (K^+ , Na^+ , Ag^+ , ...), and even trivalent such as rare earth, XO_4^{n-} a usually trivalent anion (PO_4^{3-} , VO_4^{3-} , AsO_4^{3-} , ...), also divalent such as SO_4^{2-} and even tetravalent such as SiO_4^{4-} or GeO_4^{4-} and can also be CO_3^{2-} and 'Y' a monovalent anion (F^- , OH^- , Cl^- , O^{2-} , ...), and also divalent such as CO_3^{2-} , S^{2-} , O^{2-} , ..., etc. Their structure is characterized by the presence of two non-equivalent sites '6h' and '4f' with cations labelled 'Me (II)' and 'Me (I)', respectively. Due to this particular architecture, they can form solid solutions and accept many substitutions.

[1] St. Naray-Szabo, Zeitsch-Krist. 75 (1930) 387.

[2] JC Elliott Structure et Chimie de la apatites et autres orthophosphates de calcium, vol. 18 Elsevier, Amsterdam (1994)137.

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In FRANCE apatites are present in many deposits: the Montmins mine (Allier), Mont Denise (Haute-Loire), the sands of Concarneau and the Villeder mine (Finistère), the Agly massif (Pyrénées-Orientales), the Montebras mine (Creuse), the Framont mine (Bas-Rhin) and the Raon-l'Etape mine (Vosges), at Luzenac (Ariège) among many other deposits to be reported.

Beautiful crystals can be found in the crystalline marbles of Greenville (CANADA), Panasqueira (PORTUGAL), Durango (MEXICO) and Minas Gerais (BRAZIL), and more recently in PAKISTAN, CHINA (very many mines) and SIBERIA. Apatites are used in fine gemstones in jewellery because of their very varied colours (green, yellow, blue, brown, pink or beige, and white or colourless), [Fig.2](#).



Fig.2: Mineral apatites.

[Fig.2](#) shows a series of apatites, including fluorapatite (the most important mineral in trade), chlorapatite, hydroxyapatite, and carbonate-apatite. These minerals are all calcium phosphates, differing chemically only in that fluorapatite contains fluorine; chlorapatite, chlorine; hydroxyapatite, a hydroxyl group (OH^-); and carbonate-apatite, a carbonate group (CO_3). fluorine, chlorine, hydroxyl and carbonate are substituted for each other, so that in nature most apatites are a mixture of several compounds, $\text{Ca}_5(\text{PO}_4)_3(\text{F}_x \text{ OH}_y \text{ Cl}_z \text{})$. Chloroapatite is relatively rare.

[3] D. McConnell Apatites, minéralogie appliquée, vol. 5, Springer, New York / Vienne (1963).

[4] G. Wright, G. Montel CR Acad. Sci. Paris, 268C (1969)2077.

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Calcium phosphates evolve in the natural environment towards the apatitic form, the most stable. The calcium fluoride apatite variety is most abundant in purely inorganic contexts while hydroxyapatite dominates in fossil-rich sediments. They are therefore minerals that are generally formed in hydrothermal contexts, in pegmatites but also sediments (fossil bones).

The mineral constituent of bone, enamel and dentine of teeth is essentially hydroxyapatite $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, which has a structure that differs only in detail from that of well-crystallized fluorapatite $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$, Fig.3. The main difference, in fact, the only fully established difference between the two structures, is that hydroxyapatite has a unit hexagonal cell slightly larger than that of fluorapatite. The structure of the latter was determined in 1930, by N  ray-Szab   [8] and Mehmel [9].

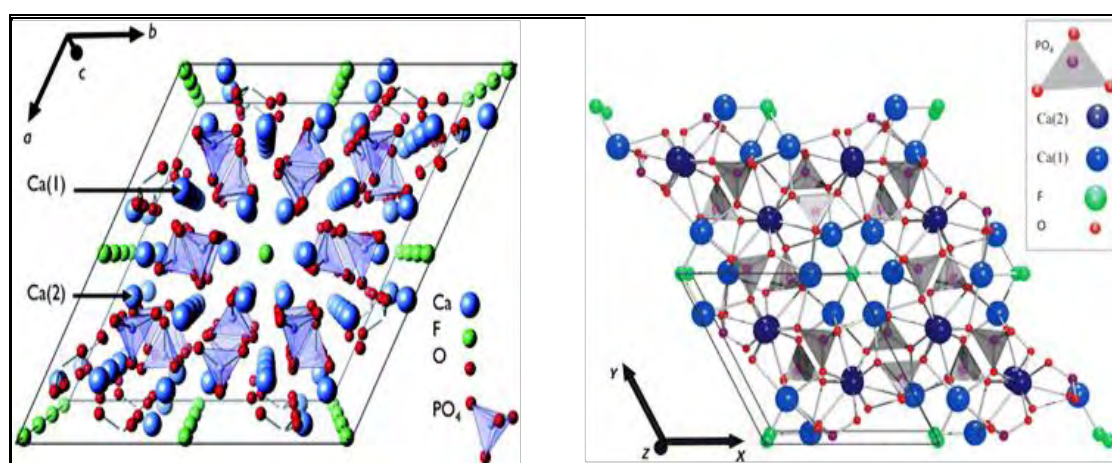


Fig. 3 : Diagrammes montrant la structure et la connectivit   des ions fluorapatite, les deux sites de calcium   tant indiqu  s respectivement en bleu fonc   et en bleu ciel (Ca (1) et Ca (2)), le fluor en vert, les ions phosphoreux en violet et les ions oxyg  ne en rouge avec les t  tra  dres gris et bleu.

[5] R.Z. LeGeros, M.H. Taheri, G.B. Quiroigico, J.P. Legeros, dans: Actes de la deuxi  me Conf  rence internationale sur le phosphore compos  s, Boston, Avril 1980, p. 89.

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[9] Mehmel, Z. Crystallogr., 75, 323 (1930).

Introduction of the Chapters

The weight composition of bone tissue according to Wollaston [10], see Table.1, shows that the calcium component of bones and teeth (involved in many physiological processes [muscle contraction, blood coagulation, etc.]), as well as phosphorus, is the fifth element making up living matter [11]. Natural phosphate apatites have a structure and chemical composition similar to that of the mineral part of calcified tissues, bones and teeth (Fig.3). They correspond to the mineral part of the vertebrate skeleton [11-13]. They belong to a large family of biomaterials used in dentistry and bone surgery [10-21].

Table .1: Weight composition of bone tissue according to Wollaston.

Element	Bone (%) [12]		Teeth (%) [13]		
	Young bone	Old bone	Enamel	Dentine	Cementum
Ca	23.4	24.6	36.1	35.0	35.5
P	11.9	12.6	17.3	17.1	17.1
CO ₃	3.57	3.99	3.0	4.0	4.4
Mg	0.40	0.51	1.2	1.2	0.9
S	-	-	0.1	0.2	0.6
Na	0.55	0.64	0.2	0.2	1.1
K	0.15	0.05	0.3	0.07	0.1
F	-	-	0.016	0.017	0.015
Cl	0.14	0.08	0.3	0.3	0.1
(Ca/P)mol	1.52	1.52	1.62	1.62	1.61

Dental enamel is formed of hydroxyapatite $\text{Ca}_5(\text{PO}_4)_3\text{OH}$. It can be transformed by "fluoridation" into the more resistant fluorapatite $\text{Ca}_5(\text{PO}_4)_3\text{F}$ (Ca/P=1.666), Fig.4. Synthetic apatite is biocompatible and has an attractive biological profile. Its chemical and crystalline structure is the same as the majority phase of the mineral part of bone and teeth. It is currently well established that hydroxyapatite is a non-toxic and stable material [22].

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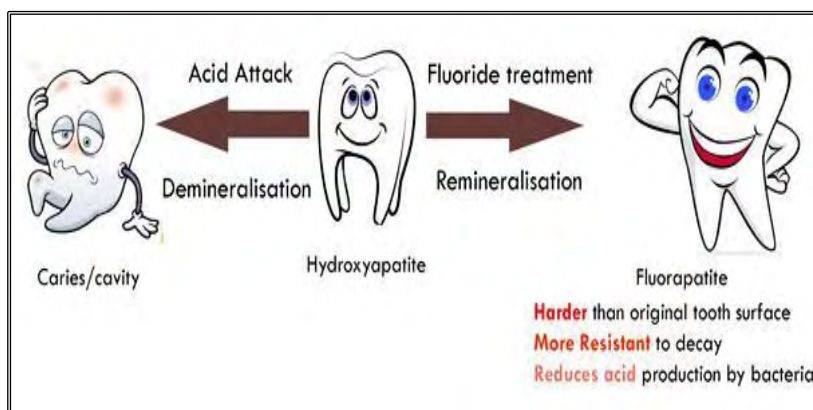


Fig.4: Hydroxyapatite transformed by fluoridation, showing the possible substitution between OH^- and F^- , in the hexagonal $\text{Ca}_5(\text{PO}_4)_3\text{OH}_{1-x}\text{F}_x$ structure.

The primary crystallographic description of the apatites $\text{Ca}_5(\text{PO}_4)_3\text{OH}_{1-x}\text{F}_x$ was provided by Beevers and McIntyre [23], who identified these two key characteristics. Firstly, the presence of a central tunnel structure, oriented along the 'c' axis, with CaO_6 (AO_6) and PO_4 polyhedra (BO_4) as corner-connected units, secondly, that the tunnels are occupied by anions (OH^- , Cl^- , F^-), see Fig.5.

On the other hand, Fluorapatite, a naturally occurring calcium phosphate, is the main apatitic ore mined in the world; see Tables .2 and .3; 80% of which is used to make H_3PO_4 .

Table.2: Mining production of $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ phosphates, in thousands of tonnes, in 2012. [World: 210,000, European Union (Finland, in 2011)].

China	89000	Brazil	6300
The United States	29200	Tunisia	6000
Morocco	28000	Egypt	3000
Russia	11300	Israel	3000
Jordan	6500	Australia	2600

Table.3 : Reserves, in millions of tons, in 2012 [Monde:67 000](1million= 10^3 mile).

Morocco	50000	South Africa	1500
China	3700	The United States	1400
Algeria	2200	Russia	1300
Syria	1800	Peru	820
Jordan	1500	Saudi Arabia	750

[22] J. A. D'Antonio, W. N. Capello, W. L. Jaffe, Multicenter three-year clinical and roentgenographic results. Clin Orthop, 100 (1992).

[23] Beevers, C. A., & McIntyre, D. B. (1946). The Atomic Structure of Fluor-Apatite and its Relation to that of Tooth and Bone Material. Mineralogical Magazine, 27(194), 254-257.

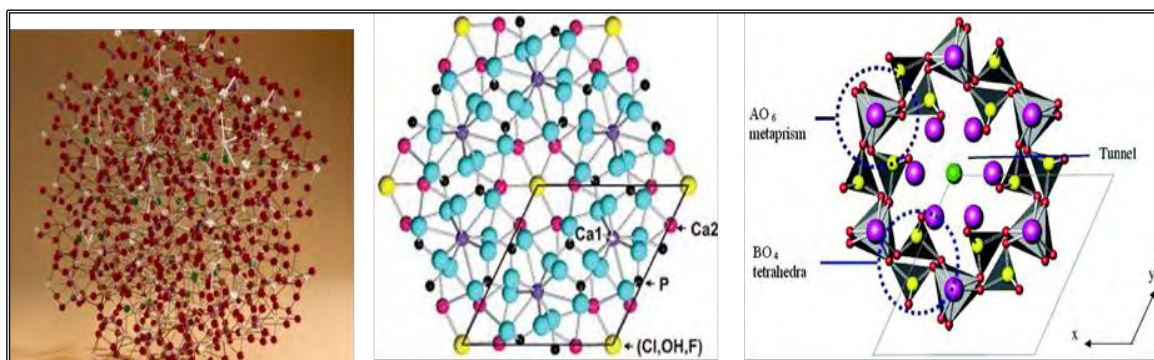


Fig.5: The primary crystallographic description of the apatites $\text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{F}, \text{Cl})$.

Natural, sedimentary phosphates are sourced from the accumulation of bones of marine species. For several years, they have been the most important in number and volume. They are distributed in several parts of the world, generally in shallow coastal areas. In Morocco the phosphate deposits are located in the mines of Ganntour in YOUSSEOUFIA and BENGUERIR, Meskala in CHICHAOUA, Oued Eddahab in BOUCRAA and Oulad Abdoun in K HOURIBGA, [Fig.6](#).

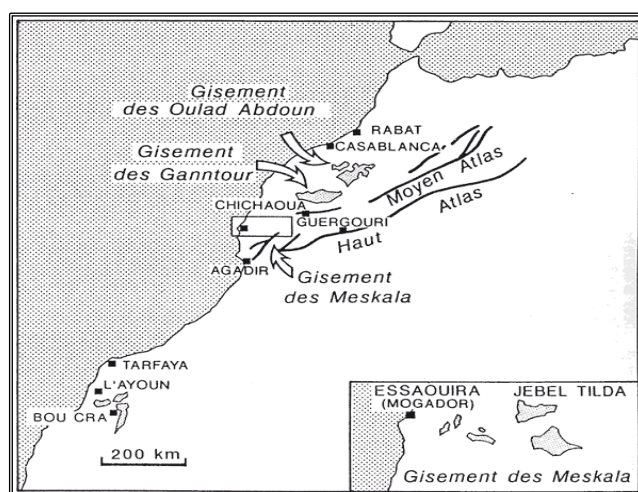


Fig.6: Sources of phosphate ores in Morocco.

The phosphate ores $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$, present an enormous reserve of the Moroccan subsoil, and they are of great importance in various fields of life. Our region Chaouïa Ouardigha and more precisely the city of K HOURIBGA, capital of phosphate in the world, recognized worldwide by its quality of phosphate and its enormous reserve, which justifies the need for scientific and technical research in the field of apatitic and phosphate materials.

Introduction of the Chapters

The possible fields of application of apatites are many and varied such as:

- ☞ Medicine: bone filling material, coating of dental implants.
- ☞ Agrochemicals: artificial fertilizers.
- ☞ Technology: fluorescent lamps and laser materials, catalysts and gas detectors due to the existence of ion conduction, etc.
- ☞ Nuclear industry: a matrix that can receive radioactive elements and fission products.

The only apatite system, where compounds having the apatite structure could be prepared without a 'Y' anion, is the apatite lead system [6, 24]. Apatites with gaps in the anion sites of the general formula $\text{APb}_4(\text{PO}_4)_3$ have been studied by several authors (A = Na, Ag, K) [6, 24-26]. These lacunar apatites derived from apatites with anion sites, born in recent years, are known by the formula $\text{Pb}_{4.5}(\text{XO}_4)_3\text{Y}_0$, despite significant anomalies observed in the stoichiometry of many synthesized apatite-structured compounds of this genus 0.5 in the composition of 'Pb²⁺' is replaced by a monovalent cation hence the formula $\text{APb}_4(\text{XO}_4)_3\text{Y}_0$ ('X' generally a pentavalent cation X^{5+} : P^{5+} , V^{5+} and As^{5+} , ..., etc.).

Mathew and al [27] and Engel et al [28] have shown in their work that stabilization of the structural type of apatite seems to be directly related to the presence of a minimum electron density in its large tunnels. These negative charges could be brought either by the anions (Y^- : F^- , Cl^- , OH^- , ...etc.), which occupy the large tunnels which encompass (6₃) axes. Each time the 'Y-' anions are removed from the network, the apatite network collapses, giving rise to a mixture of phases or a new type of structure, except in cases where the host channels are occupied or substituted by cations with isolated pairs such as 'Pb²⁺ or Bi³⁺'.

[24] M. Azrour, M. Azdouz, B. Manoun, R. Essehli, S. Benmokhtar, L. Bih, L. El Ammari, A. Ezzahi, A. Ider, A.A. Hou, Rietveld refinements and vibrational spectroscopic studies of $\text{Na}_{1-x}\text{K}_x\text{Pb}_4(\text{PO}_4)_3$ lacunar apatites ($0 \leq x \leq 1$), J. Phys. Chem. Solids. 72 (2011) 1199–1205.

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[26] R. Ternane, M. Ferid, M. Trabelsi-Ayadi and B. Piriou, Spectrochim. Acta, A(55) (1999)

[27] M. Mathew. W.E. Brown, M. Austin. T. Negas, J. Solid State Chem. 35(1980),p.69.

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Indeed, El Koumiri et al, which is the subject of the study of the first crystal structure of the lacunar apatite $\text{NaPb}_4(\text{PO}_4)_3$ [6], Manoun and many authors have reported various compounds corresponding to different types, although there are many chemical families among the "Phosphates, arsenates or vanadates". For example, $\text{APb}_4(\text{PO}_4)_3 \cdot \text{Y}_0$ (A: Na^+ , K^+ or Ag^+) [6,25,26], $\text{Na}_{1-x}\text{K}_x\text{Pb}_4(\text{PO}_4)_3$ [24], $\text{Na}_{1-x}\text{K}_x\text{Pb}_4(\text{VO}_4)_3$ [29], $\text{Na}_{1-x}\text{K}_x\text{Pb}_4(\text{AsO}_4)_3$ [30] and $\text{Na}_{1-x}\text{K}_x\text{Pb}_3\text{Ca}(\text{PO}_4)_3$ [31,32]. The stoichiometry of these materials is directly related to the cationic distribution within the crystal lattice, as would normally be predicted based on both ion size and charge compensation and occupancy at one or more sites (6h and 4f). Manoun et al have provided an excellent description of the structure, which is hexagonal with space group $P6_3/m$, which can be described as consisting of $[\text{XO}_4]^{3-}$ tetrahedra and characterized by the presence of two non-equivalent sites 6h and 4f. It appears that the ' Pb^{2+} ' ions play an essential role in maintaining the ideal apatite lattice. This role is related to the presence of $6s^2$ electron pairs that can compensate for the Coulomb imbalance due to the existence of anion vacancies in the apatite tunnels.

Our investigations on lead apatites are justified by the fact that the largest accumulation of Lead in the human body is normally contained in teeth and bones, which are mainly composed of calcium hydroxyapatite [27,33]. One of the possibilities of incorporating Lead into bone is through coupled substitution: ' $2\text{Ca}^{2+} \text{OH}^- \longrightarrow \text{Pb}^{2+} + \text{A}^+ + \Delta(\text{OH})^-$ '

[29] M. Azdouz, B. Manoun, M. Azrour, L. Bih, L. El Ammari, S. Benmokhtar, P. Lazor, Synthesis, Rietveld refinements and Raman spectroscopy studies of the solid solution $\text{Na}_{1-x}\text{K}_x\text{Pb}_4(\text{VO}_4)_3$ ($0 \leq x \leq 1$), J. Mol. Struct. 963 (2010) 258–266.

[30] B. Manoun, M. Azdouz, M. Azrour, R. Essehli, S. Benmokhtar, L. El Ammari, A. Ezzahi, A. Ider, P. Lazor, Synthesis, Rietveld refinements and Raman spectroscopic studies of tricationic lacunar apatites $\text{Na}_{1-x}\text{K}_x\text{Pb}_4(\text{AsO}_4)_3$, J. Mol. Struct. 986 (2011) 1–9.

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[32] S. Lahrich, B. Manoun, M.A. El Mhammedi, Sodium doping effect on physicochemical properties of $\text{K}_{1-x}\text{Na}_x\text{CaPb}_3(\text{PO}_4)_3$ ($0 \leq x \leq 1$) for the determination of mercury(II), Mater. Res. Bull. 59 (2014) 349–357.

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Introduction of the Chapters

Where in ' A^+ ' and (OH^-) , represent respectively a monovalent cation (or proton) and a hydroxyl vacancy. Therefore, the physicochemical results of our current work should be of great interest in understanding the mechanisms of apatite onset, substitution and stabilization in the human body.

Recently, we have found new voltammetric sensors based on a carbon paste electrode modified with the materials $Na_{1-x}K_xCaPb_3(PO_4)_3$ [32], which has been described for the determination of the trace level of mercury (II) and cadmium (II) ion by differential pulse anodic voltammetry. The results obtained by using the lacunar materials are an important tool for the quantification of mercury (II) and cadmium (II) ions in tap and seawater samples and mussels.

A.II. Natural apatites.

Phosphate rock can be of two different types: sedimentary or of volcanic origin, both associated with a large number of impurities.

Sedimentary minerals have relatively homogeneous layers, although each of them has its characteristics, depending mainly on the nature of the chemical constituents. The level of impurities in sedimentary phosphates depends on the specific local conditions, which are very similar. Compared to phosphates of volcanic origin, sedimentary phosphates contain more carbonates, fluorides and often more aluminium and iron. Being porous, sedimentary phosphates offer a larger area for chemical reactions. Most sedimentary ores contain organic matter that can generate foams during the production of phosphoric acid [34].

On the other hand, not only do phosphates of volcanic origin differ from each other, but they can also be different within the same mine.

Other types of phosphates of lesser importance also exist, such as metamorphic phosphates, which are an intermediate form of phosphate and are more complex. These are usually sedimentary rocks that have undergone alterations due to temperature and pressure,

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resulting in recrystallization. Because of their sedimentary origin, they contain the same impurities as sedimentary phosphates.

The Moroccan subsoil contains the largest sedimentary phosphate deposits in the world. Three-quarters of the world's reserves, 98% of which are in the centre of the country; Oulad Abdoun, Gantour, Ouad Eddahab and Meskala, and 2% in the south. Their geographical location and the diversity of their commercial qualities naturally give the Kingdom of Morocco a special place in the international trade of phosphate and its derivatives (phosphoric acids and fertilizers). Moroccan deposits contain many kinds of phosphate: the first phosphate contains 72% GLP (good phosphate of lime) which generally does not undergo any treatment operation except screening to eliminate large stones and waste rock, and drying to remove moisture. While the second phosphate, which is low in GLP, requires treatment operations for the removal of impurities such as screening, washing and drying or calcination, and the third phosphate contains a lot of organic matter and limestone undergoing further treatment talks about it on flotation through the use of an ester and an amine.

Table.4 shows the mass percentages in % of certain elements present in mined rocks from different regions of the world for the two types, sedimentary and volcanic origin [34]. From Table.4, it can be seen that phosphate rocks of volcanic type contain more P_2O_5 (phosphoric acid) than those of sedimentary nature.

Table.4^[34]: Mass percentage in % of certain elements in different rocks.

Phosphate rock	P_2O_5	F	CO_2	SiO_2	Al_2O_3	MgO
Sedimentary						
Khouribga (Morocco)	32.9	4.1	4.8	2.0	0.4	0.3
El Hassa (Jordan)	32.8	3.7	4.7	1.6	0.5	0.4
Kneifiss (Syria)	32.8	4.0	3.9	1.2	0.1	0.20
Hong He Zhou (China)	31.9	3.1	-	14.7	1.35	0.35
Floride (USA)	31.3	3.6	3.7	5.6	1.3	0.5
Abou Tartur (Egypt)	30.0	3.1	2.8	2.1	1.5	1.0
volcanic origin						
Palfos 88S (South Africa)	40.2	2.38	1.3	0.45	0.05	0.53
Palfos 88I (South Africa)	39.9	2.35	1.0	1.0	0.35	0.51
Palfos 80M (South Africa)	36.5	2.2	4.2	0.71	0.06	1.49

[34] MICHAEL SCHORR, ISRAEL J. LIN, Wet Process Phosphoric Acid Production Problems and Solutions, Industrial minerals, 1997, N°355, pp. 61-71

Introduction of the Chapters

Phosphoric acid resulting from the attack of the phosphate rock by sulphuric acid inevitably contains impurities, particularly metallic species where some such as cadmium arsenic and lead, must be eliminated as they present direct dangers to living beings. By way of illustration, the composition of phosphoric acid resulting from the wet process, after sulfuric acid etching of phosphate rock extracted from certain Algerian [35] and Tunisian [36] mines, is shown in Table.5:

Table.5: Composition of phosphoric acid from rock from Algeria and Tunisia.

Element (ppm)	Algeria rock ^[35]		Tunisia rock ^[36]	
	Phosphate	Acid 29% P ₂ O ₅	Acid 28% P ₂ O ₅	Acid 54% P ₂ O ₅
Cd	6.75	3.58	-	-
As	10.09	4.59	43	82
Zn	180.02	87	123	238
Pb	80.11	18	2	2
Cu	50.03	26	1	2
Hg	80.01	9	5	10
Mn	9.29	3.6	16	36
Cr	134	31.33	137	396
V	47.50	30.41	38	79
Sr	-	-	40	2
Ti	-	-	24	67
Ni	-	-	10	38

From the two Tables 4&5, it is clear that the phosphate rock is the main source of dissolved or suspended impurities in phosphoric acid from the wet process. All these metallic species can be present, for example, in the phosphates used as fertilizers, which, therefore, are a fairly important source of pollution of soil and water resources. It can be seen that the purification of phosphoric acid is a rather complex operation. This is mainly explained by the presence or formation, during the process, of species that must imperatively be eliminated (Pb, Cd, As, Zn,...). It should also be noted that impurities can be introduced during the manufacturing process, such as, for example, the 'Cl' ions brought by the washing water, which can be seawater. Sulphuric acid obtained from hydrometallurgical industries can also introduce additional impurities.

[35] SAOUD A., NABIEV M., MIMOUN H., Utilisation du diéthylthiocarbamate pour la purification de l'acide phosphorique des métaux lourds par extraction liquide-liquide.

[36] AYADI ABDEL MONEIM, Elimination du Cadmium dans l'Acide Phosphorique, Information Chimie N°345, février 1993

Introduction of the Chapters

Heavy metals are naturally present in our environment. They are found everywhere in the soil, in water, in food and even in the human body. However, above a certain concentration, they become harmful especially to living things. Consequently, the problems inherent in the release of heavy metals such as cadmium, lead, mercury, zinc, arsenic, etc. into the environment have always been a concern for public authorities and therefore also for researchers who are called upon to find solutions.

In general, the different methods currently used for the treatment of liquid waste or even the purification of certain compounds such as phosphoric acid produced from the wet process, to eliminate the heavy metals present, include, among others, adsorption, electrolysis, solubilization, flotation, precipitation, ion exchange, as well as liquid-liquid extraction,..., etc. (see [Chapter. IV](#)).

A.III. Pathway of synthesis Apatite.

The diverse application of apatites in several fields (medical, environmental ..., etc.), requires the control of the conditions of synthesis of these compounds by different methods, to study their physicochemical properties. The method of preparation depends essentially on the nature of the ions constituting the apatite [37]. A variety of synthesis routes are proposed in the literature for the preparation of apatite materials including synthesis in the aqueous phase [38,39], the sol-gel method which uses phosphorus and calcium alkoxides under conditions of pH and temperature [40] and the dry method at temperatures between 700 and 1100°C [41].

[37] S. Kadouche, utilisation des biomatériaux dans le traitement des eaux, thèse, Université Mouloud Mammeri Tizi Ouzou, Algérie (2013).

[38] H. Chaair, Optimisation de la synthèse en continu des phosphates de calcium, Thèse, Université de Toulouse, France (1993).

[39] A. Osaka, Y. Miura, K. Takeuchi, M. Asada, K. Takahashi, Calcium apatite prepared from calcium hydroxide and orthophosphoric acid, *Journal of Materials Sciences in Medicine* 2 (1991)51-55.

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[41] L. Badrour, A. Sadel, M. Zahir, L. Kimakh, A. El Hajbi, Synthesis and physical and chemical characterization of $\text{Ca}_{10-x}\text{Ag}_x(\text{PO}_4)_6(\text{OH})_{2-x}$ apatites, *Annales de chimie science des matériaux*, 23(1998)61-64.

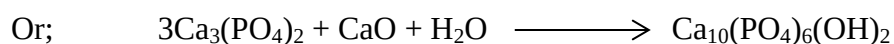
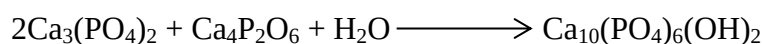
Introduction of the Chapters

According to the literature, the known dry solid-solid reaction route is the only one used in the synthesis of lacunar apatites at temperatures between 600 and 900°C [6, 24, 29, 30, 42]. Single crystals of $\text{NaPb}_4(\text{PO}_4)_3$ [6], which have been successfully grown from crystals at high temperatures, are reported, and the recovered solution is slowly cooled. The appropriate mixtures of the raw materials (Na_2CO_3 , PbO and $\text{NH}_4\text{H}_2\text{PO}_4$) were carefully ground before being subjected to heat treatment at 750°C. The solid phase obtained after 20 h of the reaction was melted at 1100°C for 10 h. The bath was slowly cooled (rate 5°C/h) to 500°C before the furnace was shut down and the system was allowed to cool down normally to room temperature.

In the case of calcium phosphate synthesis e.g. Hydroxyapatite (HAP), their preparation depends on several parameters such as pH, temperature, the concentration of reagents, cation/anion molar ratio, stirring speed, ..., etc.

1. Dry synthesis.

Solid-solid reaction synthesis involves heating the starting reaction mixture to an elevated temperature. This mixture must be perfectly homogeneous to allow a total reaction. Indeed, the synthesis of several studies has shown that the optimal conditions for the formation of HAP in the solid-state between tricalcium phosphate and tetra calcium phosphate (or tricalcium phosphate and calcium oxide) are around 1050°C in a humid atmosphere [43,44].



[42] HAMDY Besma, Synthèse, caractérisation physico-chimique et étude structurale d'apatites lacunaires à base de plomb et de bismuth, différemment substituées. Thèse de l'Université de SFAX & l'Université PAUL SABATIER, 2007.

[43] WALLAEYS R., Contribution à l'étude des apatites phosphocalciques, Ann. Chim., Vol. 7, p. 808 (1952)

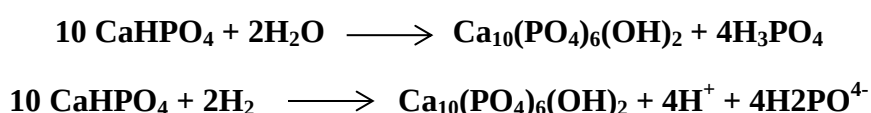
[44] BRITEL O., Possibilités de substitution dans les apatites et défloration en fonction de la pression par voie thermique de la fluorapatite synthétique et naturelle, thèse de 3ème cycle, Rabat, (1990).

2. *Hydrothermal synthesis.*

The hydrothermal technique allows compounds to react, or evolve, in a liquid at temperatures above the boiling point of the liquid. In the case of a reaction in the presence of water, it is possible to carry out this reaction at temperatures above 100°C. To obtain these conditions, it is necessary to use equipment (autoclaves) that can withstand high temperatures and pressures. At temperatures above 100°C, the water contained in the autoclave partially vaporizes, causing an increase in internal pressure. The pressure in the autoclave is therefore equal to the value of the saturating vapour pressure of the water at the given temperature.

Hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ is obtained from calcium acetate and triethyl phosphate at 350°C and 30 MPa in a water-ethanol mixture [45] or from calcium pyrophosphate at 500°C and 80 MPa [46]. Hydrothermal synthesis allows the growth of crystals of a particular shape in the case of carbonate apatite synthesis. The morphology of the crystals depends on the amount of ethanol added to the medium [47].

Teraoka et al [48] were able to obtain apatite single crystals by hydrolysis of calcium monohydrogen phosphate (CaHPO_4) associated with a temperature gradient. The reaction is written:



The hydrothermal treatment allows the formation of well-crystallized, homogeneous and evenly shaped products.

[45] T. Hattori, Y. Iwadate, T. Kato, *Adv. Ceram. Mat.*, 3(4), 426 (1988).

[46] T. Hattori, Y. Iwadate, T. Kato, *J. Mater. Sc. Let.*, 8, 305 (1989).

[47] F. Nagata, Y. Yokogawa, M. Toriyama, Y. Kawamoto, T. Suzuki, K. Nishizawa *J. Ceram. Soc. Japan*, 103, 70 (1995).

[48] K. Teraoka, A. Ito, K. Onuma, T. Tateishi, S. Tsutsumi, *J. Mater. Res.*, Vol. 14, N°6, (1999).

3. Sol-gel reaction.

The sol-gel process is based on the polymerization of organometallic precursors of the ' $M(OR)_n$ ' alkoxide type. After, controlled hydrolysis of the alkoxide in solution. The condensation of the monomers leads to 'oxo' bridges and then to an organic oxide. The progressive polymerization of these precursors forms oligomers then polymers, thus increasing the viscosity. These polymeric solutions lead to gels that allow easy shaping of materials (dense and transparent films, ultrafine powders, ceramics...) with many technological applications [49].

Cheng and al [50] have succeeded in synthesizing hydroxylated and fluorinated apatites (HA/FA) according to the procedure described in Fig.7.

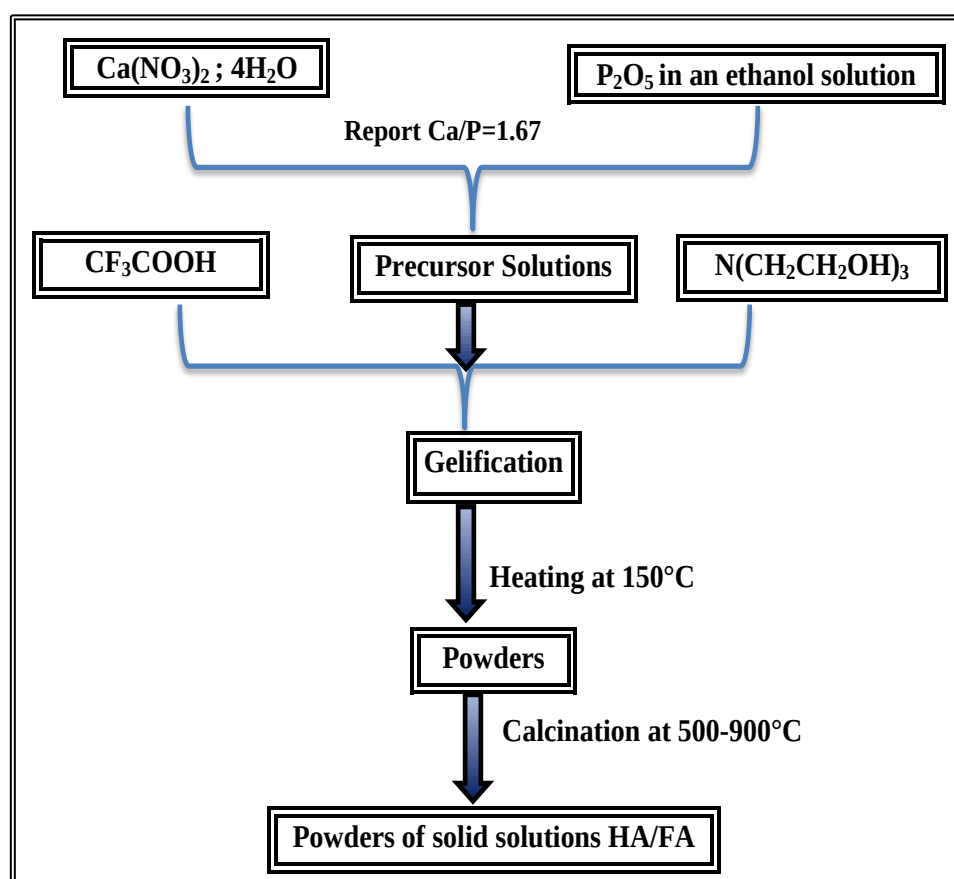


Fig.7: Diagram showing the steps for the synthesis of the HA/FA solid solution [50].

[49] LIVAGE, S., journal of non-crystalline solids, vol. 145, p.11 (1992).

[50] K. Cheng, G. Shen, W. Weng, G. Han, J. M. F. Ferreira, J. Yang, Mat. Lett. 51,37 (2001).

4. *Wet synthesis.*

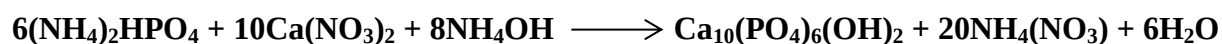
Several authors have been interested in the preparation of hydroxyapatite by wet synthesis. Two methods of wet preparation are commonly used: the Wallaеys precipitation method and the double decomposition (co-precipitation) method. These processes are currently used for industrial apatite production [51].

- Wallaеys precipitation method:

This method of synthesis, generally used to prepare phosphocalcic hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ has been implemented by R. Wallaеys [43] and improved by Trombe, Dowell and others [52]. It consists of neutralizing, first cold and then hot, orthophosphoric acid with lime $\text{Ca}(\text{OH})_2$ in the presence of phenolphthalein. A suspension is obtained consisting of hydroxyapatite mixed with lime. This suspension is filtered, dried at about 100°C away from atmospheric carbon dioxide, then heated to 900°C in a nitrogen atmosphere, and finally washed with distilled water until all traces of CaO disappear.

- Double decomposition method (co-precipitation):

This method, although slow, offers the advantage of synthesizing apatites very close to the proposed stoichiometry. It consists of adding in a controllable way drop by drop a solution of calcium nitrate in an ammoniacal solution of ammonium hydrogen phosphate brought to boiling, during the precipitation the PH is higher than 12. Precipitation is carried out for about 3 hours; the precipitate is left in contact with the stock solution for one hour, then filtered, washed with bi-distilled water and dried in an oven and calcined at 900°C before use [52-54].



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A.IV. Physico-chemical properties and different applications.

The first apatites studied correspond to the fundamental stoichiometry $M_{10}(XO_4)_6Y_2$ whatever is 'M' and 'Y' associated with the ions XO_4^{3-} . The question of lacunar apatites is controversial especially in the case of oxyapatites. It is known that some calcium hydroxyapatites are deficient in calcium [55]. The first examples of lacunar apatites have been reported in phosphate series such as $Pb_{10}(PO_4)_6O_{\square}$ or analogous compounds of barium, lead, bismuth or strontium [56-58] in mixed series such as $Pb_{10}(PO_4)_4(SiO_4)_2\square_2$ whose range of existence in the PbO , SiO_2 and P_2O_5 system is very large [59, 60]. Subsequent work on silicoapatites showed that some apparent deficiencies could be explained by a different formulation of the compound, thus lanthanum monosilicate, which could be considered as doubly deficient $La_8\square_2(SiO_4)_6\square_2$ can also be written $La_{9.33\square_{0.67}}(SiO_4)_6O_2$ showing only a slight cationic deficiency [60]. For more details see Table.6.

Recently, Tao et al [61] have successfully synthesized the two apatitic compounds $La_{10}(SiO_4)_6O_3$ and $La_{9.33}(SiO_4)_6O_2$ by the sol-gel method. The process of this synthesis is schematized as follows, Fig.8.

Nowadays the lacunar apatites are well known, the lacunae are mainly in position (2a) occupied by the anions 'Y' but they can also be found on the cation sub-grid. The two types are sometimes associated with the same compound. No compound has been known to present a gap at the site of the 'X' cations of the ' XO_4 ' tetrahedron.

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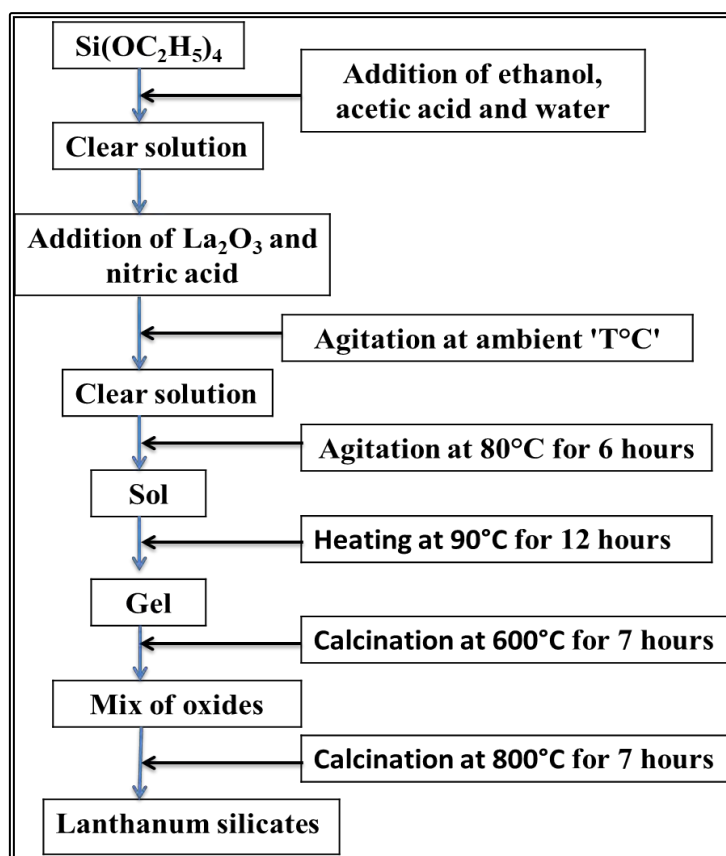


Fig.8: Schematic diagram of the preparation of lanthanum silicates by the sol-gel process ^[61].

Table.6: lacunar Lead-apatites with their crystal parameters $a(\text{\AA})$, $c(\text{\AA})$ and $v(\text{\AA}^3)$.

Apatite Formulation	crystal parameters			c/a	References
	a (Å)	c (Å)	V(Å ³)		
Pb ₉ □(PO ₄) ₆ □ ₂	9,827	7,357	615,28	0,749	[62]
Na ₂ Pb ₈ (PO ₄) ₆ □ ₂	9,725	7,190	588,9	0,739	[6]
Ag ₂ Pb ₈ (PO ₄) ₆ □ ₂	9,770	7,207	595,8	0,739	[26]
K ₂ Pb ₈ (PO ₄) ₆ □ ₂	9,827	7,304	610,9	0,743	[62]
Rb ₂ Pb ₈ (PO ₄) ₆ □ ₂	9,86	7,37	620,5	0,748	[62]
Cs ₂ Pb ₈ (PO ₄) ₆ □ ₂	9,99	7,49	647,4	0,750	[63]
Na ₂ Pb ₈ (VO ₄) ₆ □ ₂	10,06	7,346	643,9	0,730	[63]
K ₂ Pb ₈ (VO ₄) ₆ □ ₂	10,142	7,472	665,6	0,737	[57]
Bi ₂ Pb ₈ (VO ₄) ₂ (SiO ₄) ₄ □ ₂	9,76	7,26	599	0,744	[57]
Bi ₂ Tl ₂ Pb ₆ (PO ₄) ₄ (SiO ₄) ₂ □ ₂	9,78	7,34	608	0,75	[28]
Bi ₄ Pb ₈ (SiO ₄) ₆ □ ₂	9,791	7,222	599,6	0,738	[57]
NaPb ₉ (PO ₄) ₅ (SiO ₄)□ ₂	9,77	7,26	601	0,743	[57]
Na ₂ Pb ₈ (PO ₄) ₂ (SiO ₄) ₂ (SO ₄) ₂ □ ₂	9,79	7,29	606	0,744	[57]
KPb ₉ (AsO ₄) ₅ (SiO ₄)□ ₂	10,06	7,40	649	0,736	[28]

1. Apatite stability:

Several studies have been carried out on the evolution of the physical and chemical characteristic of the stability of apatites [64].

Factors that affect apatite stability include temperature, pressure and chemical composition. Favourable conditions for solid-gas reactions can be found by adjusting the processing temperature and pressure. An example is the extraction of fluor ions from natural phosphates or synthetic fluorapatites [44,65,66]. Further work has been carried out to extract cadmium and zinc from the corresponding apatites. Indeed, the study of calcocadmie or calcozinc apatites, treated at different temperatures under the 'H₂S' atmosphere, showed an extraction of 'Cd' or 'Zn' from the apatite lattice in the form of 'CdS' and 'ZnS' [67].

Furthermore, to show the compositional effect, the authors measured the heat of dissociation of synthetic apatites of the form M₁₀(PO₄)₆Y₂ (Y = F, OH) [68,69]. They found that cation size plays an important role in the formation or dissociation of these apatites. The results obtained by calorimetry show that fluorapatites are generally the most stable.

2. Diffusion process in apatites:

The diffusion process generally depends on several parameters including the existence of tunnels and steric hindrance. Indeed, the existence of two tunnels in the apatite structure gives the ions included in the tunnels high mobility. G. Montel is the first to show [70], through his work on ion exchange, those ions occupying the tunnels are mobile without giving the migration mechanisms. Subsequently, other studies have focused more specifically on ion mobility in hydroxyapatites. For examples, the proposed diffusion mechanism involves 'H⁺ and O²⁻' ions [71-76].

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3. *Electrical properties:*

Ion conduction varies with charge and ion size, with the possibility of migration within the structure. The introduction of small, non-highly polarizing ions can induce high electrical performance. Apatites are generally considered to be ionic electrolytes. The presence of tunnels in the apatite means that conduction is preferred along the tunnel axis, i.e. in the direction of the c-axis (conduction $\parallel c >$ conduction $\perp c$) [72-76].

To demonstrate the mobility of ions in apatites, electrical measurements were carried out. Several authors have established a correlation between structural properties and ion conductivity [77,78]. Comparison of the electrical properties between fluorapatite and hydroxyapatite electrolytes [79] shows that leaded fluorapatite and leaded hydroxyapatite have a higher conductivity than other apatites ($\text{Ba}_5(\text{PO}_4)_3\text{F}$, $\text{Ca}_5(\text{PO}_4)_3\text{F}$, $\text{Ba}_5(\text{PO}_4)_3(\text{OH})$ and $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$). According to the authors, this phenomenon is related to the strong polarization of the ' Pb^{2+} ' ion, also, the wide tunnels resulting from the introduction of bulky cations such as ' Ba^{2+} ' may be a second parameter influencing the variation of the ionic conductivity. A break was observed in the Arrhenius curve, at 480°C, for lead apatite. This is related to the ionocovalent ' Pb-Y ' (Y: anion in the tunnel) bond, which requires high energy to break it and release the mobile ions (F^- , H^+). Table.7 compiles a comparison of the electrical properties of the samples.

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According to these authors, conductivities are governed by an ion hopping mechanism. In fluorapatite, the conduction mechanism is related to the hopping of 'F' ions along the 'c' axis from ordinary sites to interstitial sites and vice versa. In opposition, the mobility mechanisms of the proton can be formulated as follows: proton conduction between two neighbouring 'OH' (O-H...O-H) and proton jump from one 'OH' to another through 'PO₄³⁻' ions.

Table.7: Comparison of the electrical properties of fluorapatite and hydroxyapatite samples about the physical characteristics of the 'M²⁺' cations [79].

Ions M ²⁺	Ca ²⁺	Ba ²⁺	Pb ²⁺
Fluorapatite			-3,563
log σ_{800} (S/cm)	-4,452	-3,89	0,25
Activation energy E _a (eV)	1,86	1,47	1,36
Hydroxyapatite			-4,637
log σ_{800} (S/cm)	-6,127	-5,74	0,62
Activation energy E _a (eV)	1,21	1,27	1,6
Ion radius of the M ²⁺ (Å)	0,99	1,34	1,2
Polarizability of the ion M ²⁺ 10 ⁻²⁴ (cm ⁻¹)	0,6	1,6	3,6

The conductivity in hydroxyapatite is thermally activated and depends as much on the nature of the cation 'M²⁺' (M = Ca²⁺, Ba²⁺, Pb²⁺ and Sr²⁺) as on the insertion rate of the more or less charged cations [72]. The electrical behaviour of some types of apatites has been studied by K.Yamashita et al [71] who evaluated the electrical quantities of phosphocalcic oxyhydroxyapatites containing trivalent ions Ca_{10-x}M_x(PO₄)₆(OH)_{2-x}O_x (M = La, Y).

The study of the cationic conductivity in the Pb₈K_{2-x}Na_x(PO₄)₆ system as a function of the sodium level [80] showed that the ionic conductivity increases when the sodium level increases up to the value of x = 1 and then decreases (Table.8).

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According to the authors, this phenomenon can be explained by considering the difference in tunnel dimensions. Indeed, the tunnels surrounding 'K⁺' ions are wider than those formed by 'Na⁺' ions.

Table.8: Conductivity at 800°C and activation energy of $Pb_8K_{2-x}Na_x(PO_4)_6$ samples ^[80].

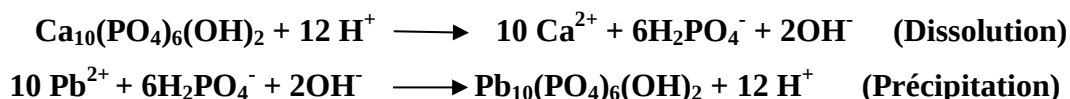
x (rate of Na ⁺)	0	0.5	1	1.5	2
log σ_{800} (S/cm)	-6.10	-4.35	-2.78	-4.40	-5.62
Activation energy E_a (eV)	2.07	1.28	1.21	1.35	1.44

4. Apatite adsorption properties:

Apatite has been widely used, due to its high adsorption and ion exchange capacity, as a material capable of immobilizing various heavy metals such as, 'Cd²⁺', 'Cu²⁺', 'Fe²⁺', 'Zn²⁺', 'Pb²⁺', 'U⁴⁺', [81-83], and various toxic organic molecules such as dyes [84] and pesticides [85,86]. Its adsorption capacity has also been exploited in catalytic reactions [87].

- Adsorption of heavy metals, e.g. 'Pb²⁺'.

Lead is one of the most toxic elements. There are several stable isotopes of lead in nature, of which '²⁰⁸Pb' is the most abundant. In this sense, several works have been carried out on the use of well-crystallized hydroxyapatites for the removal of 'Pb²⁺' ions from aqueous solutions and soils contaminated by these elements [88-90]. These studies examined the mechanism of 'Pb²⁺' removal by two processes: the dissolution of the hydroxyapatite followed by precipitation of a lead phosphate (hydroxy-pyromorphite) $Pb_{10}(PO_4)_6(OH)_2$ according to the two equations below :



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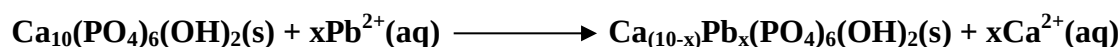
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Introduction of the Chapters

Indeed, the 'Pb²⁺' ion can partially or substitute the calcium of hydroxyapatite Ca₁₀(PO₄)₆(OH)₂ according to the following chemical equation [91] :



- Adsorption and exchange of ion:

Apatites are not only used for the adsorption of cations [92] but also the removal of anions such as 'F⁻, Cl⁻, SeO₃²⁻'. In this case, several studies on the adsorption phenomenon have been published. The study of the adsorption of selenite (SeO₃²⁻) on phosphocalcic hydroxyapatite shows that the removal of these ions depends on the pH and obeys a mechanism of anionic exchange with the 'PO₄³⁻' group by incorporation into the occupied crystallographic sites [93].

5. Theoretical modelling.

Strontium is one of the most common substituents in the structure of apatites, as in the Ca_{5-x}Sr_x(PO₄)₃Y (Y = F⁻, Cl⁻) series [94-99], as an example, the structure of Sr₅(PO₄)₃Y materials has been determined by X-ray diffraction, studied by infrared and Raman techniques [99-105], and by theoretical modelling on structural stability, electronic, vibrational and thermodynamic properties [98].

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Fig.9 shows the total densities of the Kohn-Sham states of the different apatites $\text{Ca}_5(\text{PO}_4)_3\text{Y}$ ($\text{Y}=\text{F}, \text{Cl}, \text{OH}, \text{O}_{0.5}$). They have been realized in the theoretical framework, by the Density Functional Theory (DFT) / Local Density Approximation (LDA) and pseudopotentials at zero temperature [94]. It is well known that apatite structures are insensitive to the choice of the anion in the c-axis column so that if they are eliminated as in this work, the structure is largely unchanged and remains stable, or at least metastable. The analysis of the XDOS data shows the same shape for the apatites, except the 'Cl' based material, due to the attractive inductive effect of oxygen. The more oxygen connected to the chlorine ion, the more polarization increases. The transition is due to the ' Ca^{2+} ' '3p' states and the valence bands consist of 'P and O' states linking the ' PO_4 ' groups with ' Ca^{2+} ' states also contributing to the bottom of the lower bands. The energy differences are between 5 and 6eV, except for that of (OA) with the 4eV value, which is much smaller; the results are presented in Table.9. The transition is due to some instability of the tetrahedron in the hexagonal apatite channel.

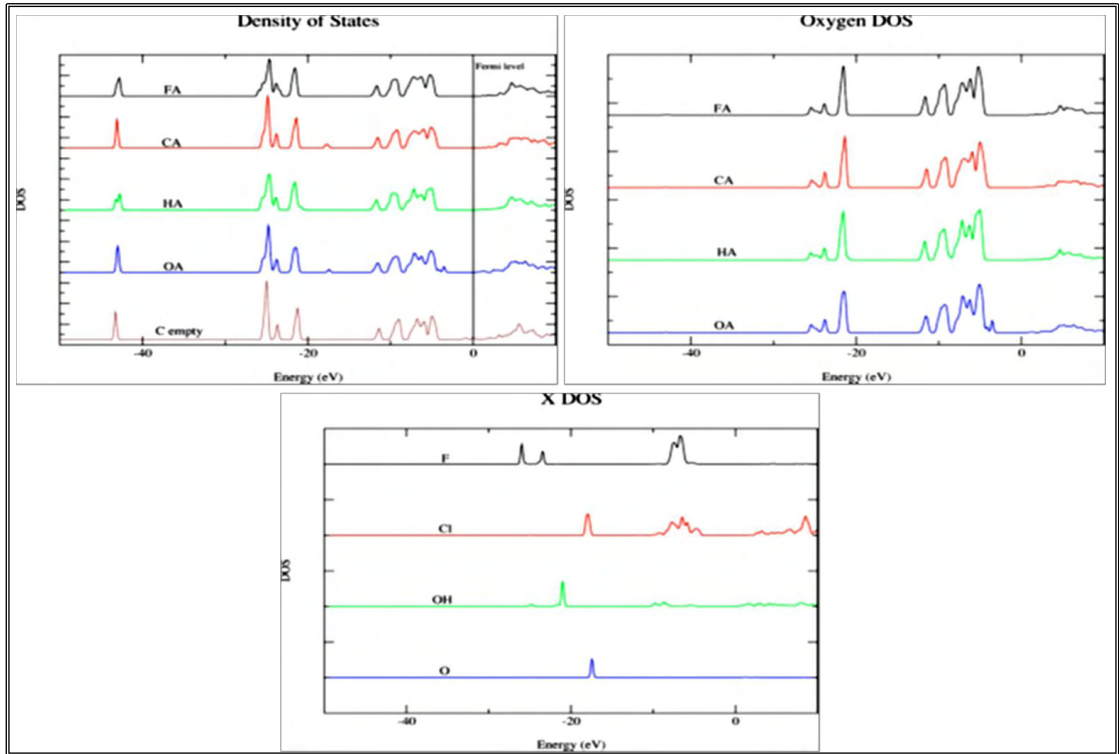


Fig.9: Density of states of $\text{Ca}_5(\text{PO}_4)_3\text{Y}$ ($\text{Y}=\text{F}, \text{Cl}, \text{OH}, \text{O}_{0.5}$) for; Total, and Partial for oxygen and of the anions along the c channel^[94].

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Table.9: Optimized 'Kohn-Sham' energies of the forbidden bands, and experimental and theoretical structural parameters for the apatites $\text{Ca}_5(\text{PO}_4)_3\text{Y}$ and $\text{Sr}_5(\text{PO}_4)_3\text{Y}$; ($\text{Y} = \text{F}, \text{Cl}, \text{OH}, \text{O}_{0.5}, \text{Br}$), and for our lacunar apatites $\text{APb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$ ($\text{A} = \text{Na}, \text{K}$).

Apatites	Khon-Sham gap (ev)	Unit-cell parameters		Ref	
		Calculated	Experimental		
Ca ₅ (PO ₄) ₃ F (FA)	5.9	S.G : P6 ₃ /m			
		a=b=9.06Å, c=6.84Å	a=b=9.398Å, c=6.878Å	Cal ^a	Expt ^a
Ca ₅ (PO ₄) ₃ Cl (CA)	5.6	S.G : P6 ₃ /m			
		a=b=9.25Å, c=6.79Å	a=b=9.628Å c=6.764Å	Cal ^a	Expt ^a
Ca ₅ (PO ₄) ₃ OH (HA)	5.4	S.G: P6 ₃		S.G: P6 ₃ /m	
		a=b=9.11Å, c=6.86Å	a=b=9.422Å c=6.885Å	Cal ^a	Expt ^a
Ca ₅ (PO ₄) ₃ O _{0.5} (OA)	4.0	S.G : P 6̄			
		a=b=9.06Å, c=6.73Å α=90.3°, β=90.0°, γ=119.9°	Cal ^a		
Sr ₅ (PO ₄) ₃ F (Sr-FAP)	5.42	S.G : P6 ₃ /m			
		a=b=9.568Å, c=7.183Å	a=b=9.678Å c=7.275Å	Cal ^b	Expt ^c
Sr ₅ (PO ₄) ₃ Cl (Sr-ClAP)	5.27	S.G : P6 ₃ /m			
		a=b=9.711Å, c=7.085Å	a=b=9.859Å, c=7.205Å	Cal ^b	Expt ^d
Sr ₅ (PO ₄) ₃ Br (Sr-BrAP)	5.27	S.G : P6 ₃ /m			
		a=b=9.796Å, c=7.101Å	a=b=9.972Å c=7.214Å	Cal ^b	Expt ^e
Lacunar apatites	Band-Gap Energy (eV)	S.G: P6 ₃ /m			
NaPb _{2.5} Sr _{1.5} (PO ₄) ₃	4.28		a=b=9.738Å c=7.198Å	This work	
KPb _{2.5} Sr _{1.5} (PO ₄) ₃	4.35		a=b=9.832Å, c=7.340Å		

^aRef : [94]. ^bRef : [98]. ^cRef : [99]. ^dRef : [100]. ^eRef : [101]

Fig.10 highlights the difference in the estimation of the electron density of states for $\text{Sr}_5(\text{PO}_4)_3\text{Y}$ apatites ($\text{Y} = \text{F}, \text{Cl}, \text{Br}$), using first-principle calculations of Ab-initio simulations of materials using the VASP software, by applying the functional density theory "DFT/Abinitio (VASP)". Local density approximation (LDA) is applied to describe the exchange-correlation energy. It is found that the main characteristics of the band structures are common to each apatite. All of these apatites are insulating materials and are characterized by an indirect bandgap. The bandgap decrease with the reduction of the electronegativity of the Y⁻ ions. Table.9 provides the calculated bandgaps and other theoretical and experimental values for each apatite, Sr-FAP, Sr-ClAP and Sr-BrAP. The DOS of these apatites is very similar with slight differences as for the band structures. The conduction band is mainly fed by the 'Sr²⁺, '4d' states with some mixing of O²⁻ '2s' and O²⁻ '2p'.

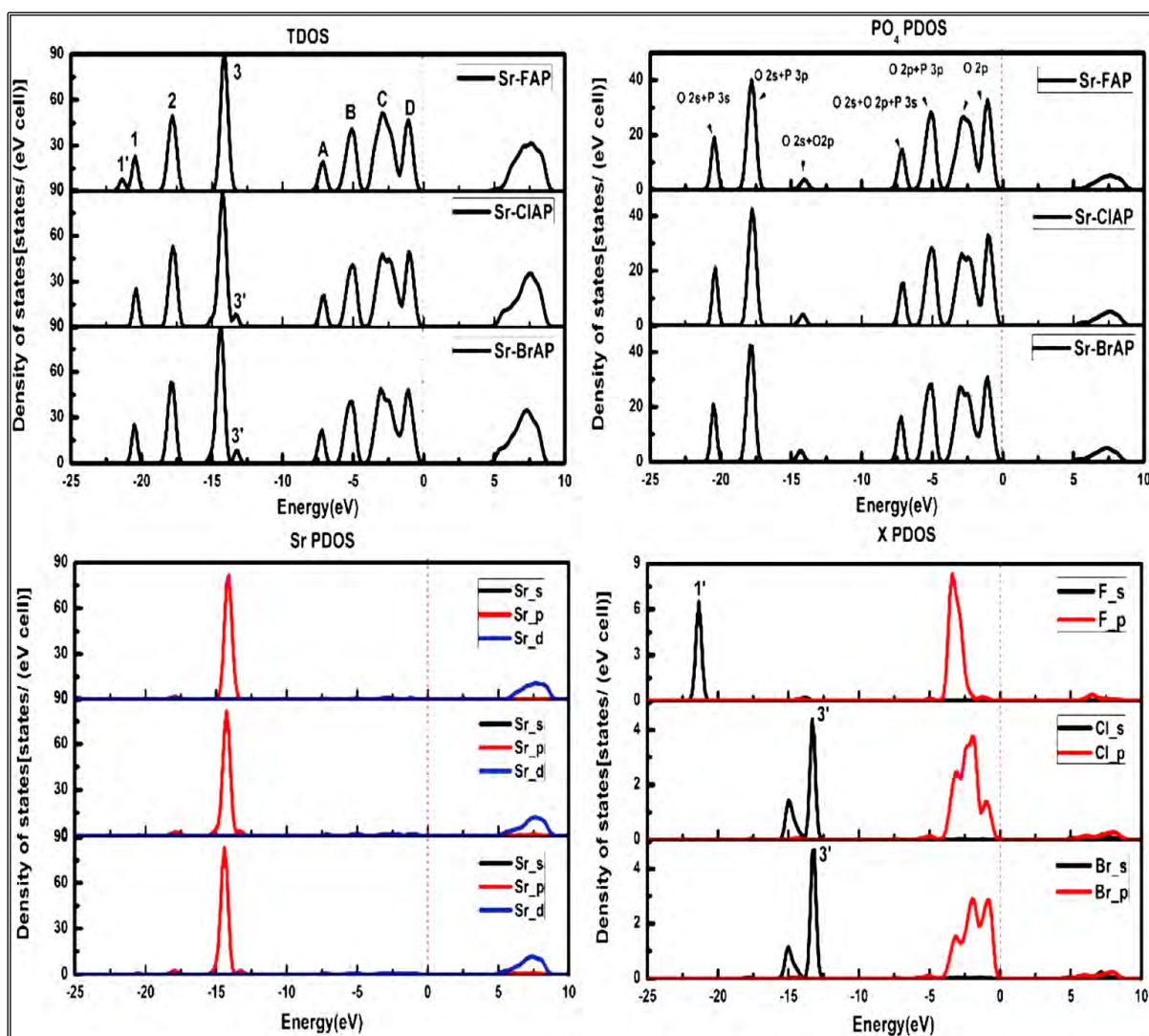


Fig.10. Apatites $Sr_{10}(PO_4)_6Y_2$ ($Y = F, Cl, Br$); Total density of states (TDOS) and partial density of states (PDOS) for Sr-FAP, Sr-ClAP and Sr-BrAP. ^[98]

6. The different applications:

Certain families of phosphates are of great technological importance in various fields of materials science chemistry. It is known that these apatites exist in a natural state and constitute the main matrix of phosphate ores. Apatites are used in various fields of application. A quick search can identify some of them, as examples:

- [102] A. Aissa, B. Badraoui, R. Thouvenot and M. Debbabi, Eur. J.Inorg. Chem., 2004, 2004, 3828–3836.
- [103] S. Zhai, S. R. Shieh, W. Xue and T. Xie, Phys. Chem. Miner., 2015, 42, 579–585.
- [104] C. E. Bonner, C. C. Chess, C. Meegoda, S. Stefanos, G. B. Loutts, Opt. Mater., 2004, 26, 17–22.
- [105] A. Schulte, S. C. Buchter and B. H. Chai, International Society for Optics and Photonics, 1995, 2380, 34–42.

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- ☞ In agriculture, they are widely used as a source of phosphate fertilizer [13].
- ☞ Their properties of absorption of organic compounds (amino acids, proteins, pesticides ...) are widely used [11,14-15,18-19].
- ☞ They are exploited as a support for high-performance liquid chromatography (HPLC) especially during the separation of biological compounds (DNA, RNA) [20].
- ☞ Phosphosilicate apatites, whose composition is close to that of natural apatites, are being considered in the field of radioactive waste disposal. They can store radioactive elements in their matrices [106], without suffering irreversible radiation damage.
- ☞ Apatites are also used in the electric lighting industry; in particular, fluorapatites doped with rare earth are used in the coating of fluorescent tubes [107].
- ☞ The synthesized materials show in particular the presence of ionic conductivity in phosphates of formula $A_3M_2(PO_4)_3$ (M^{3+} : Cr^{3+} , Fe^{3+} and $A^+ = Na^+$, Li^+ , Ag^+) and $Na_{1+x}Zr_{2-x}L_x(PO_4)_3$ ($L = Cr, Ln, Yb$) of Nasicon structure [108-113]. Conductivity has its origin in the very aerated three-dimensional organization of this structural type, which favours the migration of the monovalent cation. The optical properties are also reported in $A_3Ln(XO_4)_2$ type phases ($A = Na, K, Rb, Cs$; $Ln = \text{rare-earth}$; $X = P, V$) [114]. Their ionic conductor properties lead to their use in gas detectors (Alcohol, O_2 , H_2 , CO_2) or SOFC-type high-temperature fuel cells [115-117].

[106] J. C. Elliot, *Studies in Inorganic Chemistry*, 18, (1998).

[107] B. Piriou, D. Fahmi, J. Dexper-Guys, A. Taitai, J. L. Lacout, *J. Luminescence*, 39, 97, (1987).

[108] P.J. Panteix, *Synthèse et Caractérisation de conducteurs ioniques à structure apatitique*. Thèse de l'Université de Limoges, Limoges, (2005).

[109] P.J. Panteix, I. Julien, D. Bernache-Assollant, et al, *Synthesis and characterization of Oxide ions conductors with the apatite structure for intermediate temperature*, *Mater. Chem. Phys.*, (2006), 95, 313–320.

[110] J.E.H. Sansom, E. Kendrick, J.R. Tolchard, et al., *A comparison of the effect of rare Earth vs Si sit doping on the conductivities of apatite-type rare-earth silicates*. *J. Solid State Electr.*, (2006), 10, 562-568.

[111] P.J. Panteix, E. Béchade, I. Julien, et al., *Influence of anionic vacancies on the Ionic Conductivity of silicated rare earth apatites*, *Mater. Res. Bull.*, (2008), 43, 1223-1231.

[112] P.J. Panteix, I. Julien, P. Abelard, et al., *Influence of cationic vacancies on the ionic conductivity of oxyapatites*, *J. Eur. Ceram. Soc.*, (2008), 28, 821-828.

[113] P.J. Panteix, I. Julien, P. Abélard, et al., *Influence of porosity on the electrical properties of $La_{9.33}(SiO_4)_6O_2$ oxyapatite*, *Ceram. Int.*, (2008), 34, 1579-1586.

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All of these applications bring into play the Physico-chemical properties resulting from the structure of the apatitic network.

A.V. Apatite crystal structure.

In 1930, Nàray- Szabó [8] and Mehmél [9] were the first to determine that fluorapatite crystallizes in the hexagonal system [118-123]. The primitive mesh of apatite is a hexahedron of sides a , b and c , with $a = b$ but different from c . The angles α and β are equal to 90° and the angle γ (angle between $\vec{a}$ and $\vec{b}$) is equal to 120° . The structure of fluorapatite is shown in Table.10.

Table.10: Symmetry of sites of $\text{Ca}_5(\text{PO}_4)_3\text{F}$ atoms in space group $P6_3/m$, according to the International Crystallography Tables (Hann 1993. Schutte et al. 1997).

Atom	Multiplicity and Wyckoff Symbol	Crystallographic data
F	2 a	(0;0; $\frac{1}{4}$), (0;0; $\frac{3}{4}$)
Ca(I)	4 f	($\frac{1}{3}$; $\frac{2}{3}$; z), ($\frac{2}{3}$; $\frac{1}{3}$; z), ($\frac{1}{3}$; $\frac{1}{3}$; $z+\frac{1}{2}$), ($\frac{1}{3}$; $\frac{2}{3}$; $\frac{1}{2}-z$)
Ca(II) P O(I) O(II)	6 h	(x ; y ; $\frac{1}{4}$), (1- y ; $x-y$; $\frac{1}{4}$), ($y-x$; 1- x ; $\frac{1}{4}$), (1- x ; 1- y ; $\frac{3}{4}$) (y ; $y-x$; $\frac{3}{4}$), ($x-y$; x ; $\frac{3}{4}$)
O(III)	12 i	(x ; y ; z) (1- x ; 1- y ; 1- z) (1- x ; 1- y ; $\frac{1}{2}+z$) (x ; y ; $\frac{1}{2}-z$) (1- y ; $x-y$; z) (y ; $y-x$; 1- z) (y ; $y-x$; $\frac{1}{2}+z$) (1- y ; $x-y$; $\frac{1}{2}-z$) ($y-x$; 1- x ; z) ($x-y$; x ; 1- z) ($x-y$; x ; $\frac{1}{2}+z$) ($y-x$; 1- x ; $\frac{1}{2}-z$)

Apatite consists essentially of ions (XO_4^{3-}) arranged in two layers per lattice in which they form trigonal arrangements, Fig.11 [124]. These hexagonal arrangements are held together by 'Me' ions arranged in columns in the direction of the c -axis. The ions (XO_4^{3-}) are then deformed and their symmetry is only of the 'Cs' type (Fig.12) [118]. Also, each phosphate atom is bonded to three oxygen atoms in one column and one oxygen atom in an adjacent column (Fig.12) [118]. The metal and grouping (XO_4^{3-}) stabilize the large tunnels, in which other 'Me' ions are inserted forming triangles and in the axis of the tunnel anions stabilize the structure (Fig.11).

[114] M.Vlasse, C.Parent,R.Salmon,G.Le Fleur,P.Hagenmuller. Solide state chimistry.V:35 1980.P(318-324).

[115] K. Yamashita, H. Owada, T. Umegaki, T. Kanazawa, K. Katayama, Solid State Ionics, 40-41, 918 (1990).

[116] Y. Komine, K. Sato, Fine Ceram. Rep, 1, 4 (1983).

[117] M. Nagai, T. Nishino, Solid State Ionics, 28-30, 1456 (1988).

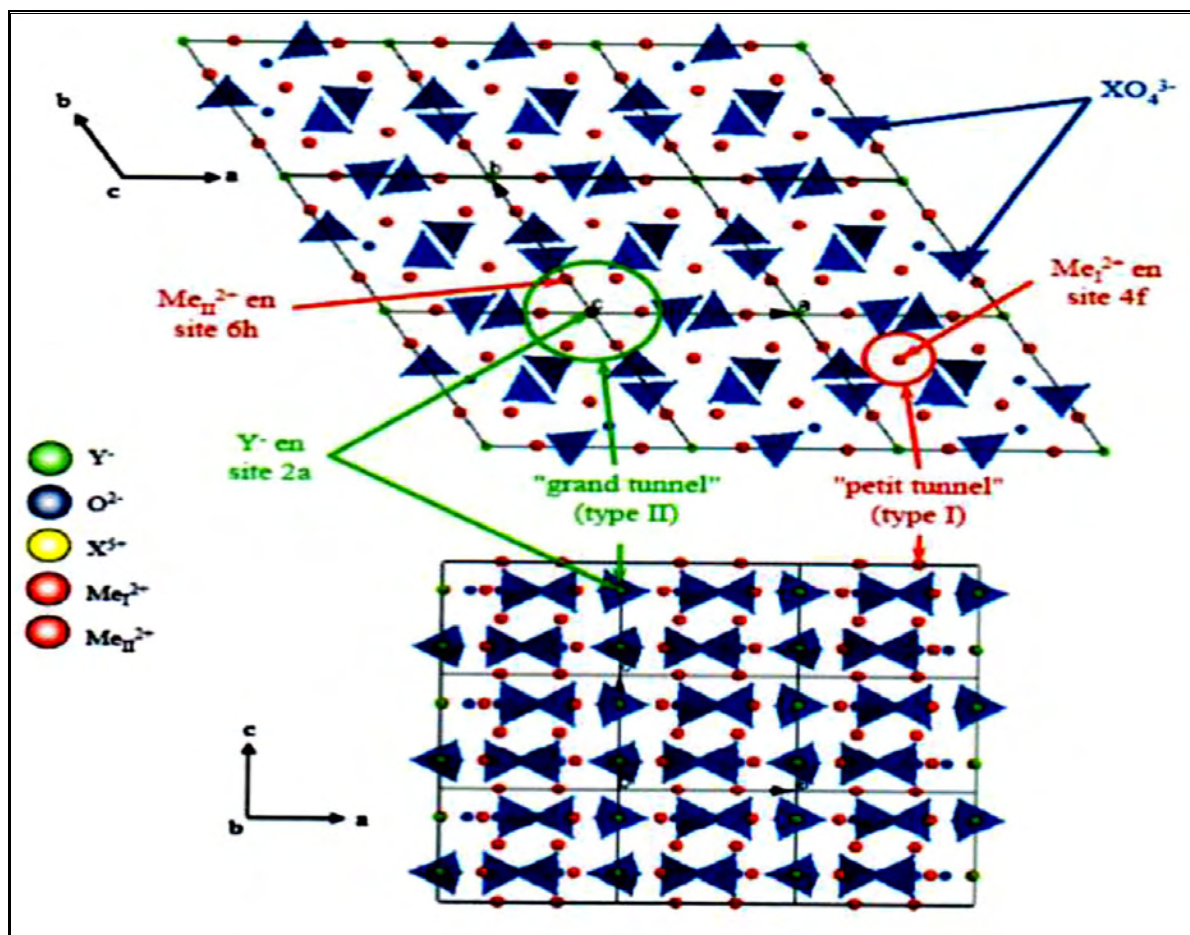


Fig.11 : Projection of the apatitic structure $[Me(I)]_4[Me(II)]_6^{6h}(XO_4)_6Y_2$, along the c -axis on the (001) plane.

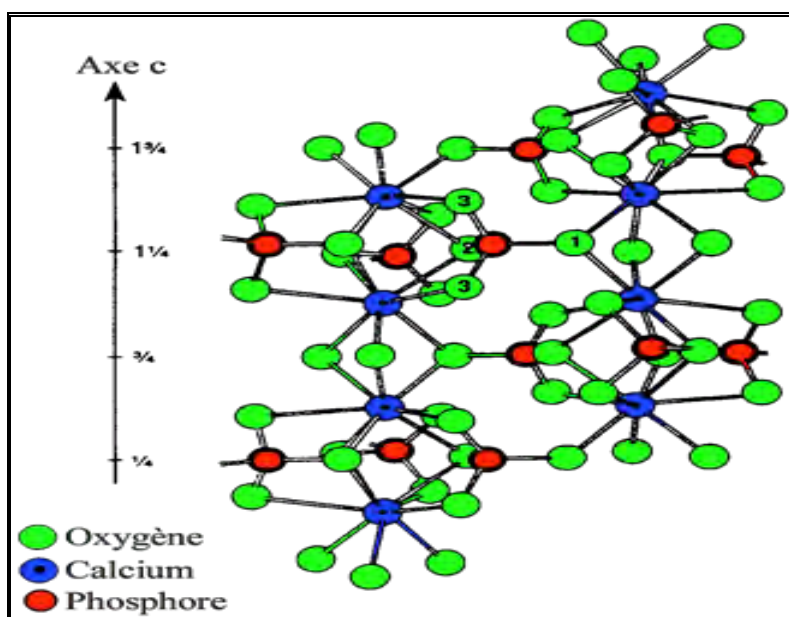


Fig.12: Partial view of the columns $M(4f)-(PO_4)$, the represented axis, parallel to the c - axis, gives the dimension of the different atomic layers ^[118].

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The first type of cations 'Me', four per mesh, is located on the positions (4f). These cations have a coordination sphere of (C_{3v}) symmetry. They are noted 'Me_I' at the '4f' site. They are coordinated to nine oxygen atoms belonging to the groups (XO_4^{3-}), [Fig.13](#) [120]. The corresponding cavity has a diameter of about 2.5 Å in the case of phosphocalcic apatites. The second type of cations 'Me' is located at the positions (6h), at the edge of the tunnel which develops along the helical stellar axis of the network. These cations noted as 'Me_{II}' at the '6h' site, are six per mesh. The symmetry of their environment is (C_s) symmetry. They are grouped by three at the vertices, of equilateral triangles offset by an angle of 60° concerning each other along the 'z' axis and located at the '¼' and '¾' dimensions, [Fig.14](#) [119]. The coordination of these Me ions (6h) is equal to six, [Fig.15](#) [120]. The geometry of their environment is of the deformed pentagonal bipyramid type. The vertices are occupied by one O(1), one O(2), four O(3) and one anion of the 'Y' tunnel (Y: Fluorine, hydroxide, chlorine, bromine, iodine,...) ([Fig.14&15](#)). The diameter of the tunnel is 4.5 Å in the case of phosphocalcic apatite. It is greater than the tunnel diameter of the site (I) ([Fig.11](#)). They give the apatite lattice ion mobility properties allowing ion exchange, or even host lattice properties, as the tunnels can be occupied by small molecules such as 'H₂O' or glycine [121]. 'Y' anions are distributed along the axis of these tunnels. Their location along this axis varies according to their nature ([Fig.14](#)). A physicochemical study on apatites has shown that the ions located in these tunnels are poorly bound to the rest of the network [120]. These ions generally have high mobility and can be easily substituted [122].

[118] C. Vignoles, Thèse, Toulouse, Université Paul Sabatier (1973).

[119] G. Bonel, Thèse, Toulouse, (1970).

[120] R. A. Young, J. C. Elliot, Arch. Biol., 11, 699 (1966).

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[124] L. Eddahby, A. Berrada, A. Boukhari, and E. M Holt., Eur. J. Solid State Inorg. Chem., t34, 527 (1997).

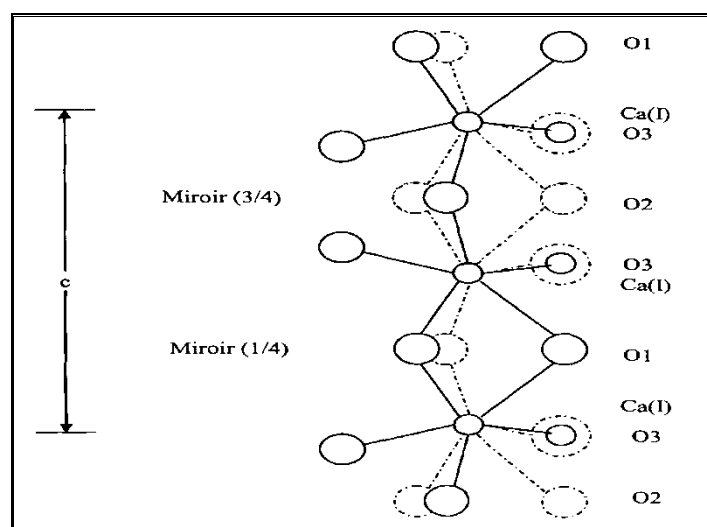


Fig.13: Environment of calcium cations $M(4f)$ in phosphocalcic fluoroapatite ^[120].

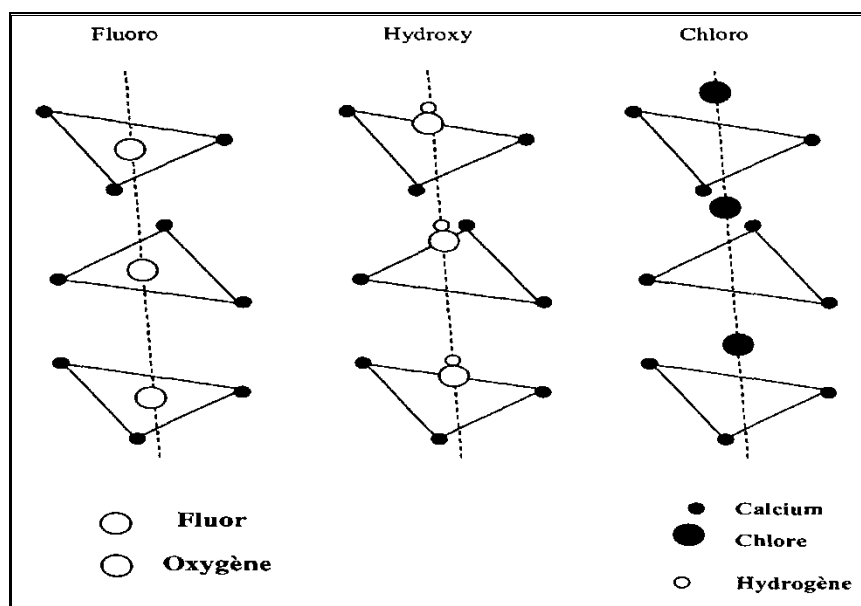


Fig.14: Environment of F^- , OH^- , Cl^- ions concerning $Ca(6h)$ triangles along the helical stellar axis ^[119].

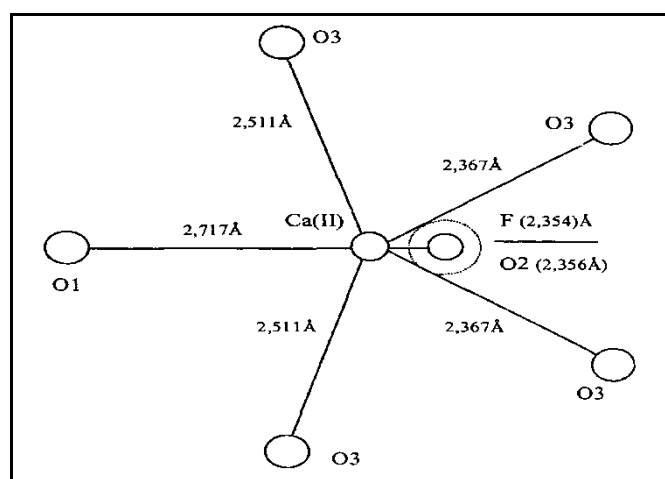


Fig 15: Environment of calcium cations $M(6h)$ in phosphocalcic fluorapatite ^[120].

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The two tunnels of the apatitic structure give these materials important physicochemical properties. Taking into account these two different crystallographic sites, the apatite must be described according to the following formula: $[\text{Me(I)}]_4^{4f}[\text{Me(II)}]_6^{6h}(\text{XO}_4)_6\text{Y}_2$. In the apatite network, several types of connections are observed. In the case of $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$, between ' Ca^{2+} ' and the oxygen of ' PO_4^{3-} ', the bonds are considered to be purely ionic. On the other hand, 'P-O' bonds have a distinctly covalent character, Kislovsklj and Coll [123] showed that 'Me-Y' bonds have an ionocovalent character.

A.VI. Possible substitutions in the apatitic network.

The integration of toxic heavy metals, such as Pb, V, As, Zn, Cd, etc., into the crystal structure of apatites is a possible solution to the problem of storing these pollutants. For example, apatite-type compounds applied to the treatment of lead-contaminated soil and water (Chen et al, 1997; Zhang and Ryan 1999; Ioannidis and Zouboulis 2003), other apatite types are also applied to the common stabilization and recycling of incineration ashes containing industrial wastes (Taylor et al. 1998; Valsami-Jones 1998; Crannell et al. 2000; Dong et al. 2002; Dong and White 2004a, b; Kim et al. 2005).

Natural apatite generally contains a large number of trace elements. A complete inventory of these elements would be time-consuming because apatite alone is likely to contain a significant concentration of elements (one-third of elements in the periodic table). For example, more than 35 trace elements are reported in some natural apatites. Table.11 summarizes some possible substitutions in the apatite structure.

Table.11: Some examples of possible substitutions in the apatite structure.

General formulation	Me_5	$(\text{XO}_4)_3$	Y
stoichiometric substitution	$\text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}, \text{Pb}^{2+},$	$\text{PO}_4^{3-}, \text{AsO}_4^{3-}, \text{VO}_4^{3-}, \text{MnO}_4^{3-},$	$\text{F}^-, \text{Cl}^-, \text{OH}^-, \text{Br}^-,$
non-stoichiometric substitution	$\text{Ln}^{3+}, \text{La}^{3+}, \text{Nd}^{3+}, \dots$ Zr^{4+} Cs^+ N^{a+} Al^{3+} lacunar	SO_4^{2-} CO_3^{2-} PO_4^{3-} HPO_4^{3-} SiO_4^{4-} GeO_4^{4-}	O^{2-} CO_3^{2-} Lacunar

Introduction of the Chapters

These substitutions have been the subject of much work [52, 119-123, 125-127]. These studies have highlighted several types of exchanges in the apatitic structure. Three types of substitution are defined:

- ☞ The first type consists of an exchange of 'Me²⁺', 'XO₄³⁻' or 'Y⁻' ions with other ions of the same charge but of different size. These apatites remain stoichiometric and only a slight deformation of the mesh is observed.
- ☞ The second type of substitution corresponds to the replacement of an ion by another ion of a different charge. The implementation of this substitution requires charge compensations, anionic or cationic or both, to ensure the electroneutrality of the crystal lattice. These ion exchanges are carried out :
 - Either in a coupled way by ensuring the stoichiometry of the material, as in the case:
$$(Ca^{2+}, PO_4^{3-}) \longrightarrow (Ln^{3+}, SiO_4^{4-}).$$
 - Or by the creation of the gaps leading to so-called non-apatite formulations stoichiometry, this variation in stoichiometry leads to a variation in the physicochemical properties of the material. This is, for example, the case of phosphocalcic hydroxyapatite which, when it is substituted by carbonate groups (Ca_{10-x}□_x(PO₄)₆(CO₃)_x(OH)_{2-x}□_x, then symbol '□' represents a Lacunar), sees its dissolution rate increase with the quantity of Lacunars.
- ☞ The last substitution by ions of different valences, such as the case of 'Pb²⁺' and 'Bi³⁺', not only causes mesh distortions but also the creation of point defects called anionic gaps, to compensate for the charges. It should be noted that these point defects appear only on sites occupied by 'Me²⁺' or on sites occupied by 'Y⁻'.

[125] G. C. Maiti, F. Freud; J. Chem. Soc. Dalton Trans. 949 (1981).

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[127] I. Mayer, A. Semadja, V. Weiss, J. of Solid State Chemistry, 34, 223 (1980).

1. Substitution in 'Y':

It is possible to consider the partial or total replacement of the anion located in the tunnel by other anions such as chlorine, fluorine... to obtain, for example, chlorapatite or fluorapatite. The 'Y' ions located in the tunnels are relatively unrelated to the rest of the network which constitutes the stable structure. The size of the tunnel gives them high mobility and therefore allows easy substitutions [128,129].

In the case of fluorapatite of the formula $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$, the fluorine can be replaced by other halogens (Cl^- , Br^- , I^-) or by the hydroxyl group ' OH^- ' [130-132]. When the fluorine substituent has a larger radius such as ' OH^- ', Cl^- , I^- , Br^- ', it no longer occupies the same position (Fig.14). Several series of apatites have been prepared, in particular the compound of general formula $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_{2-x}\text{F}_x$ [125,126]. R. Walleys [43, 133, 134] carried out total substitutions of the hydroxyl group of hydroxyapatites by fluorine, by reacting hydroxyapatite with calcium fluoride.

The substitution of a 'Y' ion located in the tunnels by an anion of the same charge and different size leads to variations in parameter (a) and parameter (c) in opposite directions [135, 136]; for example, the substitution of a 'Y' ion by a larger ion leads to an increase in parameter (a) and a decrease in parameter (c). A structural study of the location of ' Cl^- ' in phosphate chlorapatites such as $\text{Ba}_5(\text{PO}_4)_3\text{Cl}$ [137], $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$ [138], $\text{Sr}_5(\text{PO}_4)_3\text{Cl}$ [100] and $\text{Cd}_5(\text{PO}_4)_3\text{Cl}$ [139], shows that ' Cl^- ' is located at (0,0,0) in $\text{Ba}_5(\text{PO}_4)_3\text{Cl}$ and occupies the position (0,0,0.06) along the (c) axis in $\text{Sr}_5(\text{PO}_4)_3\text{Cl}$. while ' Cl^- ' occupies the centre of the metal triangle formed by 'Cd and Mn', (0,0,1/4), in $\text{Mn}_5(\text{PO}_4)_3\text{Cl}_{0.9}(\text{OH})_{0.1}$ [140] and $\text{Cd}_5(\text{PO}_4)_3\text{Cl}$.

[128] Samec, Contribution à l'Etude des Echangeurs d'ion de Structure Apatitique, Thèse, Université de Toulouse, (1965).

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[130] E. R. Kreidler and F. A. Hummel, the American Mineralogist, 55, 167 (1970).

[131] G. Montel, G. Bonel, J. C. Trombe, J. C. Heughebaert et C. Rey, 1^{er} Congrès International des Composés Phosphatés, Rabat 17-21 Oct (1977).

[132] E. R. Kreidler : P. H. D Thèse, Michigan (1967).

This leads to the conclusion that the position of the 'Cl' atom in compounds of the $M_5(PO_4)_3Cl$ [135] type depends on the size of the ' M^{2+} ' ion. It occupies the (0,0,0) position when the radius of ' M^{2+} ' is larger than that of ' Ca^{2+} ' and the (0,0,1/4) position when the radius of ' M^{2+} ' is smaller than that of ' Ca^{2+} ', whereas in the case of ' Ca^{2+} ', 'Cl' occupies an intermediate position between (0,0,0) and (0,0,1/4).

When the fluorine substituent has a very large radius like the anion 'Cl', it does not necessarily occupy the same position; hence a change in crystallographic symmetry is envisaged. In lead apatite, the mirror is transformed into a sliding plane; the mesh becomes twice as large and has a monoclinic symmetry corresponding to the space group $P2_1/b$ [141-143] as in the case of some mineral species [144] or the case of phosphocalcic chlorapatite. The structure determination by Mackie [138] revealed that chlorine is on the snare axis, in the (0, 0, 0.38) and (0, 0, 0.88) positions instead of (0, 0, 1/4) and (0, 0, 3/4) positions. Chlorine is surrounded by three oxygen atoms while fluoride ions are in the centre of a triangle formed by calcium atoms.

2. Substitution in ' Me^{2+} ':

Cationic substitutions have been extensively studied in systematic investigations [145-155]. However, these substitutions are either total or partial. This work has specified the distribution of cations at each of the two possible sites since the two positions are not equivalent. The substitution could be done on the four atoms of the site (I) or the six atoms of the site (II), which would easily explain the ' $Ca(4f)Me(6h)$ ' or ' $Ca(6h)Me(4f)$ ' formations. [156]. Nevertheless, the number of sites corresponding to a crystallographic position alone does not allow us to deduce the distribution of cations and their evolution during a progressive substitution. It also does not allow explaining the limits of the domains of existence of solid solutions when the substitution is partial. This requires analytical techniques to locate the positions of the cations in question.

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Substitution at cationic sites is feasible, as calcium can be totally or partially substituted by divalent cations (Sr^{2+} , Ba^{2+} , Pb^{2+} , Fe^{2+} , Cd^{2+} , etc ...) [8-22,115-141,145-161]. To understand the effect of cationic substitution on the formation and stability of these apatites, studies have been done [8, 9, 118]. The results showed that some cations can easily substitute for ' Ca^{2+} ' ions. These results in changes in the lattice parameters that vary according to the ion radius of the cations compared to that of the ' Ca^{2+} ' ion.

The study on stabilization of the $P6_3/m$ structure of chlorapatites and fluorapatites, carried out by Kriedler and Hummel [130], deduced the limiting size of the ions that can substitute calcium. According to these authors, the ions capable of occupying the cationic sites must have ' r_{Me} ' radii between 0.95 and 1.35Å for chlorapatites and between 0.80 and 1.35Å for fluorapatites.

In the structure of $\text{Me}_{10}(\text{PO}_4)_6\text{Cl}_2$, the location of ' Cl ' is highly dependent on the size of ' Me^{2+} ': it occupies position (2b) if ' Me^{2+} ' is larger than ' Ca^{2+} ' (this is the case of Sr^{2+} and Ba^{2+}), and position (2a) if ' Me^{2+} ' is smaller than ' Ca^{2+} ' (this is the case of Cd^{2+}). Taking into account the coordination of the ' Me^{2+} ' ions, and thus the appropriate ion radius, the following values for the ratios $r(\text{Me})/d(\text{Me-Me})$ are given in Table.12:

-
- [133] R. Wallaey, G. Chaudron, C. R. Acad. Sci., 230C, 1867 (1950) et 231C, 355 (1950).
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 - [149] J. L. Lacout, J. Assaran, J. C. trombe, C. R. Ac. Sci. Fr., Série II 5, 298(1984).
 - [150] J. L. Lacout, M. Mikou, Ann. Fr., 14, 9 (1989).

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Table.12: radii(Me)/distance (Me-Me) ratio of some Me^{2+} cations.

r_{Me}/d_{Me-Me}	Me^{2+}
0.215	Cd^{2+}
0.260	Ca^{2+}
0.282	Pb^{2+}
0.288	Sr^{2+}
0.315	Ba^{2+}

This means that in the case of $Cd_{10}(PO_4)_6Cl_2$ the triangle formed by the ' Cd^{2+} ' is vague enough for the 'Cl' ions to be placed in its centre, whereas in the case of ' Sr^{2+} ' and ' Ba^{2+} ', the triangle is narrower, so it will move the 'Cl' ions from $z = 1/4$ to $z = 1/2$. Lead apatite is located closer to strontium and barium.

3. Substitution in ' XO_4^{3-} ':

The substitution of the ' PO_4^{3-} ' group by other trivalent groups (VO_4^{3-} , AsO_4^{3-} ...) is also possible. Indeed, we know the vanado-apatites [162] or arsenic-apatites in which the PO_4^{3-} groups are substituted respectively by the VO_4^{3-} or AsO_4^{3-} groups.

In the inorganic system according to $Cd_5(XO_4)_3Y$ [163] where 'X' = As, V or P and Y = Br, Cl or I', the parameter (c) is smaller than in the calcium apatite, respectively 6.504Å, 6Å and 7.66Å [164]. This leads to the conclusion that the interatomic distances between the halogens (Y-Y) are smaller than the sum of their ionic rays. The structural refinement results of the compounds $Cd_5(PO_4)_3Cl$ [139], $Cd_5(PO_4)_3Br$ and $Cd_5(VO_4)_3Br$ [163] indicate that the formulae for these compounds are written as follows $Cd_{5-x}(XO_4)_3Y_{1-2x}$ where 'x' can reach the maximum value allowing the stress due to the distances between halogens to be removed. The apatite $Sr_{10}(CrO_4)_6F_2$ has been synthesized [165], and the resulting compound has an apatite structure with a distorted CrO_4^{3-} tetrahedron.

[151] S. Mehta, D. R. Simpson, Am. Miner., 60, 134 (1975).

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4. Substitution in ' $Y \rightarrow Y^{2-} + \square(\text{Lacunar})$ ':

Another type of substitution on the secondary axis is also possible, it is the substitution of an anion ' Y ' by another one of a different charge. Indeed, in natural apatites, francolite is a fluorinated apatite ($\text{Ca}_5(\text{PO}_4, \text{CO}_3)_3\text{F}$), which contains traces of carbonate. Several series of apatite has been prepared by substituting the ' Y ' ions located in the tunnels by bivalent ' Y^{2-} ': O^{2-} , S^{2-} or even carbonate groups. Indeed, we know $\text{Ca}_{10}(\text{PO}_4)_6\text{S}$ [52] and $\text{Ca}_{10}(\text{PO}_4)_6\text{O}$ [159]. The oxyapatite of formula: $\text{M}_{10}(\text{PO}_4)_6\text{O}\square$ (with $\text{M} = \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}, \text{Pb}^{2+}$) [166-168] is thus prepared. Note that the tunnel can receive several types of anions simultaneously.

Other reactions can be carried out from hydroxyapatite. Walley prepared for the first time a carbonated phosphocalcic apatite, the substitution mechanism obtained is written $2(\text{OH}^-) \rightleftharpoons \text{CO}_3^{2-} + \square(\text{Lacunar})'$ [134]: this made it possible to obtain the following compound $\text{Ca}_{10}(\text{PO}_4)_6(\text{CO}_3)_{0.6}(\text{OH})_{0.8}\square_{0.6}$.

The localization of the carbonate ions in the tunnel increases the parameter (a) of the hexagonal mesh of the apatite ($a=9.4468(4)\text{\AA}$) compared to that of the initial hydroxyapatite ($a = 9.4302(5)\text{\AA}$). This evolution is the consequence of the presence, in the tunnel, of ions that are larger than OH^- [119] ions.

Similarly, oxy-hydroxyapatites are also found. However, the synthesis of phosphocalcic oxyapatite $\text{M}_{10}(\text{PO}_4)_6\text{O}_x\square_x$ [140] is very delicate and in practice, a mixture of oxy-hydroxyapatites of formula $\text{M}_{10}(\text{PO}_4)_6(\text{OH})_{2x-x}\text{O}_x\square_x$ is obtained, with ($0 \leq x \leq 1$). Oxy-hydroxyapatites are highly reactive and thermally metastable and react significantly with air humidity.

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5. Substitution in ' $Y^{2-} + \square$ (Lacune) $\rightarrow 2Y'$ ':

Walley has prepared a phosphocalcium carbonated apatite [134], this preparation follows the ' $2(OH) \rightleftharpoons CO_3^{2-} + \square$ (Lacunar)' mechanism which gave rise to the following compound $Ca_{10}(PO_4)_6(CO_3)_{0.6}(OH)_{0.8}\square_{0.6}$. During the treatment, carbonate ions are substituted for hydroxide ions. To check the fixation of carbonate ions in the tunnel, this author treated the carbonated hydroxyapatite obtained with calcium fluoride. He obtained a fluorapatite with fluorine substituting hydroxide ions and carbonate ions. This evolution was followed by thermogravimetry. It was carried out according to the inverse mechanism of the above:



6. Substitution in ' $Y + M^{2+} \rightarrow M^+ +$ (Lacunar)':

Indeed there are apatites in which the 'Y' anion is absent [115]. These lacunar apatites are well known, for example, those with fluorine gaps [8, 9, 119-126]. The number of gaps can be more or less important and lead to interesting electrical, catalytic and adsorption properties. Non-occupation of some of the sites (2a) has been reported in various series of substituted apatites [8, 166-168].

7. Substitution in ' $Y + (XO_4)^{3-} \rightarrow (X'O_4)^{2-} + Y^{2-}$ ':

Due to the existence of two anionic sites in the apatite tunnels, the number of bivalent ions (O^{2-} , S^{2-} or CO_3^{2-}) can theoretically be increased. This requires compensation for the excess negative charge by introducing bivalent groups in substitution for ' PO_4^{3-} ' ions or trivalent cations in the cationic sites.

8. Substitution in ' $XO_4^{3-} + M^{2+} \rightleftharpoons X'O_4^{2-} + M^+$ ':

There are also sulfoapatites $Na_6Ca_4(SO_4)_6F_2$ in which the group ' PO_4^{3-} ' is substituted by the group ' SO_4^{2-} '. The ' PO_4^{3-} ' groups can indeed be substituted by the following bivalent groups (CO_3^{2-} , SO_4^{2-} , HPO_4^{2-} , ...) [169-171].

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Often substitutions with anions of different charge are accompanied by cationic substitution. Thus a partial substitution of the group 'PO₄³⁻' by 'SO₄²⁻' gives rise to the family of compounds, Ca_{10-x}M_x(PO₄)_{6-x}(SO₄)_xF₂, prepared by reaction in the solid-state, where 'M' = Li⁺ or Na⁺ with 0 < x < 6. The electrical neutrality of the corresponding compounds is ensured by partial replacement of the torque (Ca²⁺, PO₄³⁻) by the torque (M⁺, SO₄²⁻) [172].

Apatites with a 'Me/X' ratio of < 10/6 have cationic and anionic deficiencies, e.g. apatitic tricalcium phosphate [169]. Ca₉(PO₄)_{6-x}(HPO₄)_x(OH)_x where 0 < x < 1 where the Ca/P ratio is 1.50 or the carbonated apatite Ca₈(PO₄)₅(CO₃)₂ [173] where the Ca/P+C ratio is 8/6.

9. Substitution in 'XO₄³⁻ ↔ XO₄²⁻ + X''O₄⁴⁻' :

The replacement of the PO₄³⁻ group by a tetravalent group (SiO₄⁴⁻, GeO₄⁴⁻...) [172] is also possible. Typical examples of these compounds are Pb₁₀(SiO₄)₃(SO₄)₃F₂ and Ca₁₀(SiO₄)₃(SO₄)₃F₂. Minerals with this formula are called 'ellestadite'. The latter compound crystallizes in the monoclinic space group system *P2₁/m* [174].

10. Substitution in 'M²⁺ + (XO₄)³⁻ → M³⁺ + X'O₄⁴⁻' :

In natural apatites, of the most common compositions, corresponding to calcium phosphates: Ca₁₀(PO₄)₆(OH, F, Cl)₂, there are many coupled substitutions. For example, when a coupled substitution is carried out by exchanging a 'Ca²⁺' with rare earth 'Ln³⁺' and a 'PO₄³⁻' ion with a 'SiO₄⁴⁻' ion [175], the mineral is called britholite (Ca, Ln)₁₀(PO₄, SiO₄)₆F₂.

In this case the exchange mechanism corresponds to: Ca²⁺ + (XO₄)³⁻ ↔ Ln³⁺ + XO₄⁴⁻

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11. Substitution in anionic lacunar apatites $Pb_{4.5-x}M_x(XO_4)_3Y_0$:

It is possible to provide both cationic and anionic gaps in the same material, and even to have no monovalent anion in the apatite structure, this is the case of ; $Pb_8Na_2(PO_4)_6\Box Y_2$ [54], $APb_4(PO_4)_3\Box Y_0$ (A : Na^+ , K^+ or Ag^+) [6,25,26], $Na_{1-x}K_xPb_4(PO_4)_3\Box Y_0$ [24], $Na_{1-x}K_xPb_4(VO_4)_3\Box Y_0$ [29], $Na_{1-x}K_xPb_4(AsO_4)_3\Box Y_0$ [30] and $Na_{1-x}K_xPb_3Ca(PO_4)_3\Box Y_0$ [31,32]. All possible substitutions can be made on monovalent, divalent and also pentavalent cations, provided that the concentration of ' Pb^{2+} ' cations remains sufficient to ensure the stability of the lacunar network. Indeed, only lead apatites are known to be deficient in anions (Table.6).

12. Cationic Site Occupancy Preference:

Radiocrystallographic and thermodynamic studies have been made concerning the occupancy preference of the two non-identical sites of the apatitic structure. By substituting calcium with rare earth elements [176], the '6h' site is best occupied first, although this depends on many factors including bond lengths, stoichiometry and the type of the 'Y' mobile anion. Khattech et al [177] have shown, by studying the substitution of calcium $R(Ca^{2+})=0.99\text{\AA}$ by strontium $R(Sr^{2+})=1.6\text{\AA}$ in fluorapatite, that the substitution is preferentially oriented towards the 4f site. Moreover, although the X-ray diffraction shows a monotonous evolution with the substitution, without discerning the occupancy preference, the thermochemical results illustrate this well and cause the bond energies to be affected more than the crystal lattice geometry.

B. Bibliography on heavy metals.

B.I. Introduction.

Generally, heavy metals are natural metallic elements (metals or in some cases metalloids) characterized by a high density. Because of their increasing presence in the environment, their persistence and their widespread toxicity throughout the biotope, heavy metals have a prominent place in ecotoxicological research [178].

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The classification of heavy metals is often discussed because some toxic metals are not particularly heavy, for example, Zinc, while not all toxic elements are metals (e.g. arsenic is a metalloid). For these reasons, most scientists prefer the term trace elements or metallic trace elements to heavy metals [179]. In environmental science, the heavy metals associated with the concepts of pollution and toxicity are generally: arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), manganese (Mn), nickel (Ni), lead (Pb) and tin (Sn) [180]. From a biological point of view, two types of metals can be distinguished according to their physiological and toxic effects: essential metals and toxic metals.

- ☞ Essential metals are essential trace elements for many cellular processes and are found in very low proportions in biological tissues. For example, lack of sufficient amounts can limit the growth of certain organisms such as algae. Some of these elements can become toxic when the concentration exceeds a certain threshold, such as copper (Cu), nickel (Ni), zinc (Zn) and iron (Fe). For example, zinc (Zn) at the milli-molar concentration is a trace element that is involved in many enzymatic reactions (dehydrogenases, proteinase, and peptidase) and plays an important role in protein, carbohydrate and lipid metabolism [178].
- ☞ Toxic metals have a polluting character with toxic effects on living organisms even at low concentrations. They have no known beneficial effects on the cell, the case of mercury (Hg) and cadmium (Cd) [178]. Thus, in excessive quantities and depending on the chemical forms in which they are found, their toxicity can pose health problems and limit the use of water resources. It is therefore necessary to measure and control the concentrations of these substances [181].

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[179] G. Miquel, *Rapport sur les effets des métaux lourds sur l'environnement et la santé*, Office parlementaire d'évaluation des choix scientifiques et technologiques, N°2979 Assemblée Nationale, N° 261 Sénat-2001(365p)

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Metals enter the environment through natural processes or are derived from human activities. They are primarily arsenic, cadmium, chromium, copper, mercury, nickel, lead, selenium and zinc. In addition, these metals are released from domestic discharges, storm water and runoff, industrial and artisanal discharges, and atmospheric deposition. They are necessary for the proper development of plants. However, if they are present in too large quantities, they present a risk that must be estimated [182]. Particular attention has been paid to cadmium (Cd) and mercury (Hg), which may present a risk to the consumer because of their ubiquitous nature and their toxicity at low doses during prolonged exposure in relation to their persistence [183]. The consequences of this ubiquity would be less if it were not associated with a direct risk of contamination for humans. Humans can be at all levels of the distribution cycle of trace metal elements in the environment. He will absorb them by different routes and become himself a reservoir of these trace elements with probable consequences on his health [180].

However, anthropogenic factors, such as mining activity, can lead to a significant increase in metal concentrations in the water and sediments of the affected area [184]. Indeed, the main types of anthropogenic pollution responsible for the increase in heavy metal fluxes are first and foremost air pollution from urban and industrial activities (factory discharges, exhaust gases, etc.). Secondly, industrial pollution from human activity production plants, particularly chemical production and metallurgy. Finally, pollution linked to agricultural activities, from which the products intended to improve the physicochemical properties of the soil is often richer in heavy metals (for example fertilizers, composts and sewage sludge) [178].

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Introduction of the Chapters

Human activity has not resulted in any change in the volumes of heavy metals. Above all, it has changed the distribution of new modes of dispersion (smoke, sewers, cars, etc.) [185]. Table.13 shows the different industrial and agricultural sources of metals in the environment [186].

Table.13: Industrial and agricultural sources of metals in the environment ^[186].

Use	Metals
Batteries and other electrical appliances	Cd, Hg, Pb, Zn, Mn, Ni
Pigments and paints	Ti, Cd, Hg, Pb, Zn, Mn, Sn, Cr, Al, As, Cu, Fe
Alloys and welds	Cd, As, Pb, Zn, Mn, Sn, Ni, Cu
Biocides (pesticides, herbicides)	As, Hg, Pb, Cu, Zn, Mn, Sn
Catalysing agents	Ni, Hg, Pb, Cu, Sn
Glass	As, Zn, Sn
Fertilizers	Cd, Hg, Pb, Al, As, Cr, Mn, Sn, Ni, Cu
Plastic materials	Cd, Sn, Pb Cd, Sn, Pb
Dental and cosmetic products	Sn, Hg
Textiles	Cr, Fe, Al
Fuels	Ni, Hg, Cu, Fe, Mn, Pb, Cd
Refinery	Ni, V, Pb, Fe, Mn, Zn

B.II. Cadmium.

Cadmium is a relatively rare element with no related biological function. It appears in the environment mainly as a compound of minerals in the earth's crust. Industrial use of cadmium has accelerated the biological mobilization and transport of this element, exceeding the amounts involved in its natural cycle [187].

1. Physico-Chemical properties.

Cadmium is a chemical element whose symbol is 'Cd'. It has the atomic number 48. It is a white, soft and malleable metal, so it is commonly classified as heavy metal. This element is naturally associated with zinc in some ores. Cadmium was known until the 19th century (in 1818 the discovery of cadmium by the chemists Hermann and Stromeyer) when its Physico-chemical characteristics were revealed. Thereafter, it is used in several fields, in particular in the manufacture of batteries [188].

[183] B.K.M. Petit, Actualisation des connaissances sur les éléments biologiques et minéraux persistants dans les boues des stations d'épuration : impact sur la santé publique, Thèse, E.N.V. d'Alfort Paris (2007).

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Cadmium is characterized by high corrosion resistance, low melting point and good electrical conductivity. Its by-products have good resistance to high temperatures. Thus, it has chemical characteristics close to those of calcium, in particular the ionic radius, thus facilitating its penetration into organisms [189]. Cadmium is an element found in the aquatic environment in various physical (dissolved, colloidal, and particulate) and chemical (mineral or organic) forms. A set of physicochemical environmental variables (salinity, pH, redox potential, sedimentological characteristics, geochemical nature of particles, chloride concentration) govern cadmium transformations in the environment [190,191].

2. Use.

Cadmium has multiple uses: in particular in television screens, nuclear reactor control rods, dyes (enamel, glaze). It is used in the composition of many low-melting alloys (welds, solders) and the manufacture of certain accumulator batteries [192]. But its main uses are those of these compounds which concern anti-corrosion coatings (applied to steel by cadmium plating, cadmium protects against corrosion, particularly saline) [193], it is used in the manufacture of stabilizers for plastics [189].

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- ☞ Cadmium chloride (CdCl_2) is used in the production of plastic stabilizers and pigments, in the preparation of cadmium sulphide, in chemical analysis, photography and dyeing [194], in the manufacture of special mirrors, vacuum tubes and as a lubricant [195].
- ☞ Cadmium oxide (CdO) is mainly used in the manufacture of nickel-cadmium batteries [194], in the manufacture of resistant enamels, in heat-resistant plastics, in electroplating baths [195].
- ☞ Cadmium sulphate (CdSO_4) is used as a raw material in the manufacture of pigments and stabilizers for plastics [194]. It is also used in the manufacture of other cadmium compounds and fluorescent materials [195].
- ☞ Cadmium sulphide (CdS) is mainly used in pigments, including fluorescent and phosphorescent pigments, as a dye for textiles, paper, rubber, plastics, glass and enamels [194], and in the electronics industry [195].

3. Sources of cadmium contamination.

Cadmium released into the atmosphere comes from natural and anthropogenic sources. Cadmium in the earth's crust can be dispersed into the air by the entrainment of particles from the soil and by volcanic eruptions. However, industrial activities such as non-ferrous metal refining, combustion of coal and petroleum products, household waste incinerators and steel metallurgy are the main sources of atmospheric releases. Cadmium can enter aquatic systems through weathering and natural erosion through soil leaching (phosphate fertilizers). Also, cadmium is released from industrial landfills and the treatment of industrial and mining effluents [196].

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4. Cadmium toxicity.

Cadmium is very toxic in all its forms (metal, vapour, salts, and organic compounds) and even at low concentrations. It does not appear to be biologically essential for the metabolism of living organisms [197]. In humans, it causes in particular kidney problems where the accumulation takes place over very long periods (50 years) [198]. The main cause of human exposure to cadmium is diet (fish, bivalve molluscs, plants including vegetables rich in fibre) [199, 200].

It causes an abnormal loss of protein in the urine (proteinuria) and causes urinary dysfunction in the elderly [196]. It should be noted that in addition to food and drink, smoking is an important source of cadmium noted in all epidemiological studies [201]. The toxic effects of cadmium are not only for humans but also for plants and animals [202]. Other problems that cadmium can cause are Diarrhea, severe stomach pain and vomiting, Bone fracture, Reproductive failure and possibly even infertility, Central nervous system problems; Immune system problems; Psychological disorder; Probably DNA damage or cancer development [203].

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5. Methods of analysis for cadmium.

Spectroscopic techniques are often capable of providing qualitative and quantitative information on the elemental composition of a sample. Indeed, they are widely used for the analysis of cadmium in different matrices such as inductively coupled plasma mass spectrometry (ICP-MS), cold vapour atomic absorption spectrometry (CV-CAAS) and atomic fluorescence spectrometry (AFS) [204-207].

Electrochemical techniques also allow the determination of trace amounts of cadmium and the achievement of remarkable sensitivities [208,209], especially with the use of modified electrodes. Consequently, electrochemical techniques offer the advantage of being fast, reproducible and inexpensive with simple instrumentation [210]. Thus, the concept of modified electrodes has continued to be an important research topic for the determination of cadmium, in particular, the use of carbon-based electrodes modified with composites such as apatites [211]. These minerals have many properties that are of particular interest for these applications, namely: the capacity to receive a very large number of ions, chemical stability and thermal stability.

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6. Mechanisms of cellular protection against the toxicity of cadmium and lead.

To counter toxicity, the cell has developed certain defence mechanisms against the stress caused by heavy metals such as (Cd, Pb,..., etc). The main strategy is simple: the sequestration of free ions prevents them from disrupting the normal course of cellular functions. Cells respond to metal contamination by inducing the transcription of genes that code for "defence" or "repair" proteins. These proteins can sequester metals to neutralize their toxic effects, fight the formation of reactive oxygen species, and repair (if not inhibited by cadmium). In general, proteins with thiol groups play a key role in cellular defence against cadmium toxicity [212].

Against the toxicity of 'Cd', three main strategies are well documented:

- The presence and induction of metallothionein (MTs) expression.
- Glutathione intervenes by forming conjugates with 'Cd and Pb' via its thiol group [213].
- Induction of the expression of the 'HSP70' group of proteins (heat shock proteins) is recognized as a cellular defence mechanism against various contaminants.

MT contains many sulfhydryl groups due to its rich cysteine content, allowing the binding of several 'Cd' atoms, thus reducing the stress caused by the presence of free ions [214], which perform various functions including the maintenance of homeostasis of essential metals and protection against the toxicity of many metals. The regulation of MTs synthesis takes place at the transcriptional level [215].

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Metallothioneins (MTs), discovered in 1957 by Margoshes and Vallee. These are small proteins encoded by genes that are classified into two groups (MT1 and MT2) [216], which allows them to complex metal cations by thiol groups and thus have a high metal content, thus decreasing the availability of cadmium in the cell and reducing its toxicity [217].

Metallothioneins influence the tissue transport and distribution of cadmium and its toxicity [218], and this biochemical signal may be useful as a biomarker of effects. By definition, a biomarker is a change in an observable and/or measurable parameter at the molecular, biochemical, cellular, physiological or behavioural level that indicates the present or past exposure of an individual to at least one polluting chemical [219].

Glutathione (GSH) is a tri-peptide formed from glutamic acid, cysteine and glycine (Glu-Cys-Gly) that not only acts as a scavenger of reactive oxygen species but also has functions in the regulation of intracellular redox status [220]. The GSH system is probably the most important cellular defence mechanism against oxidative stress in the cell [213]. Similar mechanisms are also synthesized by the cell to counter this type of stress [214].

The high molecular weight protein group 'HSP70' ("Heat-shock proteins"; 70 kDa) belongs to the family of stress proteins that are induced as a result of various pathophysiological conditions such as heat shock, oxidative stress, intoxication, heavy metal exposure and tissue trauma. The expression of all classes of inducible HSP is under the transcriptional control of "Heat-Shock Factor 1" (HSF1). HSF1 is a transcription factor constitutively expressed as a monomer in the cytoplasm of human cells. However, the binding of HSF1 to DNA is insufficient to induce transcription, as complete transcription requires hyperphosphorylation of HSF1 [221].

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B.III. Lead.

Lead is naturally present in the environment. However, most of the lead concentrations found in the environment are the result of human activities [222]. In general, fuels are the main source of lead emissions to the environment. However, there are other emission sources such as industrial processes and solid waste combustion. Long-term exposure to relatively low levels of lead or short-term exposure to high levels can seriously affect human health [222].

Lead is a greyish blue metal and is found primarily in primary deposits in eruptive and metamorphic rocks where it occurs mainly as a sulphide (galena) Fig.16. It is redistributed via alteration in all rocks as carbonate (cerusite), sulphate (anglesite) and can substitute for potassium in silicate rocks and phosphates. It is, however, a metal with very low water solubility and low geochemical mobility.



Fig.16: *Galena is the natural crystallized form of lead sulphide, with its cubic crystals with metallic splinters.*

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1. The Physico-chemical characteristics of lead.

Lead exists in the oxidation states (0), (+II) and (+IV), but in the environment, it is mainly in the (+II) state. The (+IV) state exists only under severe oxidizing conditions. The (+II) degree is stable under practically all environmental conditions.

Lead is rarely in its elemental form. It exists in metallic, inorganic and organic forms. It takes an inorganic form when it is combined with certain compounds to form lead salts. Among the most common lead salts are chlorides, chromate, nitrate, phosphates, and sulphates. Organic lead is most commonly found in the form of tetramethyl lead and tetraethyl lead, two additives used to increase the octane number in gasoline [223]. The main physical and chemical characteristics of lead are given in Table.14.

Table.14: Physico-chemical characteristics of lead.

Atomic number	82
Atomic mass	207,2 g.mol ⁻¹
Electronegativity of Pauling	1,8
Density	11,34 g.cm ⁻³ à 20°C
Melting Temperature	327 °C
Boiling temperature	1755 °C
Atomic ray (Van der Waals)	0,154 nm
Ion beam	0,132 nm (+2) ; 0,084 nm (+4)
Isotopes	4
First ionization energy	715,4 kJ.mol ⁻¹
The energy of the second ionization	1450,0 kJ.mol ⁻¹
Third ionization energy	3080,7 kJ.mol ⁻¹
Fourth ionization energy	4082,3 kJ.mol ⁻¹
Fifth ionization energy	6608 kJ.mol ⁻¹
Standard potential	(Pb ²⁺ / Pb)= - 0,13 V ; (Pb ⁴⁺ / Pb ²⁺)= -1,5 V

2. Industrial uses.

World demand for lead increased from 4.5 Mt in 1970 to 6.7 Mt in 2003 [223]. Lead has interesting properties such as flexibility, resistance to corrosion and certain types of radiation, and high density, which make it useful for a variety of uses. Its flexibility and low melting temperature make it easy to work with. Its capacity for corrosion resistance makes it a suitable sealing material for use in construction (lead sheet for roofs, lead paints) and for

Introduction of the Chapters

equipment in contact with acids (lead-acid batteries, acid production). Its high density makes it effective protection against radiation or noise. The main applications of lead are the following:

- Lead-acid batteries.
- Pigment and other compounds (including stabilizers in some plastics and rubbers).
- Plaminates and extruded products (lead sheet), mainly used in the construction sector, especially for roofs.
- Alloys, mainly tin-lead alloys (solder), mainly in the electronics industry.
- Glass and ceramics.
- Paints.
- Cable sheaths.

3. Sources and pollution of lead in the environment.

3.1. Natural sources:

Lead is present in the earth's crust and all compartments of the biosphere. The average lead concentration in the earth's crust is estimated to be in the range of 13-16 mg/kg. Emissions of lead to air from wind-borne volcanic dust are estimated to be between 540 and 6000 tonnes/year [223]. Other natural processes, such as soil degradation and erosion (containing 50-75 mg lead per kg of soil) and forest fires, contribute significantly to the release of lead. However, in general, these natural processes rarely lead to elevated lead concentrations in the environment, the results of which are shown in Table.15.

Table.15: Natural air emissions of lead (in kt/year) [223].

Sources	Emissions (kt/ year)
Soil Erosion	0.3 – 7.5
Marine particles	0 – 2.8
Volcanoes	0.5 – 6.0
Forest fires	0.1 – 3.8

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3.2. Anthropogenic sources:

Emissions of 'Pb' are generally anthropogenic. They come from: Road transport; Metallurgy industries; Refineries; Chemical industries; Mining activities; Industrial waste; Waste incineration.

3.3. Air pollution by lead

Lead released into the atmosphere is a major source of environmental contamination. Once deposited on soil and plants as well as in surface waters, it can enter the food chain. Lead particles can be transported considerable distances through the atmosphere, sometimes to the point of deposition via precipitation. The airborne lead comes from industrial effluents and the use of leaded petrol. Because of the use of lead in petrol an unnatural lead cycle has been created. Lead is burned in car engines, creating lead salts (chlorides, bromides,). These lead salts enter the environment through car exhaust fumes [223].

Larger particles fall to the ground immediately and pollute the soil or surface water, while smaller particles travel long distances in the air and remain in the atmosphere. Some of this lead falls back to earth when it rains. This human-induced lead cycle is much more extensive than the natural lead cycle. In the atmosphere, inorganic lead is mainly in particulate form. The main forms of (inorganic) lead in the air are carbonates, oxides and sulphates [223].

3.4. Lead contamination of water:

Lead may be present in water, following industrial discharges or transfers between different environmental compartments (polluted soils, atmospheric fallout, spreading of sludge from wastewater treatment plants, etc.). As lead is a metal that is not very mobile, it tends to accumulate. It is eliminated from water either by migration to sediments where it is retained by adsorption on organic matter and clay minerals or by precipitation as an insoluble salt (carbonate, sulphate or sulphide), which reduces the risk of contaminating the aquatic environment in the short term. The amount of lead remaining in the solution will depend on

the pH [224]. Nevertheless, large amounts of lead that have been stored in sediments for several years could be released as a result of climatic disturbances and lead to water pollution. Lead in rivers is mainly in the form of suspended particles. On average rivers contain between 3 and 30 ppb. Seawater contains small amounts of lead 2-30 ppt [224].

4. Lead toxicity.

Exposure to lead can cause serious adverse health effects and can even be fatal at high doses. Lead can accumulate in the body, and exposure to it, even at very low doses, can be dangerous. Lead is particularly harmful to infants, young children and pregnant women, and can permanently harm children's development, including intellectual and behavioural development [223].

Lead colic is the best-known toxic effect of lead, but its main target organs are the nervous system, kidneys and blood [225]. Lead is responsible for neurological damage. In cases of mass poisoning, the neurotoxic effect of lead can result in convulsive encephalopathy and even death. In less severe cases, neurobehavioral disorders and intellectual deterioration have been observed. Lead blocks several enzymes necessary for the synthesis of haemoglobin. These blood effects lead to a decrease in the number of red blood cells and anaemia.

B.IV. The problem of the toxicity of heavy metals.

Heavy metals all have a toxic potential that depends mainly on their concentration in the medium under consideration and their bioavailability, i.e. their soluble and accessible function in organisms. Too high concentrations of even essential heavy metals are toxic to living organisms. The bioavailability of heavy metals defines their ability to be transferred from one compartment to another, thus increasing the risk of toxicity to living organisms [226]. The toxicity of heavy metals is mainly due to:

- ☞ Their non-degradable over time.
- ☞ Their toxicity at low concentrations.

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☞ Their tendency to accumulate in living organisms and concentrate along trophic chains [227].

The toxicity of a metallic element in the environment depends on the chemical form in which it exists. An example is MnVII and AsIII which is more toxic than MnII and AsV [228]. Availability and toxicity depend on the free ion concentration of the element, as well as the total concentration of the metal or the metal complex [229].

One of the characteristics of metal toxicity is the ability of metals to form complexes [230], and their toxicity also varies with dose and duration of exposure. Short-term exposure to high concentrations causes acute syndromes, while long-term exposure to low concentrations causes chronic disorders [231]. The classification of heavy metals in order of toxicity is as follows [232], $\text{Hg}^{2+} > \text{Pb}^{2+} > \text{Cd}^{2+} > \text{Cr}^{6+} > \text{Cr}^{3+} > \text{Zn}^{2+} > \text{Ni}^{2+}$. The main hazards of heavy metals are:

- ☞ They replace or substitute essential minerals.
- ☞ They change our genetic code.
- ☞ They produce free radicals.
- ☞ They neutralize the amino acids used for detoxification.
- ☞ They cause allergies.
- ☞ They damage nerve cells [233].

We must reduce the use of metallic cadmium in various industries and try to find alternatives to it.

Health and safety measures in the workplace are Respiratory protection for workers while working with blinds for eyes, face and arm and waterproof clothing.

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Can apatites lacunar be the materials with the strongest capacity to retain heavy elements ?

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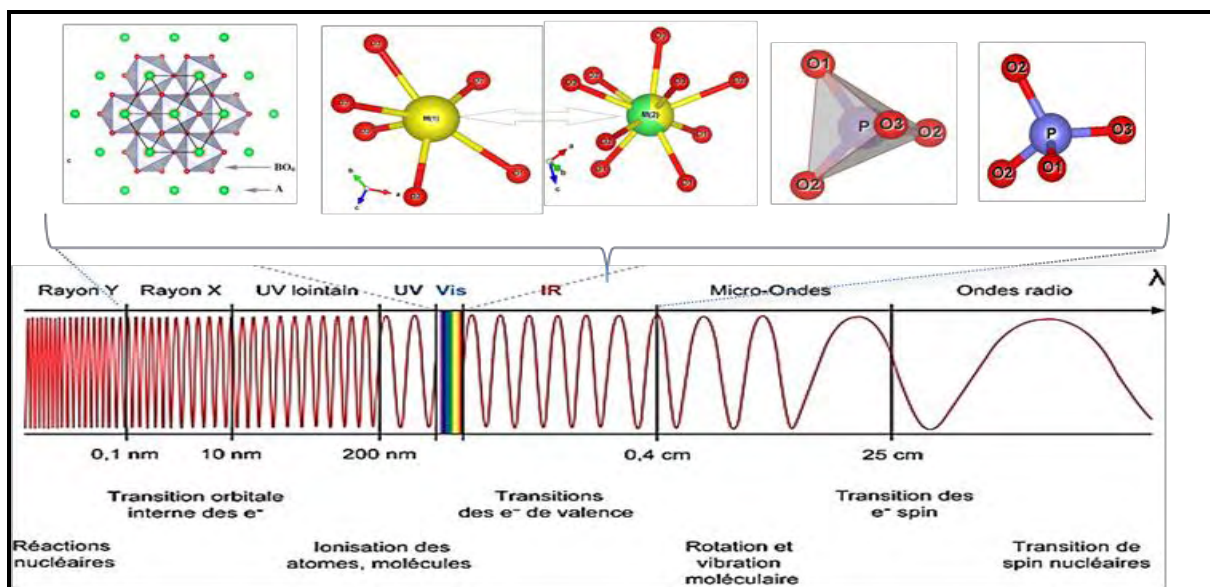
Chapter. I: Synthesis, Experimental Techniques, and Methods of Analysis.

Abstract;

This work demonstrates of Synthesis of different materials, Experimental Techniques and Methods of Analysis employed for this works. The results show can apatites lacunar is the materials with the strongest capacity to retain heavy elements. Apatite materials can form solid solutions and accept many substitutions. These oxide classes can accommodate a wide variety of metal cations while retaining their unique structure, can often be tuned or changed by elemental substitution, and materials with the same structural connectivity can be studied for different purposes.

Of all the physicochemical methods of analysis, spectroscopic methods play an important role in physical and chemical characterization. A spectroscopic method is referred to as a spectroscopic method when the sample apatite emits, absorbs or scatters electromagnetic radiation. The different spectroscopic methods are distinguished by the levels of energy they involve, or any other quantity that can be reduced to energy (lattice distances, frequency, wavelength, etc.). The main spectroscopic techniques used are (Abstract Fig. I Style):

- Absorption: X-rays, UV-visible, Infrared (IR).
- Diffusion: Raman scattering at room temperature and high temperature.



Abstract Fig. I Style: Results of X-ray Diffraction, Infrared and Raman at Room- and High-Temperature Study, and UV-Vis; Spectroscopy Techniques for Various Characterizations of Lacunar Apatites.

I. Introduction.

The apatite minerals have been attracting extensive interest from scientists, researchers and engineers in different fields, and from industry groups, with the development of advanced materials science and the applications in various fields of sciences and techniques of research and industrial sectors. The possible fields of application for apatites are many and varied.

To have an accurate picture, calcium apatites of $\text{Ca}_5(\text{PO}_4)_3\text{X}$ ($\text{X} = \text{F}, \text{Cl}, \text{OH}$, etc.) have been extensively investigated due to their significance in many fields, which vary from biomaterials and medical sciences to environmental remediation, biology, ecology, catalysis and optoelectronics [1-7]. For example, Hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$), became a widely used biomaterial in medicine, due to their proverbial industrial applications and their biological bio-activity, with applications on bone and dental implants [8-10]. Furthermore, researchers have been widely discussing by the different studies and techniques the various ionic substitutions in calcium apatites [11-16] for the sake of developing and a better understanding of the structure-properties relationship for good use of apatites.

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Strontium is one of the most common substituents in the apatite structure like in $\text{Ca}_{5-x}\text{Sr}_x(\text{PO}_4)_3\text{Y}$ ($\text{Y} = \text{F}^-, \text{Cl}^-$) to $\text{Sr}_5(\text{PO}_4)_3\text{Y}$ [17-19] their structures were determined with X-ray diffraction, studied by infrared and Raman techniques [20-23] and from theoretical investigation on the structural stability, electronic, vibrational, and thermodynamic properties. Among, these applications the apatites are known to be suitable for nuclear waste storage [24], they are of interest in biological sciences including biochemistry, biomedicine, cell biology, conservation, ecology, genetics, microbiology, because of the ready incorporation of Sr into the food chain and its subsequent incorporation in bone [25-26].

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The only apatitic system, where compounds with the apatite structure could be prepared without anion Y^- , is the lead system [27]. The apatites having vacancies in the Y anion sites with general formula $APb_{4-y}M_y(XO_4)_3$ (A: monovalent cation and M: divalent cation) have been studied by several authors (A = Na, Ag, K; M=Ca and X=P, V, As) [27-30].

Apatite materials can form solid solutions and accept many substitutions. These oxide classes can accommodate a wide variety of metal cations while retaining their unique structure, can often be tuned or changed by elemental substitution, and materials with the same structural connectivity can be studied for different purposes. That fact is the main motivation of the present work, which deals with the Synthesis, Experimental Techniques, and physicochemical analysis methods for characterization of lacunars lead-phosphates (without anions) $\{Na_{1-x}K_xPb_{4-y}\{Sr/SrCa/CaCd/Zn/Ca\}_y(PO_4)_3\}$ and hydroxyapatites $\{Ca_{10}/Zn_2(PO_4)_6(OH)_2\}$. The specimens were prepared by solid-state reaction and by aqueous solution precipitation to examine the effect of the synthesis routes on the final structural and microstructural properties of phosphorus apatites as well as their surface reactivity.

Of all the Physico-chemical methods of analysis, spectroscopic methods play an important role in physical and chemical characterization. A spectroscopic method is referred to as a spectroscopic method when the sample apatite emits, absorbs, or scatters electromagnetic radiation. The different spectroscopic methods are distinguished by the levels of energy they involve, or any other quantity that can be reduced to energy (lattice distances, frequency, wavelength, etc.). The main spectroscopic techniques used are:

- Absorption: X-rays, UV-visible, Infrared (IR).
- Diffusion: Raman scattering at room temperature and high temperature.

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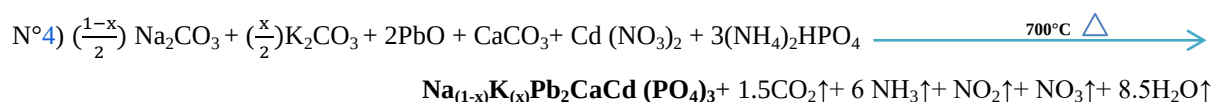
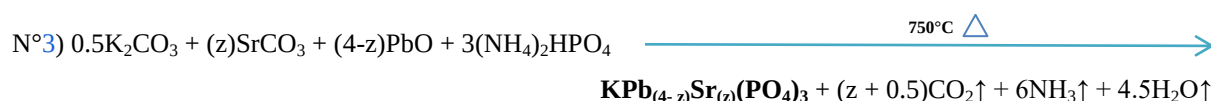
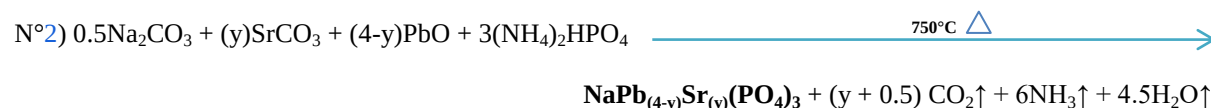
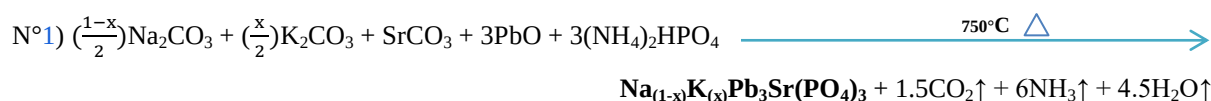
[30] S. Lahrich, M.A. Elmhammedi, B. Manoun, Y. Tamraoui, F. Mirinioui, M. Azrou, P. Lazor, Elaboration, Rietveld refinements and vibrational spectroscopic study of $Na_{1-x}K_xCaPb_3(PO_4)_3$ lacunar apatites ($0 \leq x \leq 1$), Acta Part A: Molecular and Biomolecular Spectroscopy. 145 (2015) p.22.

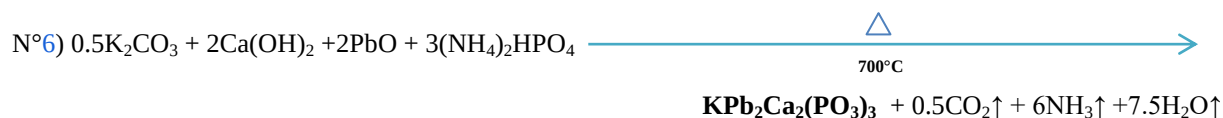
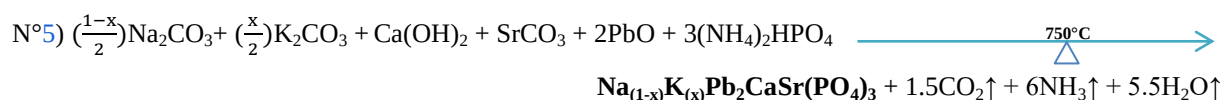
II. Synthesis of Materials.

II.1. Lacunar Apatites.

News Lacunar Apatites-type materials without anions Y^- , with the general formula $A^I Pb_{4-x} M_x (PO_4)_3 \square Y_0$, where M^{2+} are divalent cations (M : Sr^{2+} , Ca^{2+} , Cd^{2+} , Zn^{2+}) and A^I are monovalent cations (A^I : Na^+ , K^+); the compositions of Strontium-Lead-Phosphate of Sodium and/or Potassium; $Na_{1-x} K_x Pb_{4-y+z} Sr_{y+z} (PO_4)_3$ where ($0 \leq x \leq 1$) and ($0 \leq y+z \leq 1.5$) (N°1, °2 and °3), Cadmium-Calcium-Lead-Phosphate of sodium and potassium; $Na_{1-x} K_x Pb_2 Ca Cd (PO_4)_3$ ($0 \leq x \leq 1$) (N°4), Strontium-Calcium-Lead-Phosphate of sodium and potassium; $Na_{1-x} K_x Pb_2 Ca Sr (PO_4)_3$ ($0 \leq x \leq 1$) (N°5), Calcium-Lead-Phosphate of potassium; $K Pb_2 Ca_2 (PO_4)_3$ (N°6); labelled Ap-Ca, and Zinc-Lead-Phosphate of potassium; $K Pb_3 Zn (PO_4)_3$ (N°7); labelled Ap-Zn, for all were prepared by Solid-State chemical method or commonly called ‘Conventional Ceramic Synthesis method’[27].

The following solids products: Na_2CO_3 , K_2CO_3 , $SrCO_3$, PbO , $Ca(OH)_2$, $Cd(NO_3)_2$, ZnO and $(NH_4)_2HPO_4$, are obtained from Sigma-Aldrich (Steinheim, Germany) of highest purity (>99%), were weighed with an accuracy of 0.0001g and mixed in the stoichiometric quantities necessary to the reactions; N°1, °2, °3, °4, °5, °6 and °7:





The mixtures were ground in an agate mortar and placed in alumina crucibles and treated progressively at different temperatures; 300°C/12h, 500°C/24h, and T(final)=750°C/48h for reactions N°1, °2, °3 and °5, T(final)=700°C/48h for reactions N°4, °6 and °7, with intermediate regrinding to improve the homogeneity of the mixture and increase the kinetics of the solid-state reaction. Fig.1 shows the all appliances of the laboratory used in the solid-state reactions, furthermore all samples of lacunar apatites are white colours. After each thermal treatment, the products were quenched to room temperature and grounded again for the analysis step. The initial structural identification and characterization of the samples were carried out by laboratory X-ray powder diffraction.

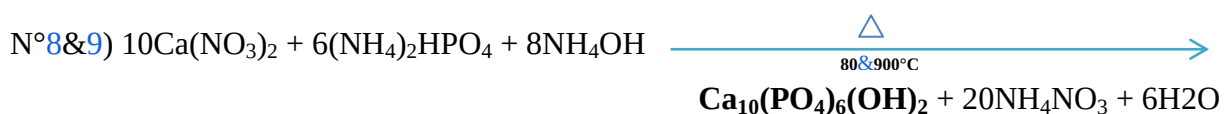


Fig.1: Appliances of the laboratory used in solid-state reactions. Analytical balance sensitivity 0.1mg, example for a sample of lacunar apatite, alumina crucibles, agate mortar, and oven NABERTHERM with and compact muffle.

II.2. Wet Preparation of Different Hydroxyapatites.

The hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 \cdot n\text{H}_2\text{O}$ (reactions N°8) refereed as HA was synthesized by co-precipitation as described previously [31]. The calcium salt solution $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (1 M, 100 mL deionized water) was added drop wisely during 3h using a peristaltic pump to a phosphate salt aqueous solution $(\text{NH}_4)_2\text{HPO}_4$ (0.06M, 1000mL deionized water) maintained at a temperature close to 80°C under continuous stirring. The pH of the suspension was around 10. After filtration, the precipitate was washed with deionized water and lyophilized for 68 h.

For the preparation of the calcined apatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, named HA_{900} , a portion of the resulted HA powder was heated at 900°C for 3h at a rate of 5°C/min. The reaction N°9 leading to the preparation of stoichiometric hydroxyapatite can be written as follows:



The Zinc-substituted hydroxyapatite $\text{Ca}_8\text{Zn}_2(\text{PO}_4)_6(\text{OH})_2 \cdot n\text{H}_2\text{O}$ (reaction N°10), named Zn-HA was obtained using the same wet chemical route as for HA, by mixing a cationic solution (100 ml) containing calcium nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$; 0.758M) and zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; 0.189M) with a solution of ammonia and phosphate ($(\text{NH}_4)_2\text{HPO}_4$; 1000 mL, 0.058 M). The reaction corresponding to the formation of Zn-HA is given by:

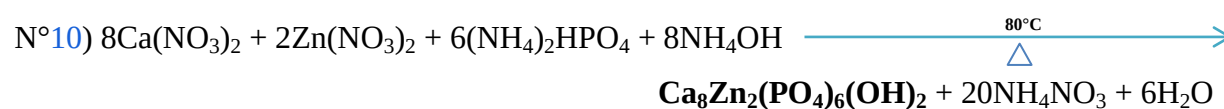


Fig.2 shows the schematic of the synthesis of different hydroxyapatite types (HA, HA_{900} , and Zn-HA) set-up used in this study.

[31] A. Barroug au J. Lemaitre, P.G. Rouxhet, Lysozyme on apatites: A model of protein adsorption controlled by electrostatic interactions, *Colloids and Surfaces*. 37 (1989) 339–355. doi:10.1016/0166-6622(89)80130-1.

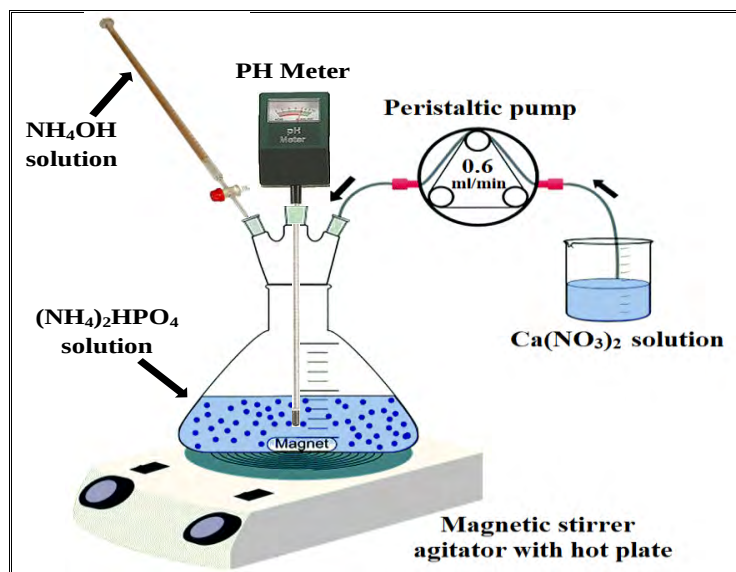


Fig.2: Schematic of the synthesis of different hydroxyapatites set-up used in this study.

III. X-ray Powder Diffraction.

III.1. History of Powder Diffraction.

The discovery of X-rays by the physicist W. C. Rontgen at the University of Wurtzburg in 1895 is a wonderful example of serendipity in science. He was the first who coined the term 'X-rays' term used ever since, even though we now know that they are short-wavelength ranging from about 0.1 Å to 10 Å electromagnetic waves, with energies ranging from about 100 eV to 10 MeV. The diffraction of X-rays realized in Munich in 1912 by Max von Laue, and later shown by W. Friedrich and P. Knipping that crystals can act as diffraction gratings for radiation of an appropriate wavelength, and the analysis of crystal structure using X-rays were developed by W. H. Bragg and his son W. L. Bragg in Leeds and Cambridge in the First World War [32].

Powder diffraction followed only two years after Bragg's successful determinations when Debye and Scherrer developed the Deby-Scherrer technique in 1916 (Debye was at that time professor in Göttingen), and in 1917 by Hull in the US.

[32] W.H. Bragg, W.L. Bragg, 'X-rays and Crystal Structure', London: Bell and Sons, (1915).

They studied and determined the structures of 'LiF' and silicon and they presented the complete theory underlying power diffraction patterns, steigende quadratsummen geordneter 'h k l' triplets to determine the unit cell dimensions". Debye's method overcomes the limitation (of larger specimens) and immensely increased the range of crystals which could be examined since so many substances can only be obtained in a finely divided crystalline; because the crystalline solid consists of three-dimensional periodic array of atoms which can be considered as extended from its unit cell. When the wavelength of an incident beam is comparable to the interatomic spacing in the crystal, the atoms can scatter and reflect the incident radiation so a diffraction pattern can be generated. The method has, therefore, opened up a new field of the greatest interest and importance.

Powder diffraction data were used for the identification of known materials or mixed phases since late 1930. This is achieved by comparing the experimental data with the standard data of the crystallographic database. The Debye-Scherrer technique had a great interest in the 70s, after the introduction by Rietveld in 1967 of a powerful method for refinement of crystal structures from a powder pattern. The Rietveld technique has greatly benefited from the revolution in the development of storage media in the last decade and the introduction of algorithms for fast phases search. Phase identification sometimes precedes a quantitative analysis of the compounds present in the sample and diffraction of powder is often the only available approach to the analyst. Initially applied to the neutron diffraction data, the method is then extended to the field of X-ray diffraction, and it was an important step to the extraction of structural information in 3D from powder diffraction patterns (1 dimension), to study the structure of crystal materials. Similarly, techniques that don't need much powder diffraction data have been introduced for modelling powder diffraction to extract the various parameters (peak position, width, shape,..., etc.) which describe individual reflections. They are used in most powder diffraction applications and they are the basis for new procedures for characterizing the microstructure properties of materials.

Crystal structure analysis from powder diffraction data has attracted considerable and ever-growing interest in the last decades. X-ray powder diffraction is best known for phase analysis ([Hanawalt files](#)) dating back to the 30s. In the late 60s, the inherent potential of powder diffraction for crystallographic problems was realized and scientists developed methods for using powder diffraction data at first only for the refinement of crystal structures. The development of ever-growing computer power profile fitting and pattern decomposition allowed to extract of individual intensities from overlapping diffraction peaks opening the way to many other applications, especially to ab initio structure determination. Powder diffraction today is used in X-ray and neutron diffraction, where it is a powerful method in neutron diffraction for the determination of magnetic structures. In the last decade, interest has dramatically improved. There is hardly any field of crystallography where the Rietveld or full pattern method has not been tried with quantitative phase analysis the most important recent application.

III.2. Production of X–Rays and Basic principles of Bragg’s Law.

X–rays are produced by the continuous bombardment of a metal anode with high–energy electrons. Upon reaching the metal anode, these electrons are decelerated by the electrons in the metal target. This produces a broad continuous spectrum of X–Rays are known by the original German term ‘bremsstrahlung’, from ‘bremsen’ (to brake) and ‘Strahlung’ (radiation) thus translating literally as ‘braking radiation’ [[33](#)]. The bremsstrahlung spectrum is dependent only on the energy of the bombarding electrons.

[33] (Rod) Nave – Hyper Physics – Georgia State University, ‘Characteristic X–Rays’, Web site: <http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/xrayc.html>

The energy of these bombarding electrons is of sufficient energy to excite an $n = 1$ (**K** shell) electron to a higher, unoccupied state. Whenever a core electron makes an electronic transition from the $n = 1$ state to an unoccupied state, it leaves a vacancy in the **K** shell. Thus, electrons in the $n = 2$ (**L** shell) or $n = 3$ (**M** shell) can make a transition into the **K** shell, simultaneously emitting electromagnetic radiation with energies of several keV. These quantized electronic transitions give rise to a discrete spectrum of sharp peaks in the intensity of X-rays at specific wavelengths and are characteristic of the anode metal. Transitions from the $n = 2$ (**L**) shell to the $n = 1$ (**K**) shell gives rise to the K_α line, whilst the K_β is a result of transitions from the $n = 3$ (**M**) shell to the $n = 1$ (**K**) shell. In addition to the **K**-series (transitions to the K shell), transitions to a vacancy in the $n = 2$ shell form the **L**-series. The lines produced by these transitions are unresolved doublets, for example, the K_α line consists of two lines corresponding to $K_{\alpha 1}$ and $K_{\alpha 2}$ radiation resulting from two **L** to **K** transitions with similar energy, differing only due to the spin multiplicity of the $2p^n$ electrons [34–37]. X-ray-production by Energy-Conversion-Events illustrated in Fig.3.

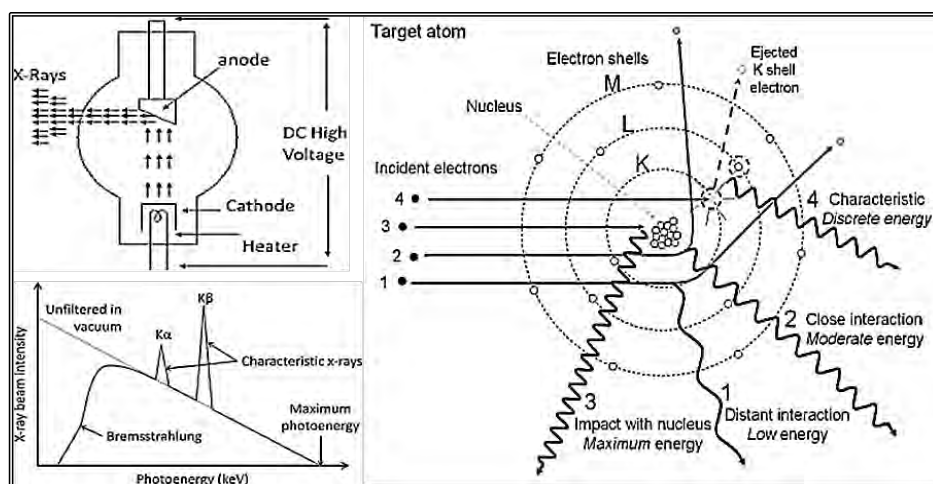


Fig.3: X-ray-production by Energy-Conversion-Events.

- [34] A.R. West, 'Solid State Chemistry and its Applications, John Wiley & Sons (Asia), (1985).
- [35] L.E. Smart, E.A. Moore, 'Solid State Chemistry: An Introduction 3rd edition (first published 1992)', Boca Raton: Taylor & Francis, (2005).
- [36] J.P. Glusker, K.N. Trueblood, 'Crystal Structure Analysis: A Primer 2nd edition (first published 1972)', New York: Oxford University Press, (1985).
- [37] V.K. Pecharsky, P.Y. Zavalij, 'Fundamentals of powder diffraction and structural characterization of materials (first published 2003)', Vol. 69, New York: Springer, (2009).

Bragg's theory of diffraction considers a crystal to be made up of parallel planes of atoms from which the incident radiation is reflected. It is constructive interference of the scattered X-rays that lead to diffraction, illustrated in Fig.4.

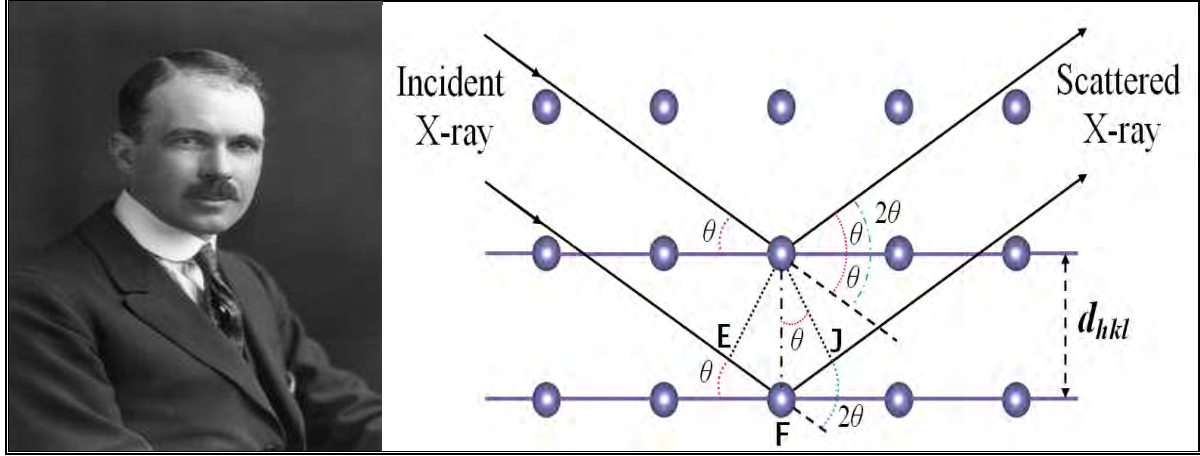


Fig.4: Sir Lawrence Bragg and diffraction of X-rays incident upon parallel planes of atoms separated by d_{hkl} distance. The angle between the incident and diffracted beams is 2θ .

The incident waves are in a phase when entering the crystal; however, some penetrate deeper than others. Constructive interference and therefore diffraction only occurs when the waves that have been scattered are in phase, and this would only happen if the extra distance travelled by the deeper penetrating waves is equal to an integer number of wavelengths $n\lambda$. This path difference between the waves scattered by atoms from adjacent $(h\ k\ l)$ lattice planes of **d-spacing** is demonstrated in Fig.3, and given by Eq.1:

$$n\lambda = EF + FJ \text{ (Eq.1)}$$

As the angle of incidence is known and the distance between the two atomic planes, known as **d-spacing**, is denoted d_{hkl} , then the path length $(EF + FJ)$ is equal to:

$$(EF + FJ) = (d_{hkl} \sin \theta + d_{hkl} \sin \theta) = 2d_{hkl} \sin \theta \text{ (Eq.2)}$$

Hence for constructive interference: $n\lambda = 2d_{hkl} \sin \theta$ (Eq.3)

The above relationship is known as Bragg's Law, and it shows that constructive interference will occur at different incident angles ' θ ' for different plane separations d_{hkl} , where ' n ' is an integer that represents the order of reflection.

III.3. Instrument D2 PHASER Diffractometer.

In the present thesis, the powder X-ray diffraction patterns were collected at room temperature on a D2 PHASER diffractometer, Fig.5 show the principles equipment of D2 PHASER, with the Bragg–Brentano geometry and (θ – θ) mode; equipped with a diffracted beam graphite monochromator; using a copper anticathode tube as radiation source discrete ($K_{\alpha 1}$ and $K_{\alpha 2}$) of corresponding ($\lambda_{K_{\alpha 1}} = 1.54056 \text{ \AA}$ and $\lambda_{K_{\alpha 2}} = 1.54439 \text{ \AA}$) wavelengths; see in *X-Ray tube* (Fig.5), superimposed to a spectrum of intensity much lower, **Cu–K α** radiation powered at 30kV and 10mA; see in *Incident beams* (Fig.5). The data produced contained both **CuK α_1** and **CuK α_2** radiation; see in *diffracted beams* (Fig.5).

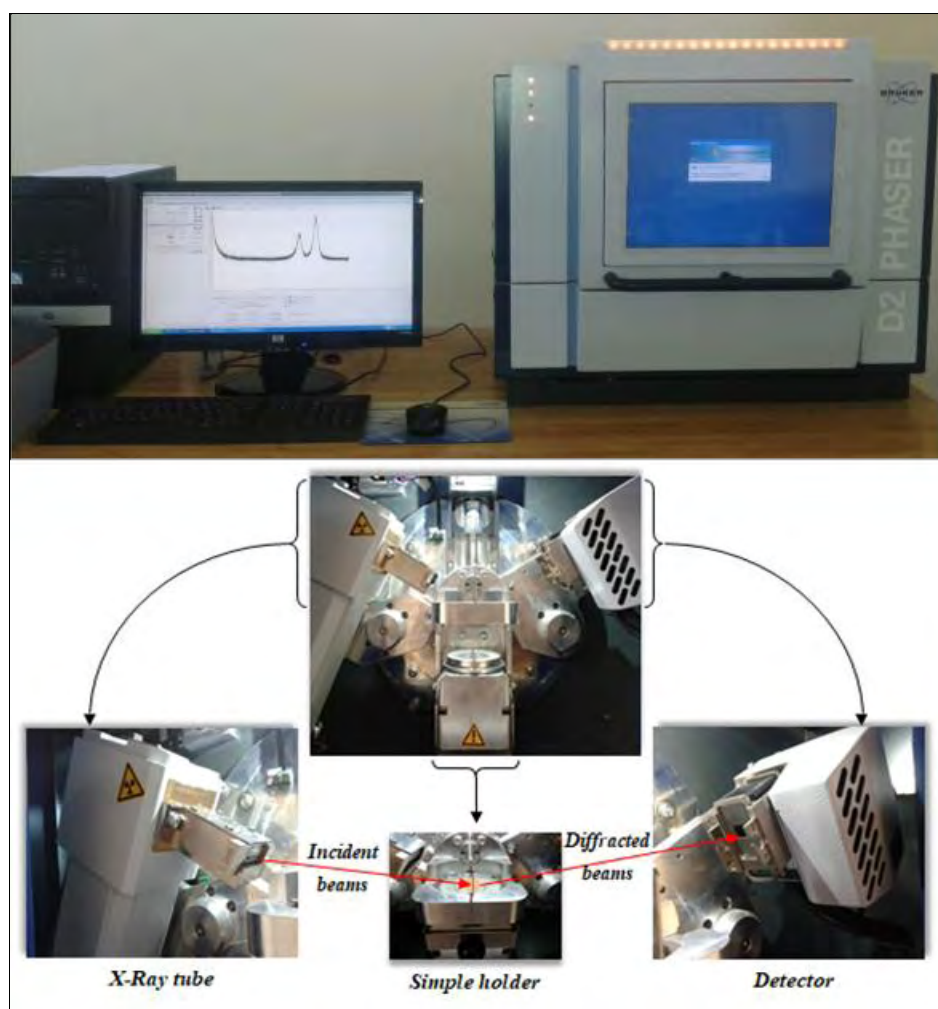


Fig.5: The principles equipment of D2 PHASER in the centre of RCAC (Regional Center for Analysis and Characterization) in Faculty of Science and Technology, University Hassan 1st, Settat.

The XRPD patterns were controlled by using Soller slits of 0.02 rad on the incident and diffracted beams (reduces peak asymmetry); divergence slit of 0.5° (adjusts beam length on the sample); anti-scatter slit of 1° (reduces background signal); receiving slit of 0.1mm; with sample spinner, see in a simple holder (Fig.5). The patterns were scanned through steps of 0.0101°(2θ), between 10 and 100(2θ) with a fixed time counting (5–10s/step), on this instrument we conducted sample routine checks (verification of purity) after each heat treatment, scanning between 15-80° in 0.02°. The EVA–software XRD was used for phase identification and quantitative phase analysis, see in Detector (Fig.5). Each crystalline solid has a characteristic XRPD pattern, which can be compared to a database of known patterns, for example, PDF–2 database, the International Centre for Diffraction Data.

III.4. Process Simulation of Differents Apatites Materials.

a) Initial Simulation Environment.

The FullProf program integrated the WinPLOTR software initially applied to facilitate the reading of X-ray diffractograms [38,39], it was an important step to the extraction of structural information; peak position (2θ and d_{hkl}), peak intensity, background. Similarly, techniques that don't need much powder diffraction data have been introduced for modelling powder diffraction patterns to extract the various lattice parameters:

$$d_{hkl} = f(h, k, l, a, b, c, \alpha, \beta, \gamma)$$

"Indexing" the diffractogram of a compound consists, from the list of reticular distances «**d–spacing**» obtained, in proposing a crystalline mesh (cubic, quadratic, orthorhombic, hexagonal, monoclinic or triclinic) which allows assigning **Miller Indices** to the "observed reflections". The reticular distances d_{hkl} are functions of the Miller indices **h**, **k**, **l**, and the mesh parameters **a**, **b**, **c**, **α**, **β** and **γ**.

[38] J. Rodriguez-Carvajal, Collected Abstracts of Powder Diffraction Meeting, (Toulouse, France), 127 (1990)

[39] T. Roisnel, J. Rodriguez-Carvajal, Mater. Sci. Forum 378-381 (2001) 118

We consider the expression: $Q(\mathbf{hkl}) = \frac{1}{d_{\mathbf{hkl}}^2} = \frac{4\sin^2 \theta}{\lambda^2}$ (Eq.4)

If $\mathbf{n}^*_{(\mathbf{hkl})}$ is the nodal distance on the row $(\mathbf{h} \ \mathbf{k} \ \mathbf{l})^*$ of the reciprocal network and $\mathbf{d}_{\mathbf{hkl}}$ the reticular distance of the family of reticular planes $(\mathbf{h} \ \mathbf{k} \ \mathbf{l})$ of the direct network, are linked by the following relationship: $\mathbf{n}^*_{[\mathbf{hkl}]} \cdot \mathbf{d}_{(\mathbf{hkl})} = 1$ (Eq.5)

$$Q(\mathbf{hkl}) = \frac{1}{d_{\mathbf{hkl}}^2} = |\mathbf{n}^*_{[\mathbf{hkl}]}|^2 = \|\mathbf{h}\mathbf{a}^* + \mathbf{k}\mathbf{b}^* + \mathbf{l}\mathbf{c}^*\|^2 =$$

$$h^2\mathbf{a}^{*2} + k^2\mathbf{b}^{*2} + l^2\mathbf{c}^{*2} + 2hka^*b^* \cos \gamma^* + 2klb^*c^* \cos \alpha^* + 2lhc^*a^* \cos \beta^* \quad (\text{Eq.6})$$

From the list of reticular distances «**d-spacing**» of the diffractogram we obtain a list of increasing values of **Q** (**Q₁**, **Q₂**, **Q₃...****Q_n**). The general problem consists of finding the unknowns **a***, **b***, **c***, **α***, **β***, **γ*** which, with triplets of integers **(h, k, l)**, make it possible to generate this list of observed "d". The difficulty increases from cubic (1 parameter) to triclinic (6 parameters). Several software programs have been developed to solve this problem. They use "trial and error" or "dichotomy" algorithms. In particular, the DICVOL and "TREOR" programs are worth mentioning. The proper functioning of these programs requires very good quality «**d_{hkl}**» observations.

In this work, we used the TREOR program to index the different diffractograms obtained, we created a file ***.don** containing the **20** experimental lines with the highest intensities and we launch the indexing by this program, the indexing results being found in the files ***.out** and ***.con** (condensed results). The program gives several possibilities of indexation, we only keep the possibility where there is 0 non-indexed line, i.e. no non-indexed line.

Fig.6 shows the result of the indexing by the "TREOR" software of the X-ray diffraction diffractogram as an example of NaPb_{2.5}Sr_{1.5}(PO₄)₃ (reaction N°2). At the end of this indexing, the software determines the nature of the crystal system, the approximate mesh parameters of the crystal system, the **Miller indices (h k l)** of each plane, the experimental **20**

and the calculated ones of each plane (**h k l**), as well as the reticular distances calculated for each plane (**h k l**).

```

** HEXAGONAL TEST ***** MAX. VOLUME= 1500.
SELECTED BASE LINES (1,2) (1,3) (2,3)
BASE LINE ONE.(HKL)-MAX= 4 4 4 MAX H+K+L= 4
BASE LINE TWO.(HKL)-MAX= 4 4 4 MAX H+K+L= 4
THIS MAY BE THE SOLUTION !!!
THE REFINEMENT OF THE CELL WILL NOW BE REPEATED
THREE CYCLES MORE. --- GOOD LUCK !

CYCLE RESULTS

0.008350 0.011470 0.000000 0.000000 0.000000 0.000000
0.008350 0.011470 0.000000 0.000000 0.000000 0.000000
0.008350 0.011470 0.000000 0.000000 0.000000 0.000000
NUMBER OF SINGLE INDEXED LINES = 20
TOTAL NUMBER OF LINES = 20
A = 9.734116 0.000104 A ALFA = 90.000000 0.000000 DEG
B = 9.734116 0.000104 A BETA = 90.000000 0.000000 DEG
C = 7.192367 0.000129 A GAMMA =120.000000 0.000000 DEG
UNIT CELL VOLUME = 590.19 A**3
H K L SST-OBS SST-CALC DELTA 2TH-OBS 2TH-CALC D-OBS
1 1 0 0.025071 0.025049 0.000022 18.221 18.213 4.8649
2 0 0 0.033394 0.033398 -0.000005 21.059 21.060 4.2153
1 1 1 0.036521 0.036519 0.000001 22.034 22.034 4.0308
0 0 2 0.045880 0.045881 -0.000001 24.737 24.737 3.5962
1 0 2 0.054247 0.054231 0.000016 26.937 26.933 3.3073
2 1 0 0.058458 0.058447 0.000011 27.983 27.981 3.1859
2 1 1 0.069922 0.069918 0.000005 30.666 30.665 2.9131
1 1 2 0.070935 0.070930 0.000004 30.893 30.892 2.8922
3 0 0 0.075145 0.075146 -0.000001 31.820 31.820 2.8100
1 1 3 0.128289 0.128282 0.000007 41.976 41.975 2.1506
4 0 0 0.133575 0.133594 -0.000018 42.874 42.877 2.1076
2 2 2 0.146082 0.146077 0.000006 44.941 44.940 2.0154
3 1 2 0.154425 0.154426 -0.000001 46.279 46.279 1.9602
3 2 0 0.158649 0.158642 0.000007 46.945 46.944 1.9339
2 1 3 0.161679 0.161680 -0.000001 47.418 47.418 1.9157
3 2 1 0.170121 0.170113 0.000008 48.719 48.717 1.8676
4 0 2 0.179473 0.179475 -0.000002 50.130 50.130 1.8183
0 0 4 0.183520 0.183525 -0.000006 50.731 50.732 1.7981
3 2 3 0.261868 0.261875 -0.000008 61.558 61.559 1.5053
5 1 1 0.270306 0.270308 -0.000002 62.652 62.653 1.4816
NUMBER OF OBS. LINES = 20
NUMBER OF CALC. LINES = 20
M( 20)= 364 AV.EPS.= 0.000066
F 20 = 241.(0.001485, 56)
M( 20)= 364 AV.EPS.= 0.000066
F 20 = 241.(0.001485, 56)

```

Fig.6: Condensed calculation results of TREOR for $\text{NaPb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$.

According to the above results confirmed by the TREOR software, all samples crystallize in the hexagonal mesh; to calculate the crystal parameters the DICVOL unit integrated into the WinPLOTR software, was used. The **d-spacings** are derived from peak positions by Bragg's law; $n\lambda = 2d \cdot \sin(\theta)$ (Eq.3), and indexing of X-ray pattern is to find a solution to the relation: $d_{hkl} = f(h, k, l, a, b, c, \alpha, \beta, \gamma)$ where **h, k, l** are the **Miller indices** and a, b, c, α, β, γ are the cell parameters. According to the results, there is sometimes a contradiction between the simulations by the DICVOL unit and TREOR software concerning some materials of the lacunar apatites, this can be explained by the presence of the phases

(second phase and sometimes third phase), considered as impurities. As an example, $\text{Pb}_3(\text{PO}_4)_2$ mixed with the material $\text{NaPb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$, Fig.7. To correct the problem, the 2θ of this impurity is eliminated, i. e. different 2θ -values from framed two lines are eliminated (Fig.7). The values of the merit $M(N)$ and $F(N)$ [40,41] are an indicator of the quality of the samples.

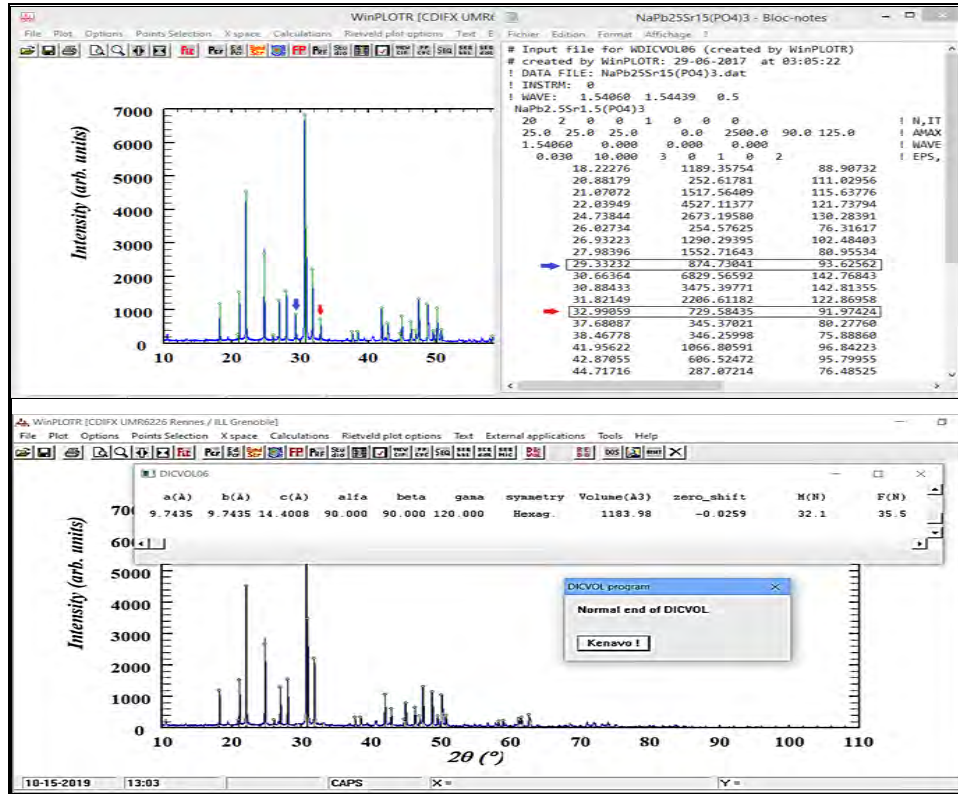


Fig.7: Removal of the impurity lines $\text{Pb}_3(\text{PO}_4)_3$ in the material $\text{NaPb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$ in the DICVOL unit.

The CAMAIL software has allowed us to calculate the approximate crystalline parameters, based on a known model of a similar structure or results of the DICVOL unit and TREOR software, to extract the hkl reticular planes. For the sample $\text{KPb}_4(\text{PO}_4)_3$ we took $d = 2.94331\text{\AA}$ and $d = 4.07361\text{\AA}$ for (121) and (111) respectively. When running the CAMAIL software; Fig.8, the structural characteristics found are: $a=b=9.832\text{\AA}$, $c=7.277\text{\AA}$ and $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$

[40] A. Boulitif, D. Lou r, J. Appl. Crystallogr. 24 (1991) 987.

[41] H. Lgaz, R. Salghi, M. Larouj, M. Elfaydy, S. Jodeh, Z. Rouifi1, B. Lakhriissi, H. Oudda, J. Mater. Environ. Sci. 7 (12) (2016) 4471-4488

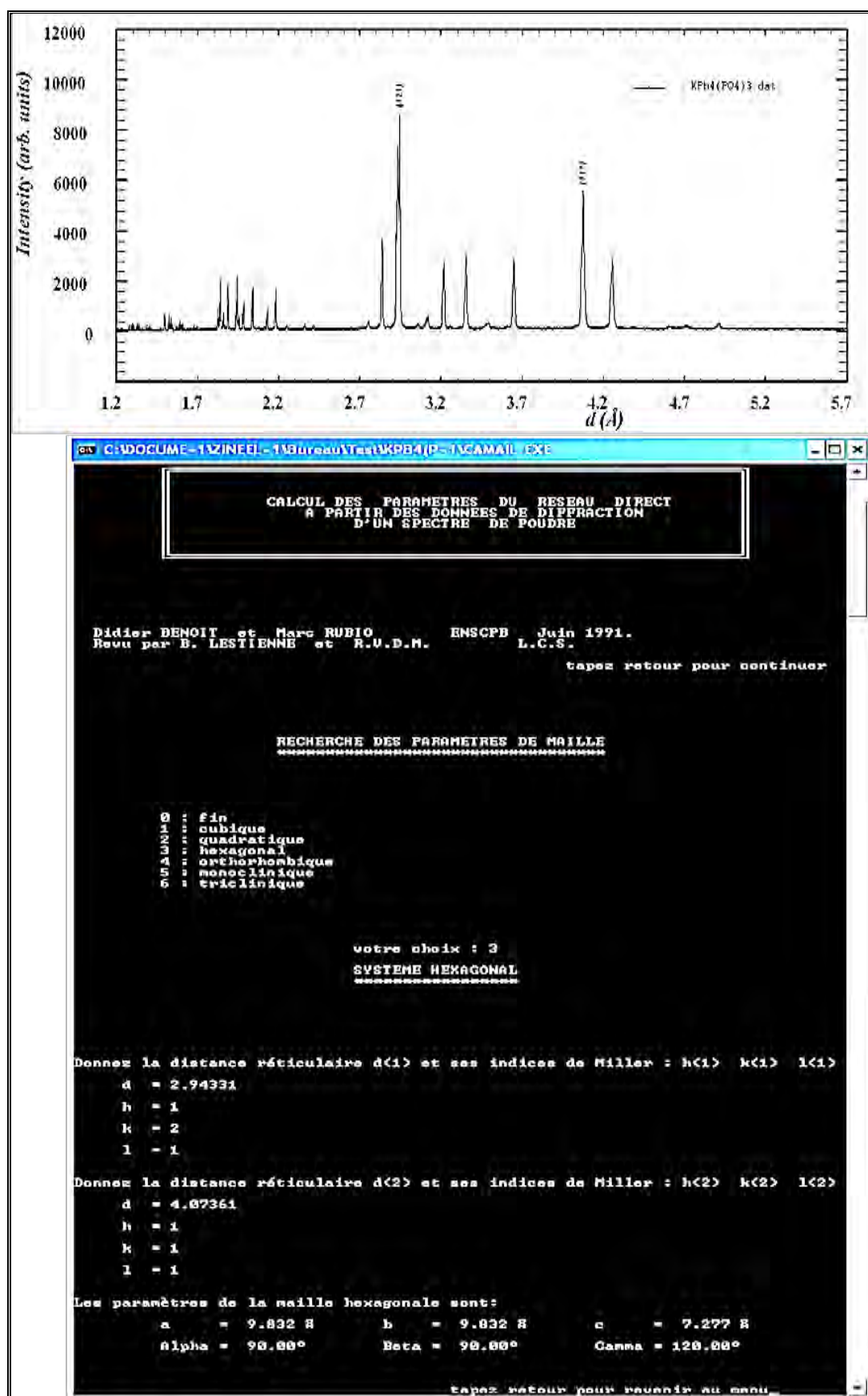


Fig.8: Identification of the crystalline parameters of $\text{KPB}_4(\text{PO}_4)_3$ from the CAMAIL software.

In comparison with the previous work of my supervisor [30,42], the variation in the mesh parameters of the 4 materials shows that the substitution of lead by M^{2+} cations ($M^{2+}=Cd^{2+}$, Ca^{2+} , Sr^{2+}) in the $NaPb_3M(PO_4)_3$ series causes a decrease in parameters (a) and (c), Table.1; this is explained by the difference in the radii of the lead-substituting cations [$r(Cd) < r(Ca) < r(Sr) < r(Pb)$]. It is important to note that the parameter (c) of $NaPb_3Cd(PO_4)_3$ has an anomaly due to the absence of Cd^{2+} in site 4f [42].

Table.1: Crystalline parameters of $NaPb_3M(PO_4)_3$ compounds; $\{M= Cd^{2+}, Ca^{2+}, Sr^{2+}, Pb^{2+}\}$.

Material	Formula	a (Å)	c (Å)	Reference
1	$NaPb_3Cd(PO_4)_3$	9.68136	7.13088	[42]
2	$NaPb_3Ca(PO_4)_3$	9.6834	7.1064	[30]
3	$NaPb_3Sr(PO_4)_3$	9.735	7.185	This work
4	$NaPb_3Pb(PO_4)_3$	9.741	7.197	

To identify the hkl planes of crystalline compounds, the DHKL software, Fig.9, is used 'd_{hkl}'. Using initially the approximate crystalline parameters obtained previously by the DICVOL unit and TREOR software, we choose the mode of the "Hexagonal" crystalline system and easily calculate all the theoretical interplanar spacing or interplanar distances and their corresponding **h**, **k**, **l**. From a file resulting from the previous step, we try to give each rai the plane (**hkl**) (Table.2) corresponding to the distance observed in the diffractogram of the compounds.

Table.2: The list of some (h k l) plans and their distances in (Å) of $NaPb_{(4-y)}Sr_{(y)}(PO_4)_3$.

y	h k l							
	(1 1 1)	(0 0 2)	(1 0 2)	(2 1 0)	(1 2 0)	(2 1 1)	(1 1 3)	(2 2 2)
0	4.03418	3.60000	3.31111	3.18849	3.18849	2.91541	2.15282	2.01709
0.5	4.02813	3.58850	3.30179	3.18620	3.18620	2.91212	2.14698	2.01407
1	4.02208	3.57700	3.29246	3.18391	3.18391	2.90884	2.14114	2.01104
1.5	4.00498	3.53800	3.26142	3.18031	3.18031	2.90079	2.12180	2.00249

[42] S.Lahrich, B. Manoun, M.A.Elmhammedi, Journal of Talanta (2015) p.40.

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NOM DU FICHIER RESULTAT : E1
PROGRAMME DE CALCUL DES DISTANCES RETICULAIRES
M.SAUX , B.LESTIENNE , R.UDM 1986 L.C.S. DU C.N.R.S.

NUMEROS DES SYSTEMES :
                                0 = FIN DU CALCUL
                                1 = CUBIQUE
                                2 = HEXAGONAL
                                3 = TRIGONAL
                                4 = QUADRATIQUE
                                5 = ORTHOROMBIQUE
                                6 = MONOCLINIQUE
                                7 = TRICLINIQUE

NUMERO DU SYSTEME ?      2

LAMBDA ?      1.54056

TETAMIN ?      5

TETAMAX ?      50

NOM DU CALCUL ?      calcE1

MODES DE RESEAU :
                                1 = PRIMITIF
                                2 = FACE A CENTREE
                                3 = FACE B CENTREE
                                4 = BASE CENTREE
                                5 = CENTRE
                                6 = FACES CENTREES
                                7 = ROMBOEDRIQUE

MODE DE RESEAU ?      1

ENTRER LES PARAMETRES DE LA MAILLE. < SEPARES PAR UN BLANC >
Valeurs de a :      9.741
Valeurs de c :      7.2

```

Fig.9: Identification of hkl planes by DHKL software for $\text{NaPb}_4(\text{PO}_4)_3$.

The AFPAR software aims to refine the different reticular planes to their corresponding reticular distances of our hexagonal structure; it has made a refinement between the observed interarticular distances and those calculated. The software executes the DHKL results, in other words, it requires the observed interplanar distances of the indexed lines and their (h k l) planes (DHKL software). Taking the example of $\text{KPb}_3\text{Sr}(\text{PO}_4)_3$, Fig.10 shows the good agreement between all lines between theory and experience with a precision of the order of 10^{-3} , which expresses a good comparison between the observed and calculated values. The results obtained are grouped in Fig.11 below. In the same way, a good refinement is obtained for the other materials.

A = 9.82696 { +/- .00046 }						
C = 7.33401 { +/- .00035 }						
H	K	L	D CALC	D OBS	Do-Dc	
3	2	5	1.1727	1.1728	.0691	10 ⁻³
5	2	2	1.2774	1.2773	-.0557	10 ⁻³
1	5	4	1.2960	1.2959	-.1836	10 ⁻³
4	1	4	1.3048	1.3049	-.1036	10 ⁻³
1	2	5	1.3346	1.3345	-.1215	10 ⁻³
0	4	4	1.3889	1.3884	-.5192	10 ⁻³
3	3	2	1.4954	1.4962	-.7120	10 ⁻³
2	3	3	1.5256	1.5254	-.2182	10 ⁻³
0	3	4	1.5399	1.5395	-.3850	10 ⁻³
2	1	4	1.5929	1.5929	-.0135	10 ⁻³
3	3	1	1.5985	1.5982	-.2370	10 ⁻³
0	4	0	1.6083	1.6082	-.0920	10 ⁻³
0	0	4	1.6838	1.6831	-.7716	10 ⁻³
0	0	4	1.8335	1.8357	2.1678	10 ⁻³
0	4	2	1.8403	1.8402	-.1068	10 ⁻³
0	3	3	1.8519	1.8532	1.2912	10 ⁻³
1	4	0	1.8571	1.8572	-.0627	10 ⁻³
2	3	1	1.8867	1.8859	-.8035	10 ⁻³
3	2	1	1.8867	1.8868	-.0968	10 ⁻³
1	2	3	1.9463	1.9454	-.8967	10 ⁻³
2	1	3	1.9463	1.9459	-.3964	10 ⁻³
1	3	2	1.9847	1.9844	-.3693	10 ⁻³
3	1	2	1.9847	1.9846	-.1693	10 ⁻³
2	2	2	2.0410	2.0398	-1.2090	10 ⁻³
2	2	2	2.0410	2.0408	-.2072	10 ⁻³
4	0	2	2.1197	2.1209	1.1346	10 ⁻³
1	1	3	2.1276	2.1278	-.1838	10 ⁻³
1	1	3	2.1887	2.1864	-2.2941	10 ⁻³
1	1	1	2.1887	2.1878	-.8917	10 ⁻³
1	3	0	2.3604	2.3608	-.4215	10 ⁻³
0	2	2	2.4181	2.4178	-.3128	10 ⁻³
1	0	3	2.8368	2.8355	-1.2593	10 ⁻³
3	0	0	2.8368	2.8370	-.2420	10 ⁻³
1	1	1	2.9388	2.9369	-1.9433	10 ⁻³
1	1	1	2.9388	2.9389	-.0587	10 ⁻³
1	1	1	2.9458	2.9452	-.5982	10 ⁻³
2	1	0	3.2166	3.2177	1.0431	10 ⁻³
2	1	0	3.2166	3.2170	-.3421	10 ⁻³
1	0	2	3.3677	3.3678	-.0741	10 ⁻³
1	0	2	3.3677	3.3660	-1.7283	10 ⁻³
0	0	2	3.6670	3.6654	-1.5583	10 ⁻³
0	0	2	3.6670	3.6659	-1.0576	10 ⁻³
1	0	1	4.0821	4.0811	-.9060	10 ⁻³
0	0	0	4.2552	4.2546	-.5879	10 ⁻³
2	0	0	4.2552	4.2546	-.5879	10 ⁻³
1	1	0	4.9135	4.9155	2.0590	10 ⁻³

Fig.10: Comparison between the d-spacings observed and calculated values of $\text{KPb}_3\text{Sr}(\text{PO}_4)_3$ by AFRAP software.

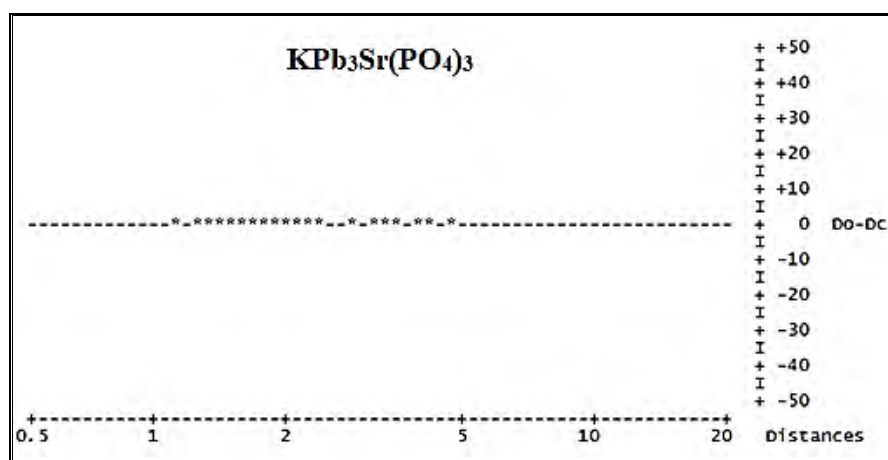


Fig.11: Refinement between the d-spacings observed and calculated of $\text{KPb}_3\text{Sr}(\text{PO}_4)_3$ AFRAP software.

Finally, to finish this part so an automatic PCR file is generated for cell refinement and integrated intensity extraction (Fig.7), the following paragraphs present in detail the information. Fig.12 shows the demo data used in this part, the diagram of structural resolution from X-Rays diffraction data, and the common procedure of cell parameters refinement is represented in the following diagram.

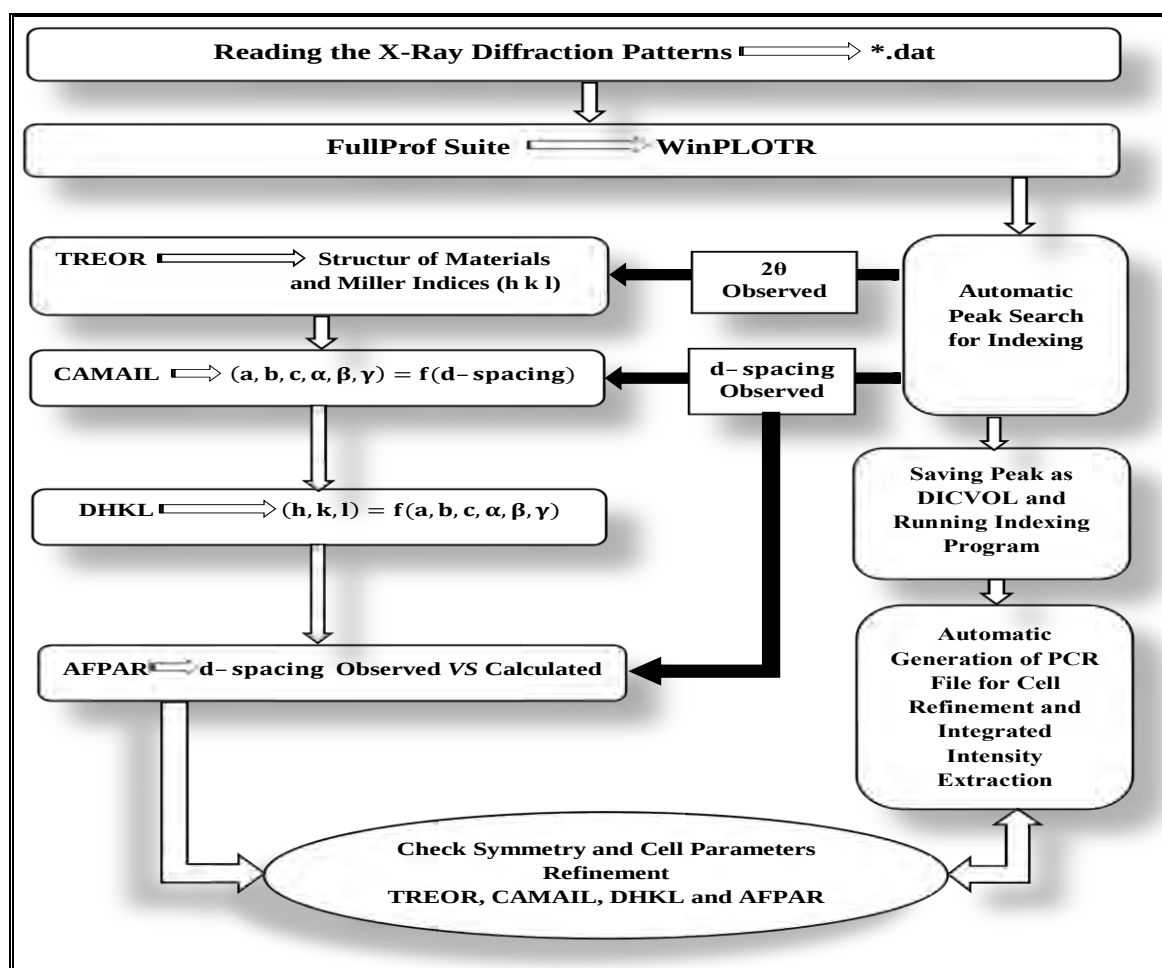


Fig.12: Diagram of structural resolution from X-Rays diffraction data.

b) Structural Refinement by Rietveld Method.

- Basic principles:

The Rietveld method is a technique that was applied originally by Hugo Rietveld in 1967 [43], is widely used to refine crystal (and/or magnetic) structure from obtained X-ray or neutron powder diffraction patterns. It is difficult to quantify the amount of structural information in a powder diffraction pattern. For most powder diffraction patterns, overlaps happen between Bragg reflections commonly found for lower-symmetry materials due to the polycrystalline nature of a powder sample. The separation of those overlapping peaks into their components allows an accurate structure to be determined. Instead of analyzing each reflection or resolving the reflection overlaps, the Rietveld method is performing a curve-fitting procedure by considering the observed intensity $y_i(\text{obs})$ of each equally spaced steps

“*i*” over the entire pattern including the background intensity and the sum of the contribution of Bragg reflections close to the “*i*” powder pattern step:

$$y_i(\text{obs}) = y_i(\text{background}) + \sum_i y_i(\text{Bragg}) \quad (\text{Eq.7})$$

A good initial structure model is required including both structural parameters (*e.g.* space group, unit cell parameters, and atomic positions) and instrumental details (*e.g.* peak shape, background). The calculated intensities $y_i(\text{calc})$ will be the sum of the contributions of the phases φ present in the sample. For the “*i*” step, several Bragg reflections can contribute to the intensity. The expression of the calculated profile intensity will be given as follows:

$$y_i(\text{calc}) = \sum_{\varphi} S_{\varphi} \sum_{hkl} L_{\varphi,hkl} |F_{\varphi,hkl}|^2 \Omega(2\theta_i - 2\theta_{\varphi,hkl}) A_{\varphi,hkl} P_{\varphi,hkl} C_{\varphi,hkl} + y_i(\text{bac}) \quad (\text{Eq.8})$$

Where S_{φ} is the scale factor of the phase φ , $L_{\varphi,hkl}$ contains the Lorentz, polarization and multiplicity factors, $F_{\varphi,hkl}$ is the structure factor which includes nuclear and magnetic structure factors if applicable, $\Omega(2\theta_i - 2\theta_{\varphi,hkl})$ is the peak shape function which describes the effects of the instrument and the sample on the reflection profile ‘*A*’ is the absorption factor of the instrument and the sample on the reflection profile, $A_{\varphi,hkl}$ is the absorption factor, $P_{\varphi,hkl}$ is the preferred orientation function, $C_{\varphi,hkl}$ includes special corrections (non-linearity, efficiencies, special absorption corrections, extinction, etc), $y_i(\text{bac})$ is the background intensity at step ‘*I*’ of the diffraction pattern. During the refinement cycles, each of these terms and its parameters may be varied to improve the match between observed and calculated diffraction patterns, *i.e.* to minimize the residual value.

The Rietveld method consists of refining a crystal (and/or magnetic) structure by minimizing the differences between the observed intensity $y_i(\text{obs})$ and the calculated intensity $y_i(\text{calc})$, important structural information may be obtained. Therefore, the quantity minimized in the least-square refinement is the residual S_y :

[43] H.M. Rietveld, Acta Cryst, 22, 151 (1967).

$$S_y = \sum_i \frac{[y_i(\text{obs}) - y_i(\text{calc})]^2}{y_i(\text{obs})} = \sum_i w_i [y_i(\text{obs}) - y_i(\text{calc})]^2 \quad (\text{Eq.9})$$

Where $w_i = 1/\sigma_i^2$ is the statistical weight that equals to $1/y_i(\text{obs})$ (σ_i^2 : being the variance of the observation y_i), and $y_i(\text{calc})$ is the intensity of each step which can be calculated by a mathematical expression that includes the factors related to both the structure and the non-diffraction terms.

The least-squares refinement aims to minimize the sum of the residual over all data points. The fitting results can be estimated by examining visually a plot of the difference between observed and calculated patterns, which should ideally be a straight line. There are also several numerical terms known as reliability or **R-Factors** that can be used to estimate the goodness of the least-square refinements. These residual values are defined as follows:

$$\text{Profile Factor :} \quad R_p = \frac{\sum |y_i(\text{obs}) - y_i(\text{calc})|}{\sum y_i(\text{obs})} \quad (\text{Eq.10})$$

$$\text{Weighted Profile Factor:} \quad R_{wp} = \left[\frac{\sum w_i [y_i(\text{obs}) - y_i(\text{calc})]^2}{\sum w_i (y_i(\text{obs}))^2} \right]^{\frac{1}{2}} \quad (\text{Eq.11})$$

$$\text{Expected Profile Factor:} \quad R_{exp} = \left[\frac{n-p+c}{\sum w_i [y_i(\text{obs})]^2} \right]^{\frac{1}{2}} \quad (\text{Eq.12})$$

$$\text{The goodness of Fit:} \quad \chi^2 = \left[\frac{R_{wp}}{R_{exp}} \right]^2 = \frac{\sum w_i [y_i(\text{obs}) - y_i(\text{calc})]^2}{n-p+c} \quad (\text{Eq.13})$$

$$\text{Bragg R-Factor:} \quad R_B = \frac{\sum |I_h(\text{obs}) - I_h(\text{calc})|}{\sum I_h(\text{obs})} \quad (\text{Eq.14})$$

$$\text{Crystallographic RF-Factor:} \quad R_F = \frac{\sum |F_h(\text{obs}) - F_h(\text{calc})|}{\sum F_h(\text{obs})} \quad (\text{Eq.15})$$

$$\text{Conventional Profile Factor:} \quad cR_p = \frac{\sum |y_i(\text{obs}) - y_i(\text{calc})|}{\sum |y_i(\text{obs}) - y_i(b)|} \quad (\text{Eq.16})$$

$$\text{Conventional Weighted Profile Factor:} \quad cR_{wp} = \left[\frac{\sum w_i [y_i(\text{obs}) - y_i(\text{calc})]^2}{\sum w_i [y_i(\text{obs}) - y_i(b)]^2} \right]^{\frac{1}{2}} \quad (\text{Eq.17})$$

In the above notation, **n** is the total number of points used in the refinement; **p** is the number of refined parameters; **c** is the number of constraints, and (**n** – **p** + **c**) represents the number of degrees of freedom. In certain cases, the Bragg reflection is labelled by ‘**h**’. Conventional Rietveld **R-Factors**: **cR_p** and **cR_{wp}**, are calculated as above but using background-corrected counts; where **y_i(b)** represents the number of calculated groundstrokes at the step “**i**”. *Note*: In this thesis will be given the conventional factors **cR_p** and **cR_{wp}**, that is to say, that the calculated and observed intensities are corrected to the background noise which implies that in the calculation of **cR_p** and **cR_{wp}**, the denominators become lower whereas the numerators do not vary, so **cR_p** and **cR_{wp}** are more important than **R_p** and **R_{wp}** but more realistic [44].

All refinements of materials structures from X-Ray powder diffraction patterns in this thesis were carried out with the Rietveld method using the package of FullProf program developed by J. Rodriguez-Carvajal and T. Roisnel [38,39]. This program handles all of the corrections, peak shape functions, background fitting, as well as structural and instrumental effects, through means that are described in the FullProf technical reference [45]. The Rietveld refinement program, therefore, adjusts refinable parameters until the residual (Eq.9) is minimized to obtain the best fit between the observed and calculated profiles.

A new development in the quantitative analysis using the Rietveld analysis by refining the multiple phases was used for better identification of phases. Information’s content of a powder diffraction pattern is illustrated in the following Fig.13.

[44] E. Jansen, W. Schafer, G. Will, J. App. Cryst., 27, 492 (1994).

[45] J. Rodriguez–Carvajal, ‘An introduction to the program fullprof 2000’, Saclay, July (2001).

[46] C. Rey, C. Combes, C. Drouet, H. Sfihi, Chemical Diversity of Apatites, Adv. Sci. Technol. 49 (2006) 27–36. doi:10.4028/www.scientific.net/AST.49.27.

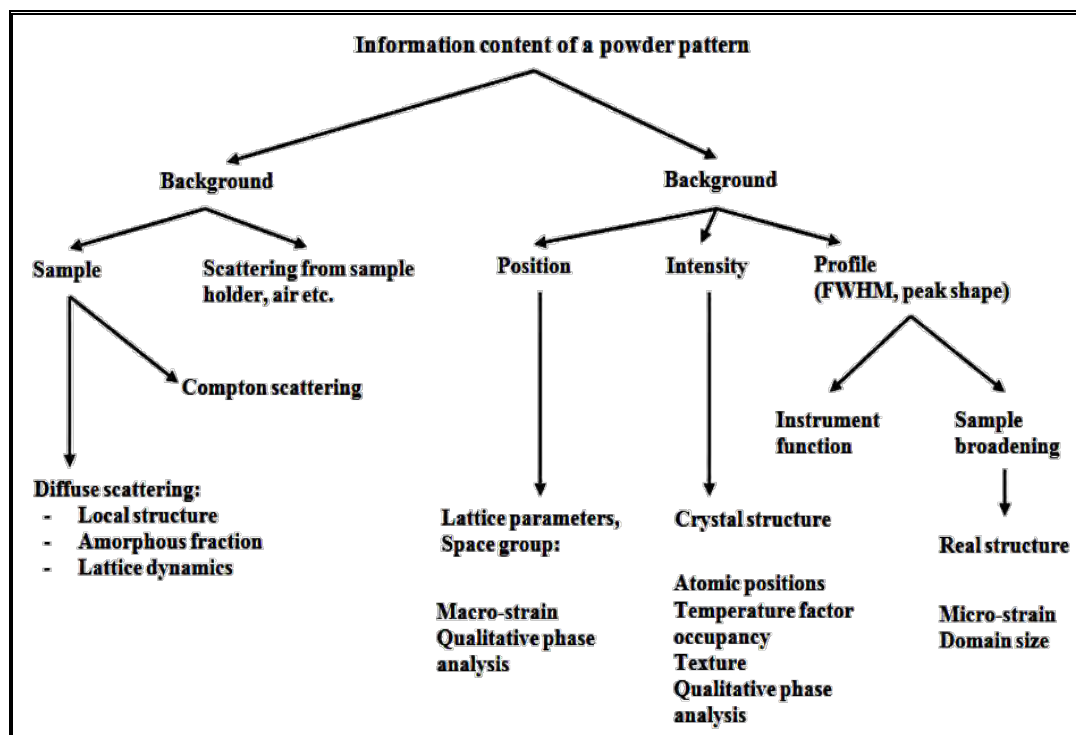


Fig.13: Information content of a powder pattern.

- Refinement of the Apatites Materials.

The X-ray powder diffraction patterns of the synthesized apatites, which are comparable to those reported earlier of the Lacunar apatites; $\text{Na}_{1-x}\text{K}_x\text{PbCa}(\text{PO}_4)_3$ [30] and for $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ [46]. Indexing of the X-ray powder patterns was performed using the software DICVOL.

The first 20 peak positions, with a maximal absolute error of 0.03° (20), were used as input data. The data were calibrated externally using the zero shift of the Rietveld refinement. All the found compositions were assigned to a hexagonal apatite structure. The structural refinements were done using the Rietveld method with the Fullprof program integrated into WINPLOTR software. The starting models for Rietveld refinements were taken from References [30] and [42]. As a starting model in the PCR file, we used the atomic coordinates of $\text{Na}_{1-x}\text{K}_x\text{Pb}_3\text{Ca}(\text{PO}_4)_3$ [30] with space group ***P6₃/m***. Hence the needs of 34 structural and non-structural parameters were allowed to vary to adjust the refinement. This includes; 17 atomic parameters (including positions, occupancies, and isotropic thermal displacements), 6

background coefficients, 1 scale factor, 1 zero point, 3 cell parameters, 2 line asymmetry parameters, using a pseudo-Voigt function, 3 half-width parameters, these half-widths of the diffraction peaks as a function of '2 θ ' was evaluated by the Caglioti equation. Also, one preferred orientation parameter was refined in the direction of the diffraction vector perpendicular to (001). For example, Fig.14 shows the automatic generation of PCR files for Rietveld's first refinement plot of $\text{KPb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$. The agreement between the theoretical and experimental diffractogram is given by the values of the Reliability factors **R_p**, **CR_p**, **R_{wp}**, and **CR_{wp}** defined by the previous equations; Eq.10&11&16&17.

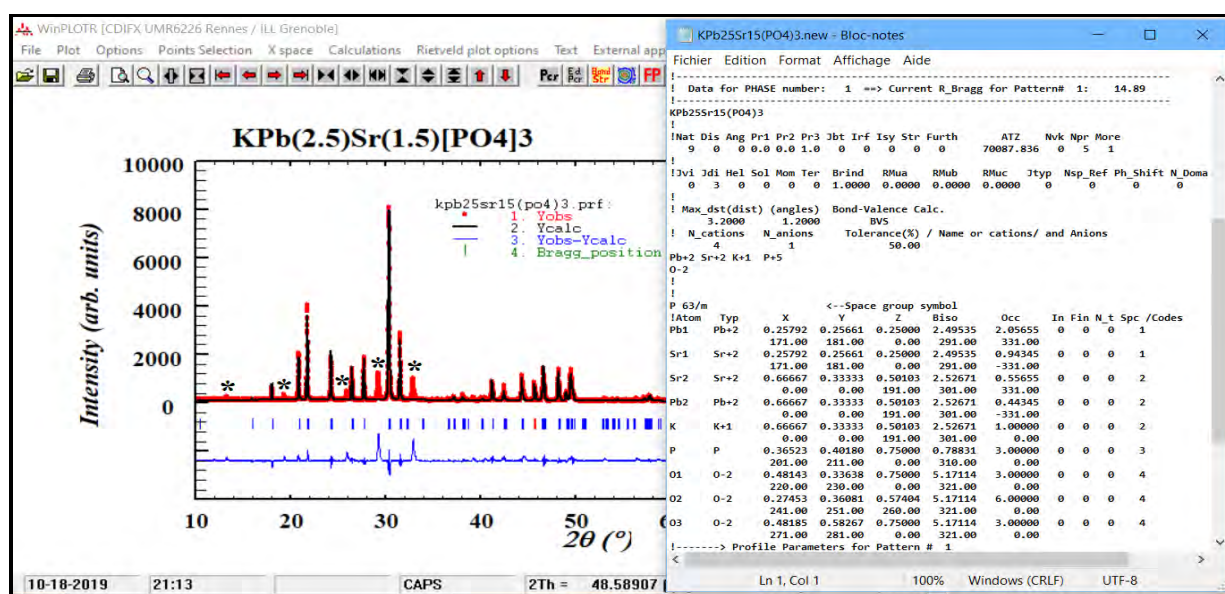


Fig.14: Automatic generation of PCR file for Rietveld first refinement plot of $\text{KPb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$.

Rietveld's first refinements plot of $\text{KPb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$ (Fig.14), showed that all the reflections could be indexed in the spatial group **P6₃/m** (N°. 176), except for the reflections which are indicated by the stars. The additional peaks have been detected by the HighScore program [47], they were assigned to the compound $\text{Pb}_3(\text{PO}_4)_2$ [48,49] (Fig.7). Fig.15 shows the detection of a minor phase $\text{Pb}_3(\text{PO}_4)_2$ by the HighScore program [47].

[47] T. Degen, M. Sadki, E. Bron, U. König, G. Nénert; Powder Diffraction 29 (2014) S13-S18

[48] Argyle, Hummel., J. Am. Ceram. Soc., 43, 452, (1960)

[49] C. Joffrin, J.P. Benoit, L. Deschamps, M. Lambert, Étude par diffraction et diffusion de rayons X de la transition de phase ferroélastique du phosphate de plomb : $\text{Pb}_3(\text{PO}_4)_2$, J. Phys. 38 (1977) 205–213.

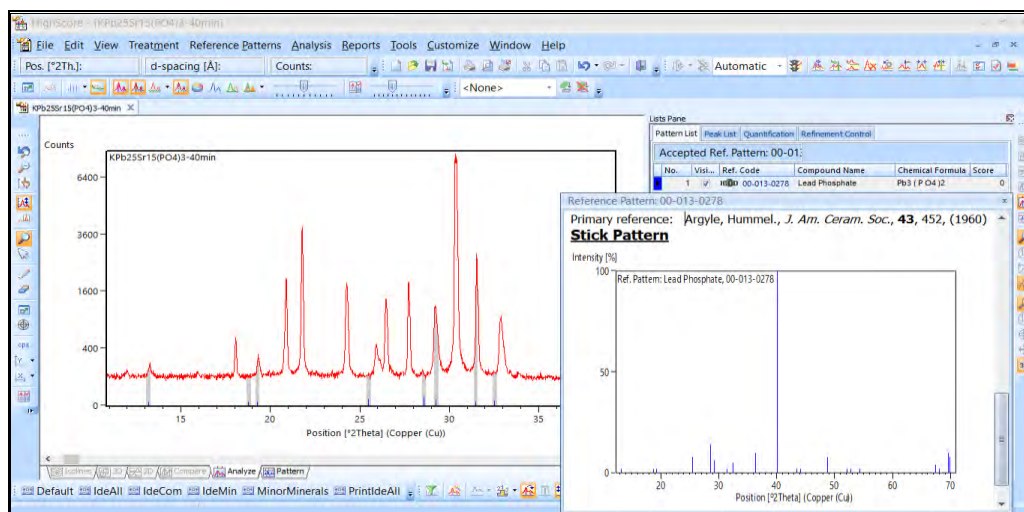


Fig.15: Detection of a minor phase $Pb_3(PO_4)_2$ by the HighScore program.

The final plot of Rietveld refinement of $KPb_{2.5}Sr_{1.5}(PO_4)_3$ is given in Fig.16 the refinement was run with the presence of the second phase as impurity type ($Pb_3(PO_4)_2$). At this stage of the refinements, the structural model indicators converged to the very satisfactory values of the reliability factors (Eq.10&11&16&17); as illustrated in Chapter. III.

To avoid repetition in the following chapter; in Figs.16&14, upper symbols illustrate: the observed data $N^{\circ}1$, and the calculated pattern (solid line) for $N^{\circ}2$, the lower curve is the difference diagram schematize in the $N^{\circ}3$ and the vertical markers show calculated positions of Bragg reflections for two phases in $N^{\circ}4$.

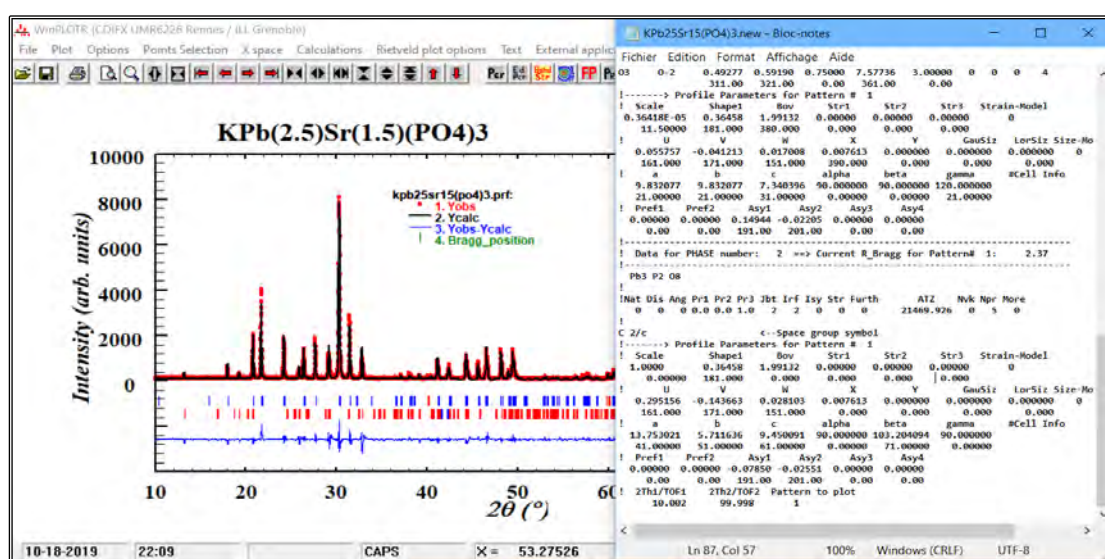


Fig.16: Final plot of Rietveld refinement of $KPb_{2.5}Sr_{1.5}(PO_4)_3$, the refinement was done with $Pb_3(PO_4)_2$ the second phase.

IV. Raman and Infrared spectroscopy.

The main spectroscopies employed to detect vibrations in molecules are based on the processes of infrared absorption and Raman scattering. They are widely used to provide information on chemical structures and physical forms, to identify substances from the characteristic spectral patterns (fingerprinting), and to determine quantitatively or semi-quantitatively the amount of a substance in a sample. Samples can be examined in a whole range of physical states; for example, as solids, liquids or vapours, in hot or cold states, in bulk, as for microscopic particles, or as for surface layers.

IV.1. History of Raman.

The phenomenon of inelastic scattering of light was first postulated by Smekal in 1923 [50] and first observed experimentally in 1928 by Raman and Krishnan [51]. The Indian Association for the Cultivation of Science: At this institute, Sir C. V. Raman discovered in 1928 that when a beam of coloured light entered a liquid, a fraction of the light scattered by that liquid was of a different colour. Raman showed that the nature of this scattered light was dependent on the type of sample present. On Fig.17 the original experiments were done by visual observation, precise measurements were made with this quartz spectrograph and first made public by Raman in a lecture in Bangalore, *"I propose this evening to speak to you on a new kind of radiation or light emission from atoms and molecules."* With these words, Professor C.V. Raman of CALCUTTA University began his lecture to the South Indian Science Association in BANGALORE on March 16, 1928 [52].

[50] A. Smekal, Naturwissenschaften, 43, 873 (1923).

[51] C.V. Raman, K.S. Krishnan, Nature, 121, 501 (1928).

[52] Book online, DK Indian Icon Series, DK India, New Delhi, 2018. Pb. Rs 250 28 February 2018.

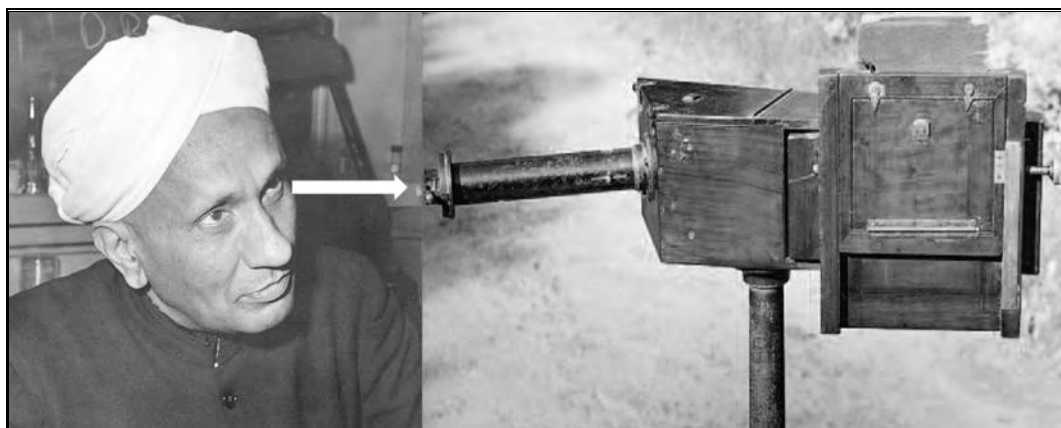


Fig.17: *Pr. Chandrasekhara.Venkata. Raman with the quartz spectrograph; the original experiments were done by visual observation.*

Profesor C.V Raman proceeded to describe a discovery that resulted from a deceptively simple experiment. It was conducted far from the great centres of scientific research in the Western world and used inexpensive equipment. Although one of the initial experiments required only a mercury lamp, a flask of benzene, and a direct vision pocket spectroscope, the results would capture the attention of scientists around the world and bring many accolades, including the Nobel Prize, to their discoverer. The experiments are discussed in detail below.

At the time of the discovery, the 40-year-old Raman held the Palit Chair for physics at CALCUTTA University. His research, however, was conducted at the Indian Association for the Cultivation of Science (IACS), CALCUTTA, which was established by Mahendra Lal Sircar in 1876 as the first basic research centre in India. Educated entirely in India, Raman made his first trip to London in 1921, where his reputation in the study of optics and especially acoustics was already known to the English physicists J. J. Thomson and Lord Rutherford, who gave him a warm reception. Raman's speciality had been the study of the vibrations and sounds of stringed instruments such as the violin, the Indian veena, and tambura, and the uniquely Indian percussion instruments, the tabla, and the mridangam.

But it was the return trip from London to Bombay aboard the "SS Narkunda" that would change forever the direction of Raman's future. During the fifteen-day voyage, his restless and probing mind became fascinated with the deep blue colour of the Mediterranean. Unable

to accept Lord Rayleigh's explanation that the colour of the sea was just a reflection of the colour of the sky, Raman proceeded to outline his thoughts on the matter while still at sea and sent a letter to the editors of the journal *Nature* when the ship docked in Bombay. A short time later Raman was able to show conclusively that the colour of the sea was the result of the scattering of sunlight by the water molecules. Ironically, it was the same argument that Rayleigh (John William Strutt RAYLEIGH, Nobel Prize in Physics 1904) had invoked when explaining the colour of the sky the blue was the result of the scattering of sunlight by the molecules in the air. Raman was now obsessed with the phenomenon of light scattering. His group in CALCUTTA began an extensive series of measurements of light scattered primarily by liquids but also by some solids. As a result, Raman was able to explain the blue colour observed in the ice of Alpine glaciers (Fig.18).

Analysis of light scattered by a liquid is not an easy task, and much of the early work in CALCUTTA was done by the visual observation of colour rather than precise measurements of the light's wavelength as shown in Fig.18.

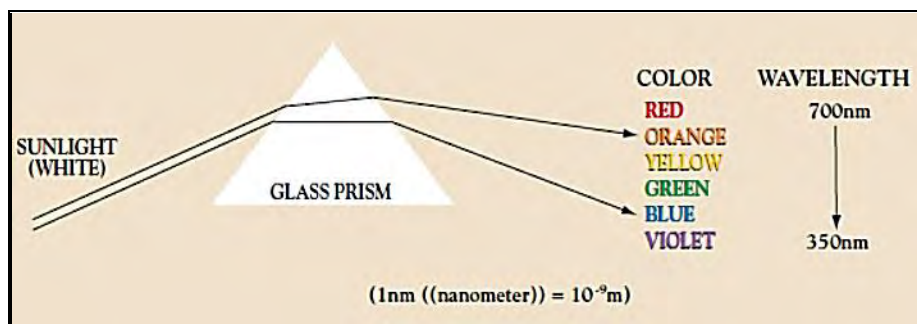


Fig.18: Visual observation of light scattered by alpine glaciers.

The violet light of the solar spectrum is isolated with a violet filter and passed through the liquid sample. Most of the light emerging from the liquid sample is the same colour as the incident violet beam: the so-called Rayleigh scattered light. However, Raman and K. S. Krishnan were able to show that some of the scattered light was a different colour, which they could isolate by using a green filter placed between the observer and the sample. The advantage of using visual observation is that several substances can be studied quickly. In his

first report to Nature, titled “A New Type of Secondary Radiation,” Raman indicated that approximately 60 different liquids had been studied, and all showed the same result; some scattered light had a different colour than the incident light. “It is thus,” Raman said, “a phenomenon whose universal nature has to be recognized.” The fundamentals of Raman’s crucial experiment are outlined in Fig.19.

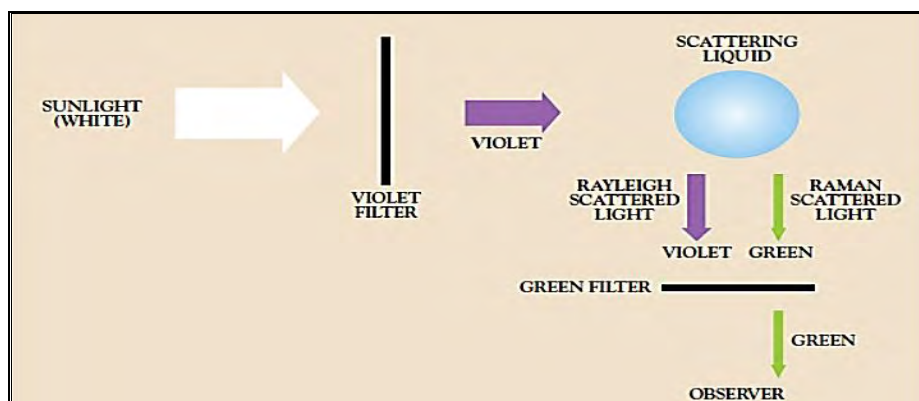


Fig.19: Raman’s crucial experiment.

The Raman Effect is very weak; only one in a million of the scattered light particles, or photons, actually exhibits the change in wavelength. This explains, in part, why the effect was not discovered earlier. In all of the early light-scattering studies, the excitation source was sunlight, which Raman has described as being plentiful in CALCUTTA, but it still lacked the desired intensity. The acquisition in 1927 by the IACS of a seven-inch (18cm) refracting telescope enabled Raman to condense the sunlight and create a more powerful light source for his studies. By early 1928, mercury arc lamps were commercially available, and he switched to this even more intense light source. Raman knew that visual and qualitative observations alone would not be sufficient information. He methodically set out to measure the exact wavelengths of the incident and Raman scattering by replacing the observer with a pocket spectroscope. He ultimately replaced it with a quartz spectrograph with which he could photograph the spectrum of the scattered light and measure its wavelength. These quantitative results were first published in the Indian Journal of Physics on March 31, 1928.

Although Raman's original experiments were done by visual observation, precise measurements were made with this quartz spectrograph given the first Raman spectra, photographed in 1928 are outlined in Fig.20. First made public by Raman in a lecture in BANGALORE on March 16, 1928.

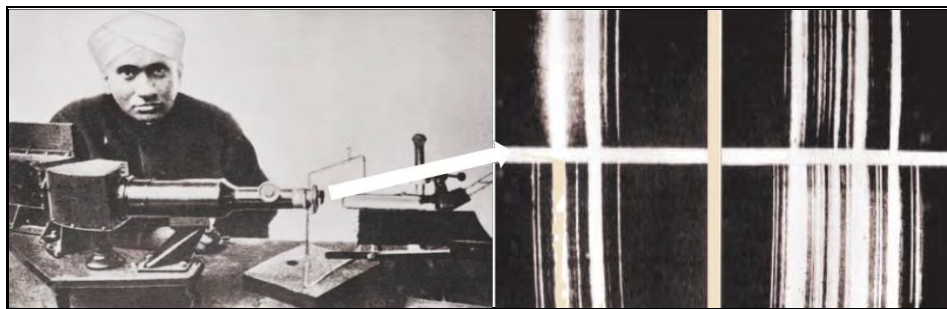


Fig.20: Raman's original experiments were done by visual observation; precise measurements were made with this quartz spectrograph given the first Raman spectra, photographed in 1928.

Other scientists quickly understood the significance of this phenomenon as an analytical and research tool and called it the Raman Effect. This method became even more valuable with the advent of modern computers and lasers. Its current uses range from the non-destructive identification of minerals to the early detection of life-threatening diseases. For his discovery, Raman was awarded the Nobel Prize in physics in 1930.

As we mentioned before, the Handbook of Raman spectroscopy [53] is a non-destructive method allowing characterizing the molecular composition and the material structure. Raman scattering results from light-matter interaction and provides access to molecular and crystal (phonon) vibrations. This technique is complementary to infrared spectroscopy [54] which also allows studying the vibrational modes of a material. The applications very diverse [55–58] concern the physics and chemistry of materials, biology, ..., etc.

[53] I.R. Lewis, H.G.M. Edwards, Ed., 'Handbook of Raman spectroscopy', ISBN: 0-8247-0557-2, Marcel Dekker, Inc – New York (2001).

[54] E. Schuller, R. Claus, H.J. Falge, G. Borstel, Z. Naturforsch, 32, 47 (1977).

[55] P.J.Caspers, G.W. Lucassen, R. Wolthuis, H.A. Bruining and G.J. Puppels, Biospectroscopy 4, S31, (1998).

IV.2. History of Infrared & Infrared Technology.

William Herschel, who discovered infrared rays, was a renowned British astronomer of German (German-British) origin. He was born in 1738 in Germany. Sent to England for his military obligations, he settled there permanently. Herschel was also a musician, composer, and mathematician: he was a jack-of-all-trades. He composed 24 symphonies, concertos, sonatas...etc. At the same time, Herschel was interested in astronomy. In 1776, Herschel built his first telescope, [Fig.21](#). He was an outstanding observer: he carried out his observations with great rigour. It is thanks to this very methodical work that he discovered the planet Uranus by chance in 1781. Following this famous discovery, King George III awarded him the title "King's Astronomer". Later, he discovered the two satellites of Uranus: Titania and Oberon as well as two satellites of Saturn: Mimas and Enceladus. During his long life, Herschel made many discoveries and built multiple telescopes, each one more powerful than the other. For these incredible discoveries, Herschel was appointed president of the Royal Astronomical Society. He died in 1822. [\[59\]](#)

The name infrared comes from the Latin word ‘infra’, meaning “below”. Red is the colour of the longest wavelengths of visible light. Infrared light has a longer wavelength than red light. A longer wavelength means it has a lower frequency than red, hence “below”.

[56] A. Cvetkovic, A.J.J. Straathof, D.N. Hanlon, S. Van Der Zwaag, R. Krishna, L.A.M. Van Der Wielen, *Biotechn. Bioeng.*,86, 389 (2004).

[57] MIT: research in biomedical optics, ‘Raman spectroscopy for measurement of blood analytes’, Web site:http://web.mit.edu/spectroscopy/research/biomedresearch/Raman_blood.html

[58] Philips Research Press Release, Philips demonstrates biosensor technologies for high-sensitivity molecular diagnostics, Web site:<http://www.research.philips.com/newscenter/archive/2005/051020-biosensors.html>

[59] Investigation of the Powers of the Prismatic Colors to Heat and Illuminate Objects; With Remarks, That Prove the Different Refrangibility of Radiant Heat. To which is Added, an Inquiry into the Method of Viewing the Sun Advantageously, with Telescopes of Large Apertures and High Magnifying Powers. By William Herschel.

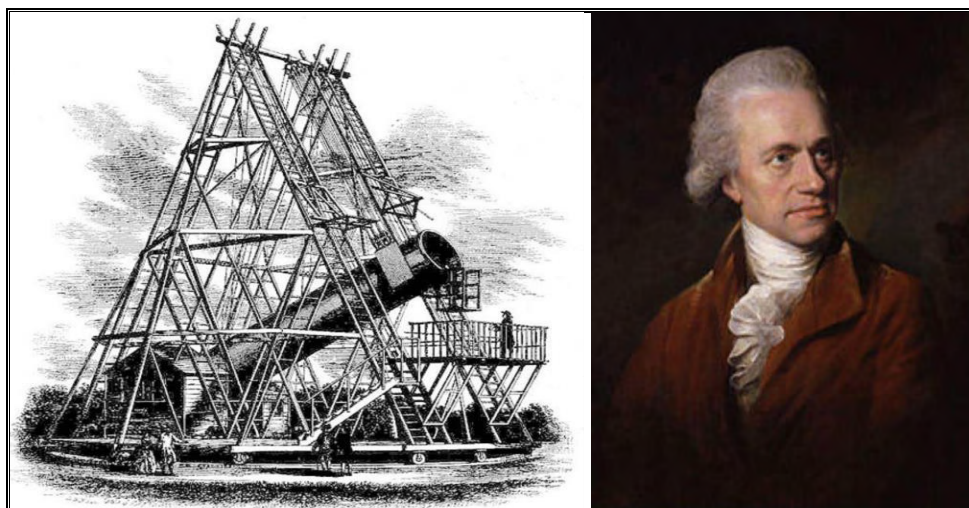


Fig.21: representing the Herschel telescope with a focal length of 40 feet (12 m) and an aperture of 48 inches (122 cm).

Thanks to his original articles [60,61], we were able to understand Herschel's approach. Herschel was very interested in the sun. He liked to observe it through his telescope. But, to avoid burning or damaging his eyes, he used different coloured filters with which he could look at the sun. As he used them, he noticed that the filters produced a different level of heat and that this temperature change seemed to be related to the colour of the filter. Herschel wrote in his essay: "In a series of experiments I have sometimes performed, touching on the method of observing the sun with large telescopes, to my best advantage I used various combinations of differently coloured darkening glasses. What seemed remarkable was that, when I used some of them, I felt a sensation of warmth, even though I had little light; while others gave me a lot of light with little sensation of warmth." This led Herschel to conduct an experiment, based on the one Isaac Newton conducted. Newton demonstrated with a prism that light breaks down into an arc-sky called the colour spectrum.

Herschel took the experiment a step further in 1800 [60,61] when he passed sunlight through a prism, which projected the solar spectrum onto a table. The solar spectrum contains all the colours that make up sunlight, i.e. violet, blue, green, yellow, orange and red, Fig.22.

[60] Experiments on the Refrangibility of the Invisible Rays of the Sun. By William Herschel

[61] POUR LA SCIENCE N°423 JANVIER 2013, article « Herschel et l'énigme des Infrarouges. »

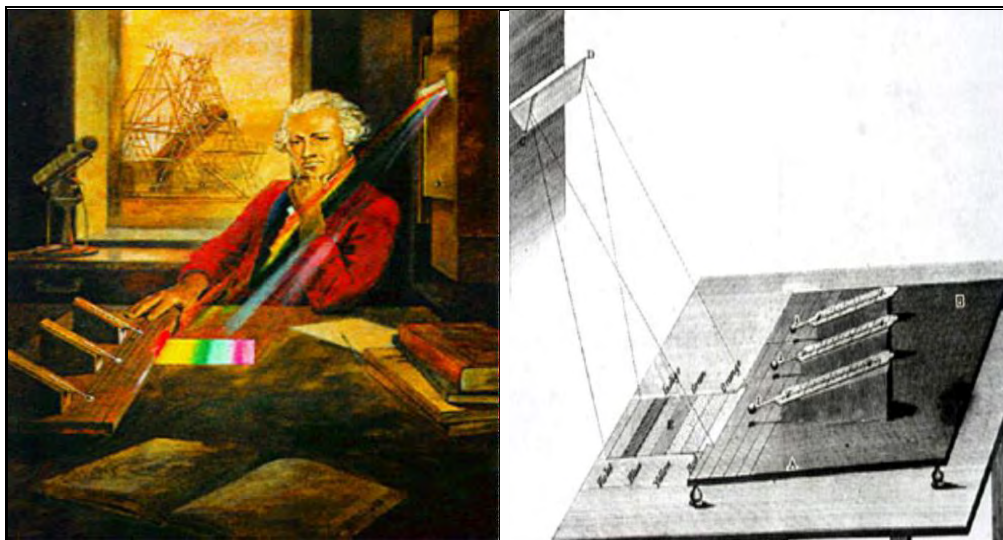


Fig.22: *Herschel discovered that there was another kind of light, invisible this time. The rays he discovered beyond the red are now called the Infrared.*

He made his great discovery on April 24, 1800. On that day he took three mercury thermometers, blackened the ends of which he placed them on a piece of metal as small inclined support so that they would not move, covered with a sheet of white paper. He placed the support so that thermometer 'T.1' could take the value in the radius of the chosen colour spectrum and the other two 'T.2' and 'T.3' in the shade. These were used as standard thermometers. Again, he made the spectrum of the sun appear with the help of a prism: red being the colour just in front of the holder. He then measured with thermometer 'T.1' the temperature in what he called "*the margin of the disappearance of the red rays*". He did the same experiment several times with different thermometers and concluded as follows: "*The experiments carried out proved that the thermal power of the prism's colours is far from being divided equally and that red rays are mainly dominant in this area*". Herschel then discovered that the temperature of red is higher than that of green and that the temperature of green is higher than that of violet. [62,63]

[62] Experiments on the Solar, and on the Terrestrial Rays that Occasion Heat; With a Comparative View of the Laws to Which Light and Heat, or Rather the Rays Which Occasion Them, are Subject, in Order to Determine Whether They are the Same, or Different. Part I. By William Herschel.

[63] AMERICAN SCIENTIST, the magazine of Sigma Xi, The Scientific Research Society Volume 100, Number 3, Page: 218 MAI JUIN 2012, article « Herschel and the puzzle of infrared. »

For more details, we present the Herschel experiment carried out by the high school students Clémence DUFLOS and Anthony FORTIN [64].

First, they painted the tips of the thermometers with black shoe polish, Fig.23. This allows to better absorb the received light (because a black body absorbs all the visible radiation it receives) and to transform it into heat. Thus, the thermometers will capture the received heat better and faster.



Fig.23: Thermometers with black shoe polish ^[64].

The second thing, they cut a hole with a cutter to just let some of the sun's rays pass through the prism. They then fixed the prism with scotch "The scotch must only be on the sides of the prism because if the scotch goes through the prism, the spectrum will not be whole, it will be cut with a black band > the scotch". Then they cut a line at the bottom of the cardboard with a cutter, this allowed the thermometer to be held, Fig.24.

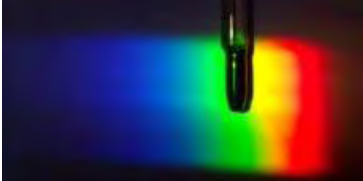
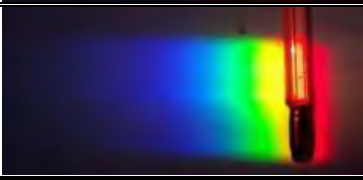


Fig.24: Experimental procedure ^[64].

[64] Clémence DUFLOS et Anthony FORTIN, Lycée BRANL Olympiades de Physique France.

They used two different thermometers 'T₁ and T₂' one after the other, both to measure the ambient temperature and then in the violet, green, red, and finally Infrared rays. Table.3 shows the temperatures they found:

Table.3: Temperatures with the experiments ^[64].

Temperatures	Experiment
Ambient temperatures inside the box : T ₁ > 16°C and T ₂ > approx. 15.2°C	
Temperatures in the purple : T ₁ > approx. 16.2°C and T ₂ > approx. 15.2°C	
Temperatures in the green : T ₁ > 17°C and T ₂ > 17°C	
Temperatures in the red: T ₁ > 18°C and T ₂ > 18°C	
Temperatures in the Infrared: T ₁ > approx. 18.2°C and T ₂ > approx. 18.4°C	

In the end, experiments show that temperatures are gradually increasing from violet to infrared, whether with the first thermometer or the second. Fig.25 shows the graph, showing the temperature rise between the ambient temperature and the temperature in the visible spectrum and beyond for the 'T₁' thermometer. It can be seen here that the temperature tends to rise and that this rise continues beyond the red light in the Infrared.

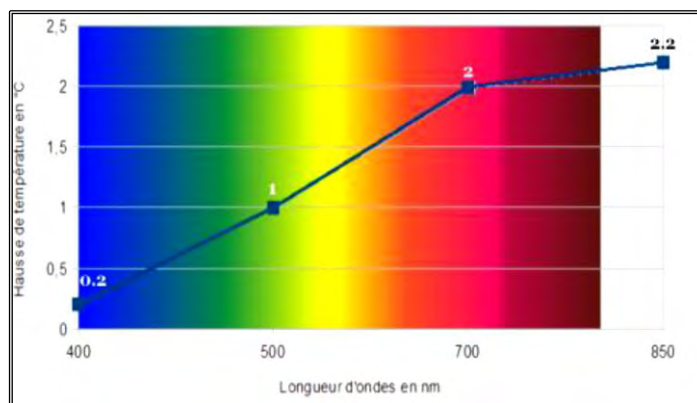


Fig.25: Temperature differences between the ambient temperature and the temperature in the colours of the spectrum ^[64].

Returning to Herschel [65], he decided to make the same experiments but on the side of the purple colour. And there, he noticed that nothing happened. The temperature of the thermometer 'T.1' was the same as that of the standard thermometers.

IV.3. Instrument.

a) Raman spectroscopy.

- Raman Spectroscopy at Room Temperature.

The Raman spectra measurements at room-temperature in Fig.26, were carried out in the Department of Earth Sciences, Uppsala University [27,66-70]. The key system components include a high-throughput, single-stage imaging spectrometer (HoloSpec f/1.8i, Kaiser Optical Systems, Inc.) equipped with a holographic transmission grating and thermoelectrically cooled two-dimensional multichannel CCD detector (Newton, Andor Technology, 1600×400 pixels, thermoelectrically cooled down to -60 °C), an argon-ion laser (Spectra-Physics, 514.5 nm, 20 mW), and an optical imaging system (magnification 20×, spatial resolution ~1 μm). Two holographic notch filters (Kaiser Optical Systems, Inc.) blocked the Rayleigh line.

[65] Investigation of the Powers of the Prismatic Colours to Heat And Illuminate Objects; With Remarks, That Prove the Different Refrangibility of Radiant Heat. To Which is Added, an In querying to the Method of Viewing the Sun Advantageously, with Telescopes of Large Apertures and High Magnifying Powers. By William Herschel.

[66] M.Azdouz, B.Manoun, M.Azrou, L.Bih, L.ElAmmari, S.Benmokhtar, P. Lazor, J.Mol. Struct. 963(2010)258.

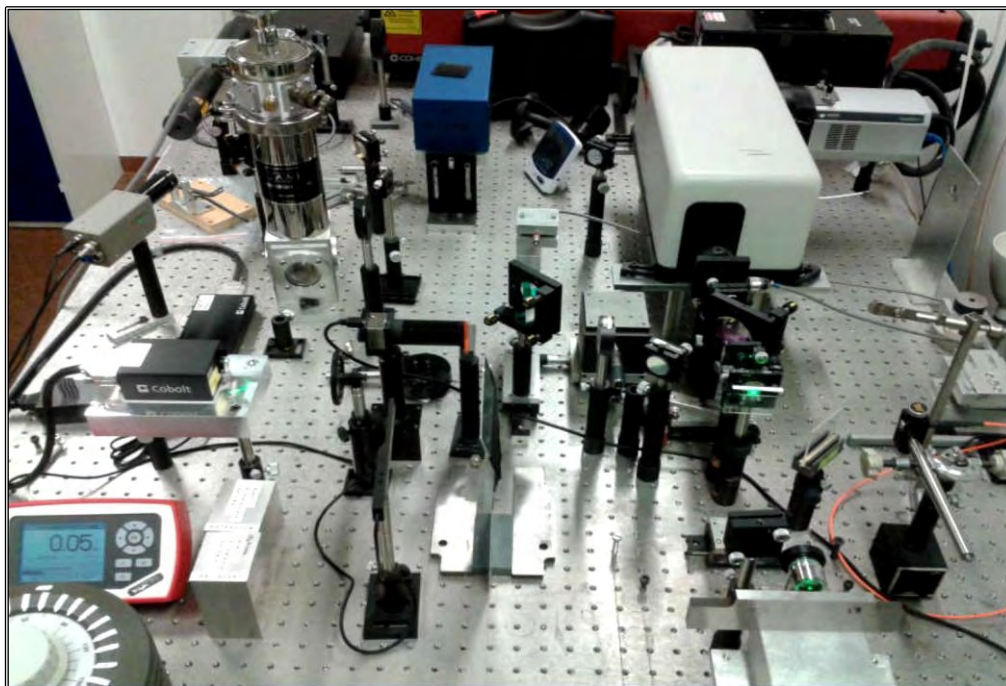


Fig.26: Raman spectroscopic system in the Department of Earth Sciences, Uppsala University, Sweden.

The scheme of the spectrometer in Fig.27, was calibrated by fluorescence lines of a neon lamp. Non-polarized Raman spectra were collected in the back-scattering geometry, in the range of $180\text{--}2280\text{ cm}^{-1}$, at a resolution of about 3 cm^{-1} . The precisions of spectral measurements, as estimated from the wavelength calibration procedure and peak fitting results, were 1.5 and $0.1\text{--}0.4\text{ cm}^{-1}$, respectively. The acquisition time varied from 30 s to 5 min .

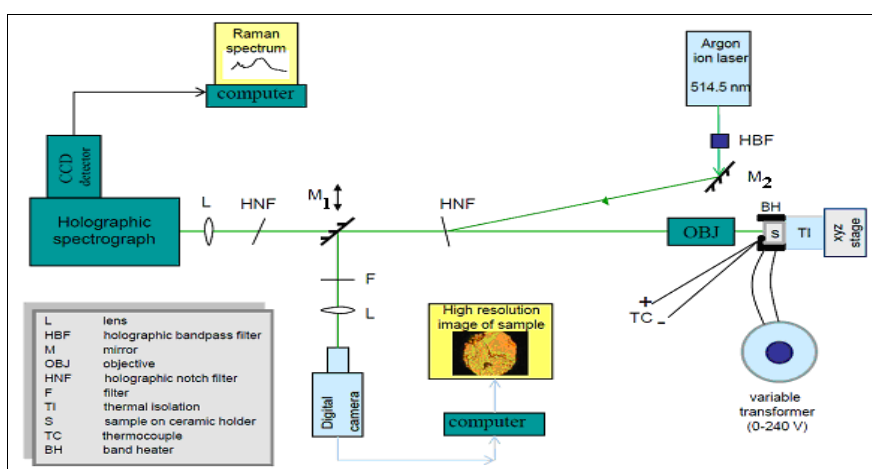


Fig.27: Principal layout scheme of the Raman experimental setup.

- Raman Spectroscopy at High Temperature.

The Raman spectra of the lacunar apatites: $\{\text{Na/K}\}\text{Pb}_{3/2}\{\text{Sr/CaCd/SrCa}\}(\text{PO}_4)_3$, were made at high temperatures ranging from ambient to 773K and at atmospheric pressure. Heating was accomplished by using a mica insulated band heater (DuraBand, Tempco Electric Heater Corporation) mounted around the sample 'ceramic holder, Fig.28' and connected to a 'variable transformer, Fig.28'. Temperature changes during the heating/cooling cycles were induced and controlled by adjusting the transformer's voltage (0–240 V) and monitored with an accuracy of $\pm 1^\circ\text{C}$ by the K-type 'thermocouple adjacent', Fig.28 to the sample. During spectral acquisitions, temperatures were stabilized to within 1 and 3 $^\circ\text{C}$, for the low and high-temperature measurements respectively.

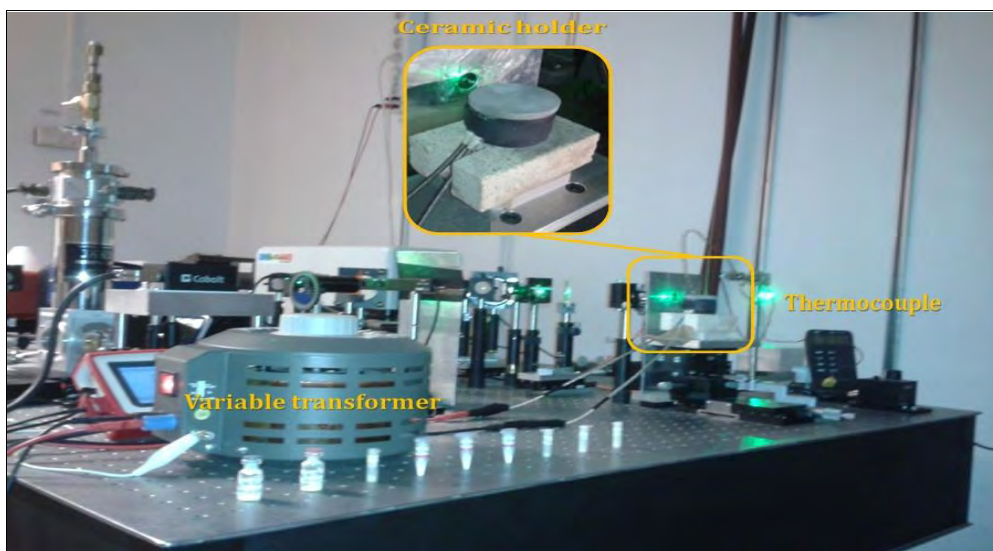


Fig.28: Picture of the real installation of the Raman spectrometer in the Department of Earth Sciences, Uppsala University, Sweden.

The Raman spectrum then consists of fine bands with frequencies between -767.59 and 1688 cm^{-1} . The Raman intensity corresponds to a maximum centred around the zero position of the eigenmode of vibration.

-
- [67] B.Manoun, M.Azdouz, M.Azrou, R.Essehli, S.Benmokhtar, L.ElAmmari, A.Ezzahi, A.Ider, P.Lazor, J.Mol. Struct.986(2011)1.
[68] H. Bih, L. Bih, B. Manoun, M. Azdouz, S. Benmokhtar, P. Lazor, J. Mol. Struct. 936 (2009) 147–155.
[69] S.Lahrich, B.Manoun and M.A. El Mhammedi, Journal of Applied Surfaces and Interfaces, 7(2017)17.
[70] S.Louihi, M.Azdouz, Z.Chchiyai, B.Manoun, Y.Tamraoui, A.Nia, E.Magha, J.Biya, P.Lazor, Journal of Applied Surfaces and Interfaces, Journal of Applied Surfaces and Interfaces 28(2018)35.

b) Infrared Spectroscopy.

Infrared radiation is electromagnetic radiation with a wavelength between 800nm and 1mm. It lies between visible light and microwaves. Within this wavelength range, different types of infrared radiation can be distinguished, ranging from Near-Infrared to Far-Infrared.

The infrared spectra of the prepared samples in the spectral range between 1300 and 400 cm^{-1} were recorded using a type SP-FTIR spectrometer (The Fourier transform infrared spectroscopy), using powdered spectroscopic grade KBr and 1% of the material with the manufacturing conditions of pellets (mid-IR). The Spotlight 400 FT-IR Imaging System in Fig.29, combines high sensitivity and rapid imaging with ease-of-use. The ability to image large sample areas rapidly at high spatial resolution extends FT-IR microscopy into new applications.



Fig.29: Picture of the Spotlight 400 FT-IR Imaging System, in laboratories of the MSN department, Mohammed VI Polytechnic University, Benguerir.

IV.4. Group theory analysis of Raman and Infrared active modes.

The group theory analysis of Raman-, and Infrared-active modes for the characterization of the apatite crystals are widely studied in the lead-phosphorus, -vanadium, and -arsenic apatite structures, for more details see [30,71]. Factor group analysis of the $\text{APb}_{4-x}\text{M}_x(\text{XO}_4)_3$ shows the internal and external modes for the tetrahedral phosphates ions. The

normal modes of vibration can be classified among the irreducible representations yielding to the optical phonon modes of C_{6h} as bellow.

$$\Gamma_{opt} = 12A_g + 8E_{1g} + 12E_{2g} + 8A_u + 12B_u + 8B_g + 12E_{1u} + 8E_{2u}$$

Note that we did not subtract the modes related to $2a$ sites (6_3 axes), which are vacant in the lacunars apatites structures. These are further developed in the already published references [28,29]. The formula developed of internal and external mode contribution of the $[PO_4]^{3-}$ groups to the Raman- and Infrared-active vibrations can be deduced by the factor group analysis as f follows.

$$\begin{aligned} \Gamma(PO_4) = & 6A_g (\nu_1 + \nu_2 + 2\nu_3 + 2\nu_4) + 3E_{1g} (\nu_2 + \nu_3 + \nu_4) + 6E_{2g} (\nu_1 + \nu_2 + 2\nu_3 + 2\nu_4) + 3A_u (\nu_2 + \nu_3 + \nu_4) \\ & + 6E_{1u} (\nu_1 + \nu_2 + 2\nu_3 + 2\nu_4) \end{aligned}$$

In real crystal structures, tetrahedra are generally deformed and distributed in crystallographic sites of low symmetry. In this case, all vibration modes can become active in Raman and infrared. In the majority of materials containing tetrahedral groups such as BO_4 , AsO_4 , SO_4 , CrO_4 , ..., etc., the vibration frequencies assigned to the different vibration modes of the tetrahedron appear in Fig.30, in the following order (for more details see Annex. I):

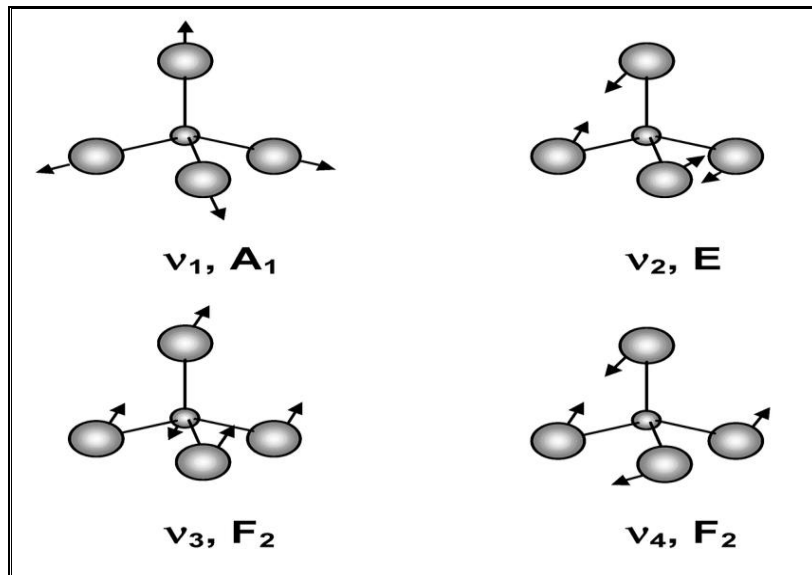


Fig.30: Normal modes of vibration of a molecule tetrahedral ' XY_4 ' of symmetry ' T_d ' [72].

[71] R. Ternane, M. Ferid, M. Trabelsi-Ayadi and B. Piriou, Spectrochim. Acta, A (55) (1999) 1793.

[72] H. Poulet et J. P. Mathieu, Spectres de vibration et symétrie de cristaux (1970).

According to Fig.31, the vibration modes of $[\text{PO}_4]^{3-}$ tetrahedra the compositions of the phosphate apatites, are interpreted using the factor group ' C_{6h} ' and the space group $P6_3/m$. The formula of internal and external mode contribution, of the $M(1/2) - [\text{PO}_4]^{3-}$ groups to the Raman- and Infrared-active vibrations where: The " A_g , E_{1g} and E_{2g} " normal modes are Raman-active, whereas " A_u and E_{1u} " normal modes are infrared active [73]. The subscripts (**g**) and (**u**) are used to describe modes that are respectively symmetric (**g** = gerade) and antisymmetric (**u** = ungerade) concerning the symmetry centre. The notations (**V**) of molecular or internal vibrations, for instance, it is agreed to describe the symmetric stretching vibration of phosphate groups (an **A** and **E** active modes of vibrations) as ' V_1 (P-O_n)' mode, the symmetric bending vibration as ' V_2 ', for the antisymmetric stretching vibration as ' V_3 ' and the antisymmetric bending vibration as ' V_4 ', the other vibrations are the external modes. Referring to the X-ray diffraction, the structure remains similar for the compositions of the lacunar apatites, this observation is well confirmed by the same number of bands active by infrared and Raman for all compounds.

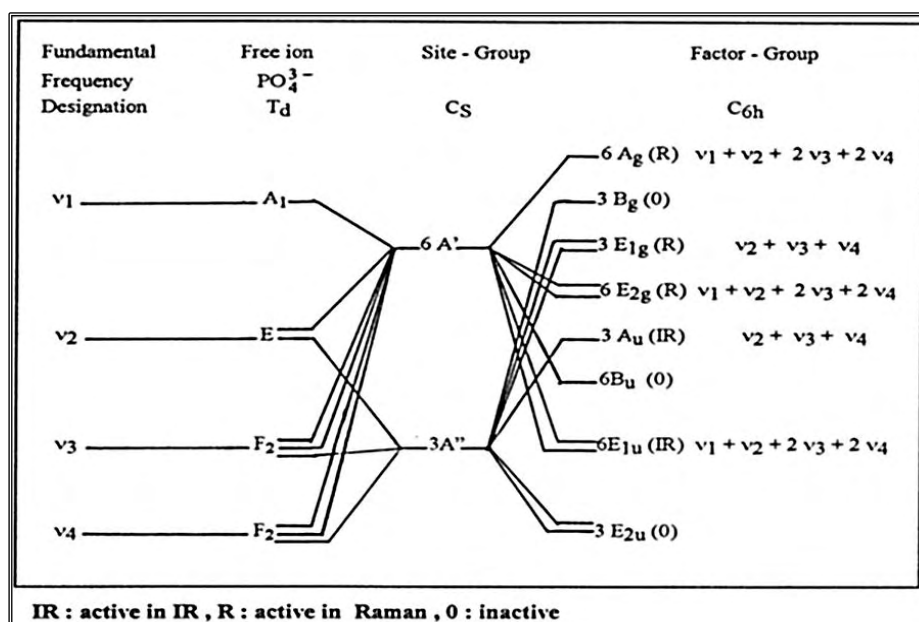


Fig.31: The factor group isomorphous with the space group $C_{6h}^2 - P6_3/m$ is C_{6h} .

[73] E. Kroumova, M.I. Aroyo, J.M. Perez-Mato, A. Kirov, C. Capillas, S. Ivantchev, H. Wondratschek, Bilbao Crystallographic Server : Useful Databases and Tools for Phase-Transition Studies, Phase Transitions. 76 (2003) 155–170.

All measurements were performed at several temperatures. The spectral parameters of Raman and Infrared bands, such as active modes (wavenumbers), spectral lines intensity, and full width at half maximum (FWHM), were determined using a fitting procedure with LabSpec software version .5 and 2.

Fig.32 shows the deconvolution results (The Assignments of observed Raman and Infrared bands at ambient temperature) in the two respective Raman and Infrared spectra for example of the compound $\text{NaPb}_2\text{CaCd}(\text{PO}_4)_3$ recorded at ambient conditions. As achieved by the LabSpec software V.5. First of all, the hydroxyl asymmetric stretching is not observed in both Infrared and Raman spectra around $3000\text{--}4000\text{ cm}^{-1}$, is verified (Cuscó et al. 1998; Rehman and Bonfield. 1997; Tsuda and Arends. 1994; Zakharov et al. 2004). This confirms that this type of apatite does not contain any hydroxyl group or water intercalated in apatite tunnels (for more details see Annex. I).

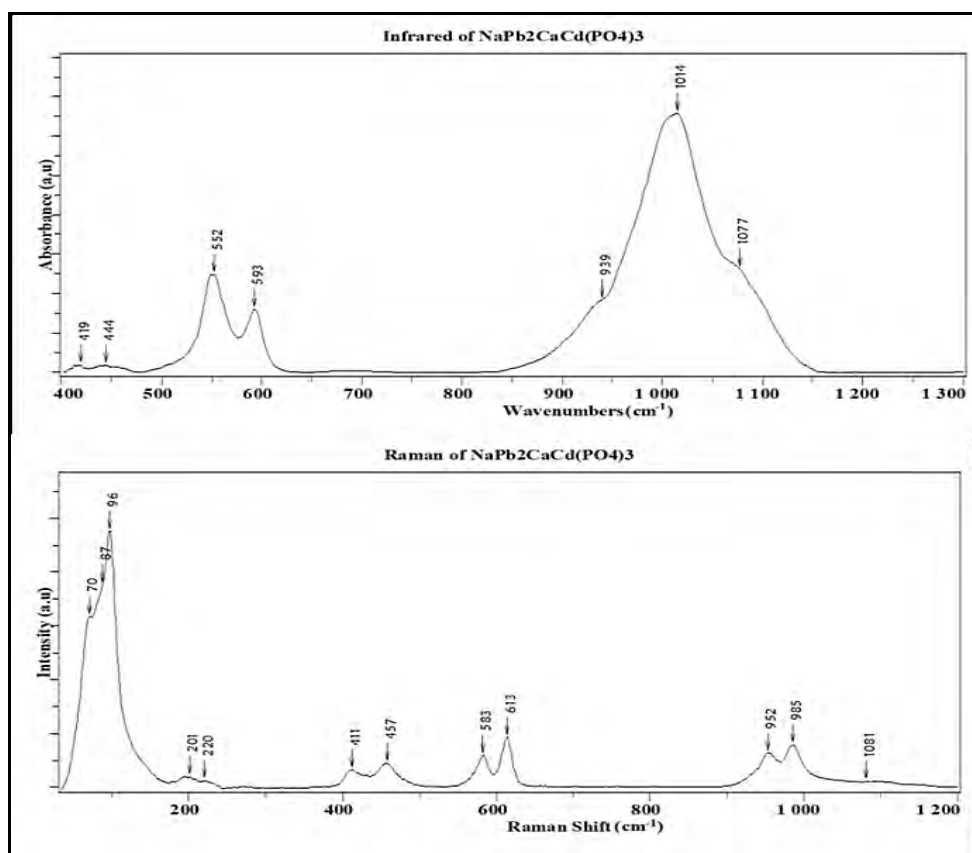


Fig.32: Infrared and Raman spectra of $\text{NaPb}_2\text{CaCd}(\text{PO}_4)_3$, after deconvolution by LabSpec software version .5, recorded at ambient conditions.

V. Optical Absorption and Energy Gap Study.

V.1. Instrument.

In the present investigation, the optical absorption experiments were carried out by PerkinElmer LAMBDA™ 1050 UV/Vis/NIR spectrometer in Fig.33, equipped with an integrating sphere in the range of 250-2000 nm with 1 nm interval to accurately get the optical absorption edge in near and far UV. Using a sample holder that needs a quantity of 0.5 g of the powder prepared as a cylindrical pellet using a manual hydraulic press, then sintered at 700 °C for 8 hours, the final pellets are with a thickness of more than 1 mm. The spectra were converted from reflectance to absorbance by using the computer program UV WinLab DPV which is based on solving the Kubelka–Munk function [74]. The optical band gap energy was estimated using the onset of the absorption edge by Tauc plots [75].

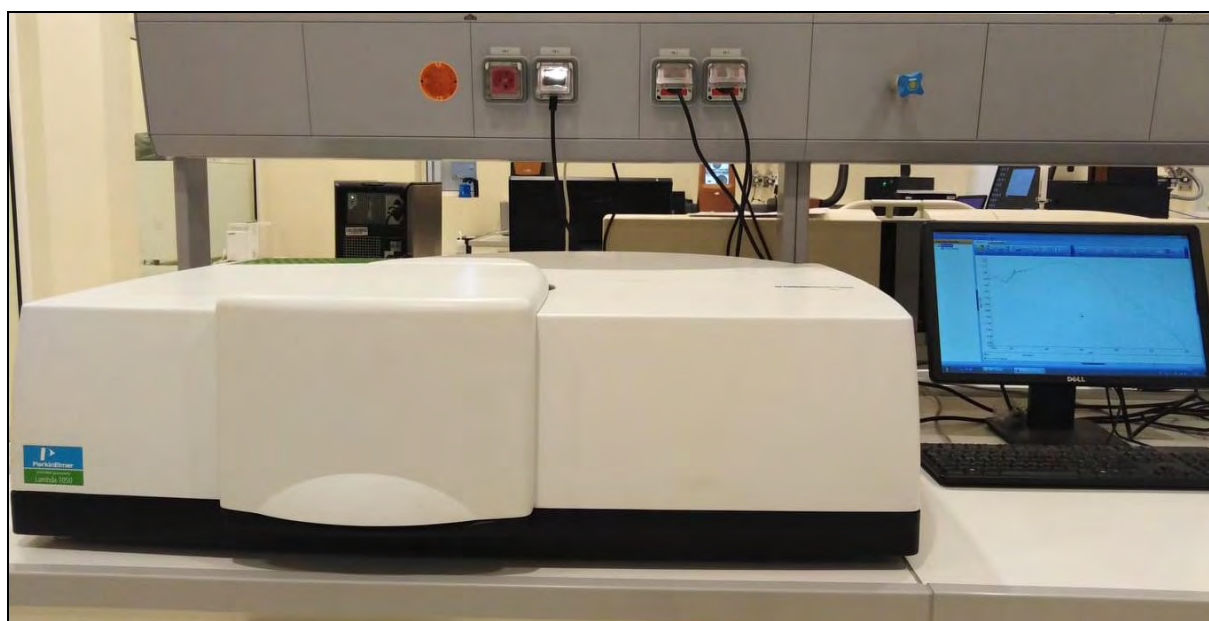


Fig.33: Picture of the PerkinElmer LAMBDA™ 1050 UV/Vis/NIR spectrometer, in laboratories of the MSN department, Mohammed VI Polytechnic University, Benguerir.

[74] P. Kubelka, F. Munk, An Article on Optics of Paint Layers (engl. Übersetzung), Z. Tech. Phys. 12 (1931) 593–601.

[75] J. Tauc, Optical properties and electronic structure of amorphous Ge and Si, Mater. Res. Bull. 3 (1968) 37–46. doi:10.1016/0025-5408(68)90023-8.

V.2. Optical absorption.

The optical studies give pertinent insight into the material behaviour such as the cut-off edge of the optical absorption, transparency to visible light, impurity absorption, which can occur at any energy in the absorption spectrum. These properties depend on the electronic band structure configuration, morphology, synthesis roots, as well as the annealing effect of crystal structure, chemical pressure, and polyhedral distortion degrees [76-79]. Many experimental studies on powder materials are being carried out using a small quantity of the sample. Hence, sampling becomes a key issue for this type of analysis. There is no standard method of powder sample preparation in UV-visible/far-ultraviolet spectroscopy investigation. Usually, powder samples are filled into a rectangular or cylindrical sample holder with a surface of at least 1.5 square centimetres. The powder should form at least one mm thickness layer for all incidents of light to be absorbed or scattered before reaching the back surface of the sample.

The solid UV visible / far-ultraviolet spectra of all compounds were measured in the range 250 nm to 800 nm at room temperature. Fig.34 shows the evolution of the absorption coefficient of reflectance $F(R)$ as a function of the wavelength in the range of variation (250-300nm) at room temperature, the intense band (λ_{Max}) of the series $Na_{1-x}K_xPb_2SrCa(PO_4)_3$ is determined by LabSpec® software.

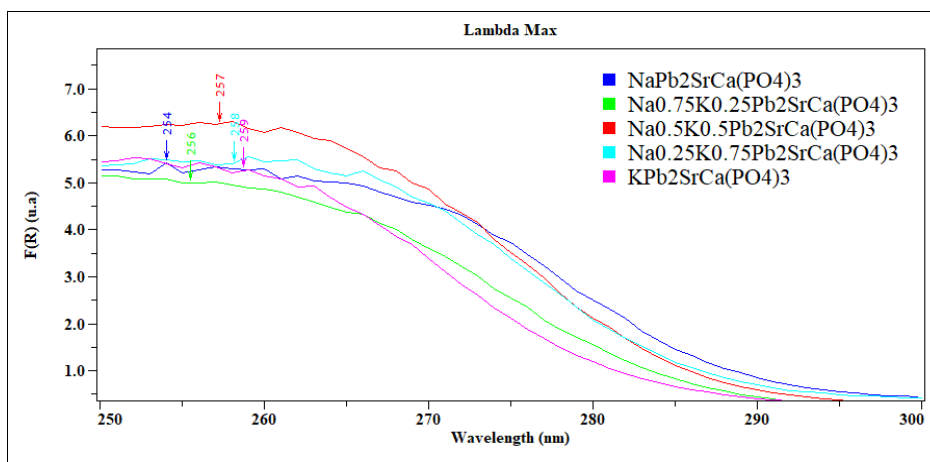


Fig.34: Lamda Max in UV visible / Far-Ultraviolet of the series $Na_{1-x}K_xPb_2SrCa(PO_4)_3$.

V.3. Optical Energy Gap.

The Bandgap is a tunable property and numerous parameters like synthesis route and thermodynamic conditions, surface morphology, crystal structure, the atomic percentage of substitution, and the degree of distortion are directly linked to optical absorption and bandgap. The theory of Kubelka-Munk function was proposed by P. Kubelka and F. Munk [74], [79] to calculate the E_g in the case of Reflectance spectra recorded from powder materials. When the thickness of the sample is in the relevant limitation then it does not influence the reflectance. Hence, the Kubelka-Munk equation at any wavelength can be written as:

$$\frac{K}{S} = \frac{(1 - R)^2}{2R} \equiv F(R) \quad (\text{Eq. 18})$$

Where S is the scattering coefficient, K is the absorption coefficients, R is the diffuse reflectance and $F(R)$ is called the Kubelka-Munk function. The predominant mechanism of the band to band transitions, which are responsible for the shape of the absorption edge of all series, was determined by analysis of the dependence $[F(R) \cdot h\nu]$ as a function of $(h\nu)$. The relation between the absorption coefficient and the incident photon energy $(h\nu)$ can be determined using Tauc's relationship in the high absorption region, as follows [75,76]:

$$F(R) \times h\nu = A(h\nu - E_g)^n \quad (\text{Eq. 19})$$

Where $F(R)$ is the linear absorption coefficient, $\nu = C/\lambda$ is the light frequency, with λ is a wavelength (meter) and C is the speed of light $= 3.0 \times 10^8$ (meter/sec), h = Planks constant $= 6.626 \times 10^{-34}$ Joules sec, ' A ' is a constant depending on the transmittance properties of E_g (eV) who is the bandgap energy where " $1\text{eV} = 1.6 \times 10^{-19}$ " Joules. The index n is determined by the nature of the electron transition during the absorption process, this index decides the transition nature; it's also called the power of probabilities. Four possible values which are ' $1/2$, 2 , $3/2$, or 3 ' corresponding respectively to direct allowed, indirect allowed, direct forbidden, and indirect forbidden types.

[76] G.P. Joshi, N.S. Saxena, R. Mangal, A. Mishra, T.P. Sharma, Bandgap determination of Ni-Zn ferrites, Bull. Mater. Sci. 26 (2003) 387–389. doi:10.1007/BF02711181.

Experimentally, to determine the optical band gap (E_g), we can plot $[F(R)*h\nu]^{1/n}$ versus the photon energy ($h\nu$) using the data obtained from the optical absorption spectra. It reveals that the obtained plots give a straight line in a certain region. To obtain the value and the transitional nature of the bandgap (E_g) of apatites materials, we proceed by plotting $[F(R)*h\nu]^{1/n}$ with the four power probabilities of 'n' versus the photon energy ($h\nu$) for this new lacunar apatite series, it was found that the most suitable and adequate plot is that when 'n = 2'. According to Tauc plot results: $A(h\nu - E_g) = 0$, as tabulated in Fig.35 we can extend the straight line to intercept (hν)-axis at $[F(R)*h\nu]^{1/2} = 0$ and for $F(R) = 0$, to estimate the values of the indirect allowed gap energy and cut-off absorption shift of the compound $\text{NaPb}_2\text{CaSr}(\text{PO}_4)_3$ (as shown in Fig.35).

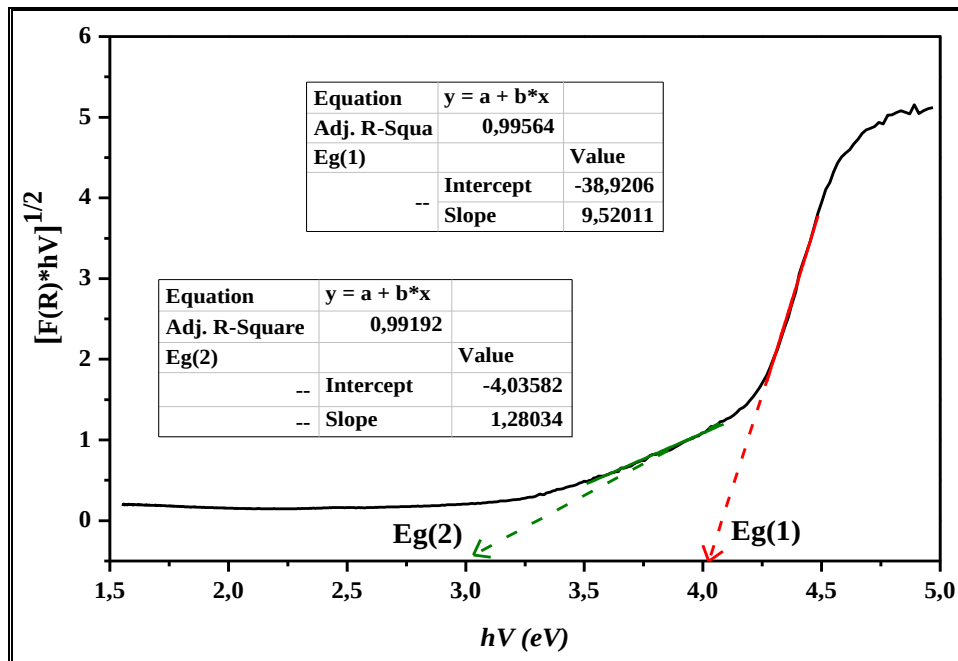


Fig.35: $[F(R)*h\nu]^{1/2}$ and of $F(R)$ for $\text{NaPb}_2\text{CaSr}(\text{PO}_4)_3$ lacunar apatites, depending upon the incident photon energy ($h\nu$) and the optical absorption.

- [77] E. Kim, Z.-T. Jiang, K. No, Measurement and Calculation of Optical Band Gap of Chromium Aluminum Oxide Films, Jpn. J. Appl. Phys. 39 (2000) 4820–4825. doi:10.1143/JJAP.39.4820.
- [78] R. Kitamura, L. Pilon, M. Jonasz, Optical constants of silica glass from extreme ultraviolet to far-infrared at near room temperature, Appl. Opt. 46 (2007) 8118. doi:10.1364/AO.46.008118.
- [79] P.R. Wessel, Reflectivity of Silver-Gold Alloys in the Spectral Region 1.8-5.0 eV, Phys. Rev. 132 (1963) 2062–2064. doi:10.1103/PhysRev.132.2062.

VI. Surface Area Analysis.

VI.1. BET theory.

Brunauer – Emmett – Teller; [Fig.36](#), they were working on ammonia catalysts the first method to measure the specific surface of finely divided and porous solids, theory aims to explain the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of materials. In 1938, Stephen Brunauer, Paul Hugh Emmett, and Edward Teller published the first article about the ‘BET’ theory in the Journal of the American Chemical Society [\[80\]](#). The ‘BET’ theory applies to systems of multilayer adsorption and usually utilizes probing gases that do not chemically react with material surfaces as adsorbates to quantify specific surface area. Nitrogen is the most commonly employed gaseous adsorbate used for surface probing by ‘BET’ methods. For this reason, the standard ‘BET’ analysis is most often conducted at the boiling temperature of ‘N₂’ (77 K). Further probing adsorbates are also utilized, albeit with lower frequency, allowing the measurement of surface area at different temperatures and measurement scales. These have included argon, carbon dioxide, and water. Specific surface area is a scale-dependent property, with no single true value of the specific surface area definable, and thus quantities of the specific surface area determined through ‘BET’ theory may depend on the adsorbate molecule utilized and its adsorption cross-section [\[81\]](#).

[80] Brunauer, Stephen; Emmett, P. H.; Teller, Edward (1938). "Adsorption of Gases in Multimolecular Layers". *Journal of the American Chemical Society*. 60 (2): 309–319. doi:10.1021/ja01269a023. .

[81] Hanaor, D. A. H.; Ghadiri, M.; Chrzanowski, W.; Gan, Y. (2014). "Scalable Surface Area Characterization by Electrokinetic Analysis of Complex Anion Adsorption" (PDF). *Langmuir*. 30 (50): 15143–15152. doi:10.1021/la503581e. PMID 25495551.



Fig.36: BET- Named after Stephen Brunauer, P.H. Emmet, and Edward Teller respectively.

The concept of the theory is an extension of the Langmuir theory, which is a theory for monolayer molecular adsorption, to multilayer adsorption with the following Assumptions, Fig.37:

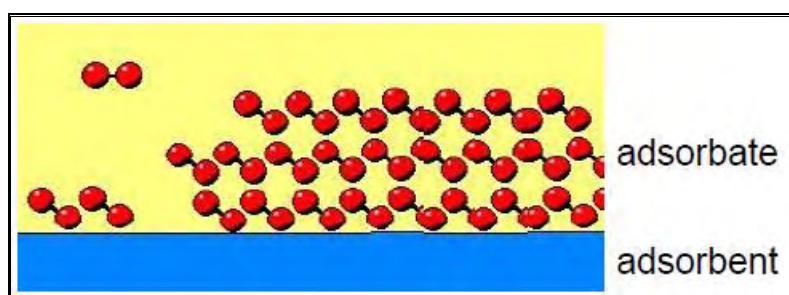


Fig.37: BET model of multilayer adsorption, that is, a random distribution of sites covered by one, two, three, etc., adsorbate molecules.

1. Homogeneous surface.
2. No lateral interactions between molecules.
3. Uppermost layer is in equilibrium with the vapour phase.
4. First layer; Heat of adsorption ' E_{ADS} ' and higher layers; Heat of condensation ' E_{COND} '.
5. At saturation pressure, the number of layers becomes infinite.

From this, BET derived the resulting equation is:
$$v = \frac{v_m c p}{(p_0 - p) \left\{ 1 + (c - 1) \left(\frac{p}{p_0} \right) \right\}} \quad (\text{Eq. 20})$$

A more convenient form is the following:
$$\frac{p}{v(p_0 - p)} = \frac{1}{v_m c} + \frac{(c - 1) * p}{v_m c * p_0} \quad (\text{Eq. 21})$$

Where ' p ' and ' p_0 ' are the equilibrium and the saturation pressure of adsorbates at the temperature of adsorption, v is the adsorbed gas quantity (for example, in volume units), and ' v_m ' is the monolayer adsorbed gas quantity. ' c ' is the 'BET' constant defined by the equation: $c \approx e^{\frac{E_{ADS}-E_{COND}}{RT}}$ (Eq. 22) and $E_{ADS} \gg E_{COND}$.

Where ' E_{ADS} ' is the heat of adsorption for the first layer, and ' E_{COND} ' is that for the second and higher layers and is equal to the heat of condensation.

Equation (Eq. 21) is an adsorption isotherm and can be plotted as straight line with $\{\frac{p}{v(p_0-p)}\}$ on the y-axis and $\{\frac{p}{p_0}\}$ on the x-axis according to experimental results, Fig.38. This plot is called a 'BET' plot. The linear relationship of this equation is maintained only in the range of $\{0.05 < \frac{p}{p_0} < 0.35\}$. The value of the slope $\{A\}$ and the y-intercept $\{I\}$ of the line are used to calculate the monolayer adsorbed gas quantity $\{v_m\}$ and the BET constant $\{c\}$.

The following equations can be used: $v_m = \frac{1}{A+I}$ (Eq. 23) and $c = \frac{A}{I}$ (Eq. 24)

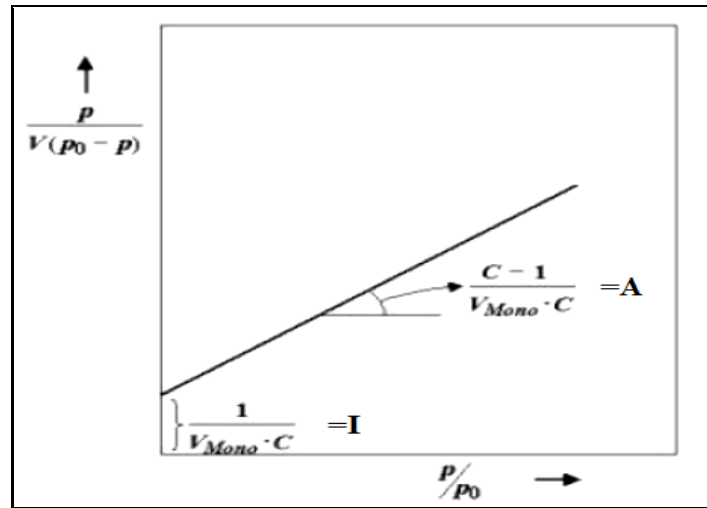


Fig.38: BET plot of adsorption isotherm, plotted as a straight line with $\{\frac{p}{v(p_0-p)}\}$ on the y-axis and $\{\frac{p}{p_0}\}$ on the x-axis according to experimental results.

The BET method is widely used in materials science for the calculation of surface areas of solids by physical adsorption of gas molecules. The total surface area ' S_{total} ' and the specific surface area ' S_{BET} ' are given by equations:

$$S_{total} = \frac{v_m N s}{v} \quad (\text{Eq. 25}) \quad \text{And} \quad S_{BET} = \frac{S_{total}}{a} \quad (\text{Eq. 26})$$

where ' v_m ' is in units of volume which are also the units of the monolayer volume of the adsorbate gas, ' N ' is Avogadro's number, ' s ' the adsorption cross-section of the adsorbing species, ' v ' the molar volume of the adsorbate gas, and ' a ' the mass of the solid sample or adsorbent.

VI.2. Instrument.

The surface-specific area (SSA) of the crystals $\text{KPb}_2\text{Ca}_2(\text{PO}_3)_3$ (N°6), $\text{KPb}_3\text{Zn}(\text{PO}_4)_3$ (N°7) $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (N°8&9) and $\text{Ca}_8\text{Zn}_2(\text{PO}_4)_6(\text{OH})_2$ (N°10); was determined by the 'BET' method, using ' N_2 ' adsorption in Micromeritics Gemini VII 1014 Instrument, Fig.39. Gemini utilizes a unique adaptive rate dosing algorithm and is a special case of the static volumetric technique. Speed and sensitivity are unsurpassed by other static volumetric instruments. Micromeritics invented the balance tube design, which negates free-space errors introduced by thermal gradient variations or by initial mismeasurement of free space.

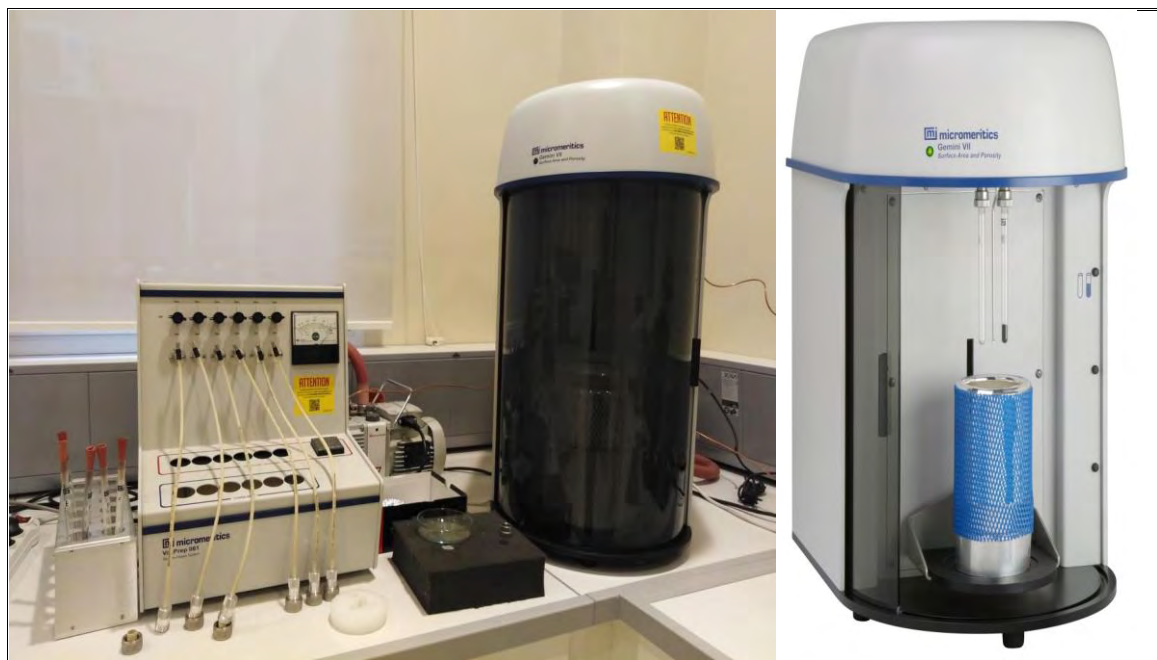


Fig.39: Picture of the Micromeritics Gemini VII 1014, in laboratories of the MSN department, Mohammed VI Polytechnic University, Benguerir.

The Gemini permits low surface area measurements without requiring krypton and the use of a servo valve controls the rate of gas flow into the sample tube to accurately attain target pressures without pressure overshoot. The sample controls the rate at which the gas is delivered thus accelerating the delivery of the analysis gas. This results in a surface area analyzer that is as fast as the physics of adsorption allows.

Micromeritics' Gemini utilizes an adaptive rate, static volumetric technique. It is the first gas sorption method that adapts the rate at which gas is delivered to the sample to the rate at which it is adsorbed. Each pressure point is allowed to equilibrate before the next point is taken. The Gemini has, as [Fig.40](#), illustrated below, two gas reservoirs (A) which are filled with equal volumes of the desired adsorptive, usually nitrogen. From the reservoirs, gas is metered into the sample and balance tubes by way of a servo valve that reacts to the rate of adsorption. A transducer (B) monitors pressure within the sample tube. In a typical dose-and-wait analytical system, the pressure within the sample tube decreases after each dose as the sample adsorbs gas. This is not the case with the Gemini. A transducer (B) causes a fast response servo valve (C) to increase or restrict the flow of gas to the sample tube as necessary to maintain a constant equilibrium pressure within the sample tube as adsorption occurs. A transducer (D) located between the sample and balance tubes detects any pressure difference between the two tubes and causes another servo valve (E) to adjust the pressure within the balance tube to negate any pressure differential. A third pressure transducer (F) monitors the pressure between the two reservoirs to determine the differential quantity of gas, the difference being the quantity that is adsorbed on the sample. These methods of dosing and differential quantity detection enable the Gemini to accurately determine adsorption characteristics at a speed and sensitivity level unsurpassed by other static volumetric instruments. [\[82\]](#)

[82] Micromeritics Instrument Corporation 4356 Communications Drive Norcross, GA 30093 USA

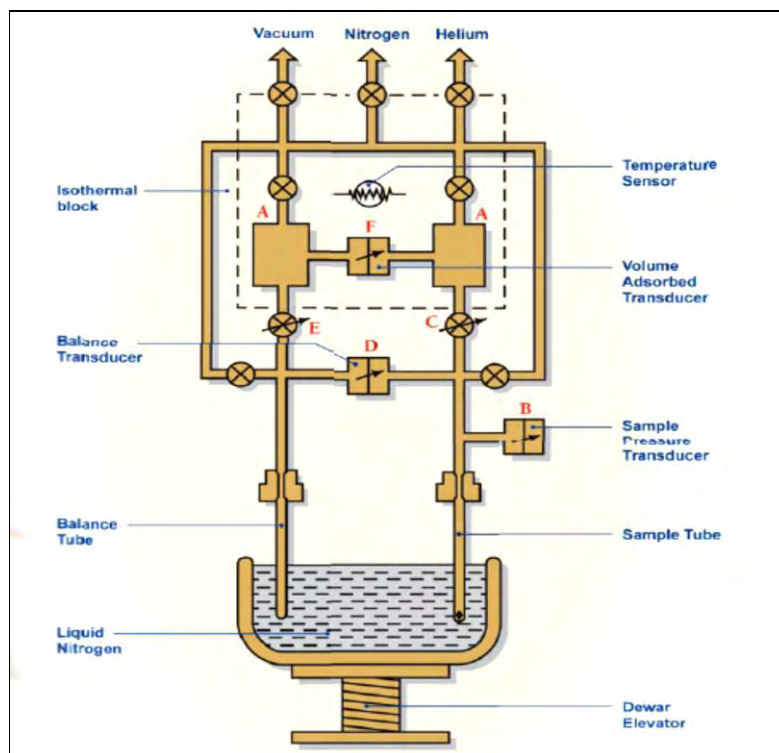


Fig.40: The Gemini Technique ^[82].

VII. Inductively Coupled Plasma Emission Spectroscopy (ICP-OES).

VII.1. Instrument.

The tests of demineralization of Phosphoric Acids 29% and 54%, carried out at the Central Laboratory OIS/L/Q of Maroc Chemistry, SAFI, for 25 days from 05/07 to 31/07, 2017, and the analyses list of the experimental tests, carried out on each of the apatites lacunars, by ICPE-9000 (Shimadzu Europa GmbH), [Fig.41](#) (for more details see [Chapter. IV](#)).

ICPE-9000 ([Fig.41](#)) is a simultaneous ICP-OES spectrometer utilizing a vacuum-type echelle optical system in combination with a large-scale CCD detector designed for stable performance over extended periods. The ICPE-9000's innovative Mini Torch minimizes cost by reducing the consumption of argon gas to half that of conventional torches. The ICPE-9000 features easy-to-use, innovative ICPEsolution Software, which offers such features as a Method Development Assistant and a Diagnosis Assistant and easily handles automatic wavelength optimization as well as interference corrections (for more details see [Annex. I](#)).

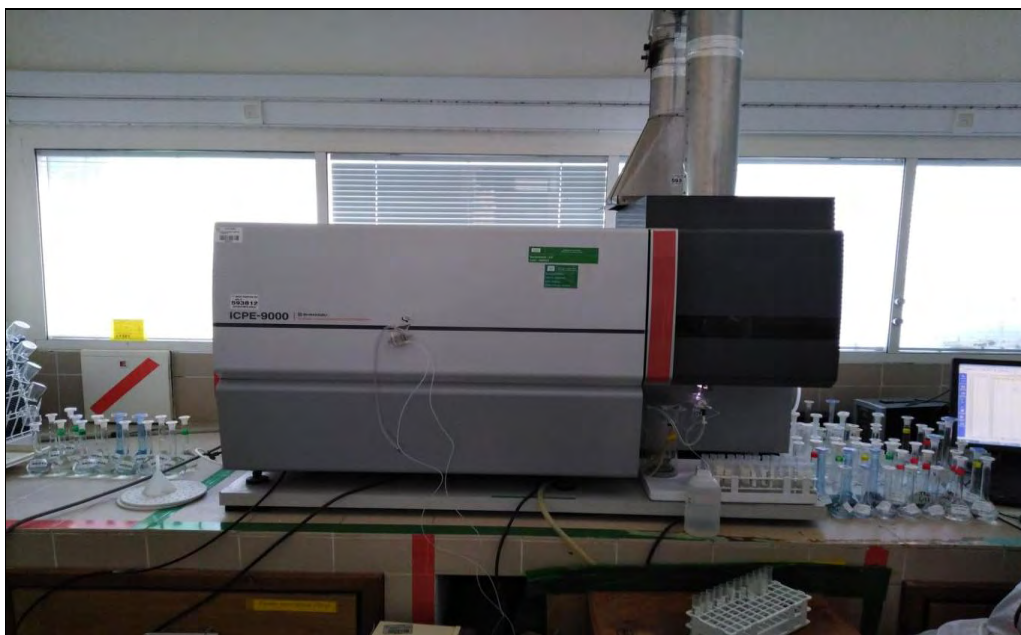


Fig.41: ICPE-9000 (of Shimadzu Europa GmbH) in the Central Laboratory OIS/L/Q of Maroc Chemistry, SAFI.

VII.2. Principle.

ICP, an abbreviation for Inductively Coupled Plasma, is one method of optical emission spectrometry. When plasma energy is given to an analysis sample from outside, the component elements (atoms) are excited. When the excited atoms return to a low energy position, emission rays (spectrum rays) are released and the emission rays that correspond to the photon wavelength are measured. The element type is determined based on the position of the photon rays, and the content of each element is determined based on the rays' intensity. To generate plasma, first, argon gas is supplied to the torch coil, and a high-frequency electric current is applied to the work coil at the tip of the torch tube. Using the electromagnetic field created in the torch tube by the high-frequency current, argon gas is ionized and plasma is generated. This plasma has high electron density and temperature (10000K) and this energy is used in the excitation-emission of the sample. Solution samples are introduced into the plasma in an atomized state through the narrow tube in the centre of the torch tube, in [Fig.42](#) (for more details see [Annex. IV](#), [Figs.7&8&9](#)).

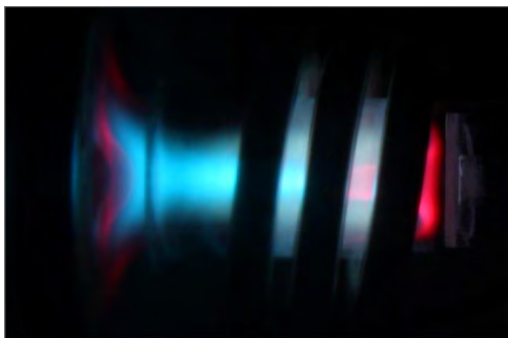


Fig.42: ICP Plasma « torch ».

VIII. Electrochemical Impedance Spectroscopy (EIS).

VIII.1. Principle of the method.

The impedance spectroscopy method is a technique that is increasingly used in the analysis and study of materials used in different sectors of research and development, for example, electrochemistry, electrical engineering, microelectronics, pharmaceutical industry, etc. Electrochemical Impedance Spectroscopy (EIS) is nowadays being extended in various applications to cover the following areas:

- Corrosion and its inhibition
- Organic electrochemistry and the study of adsorption phenomena
- Photo-electrochemistry
- The semiconductor/electrolyte interface
- Bio-electrochemistry

In the field of corrosion, electrochemical impedance measurement shows several advantages. It allows the precise determination of the corrosion rate even though the metal is covered with a protective layer. It also allows the evaluation of the inhibition rate, the characterization of different corrosion phenomena (dissolution, passivation, pitting...), and the study of the reaction mechanisms at the electrochemical interface.

The concept of impedance, therefore, allows a good identification of electrochemical processes; the different time constants represent the different stages of the electrochemical

reaction. Thus the charge transfer resistance and the diffusion or Warburg impedance reflect the charge transfer at the interface and the material transfer, respectively [83].

The principle of this technique is based on the application of a low sinusoidal voltage to the material under test. The analysis of the amplitude and phase shift of the response current gives access to the real and imaginary parts of the complex impedance ' Z^* '. Measurements are made by sweeping a generally wide range of frequencies or frequency spectrum. This is where the name spectroscopic method comes from.

Electrochemical impedance spectroscopy is a transient method that provides information on the elementary steps of the overall electrochemical process. Its principle consists of superimposing a low amplitude sinusoidal potential modulation on the electrode potential and monitoring the current response of the disturbing signal at different frequencies.

At the time to the value of the electrode potential is expressed as a function of its stationary component ' E_0 ' and a sinusoidal term, where ' ω ' represents the signal pulse and ' ΔE ' its amplitude: $E_t = E_0 + \Delta E \sin(\omega t)$ (Eq.27).

The sinusoidal disturbance of the potential induces a sinusoidal current superimposed on the stationary current and shifted in phase by an angle ' ϕ ', its value is given by:

$$I_t = I_0 + \Delta I \sin(\omega t - \phi) \text{ (Eq.28)}$$

In a sinusoidal regime, the relationship between the current flowing through a circuit and the voltage applied across it can be expressed by the equation, ' Z ' is the impedance, the equivalent of resistance in the case where the current is constant: $E = IZ$ (Eq.29)

The value of impedance ' Z ' will depend on the resistances in the circuit, but will also include a contribution from the inductors and capacitors.

[83] S. R. Taylor, E. Gileadi, Physical Interpretation of the Warburg Impedance, CORROSION. 1995;51(9):664-671.

The impedance can be represented either in polar coordinates ($|Z|$, φ) or in cartesian coordinates ($\text{Re}(Z)$, $\text{Im}(Z)$): $Z(\varphi)=|Z|\exp(j\varphi) = \text{Re}(Z) + j\text{Im}(Z)$ (Eq.30)

The graphical representation of an impedance $Z=Z_{\text{re}}+jZ_{\text{im}}$ in the complex plane for different frequencies is called the Nyquist diagram. The imaginary part of the impedance is plotted against the real part, Fig.43.

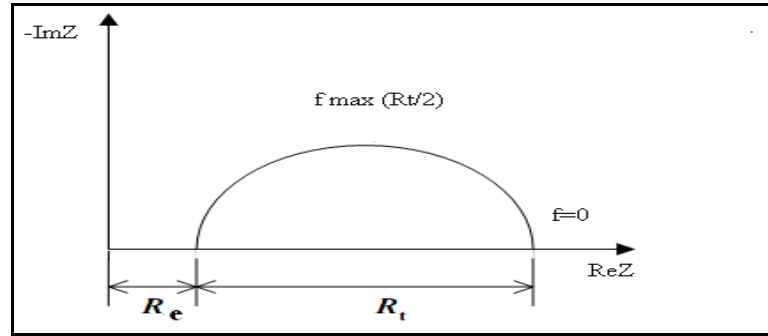


Fig.43: Impedance diagram of the Nyquist.

It is possible to relate the results of complex impedance measurements to the Physico-chemical properties of the material through modelling by equivalent electrical circuits. This method gives access to various information. The use of impedance spectra by modelling equivalent electrical circuits allows many quantities to be obtained, such as ion diffusion coefficients, conductivity, and resistance due to charge transfer across the membrane.

The study of the impedances of electrochemical cells consists of tracing the impedance diagram in the "NYQUIST plane of electrochemistry" giving the opposite of the imaginary part of the impedance as a function of its real part when the frequency varies. For example, the impedance diagram of the (R, C) parallel circuit in the NYQUIST plane is shown in Fig.44. It is a semicircle intersecting the x-axis at abscissa '0' and 'R', described by increasing frequency from right to left and reaching a maximum.

To simplify the treatment of the electrochemical cell, we first analyze the spectra of the dielectric functions of the measurements performed by the Z.view software version 2.2 to determine if the equivalent circuit that models our spectra.

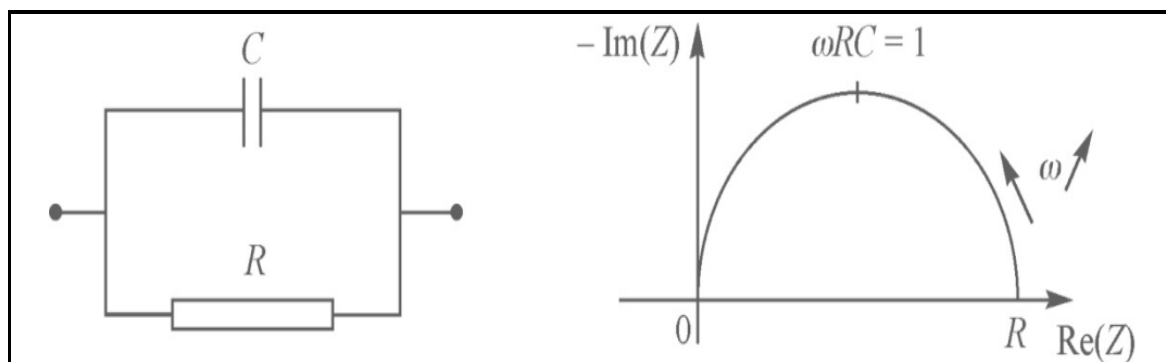


Fig.44: Circuit parallèle (R, C) et son diagramme d'impédance dans le plan de Nyquist.

The interpretation of impedance diagrams allows studying the dynamics of electrochemical systems, transfer resistance, material transport, and conductance. The measurement of the conductivity of a solution can be carried out by this method, which makes it possible to dispense with the choice of measurement frequency and to determine all the characteristics (resistances, capacities) of the system.

The experimental set-up used during our studies is shown in Fig.45. It includes a potentiostat, a three-electrode electrochemical cell, and a computer for instrument control and data processing.

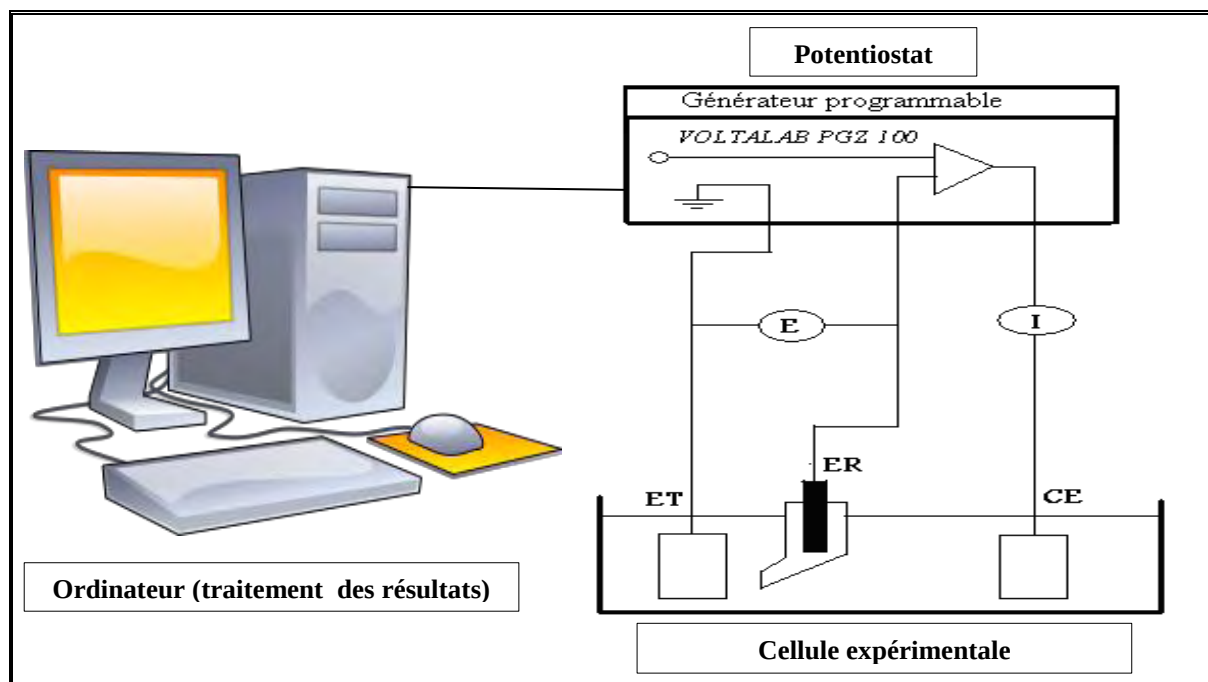


Fig.45: Electrochemical Impedance Measuring instrument.

a) Working electrodes:

The working electrode (ET) is also called an indicator electrode, it is in contact with it that the oxidation or reduction reaction of the analysis will occur following the variation of potential. In general, the working electrode must be stable over a very long period with a good signal-to-noise ratio of the background and must also be easy to handle and condition. Also, the solutes to be analyzed must develop fast electrochemical reaction kinetics in a wide range of accessible potential [84]. It can be of different kinds, namely:

- Metals (mercury, platinum, gold, silver, copper, or nickel for example, or alloys).
- Non-metallic materials (graphite or vitreous carbon for example).
- Organic materials such as conductive polymers for example.

The working electrode used for the analysis can then be chosen in particular according to the oxidation or reduction potential of a particular species to be analyzed, such as lacunar apatite.

b) Reference electrodes:

The reference electrode (ER) has a specific and constant potential. As the name implies, it serves as a reference to the potentiostat to apply an exact potential difference between this electrode and the working electrode, and thus to vary the potential applied to the working electrode in an exact and known manner. The saturated calomel electrode was the most frequently used electrode [85]. The reference potential values 'ER' about the normal hydrogen electrode (ENH) is 0.244 V for the calomel (KCl) electrode and 0.197 V for the silver chloride (AgCl) electrode at 25°C.

[84] P.T. Kissinger, W.R. Heinemann, Laboratory Techniques in Electroanalytical Chemistry, Marcel Dekker, New York (1984).

[85] C. Lamy, Conséquences de la dégénérescence des corps cellulaires dopaminergiques de la substance noire sur neurotransmission dopaminergique dans le boyau caudé : Approches méthodologiques en microdialyse et voltamétrie, Ecole pratique des Hautes Etudes (2007).

c) Auxiliary electrodes:

The auxiliary electrode (EA) is chosen so that its electrochemical properties do not affect the behaviour of the working electrode: during electrolysis, there must be no production of species that can reach the working electrode and cause parasitic reactions there. In the analysis, this three-electrode arrangement is proposed to minimize the effects of the ohmic drop, which has the effect of reducing the deformation of the voltammograms. Consequently, the auxiliary electrode ensures the passage of the current generated by the studied reactions to the working electrode.

VIII.2. Experimental device.

Lacunar apatites $\{K/Na\}Pb_{2.5}Sr_{1.5}(PO_4)_3$ used as corrosion inhibitors are compounds that, when added in low concentration to the corrosive medium, slow down the corrosion process of carbon steel 'MS' placed in contact with a hydrochloric acid solution. They used a circular cross-section of the 'MS' rod exposed to the corrosive solution in electrochemical measurements was 0.2cm^2 , was studied using electrochemical and impedance spectroscopy (EIS) at different concentrations and temperatures, in Laboratory of MNE, Faculty of Science, University Mohamed-V, Agdal-Rabat (For more details see [Chapter. V](#)).

Electrochemical impedance measurements are carried out using an experimental set-up comprising three electrodes identical to those described above. The equipment for polarization and frequency measurement consists of a transfer function analyzer. The potentiostat or galvanostatic regulation is done using a VersaSTAT.4 potentiostat (for more details see [Annex. V](#)), which allows the introduction and analysis of the low amplitude sinusoidal disturbance and at the same time the impedance measurement. A generator of the transfer function analyzer allows programming the frequency sweep by setting the minimum and maximum frequencies and the step of a logarithmic frequency progression. Thus, the frequency for which the impedance is measured is automatically changed.

Impedance measurements were performed in potentiostat mode at corrosion potential. In a frequency range from 10mHz to 1MHz and a low amplitude sinusoidal disturbance of 10mV. The electrode is held at 'E_{corr}' for 60 min before each measurement. This whole process is managed by a microcomputer, Fig.46.

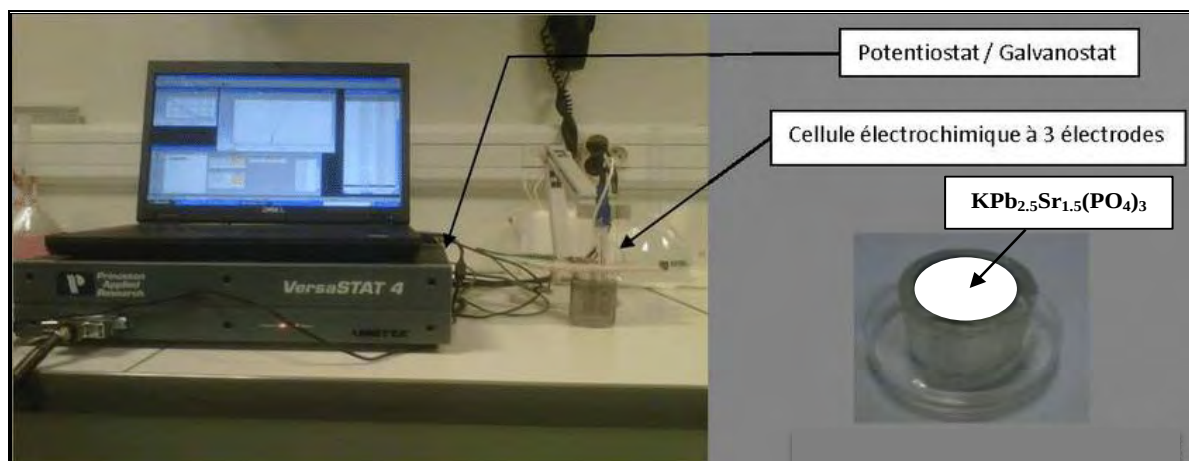


Fig.46: Experimental device for electrochemical measurements.

Fig.47 shows the working electrode divided into two sub-electrodes. Between the sub-electrodes, a physical separator made of epoxy resin material, inert and usable at 80°C, would be used to obtain the electrochemical response of each part independently of the other. These point measurements would allow a better understanding of the phenomena involved in the coupling of surfaces covered with different products or materials by removing the biases induced by the distance between the two electrodes. The test representative of the real case would involve a small area covered with lacunar apatite (electrode 1) surrounded by a larger area covered with Teflon (abbreviation for tetrafluoro-ethylene and addition of the termination) (electrode 2).

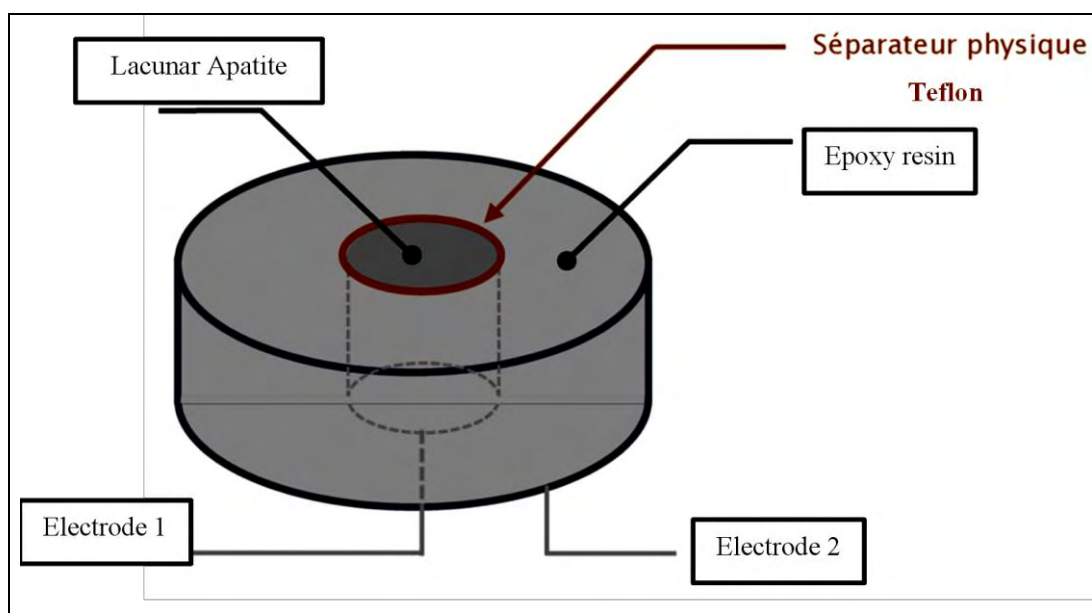


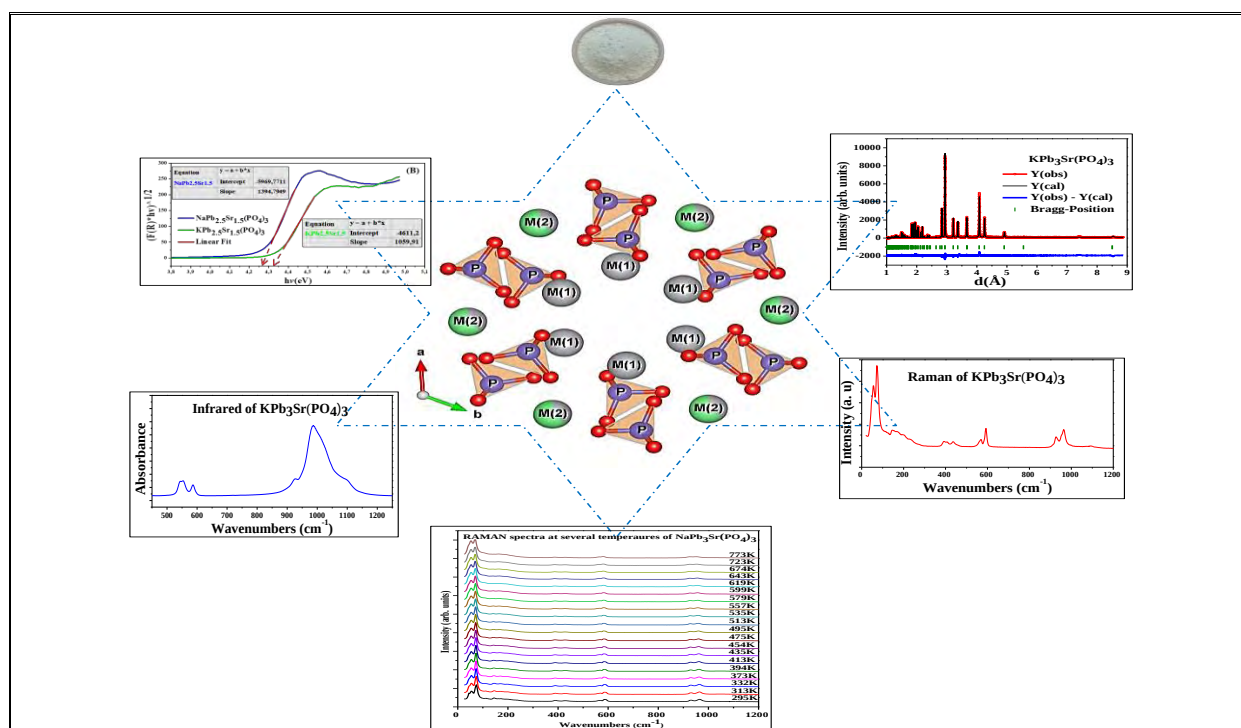
Fig.47: mounting of the working electrode divided into two sub-electrodes.

Chapter. II: Crystallographic & Vibrational Studies and Optoelectronic Properties of News Series of Lacunar Apatites type



Abstract;

This work demonstrates the effect of two substitution patterns with mono (Na/K) and divalent (Pb/Sr/Ca/Cd) cations on news series of lacunar apatites $\text{Na}_{1-x}\text{K}_x\text{Pb}_{4-y/2}\{\text{Sr}_y/\text{Ca}/\text{Cd}\}(\text{PO}_4)_3$, in the system of $(\text{Na}/\text{K})_2\text{O}-\{\text{Sr}/\text{Ca}/\text{Cd}\}\text{O}-\text{PbO}-\text{P}_2\text{O}_5$ were successfully synthesized using a solid-state chemical reaction. Because of the importance of these types of materials various properties afforded by this versatility. Properties can often be tuned or changed by elemental substitution, and materials with the same structural ($P6_3/m$) connectivity employed can be studied for different purposes and various characterizations. It seems to us of interest to perform the structural, Vibrational, and Optical studies, by using X-ray Diffraction, and Raman, Infrared, and UV-Vis spectroscopy techniques. The results of physical and chemical properties can be analyzed for the engineering aspects of materials structure, surfaces, and interfaces (Abstract Fig. II Style). We hope that our work could provide useful guidance for future experimental and theoretical studies.



I. Introduction.

The elaborations of {Strontium/Calcium/Cadmium}-Lead Phosphate, of Potassium and Sodium without Y anion vacancies $\text{Na}_{1-x}\text{K}_x\text{Pb}_{4-y/2}\{\text{Sr}/\text{Ca}/\text{Cd}\}_y(\text{PO}_4)_3$ (N°1, °2, °3, °4, °5: in Chapter. I), caught our particular attention. In the present study field, we have used X-ray Diffraction and Raman, Infrared, and UV-Vis spectroscopies to explain and to report on the structure stability at room and high temperatures as well as the optical properties, as for typical physical characteristics and properties of the polycrystalline solids. These are the most fundamental among a variety of technical instruments available that have been frequently employed. Apatites are very useful for various applications in sciences and engineering related to energy and device performance. The results of physical and chemical properties can be analyzed for the engineering aspects of materials structure surfaces and interfaces.

$\text{Na}_{1-x}\text{K}_x\text{Pb}_{4-y}\{\text{Sr}/\text{Ca}/\text{Cd}\}_y(\text{PO}_4)_3$, are similar to other lacunar materials [1-3]. Indexing of X-ray powder diffraction patterns for these compositions was performed using the computer program DICVOL [4]. The first 32 peaks positions, with a maximal absolute error of 0.03° (2θ), were used as input data. The X-ray diffraction pattern for all the compositions was assigned to a hexagonal apatite structure. The space group $P6_3/m$ (N°176), and the atomic positions of the lacunar apatitic structure $\text{Na}_{1-x}\text{K}_x\text{Pb}_3\text{Ca}(\text{PO}_4)_3$ [5], were used as starting sets in the refinement procedure for the samples $\text{Na}_{1-x}\text{K}_x\text{Pb}_{4-y}\{\text{Sr}/\text{Ca}/\text{Cd}\}_y(\text{PO}_4)_3$, with ($0 \leq x \leq 1$) and ($0 \leq y \leq 1.5$).

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- [1] M. El Koumiri, S. Oishi, S. Sato, L. El Ammari, B. Elouadi, The crystal structure of the lacunar apatite $\text{NaPb}_4(\text{PO}_4)_3$, Mater. Res. Bull. 35 (2000) 503–513.
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The Rietveld refinement of the observed powder XRD data is initiated with the scale and background parameters followed by a progressive refinement of the remaining profile parameters. The background is fitted with a third-order polynomial function. The peak shape is fitted with a Pseudo-Voigt profile function. After an appreciable profile matching, the position parameters and isotropic atomic displacement parameters of individual atoms were also refined. Finally, the occupancy factors were refined and the cation substitution was tested. The two sites 6h and 4f with cations labelled M(1) and M(2) respectively, were imposed to be fully and complementarily occupied by $\text{Pb}^{2+}(1)/\{\text{Sr}/\text{Ca}/\text{Cd}\}^{2+}(1)$ and $\text{Na}^+/\text{K}^+/\text{Pb}^{2+}(2)/\{\text{Sr}/\text{Ca}\}^{2+}(2)$, respectively. The occupancy factors of O and P were assumed as constant, in agreement with the apatite stoichiometry. The fractional atomic coordinates were refined, starting from the atomic positions in $\text{Na}_{1-x}\text{K}_x\text{Pb}_4(\text{PO}_4)_3$ [6]. In the last refinement cycles, the optimization of 40 variables (structural and non-structural parameters) and one preferred orientation parameter was refined in the direction of the diffraction vector perpendicular to (0 0 1). (For more details. see [Chapter. I. \(III.4.2.b\)](#))

The results of the Rietveld refinements showed that these polycrystalline solutions are continuously adopting the **$P6_3/m$** space group. On the elastic limits of metal polycrystals $\text{Na}_{1-x}\text{K}_x\text{Pb}_{4-y}\{\text{Sr}/\text{Ca}/\text{Cd}\}_y(\text{PO}_4)_3$ with $0 \leq x \leq 1$ and $0 \leq y \leq 1.5$. The existence of this type of lacunar apatite is conditioned by the presence of a majority of Pb^{2+} divalent cations are located in the 6h positions [1-3,5-9]. The formulation of these compounds could be written as formula $\text{M}(1)_4\text{M}(2)_4[\text{PO}_4]_3$.

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The structure can be described as built up from $[PO_4]^{3-}$ tetrahedra, M(1) of sixfold coordination cavities of whose $Pb^{2+}(1)/\{Sr/Ca/Cd\}^{2+}(1)$ cations are located in the (6h) site which delimit void hexagonal tunnels running along (0 0 1) (M(1). Fig.1). These tunnels are connected by M(2) cations of mixed sites (4f), half occupied by $Pb^{2+}(2)/\{Sr/Ca\}^{2+}(2)$ $\{0 \leq y \leq 1.5\}$ divalent cations and half by Na^+ or K^+ , as with Na^+/K^+ homogeneous for $0 \leq x \leq 1$ with mixed monovalent cations have been investigated rather thoroughly [1,2,5-7] (M(2). Fig.1). The hexagonal tunnel with a much larger section M (6h) is surrounded by divalent cations (M(1); Fig.1). These cations $Pb^{2+}(1)/\{Sr/Ca/Cd\}^{2+}(1)$ are inserted into six-fold sites that constitute the walls of the tunnels, each polyhedron is linked to 4 $[PO_4]^{3-}$ tetrahedra via corners and to one $[PO_4]^{3-}$ via edge (M(1). Fig.1). The small tunnel which corresponds to the mixed site M(4f), these cations are coordinated to nine oxygen anions belonging to six distinct tetrahedra; each polyhedron is linked to 3 $[PO_4]^{3-}$ tetrahedra via corners and to three others via edges (M (2); Fig.1).

As already found in relative lead compounds, the heavy atoms, which carry a lone electron pair, are preferentially localized in (6h) sites. This allows the formation of a metal triangle stabilizing the structure by the overlap of the lone electron pairs. The existence of this type of lacunar apatite is conditioned by the presence of lone pair cations Pb^{2+} . In the case of $A^I Pb_4(PO_4)_3$ ($A^I = Na, K; X = P, V, As$)[6-9]. Therefore, the formulation of our materials could be written as $Na_{1-x}K_xPb(2)_{1-y}\{Sr/Ca\}(2)_yPb(1)_{3-z}\{Sr/Ca/Cd\}(1)_z(PO_4)_3$. The stereo-activity of Pb^{2+} cations is manifested only for those occupying the octahedral sites living empty hexagonal tunnels (6h). The other lead cations, located in the mixed sites (4f), outside such tunnels, do not seem to be stereo-active (Fig.2). This stabilization is interpreted by the orientation of the lone pairs $6s^2$ within the tunnels. El Koumiri et al. [1] and Manoun et al. [5-9], showed previously that while $Pb^{2+}(2)$ cations with an inactive lone pairs $6s^2$ are engaged in an almost ionic bond $Pb^{2+}(2)/\{Sr/Ca\}^{2+}(2)/Na^+/K^+-O$, in the mixed site M(4f). For M(1) site,

$\text{Pb}^{2+}(1)/\{\text{Sr}/\text{Ca}/\text{Cd}\}(1)-\text{O}$ is more covalent in character and the $6s^2$ lone pair of $\text{Pb}^{2+}(1)$ is active. Note that the presence of lone pair electrons can distort the oxygen polyhedra, and this explains clearly our X-ray results.

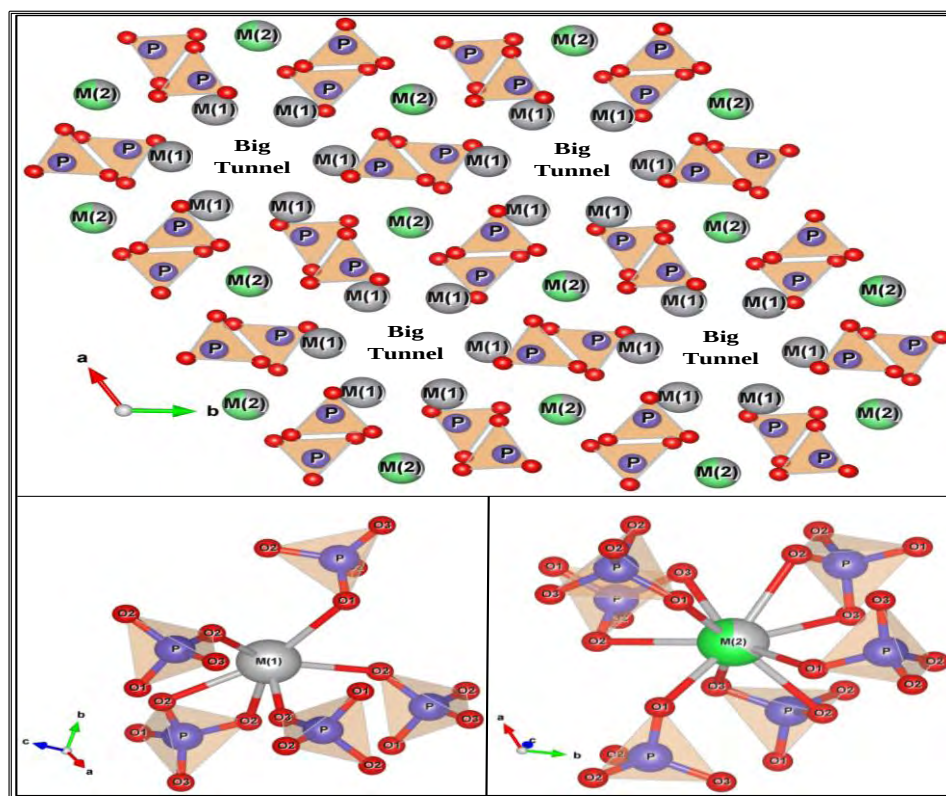


Fig.1: Structural view of $\text{Na}_{1-x}\text{K}_x\text{Pb}_{4-y/2}\{\text{Sr}/\text{Ca}/\text{Cd}\}_y(\text{PO}_4)_3$. The large tunnel of lacunar apatite illustrates the metal and oxygens arrangement around $\text{M}(6h)$ and $\text{M}(4f)$ sites connected to the $[\text{PO}_4]^{3-}$ tetrahedra.

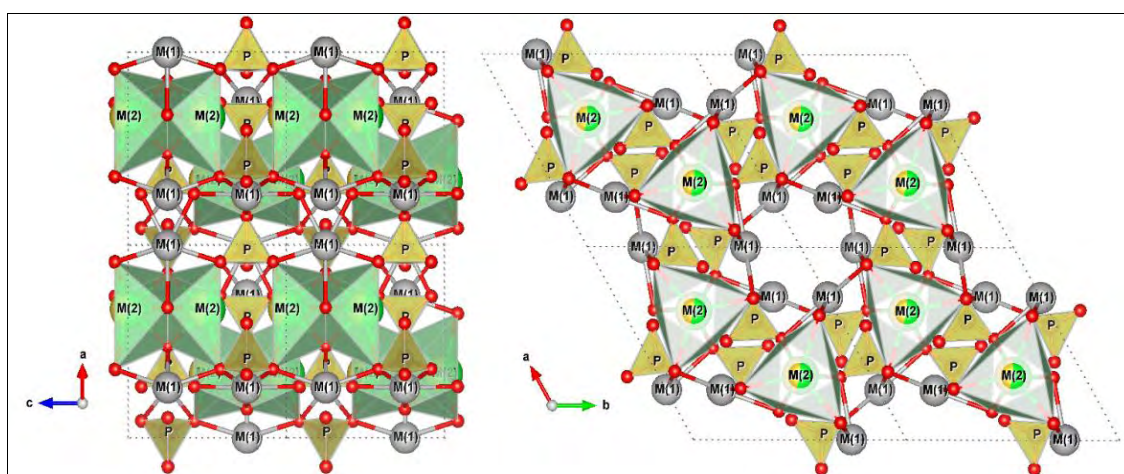


Fig.2: Polyhedral view in the ab -plane of the crystal structure of $\text{A}^{\text{I}}\text{Pb}_4(\text{PO}_4)_3$.*

Since the $\text{Na}_{1-x}\text{K}_x\text{Pb}_{4-y/2}\{\text{Sr}_y/\text{Ca}\}(2)_y\text{Pb}(1)_{3-z}\{\text{Sr}/\text{Ca}/\text{Cd}\}(1)_z(\text{PO}_4)_3$ specimens are polycrystalline powder, we cannot precisely assign the observed modes using a combination of the single-crystal orientation and the polarized Raman scattering. The bands observed in the infrared and Raman active spectra of these compounds do not differ significantly from those observed [1,2,5-7] and those of calcium hydroxyapatite whose factor group is C_{6h}^2 for ($P6_3/m$) [10,11]. However, the observed Infrared and Raman modes can be classified into two for IR and three for RAMAN. These general families of lattice vibrations; Lattice Mode ($\text{M}(2)\text{-O}_9$ and $\text{M}(1)\text{-O}_6$), are observed at frequencies below 300 cm^{-1} , as well as translational and rotational modes of $[\text{PO}_4]^{3-}$ tetrahedra, greater than of 400 cm^{-1} . First of all, the hydroxyl asymmetric stretching is not observed in both Infrared and Raman spectra around $3000\text{-}4000\text{ cm}^{-1}$ (Cuscó et al., 1998; Rehman and Bonfield, 1997; Tsuda and Arends, 1994; Zakharov et al., 2004). This confirms that this type of apatite does not contain any hydroxyl group or water intercalated in apatite tunnels.

In this work, UV-Vis spectroscopy was employed to obtain the absorption domain of these materials as well as calculating the optical bandgap. Generally, the light at a wavelength in the neighbourhood of 300 nm consists of weak energy photons. The Relating, to or being the shortest wavelengths of radiation in the ultraviolet spectrum and especially those between 100 and 350 nanometers. These measurements in the Ultraviolet/Visible region (UV-Vis) cover wavelengths from about 250 nm to 800 nm .

The lacunar apatite is composed of an optical material exhibiting light transmission characteristics in the far-ultraviolet region. This argument provides transitions among the electronic energy levels of the apatitic molecule.

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The values of the indirectly allowed energy gap of the crystal structure of apatites $Na_{1-x}K_xPb_{4-y/2}\{Sr_y/CaCd/CaSr\}(PO_4)_3$ depending on the effect of {Strontium/Calcium/Cadmium} and of potassium substitutions as a function of x&y are discussed. These types of materials can be electrically semiconductor [12-15] and visibly transparent, with a highly unique combination of properties. Generally, P^{5+} is pentavalent and contributes five valence electrons; these may act either as a potential donor or acceptor, called an amphoteric dopant. It has been reported that low carrier concentration may lead to low mobility in oxide apatitic due to the suppression and passivation of anionic vacancies. Considering O-bonding, oxygen radicals preferentially react with P° radicals because the most favourable chemical bond-forming stabilization in the crystalline state gives ‘P–O’ [12-14]. Thus, oxygen anions react mainly with M(2)-O₉ and M(1)-O₆ sites, where there are monovalent cations ‘Na⁺/K⁺’ and divalent cations $Pb^{2+}/\{Sr/Ca/Cd\}^{2+}$, see Fig.3. Because the low-energy-loss region reflects the valence and conduction band structures of solids. This indicates that the electron carrier concentration is decreased or increases by the existence of ‘Na⁺/K⁺’ and ‘ $Pb^{2+}/\{Sr/Ca/Cd\}^{2+}$ ’ cations, according to x&y, resulting in the decreased or increase of {E_g}.

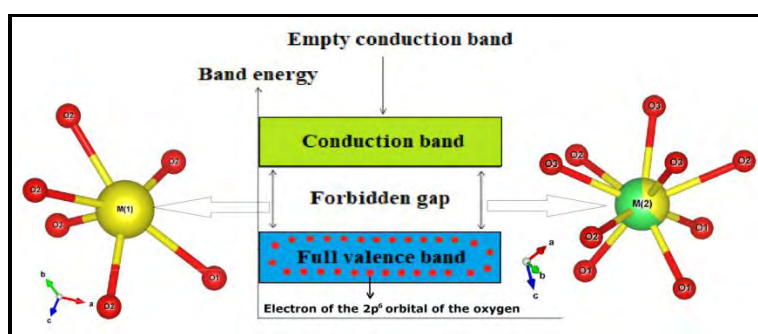


Fig.3: Electronic structure of lacunar apatites.

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As the ' $\text{K}^+/\{\text{Sr}/\text{Ca}/\text{Cd}\}^{2+}$ ' content increased, the gap between the conduction band $\{\text{Ec}\}$ and Fermi level $\{\text{EF}\}$ have slightly varied. However, because of the difficulties in deriving the relationship between the structural stability of the lacunar apatite, and the Fermi level of the oxide bandgap, the study of this issue has remained very limited until now.

II. News Series of $\text{Na}_{1-x}\text{K}_x\text{Pb}_{4-y/2}\text{Sr}_{y/2}(\text{PO}_4)_3$.

II.1. Structural Analysis.

The pictures of the X-ray powder diffraction patterns show is as [Fig.4](#). $\text{Na}_{1-x}\text{K}_x\text{Pb}_{4-y/2}\text{Sr}_{y/2}(\text{PO}_4)_3$, are similar to other lacunar materials [[1-3,5-9](#)]. Rietveld's first refinements, watched in [Fig.5](#), to justify all the observed reflections for the compositions ($0 \leq x \leq 1$) and ($0 \leq y/2 \leq 1.5$), could be indexed in the space group $P6_3/m$ (N°176). Except for reflections indicated at 2θ successively, between 17° and 35° for $y=0.5$, $y=1.5$, $z=0$ and $z=1.5$ with of low intensity (the stars indicated in [Fig.4](#)). The additional peaks have been detected by the HighScore program ([PANalytical. 2003](#)), they were assigned to the compound $\text{Pb}_3(\text{PO}_4)_2$ [[16,17](#)]. The results of the first refinements are shown in [Table.1](#), with estimated deviations in parentheses.

Two phases presented in [Fig.6](#) illustrate how perceptual the indicators of the quality of the structural models respectively for $\text{Na}_{1-x}\text{K}_x\text{Pb}_{4-y/2}\text{Sr}_{y/2}(\text{PO}_4)_3$ and $\text{Pb}_3(\text{PO}_4)_2$ carried out in the $P6_3/m$ and $C2/c$ space groups respectively. The results of the reliability factors, the judges to be a very satisfactory result, displays the agreement obtained between observed and calculated diffraction profiles. For more details of the second refinement see [Table.2](#). The finals resulting data, interatomic bond distances, and angles are given in [Table.3](#). The atomic coordinates, isotropic temperature factors, and occupation in the 6h and 4f sites as a function of the amount of potassium (x) and strontium ($y/2$) are listed in [Table.4](#), for all, with their estimated deviations in parentheses.

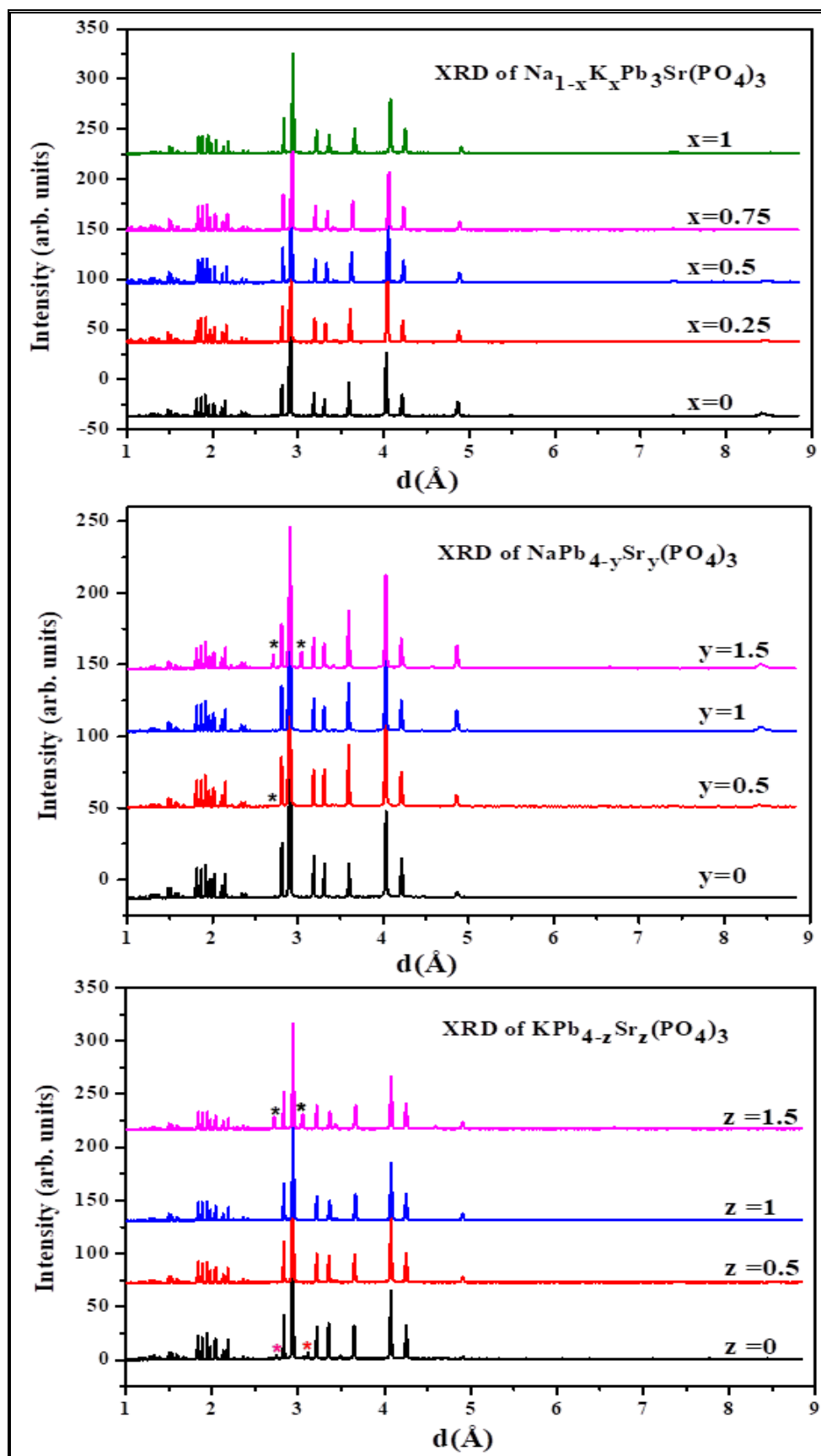


Fig.4: X-Ray powder diffraction patterns [$I = f(d(h\ k\ l))$], for $\text{Na}_{1-x}\text{K}_x\text{Pb}_{4-y/2}\{\text{Sr}_y/\text{CaCd}/\text{CaSr}\}(\text{PO}_4)_3$.

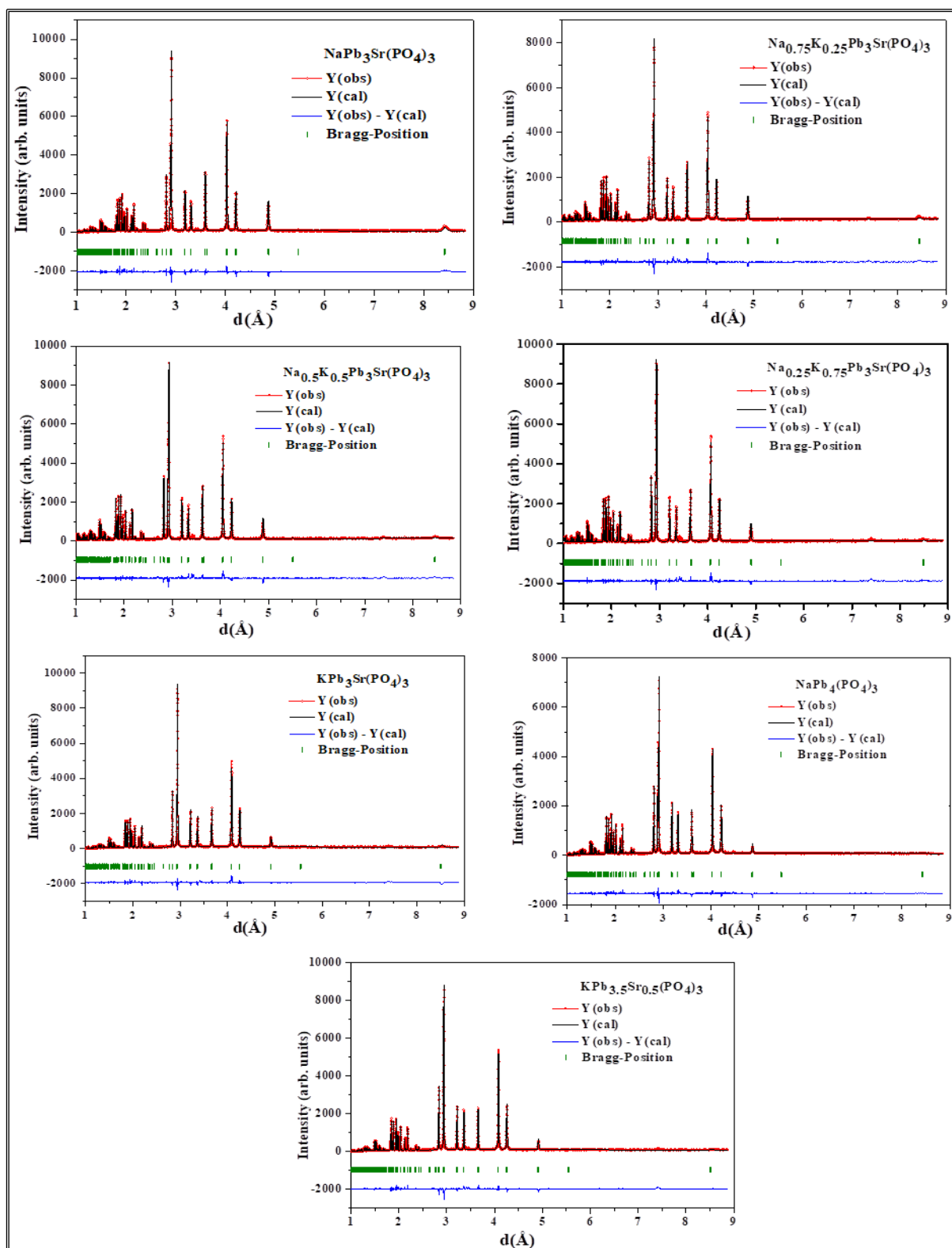


Fig.5: Rietveld first refinements plot of $\text{Na}_{1-x}\text{K}_x\text{Pb}_{4-y/2}\text{Sr}_{y/2}(\text{PO}_4)_3$. The symbols illustrate: the observed data $N^{\circ}1$ and the calculated pattern for $N^{\circ}2$, the lower curve is the difference diagram schematize in the $N^{\circ}3$ and the vertical markers show calculated positions of Bragg reflections in $N^{\circ}4$.

Table.1: Details of Rietveld's first refinement conditions plot of $\text{Na}_{1-x}\text{K}_x\text{Pb}_{4-y/2}\text{Sr}_{y/2}\text{Zr}_{z/2}(\text{PO}_4)_3$.

Materials		$\text{Na}_{1-x}\text{K}_x\text{Pb}_3\text{Sr}(\text{PO}_4)_3$ ($0 \leq x \leq 1$)					$\text{NaPb}_4(\text{PO}_4)_3$	$\text{KPb}_{3.5}\text{Sr}_{0.5}(\text{PO}_4)_3$
$x \& y \& z$		0	0.25	0.5	0.75	1	0	0.5
Zero-point (deg.2 θ)		0.0030(11)	-0.0080(13)	0.0093(10)	0.0502(11)	0.0359(9)	0.0153(7)	0.0421(9)
Pseudo-Voigt function [PV= $\eta L + (1 - \eta) G$]	η	0.5828(59)	0.5560(60)	0.5150 (17)	0.6570(70)	0.3412(71)	0.6510(71)	0.59031(69)
Caglioti parameters	U	0.0467(19)	0.0355(16)	0.0202(12)	0.0234(13)	0.0404(26)	0.0329(14)	0.0512(23)
	V	-0.0209(15)	-0.0085(13)	-0.0079(9)	-0.0071(11)	-0.0220(20)	-0.0246(12)	-0.0275(18)
	W	0.0074(1)	0.0054(2)	0.0056(2)	0.0056(2)	0.0103(4)	0.0099(2)	0.0106(3)
N°. Of reflections		472	511	503	512	496	468	524
N°. Of refined parameters		33					32	33
Space group		$P 6_3/m$						
a (Å)		9.73636(14)	9.75449(16)	9.77839(13)	9.80342(14)	9.83099(15)	9.74084(11)	9.83312(10)
c (Å)		7.19172(11)	7.22093(13)	7.25535(10)	7.29119(12)	7.33274(13)	7.20379(9)	7.31608(11)
V (Å ³)		590.41(1)	595.02(2)	600.79(1)	606.85(2)	613.75(6)	591.95(1)	612.621(9)
Z		2						
Atom Number		9	10			9	7	9
User-weighted Chi2		1.94	2.00	2.06	2.06	1.83	1.60	1.79
%R _F		5.11	4.01	3.71	3.75	4.89	6.44	5.37
%R _B		5.37	5.91	5.60	5.29	5.46	5.78	5.72
%R _p		8.45	7.77	7.48	7.51	8.25	8.11	8.26
%R _{wp}		11.6	10.50	10.30	10.70	11.3	11.4	11.5
%cR _p		13.7	15.00	14.30	13.90	13.9	14.1	14.0
%cR _{wp}		16.0	16.40	16.00	16.30	16.1	16.5	16.3

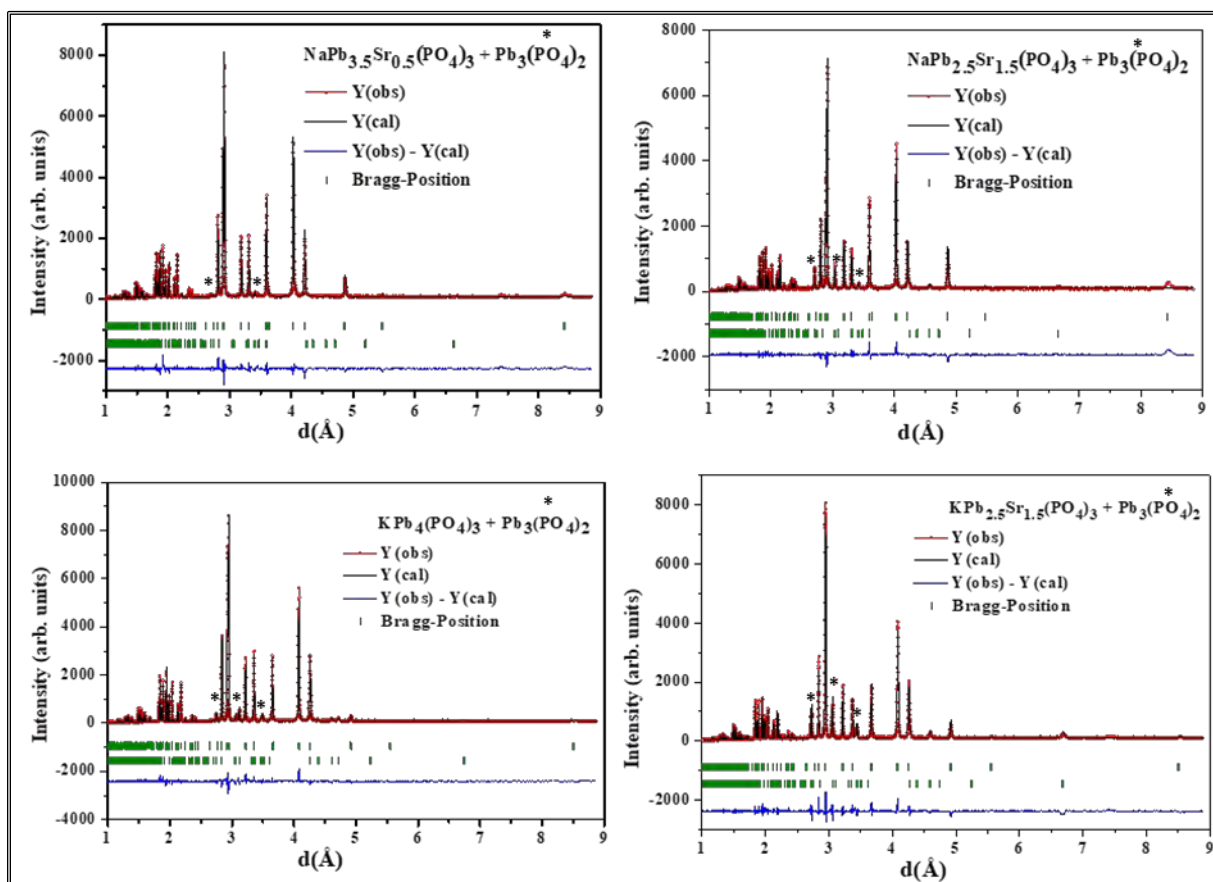


Fig.6: Rietveld second refinement of the two phases.

Table.2: Details of the second refinement plot of $\text{Na}_{1-x}\text{K}_x\text{Pb}_{4-y/2}\text{Sr}_y(\text{PO}_4)_3$ and $\text{Pb}_3(\text{PO}_4)_2$.

Materials		KPb _(4-z) Sr _z (PO ₄) ₃				NaPb _(4-y) Sr _y (PO ₄) ₃			
$\text{z}\&\text{y}$		0	Pb ₃ (PO ₄) ₂	1.5	Pb ₃ (PO ₄) ₂	0.5	Pb ₃ (PO ₄) ₂	1.5	Pb ₃ (PO ₄) ₂
Zero-point (deg.2θ)		0.0394(7)		0.0525(10)		0.0190(10)		0.0132(13)	
Pseudo-Voigt function [PV=ηL ₊ + (1-η) G]	η	0.4662(6)		0.3646(5)		0.5524(82)		0.3624(74)	
Caglioti parameters	U	0.0267(12)	0.1337(12)	0.0558(12)	0.2952(12)	0.0058(16)	0.2905(16)	0.1142(48)	0.3310(48)
	V	- 0.0225(11)	- 0.0751(11)	- 0.0412(11)	- 0.1437(11)	- 0.0051(14)	- 0.1763(14)	- 0.0535(33)	- 0.1867(33)
	W	0.0091(1)	0.0192(1)	0.01701(2)	0.02810(2)	0.0065(3)	0.0408(3)	0.0127(5)	0.0404(5)
N°. Of reflections		468	746	526	752	468	733	466	740
N°. Of refined parameters		32	7	33	7	33	7	33	7
Space group		P 6 ₃ /m		C 2/c		P 6 ₃ /m		C 2/c	
a (Å)		9.83640(10)	13.80480(8)	9.83208(4)	13.75302(5)	9.7351(2)	13.6259(9)	9.73840(20)	13.67926(73)
b (Å)		7.30510(10)	5.68050(2)	7.34040(2)	5.71164(4)	7.1968(2)	5.6581(3)	7.19789(16)	5.68412(23)
c (Å)			9.45590(4)		9.45009(2)		9.3819(5)		9.39859(50)
Beta		120.00	102.438(4)	120.00	103.204(4)	120.00	103.497(5)	120.00	103.235(4)
V (Å ³)		612.11(1)	724.11(6)	614.53(2)	722.70(2)	590.67(2)	703.34(7)	591.17(2)	711.37(6)
Z		2	4	2	4	2	4	2	4
Atom Number		9	7	9	7	9	7	9	7
User-weighted Chi2		2.27		2.82		2.77		1.91	
%R _F		3.35	3.20	2.47	0.90	4.00	0.83	2.64	0.746
%R _B		5.14	1.59	4.74	2.37	5.81	1.64	5.27	1.53
%R _p		9.14		10.5		10.4		9.19	
%R _{wp}		12.4		14.0		14.1		12.7	
%cR _p		13.9		16.0		15.0		13.4	
%cR _{wp}		16.6		18.7		18.0		16.6	

Table.3: Selected interatomic distances in (Å) and O-P-O in (°) angles.

Materials	Na _{1-x} K _x Pb ₃ Sr(PO ₄) ₃					KPb _(4-z) Sr _z (PO ₄) ₃			NaPb _(4-y) Sr _y (PO ₄) ₃		
$\text{x}\&\text{z}\&\text{y}$	0 (y=1)	0.25	0.5	0.75	1 (z=1)	0	0.5	1.5	0	0.5	1.5
M(1)-O ₁	2.861(2)	2.793(2)	2.791(2)	2.800(2)	2.816(2)	2.809(2)	2.705(2)	2.928(4)	2.806(2)	2.808(4)	2.803(4)
2*M(1)-O ₂	2.503(6)	2.583(8)	2.572(8)	2.571(8)	2.581(7)	2.514(1)	2.499(7)	2.515(6)	2.493(9)	2.740(6)	2.534(2)
2*M(1)-O ₂	2.583(2)	2.554(1)	2.597(1)	2.622(1)	2.683(2)	2.590(1)	2.733(2)	2.754(2)	2.682(1)	2.434(7)	2.602(2)
M(1)-O ₃	2.160(1)	2.227(1)	2.156(1)	2.167(1)	2.080(1)	2.336(2)	2.159(2)	2.150(2)	2.254(2)	2.109(3)	2.088(4)
<M(1)-O>	2.527	2.539	2.529	2.540	2.540	2.562	2.524	2.587	2.559	2.523	2.507
3*M(2)-O ₁	2.485(5)	2.526(5)	2.568(5)	2.571(5)	2.579(4)	2.569(4)	2.566(5)	2.551(9)	2.428(7)	2.514(4)	2.588(4)
3*M(2)-O ₂	2.872(1)	2.853(9)	2.854(9)	2.853(1)	2.841(1)	2.972(1)	2.823(1)	2.830(2)	2.896(1)	2.709(7)	2.835(6)
3*M(2)-O ₃	2.671(5)	2.678(5)	2.700(1)	2.723(1)	2.859(1)	2.764(3)	2.854(4)	2.773(2)	2.700(1)	2.704(3)	2.701(4)
<M(2)-O>	2.676	2.686	2.707	2.716	2.760	2.768	2.748	2.718	2.675	2.642	2.708
P-O ₁	1.542(9)	1.515(1)	1.505(1)	1.501(1)	1.562(1)	1.578(1)	1.590(1)	1.543(2)	1.556(2)	1.577(5)	1.525(2)
2*P-O ₂	1.581(4)	1.553(1)	1.539(9)	1.548(1)	1.516(4)	1.536(1)	1.574(4)	1.570(1)	1.534(1)	1.531(3)	1.549(2)
P-O ₃	1.596(6)	1.511(7)	1.595(2)	1.597(2)	1.558(1)	1.563(7)	1.543(6)	1.566(1)	1.554(7)	1.548(5)	1.544(3)
<P-O>	1.573	1.526	1.546	1.549	1.545	1.559	1.569	1.560	1.548	1.552	1.539
2*O ₁ -P-O ₂	112.6(4)	113.1(9)	111.2(8)	111.5(1)	108.4(4)	110.1(1)	108.8(4)	108.2(1)	110.9(1)	118.8(2)	106.3(3)
O ₁ -P-O ₃	107.9(4)	112.8(5)	110.4(1)	110.0(1)	102.6(1)	100.3(5)	105.1(4)	104.2(1)	111.3(2)	108.6(3)	109.1(4)
O ₂ -P-O ₂	103.5(2)	99.4(8)	104.0(8)	105.9(9)	111.9(2)	111.5(1)	115.8(2)	116.1(6)	109.4(9)	88.9(2)	104.1(3)
2*O ₂ -P-O ₃	110.1(3)	108.8(7)	109.9(1)	108.9(1)	112.5(8)	112.1(8)	108.9(3)	109.8(1)	107.1(8)	110.2(2)	115.2(2)
<O-P-O>	108.5	108.5	108.9	109.1	108.8	108.5	109.6	109.6	109.7	106.6	108.7

Table.4: Final refined structural parameters for $\text{Na}_{1-x}\text{K}_x\text{Pb}_{4-y/2}\text{Sr}_{y/2}(\text{PO}_4)_3$.

Ion	Wyckoff	Sym	x/a	y/b	z/c	B ($\text{\AA}^2$)	Occupancy	x&y&z
M(I)= Pb_{3-y&z}(1)/Sr_{y&z}(1)	6h	M	Na_{1-x}K_xPb₃Sr(PO₄)₃			x		
			0.2573(2)	0.2591(1)	3.99(3)	2.632(3)/0.368(3)	0(y=1)	
			0.2578(2)	0.2598(2)	0.89(2)	2.545(6)/0.455(6)	0.25	
			0.2578(2)	0.2597(1)	1.22(2)	2.537(6)/0.463(6)	0.5	
			0.2580(2)	0.2596(2)	1.15(2)	2.483(7)/0.517(7)	0.75	
			0.2576(2)	0.2584(2)	1.89(3)	2.245(3)/0.755(3)	1(z=1)	
			NaPb_{4-y}Sr_y(PO₄)₃			y		
			0.2555(2)	0.2581(2)	4.19(3)	3	0	
			0.2550(2)	0.2590(2)	0.25	2.808(6)/0.192(6)	0.5	
			0.2583(2)	0.2613(1)	1.47(2)	2.126(6)/0.874(6)	1.5	
			KPb_{4-z}Sr_z(PO₄)₃			z		
			0.2523(2)	0.2568(2)	3.48(2)	3	0	
			0.2555(2)	0.2587(2)	0.25	2.661(6)/0.339(6)	0.5	
			0.2565(3)	0.2575(3)	2.08(5)	2.063(11)/0.937(11)	1.5	
M(2)= Pb_{1-y&z}(2)/Sr_{y&z}(2)/Na_{1-x}/K_x	4f	3	Na_{1-x}K_xPb₃Sr(PO₄)₃			x		
			0.5021(10)	4.14(3)	0.368(3)/0.632(3)/1	0(y=1)		
			0.5022(9)	1.12(8)	0.455(6)/0.545(6)/0.75/0.25	0.25		
			0.5025(9)	1.34(8)	0.463(6)/0.537(6)/0.5/0.5	0.5		
			0.5038(9)	1.31(8)	0.517(7)/0.483(7)/0.25/0.75	0.75		
			0.5045(8)	3.67(8)	0.755(3)/0.245(3)/1	1(z=1)		
			NaPb_{4-y}Sr_y(PO₄)₃			y		
			0.5104(8)	3.62(6)	1/1	0		
			0.4994(9)	2.61(8)	0.692(6)/0.308(6)/1	0.5		
			0.5028(10)	5.12(4)	0.374(6)/0.626(6)/1	1.5		
			KPb_{4-z}Sr_z(PO₄)₃			z		
			0.5076(7)	2.63(8)	1/1	0		
			0.5046(9)	4.87(8)	0.839(6)/0.161(6)/1	0.5		
			0.5059(16)	2.62(2)	0.437(11)/0.563(11)/1	1.5		
P	6h	M	Na_{1-x}K_xPb₃Sr(PO₄)₃			x		
			0.3787(8)	0.4045(7)	1.80(2)	0(y=1)		
			0.3811(9)	0.4055(9)	0.91(2)	0.25		
			0.3775(8)	0.4054(8)	0.75	0.85(2)	3	
			0.3770(9)	0.4039(8)	1.19(2)	0.75		
			0.3744(9)	0.4080(8)	1.63(2)	1(z=1)		
			NaPb_{4-y}Sr_y(PO₄)₃			y		
			0.3793(10)	0.4007(9)	1.99(2)	0		
			0.3824(9)	0.4137(9)	0.75	1.47(2)	3	
			0.3785(8)	0.4177(8)	1.04(5)	1.5		
			KPb_{4-z}Sr_z(PO₄)₃			z		
			0.3574(9)	0.3939(9)	1.16(2)	0		
			0.3719(8)	0.4011(8)	0.75	1.93(9)	3	
			0.3766(13)	0.4104(12)	0.74(7)	1.5		
O(1)	6h	M	Na_{1-x}K_xPb₃Sr(PO₄)₃			x		
			0.4887(1)	0.3329(1)	5.91(9)	0(y=1)		
			0.4802(2)	0.3256(15)	2.73(2)	0.25		
			0.4751(2)	0.3256(15)	0.75	2.93(2)	3	
			0.4751(2)	0.3256(17)	3.42(2)	0.75		
			0.4751(1)	0.3256(9)	1.81(2)	1(z=1)		
			NaPb_{4-y}Sr_y(PO₄)₃			y		
			0.4878(21)	0.3258(19)	6.66(3)	0		
			0.4846(22)	0.3290(20)	0.75	6.61(2)	3	
			0.4724(14)	0.3309(16)	2.73(2)	1.5		
			KPb_{4-z}Sr_z(PO₄)₃			z		
			0.4747(12)	0.3278(9)	5.64(2)	0		
			0.4712(11)	0.3139(9)	0.75	4.70(3)	3	
			0.4846(12)	0.3383(12)	7.58(5)	1.5		
O(2)	12i	1	Na_{1-x}K_xPb₃Sr(PO₄)₃			x		
			0.2627(1)	0.3489(9)	0.5774(11)	5.91(9)	0(y=1)	
			0.2624(1)	0.3528(9)	0.5860(10)	2.73(2)	0.25	
			0.2658(1)	0.3541(9)	0.5828(10)	2.93(2)	0.5	
			0.2674(1)	0.3554(10)	0.5805(11)	3.42(2)	0.75	
			0.2746(1)	0.3597(9)	0.5787(10)	1.81(2)	1(z=1)	
			NaPb_{4-y}Sr_y(PO₄)₃			y		
			0.2743(13)	0.3514(11)	0.5762(12)	6.66(3)	0	
			0.2544(10)	0.3678(9)	0.6009(11)	6.61(2)	0.5	
			0.2658(10)	0.3544(9)	0.5804(10)	2.73(2)	1.5	
			KPb_{4-z}Sr_z(PO₄)₃			z		
			0.2559(15)	0.3400(12)	0.5762(12)	5.64(2)	0	
			0.2741(11)	0.35978(9)	0.5677(11)	4.70(3)	6	
			0.2787(22)	0.3610(15)	0.5685(16)	7.58(5)	1.5	
O(3)	6h	M	Na_{1-x}K_xPb₃Sr(PO₄)₃			x		
			0.4876(1)	0.5931(20)	5.91(9)	0(y=1)		
			0.4801(2)	0.5840(19)	2.73(2)	0.25		
			0.4888(2)	0.5926(18)	0.75	2.93(2)	3	
			0.4883(2)	0.5909(19)	3.42(2)	0.75		
			0.5016(2)	0.5855(20)	1.81(2)	1(z=1)		
			NaPb_{4-y}Sr_y(PO₄)₃			y		
			0.4787(20)	0.5847(19)	6.66(3)	0		
			0.4961(20)	0.5954(20)	0.75	6.61(2)	3	
			0.4953(17)	0.5982(20)	2.73(2)	1.5		
			KPb_{4-z}Sr_z(PO₄)₃			z		
			0.4762(20)	0.5737(21)	5.64(2)	0		
			0.4949(23)	0.5778(21)	0.75	4.70(3)	3	
			0.4928(33)	0.5919(23)	7.58(5)	1.5		

It should be noted that the refinements of $\text{Na}_{1-x}\text{K}_x\text{Pb}_{4-y/2}\text{Sr}_{y/2}(\text{PO}_4)_3$; show that there are two symmetrically non-equivalent cations sites labelled M(1) and M(2), residing respectively in the hexagonal site 6h and 4f. The occupation of monovalent ($0 \leq x \leq 1$) and divalent cations ($0 \leq y/2 \leq 1.5$), in the non-equivalent sites behind the variation of the structural parameters for structure hexagonal. For that, we have illustrated the simulation results on a particular case of the percentages (%) of occupation of these cations Pb^{2+} and Sr^{2+} in Table.5. Noted that $[\text{M}(1) / 3] * 100(\%)$ for '6h' site. For 4f site $[\text{M}(2) / 2] * 100(\%)$ and 50% the percentages of occupation who stays for monovalent cations is fixed in the site 4f (Na/K).

Indeed, as Fig.4 show the results according to X-ray diffraction presented for all the diffractograms have the same shape with two notable differences; the intensity and the orientations or the shift of the reticular planes concerning each other. The results of the Rietveld refinements showed in Figs. 5 and 6 reflect the offset of the lattice spacings $d(h\ k\ l)$ values indicated in Table.5. For example, the two most intense lattice distances $d(1\ 2\ 1)$ and $d(1\ 1\ 2)$ in powder XRD patterns of $\text{Na}_{1-x}\text{K}_x\text{Pb}_{4-y/2}\text{Sr}_{y/2}(\text{PO}_4)_3$ schematized in Fig.7. This pedagogical tool shows reticular planes inside a crystal, using a simple hexagonal (unit cell size). Became, the X-ray spectral lines measure shifts and bursting, for peaks of the most intensity are towards larger angle shows a shift on the diffractogram schematized online for two Lattice planes $d(1\ 2\ 1)$ and $d(1\ 1\ 2)$. This is based on Bragg's equation: $n\lambda = 2d \sin(\theta)$. Because potassium and lead are larger ionic radius $r(\text{K}^+) = 1.55\text{\AA}$ and $r(\text{Pb}^{2+}) = 1.19\text{\AA}$ respectively, when compared with sodium $r(\text{Na}^+) = 1.24\text{\AA}$ and strontium $r(\text{Sr}^{2+}) = 1.18\text{\AA}$, see Ionic Radii [18].

[18] B.Y.R.D. Shannon, M. H. N.H. Baur, O.H. Gibbs, M. Eu, V. Cu. Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides Central Research and Development Department, Experimental Station, E. L Du Pont de Nemours The effective ionic radii of Shannon & Prewitt [Acta. (1976).

Table.5: The occupancy rate in (%) and $d(h\ k\ l)$ lattice planes for $\text{Na}_{1-x}\text{K}_x\text{Pb}_{4-y/2}\text{Sr}_{y/2}(\text{PO}_4)_3$.

x&y&z	M(1)		M (2)		d (1 2 1)	d (1 1 2)
	Pb ²⁺ (1)	Sr ²⁺ (1)	Pb ²⁺ (2)	Sr ²⁺ (2)		
Na _{1-x} K _x Pb ₃ Sr(PO ₄) ₃						
0 (y)	87.73	12.27	18.4	31.60	2.9137	2.8924
0.25	84.83	15.17	22.75	27.25	2.9202	2.9019
0.5	84.57	15.43	23.15	26.85	2.9284	2.9133
0.75	82.77	17.23	25.85	24.15	2.9371	2.9252
1 (z)	74.83	25.17	37.75	12.25	2.9468	2.9389
NaPb _(4-y) Sr _y (PO ₄) ₃						
0	100.00	0.00	50	0	2.9156	2.8960
0.5	93.60	6.40	34.6	15.4	2.9136	2.8936
1.5	70.87	29.13	18.7	31.3	2.9146	2.8942
KPb _(4-z) Sr _z (PO ₄) ₃						
0	100.00	0.00	50	0	2.9462	2.9323
0.5	88.70	11.30	41.95	8.05	2.9461	2.9348
1.5	68.77	31.23	21.85	28.15	2.9474	2.941

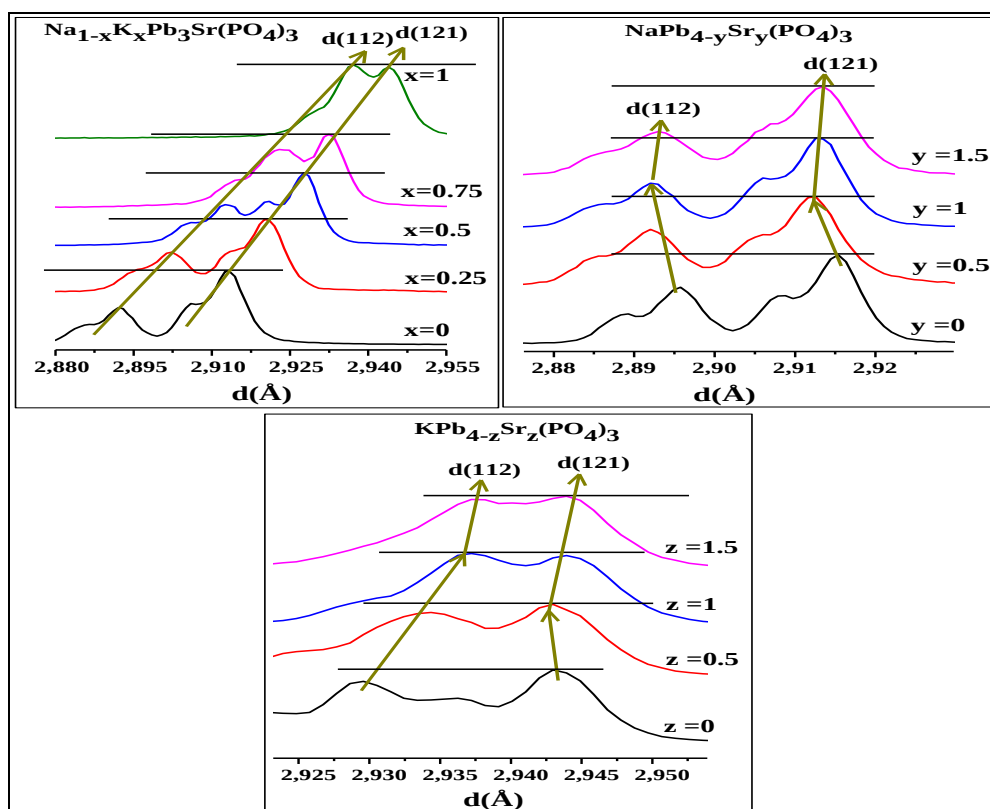


Fig.7: Shift and difference between intensity for distances $d\ (1\ 2\ 1)$ and $d\ (1\ 1\ 2)$ as a function of $x\&y\&z$ in $\text{Na}_{1-x}\text{K}_x\text{Pb}_{4-y/2}\text{Sr}_{y/2}(\text{PO}_4)_3$.

The interatomic distances and angles are reasonable, this is similar and agree well with those found in $\text{Na}_{1-x}\text{K}_x\text{Pb}_4(\text{PO}_4)_3$ [6] and also with other similar compounds. Where the M(1)–O in the site (6h) distances vary from 2.088Å to 2.928Å for $\text{Pb}^{2+}(1)/\text{Sr}^{2+}(1)$ –O. M(2)–O in the mixed site (4f), and from 2.428Å to 2.972Å for $\text{Pb}^{2+}(2)/\text{Sr}^{2+}(2)/\text{Na}^+/\text{K}^+$ –O. ‘P–O’ is with an average value of 1.5Å and the ‘O–P–O’ angles are between 99.4° and 118.8° (Table.3).

The Rietveld simulations results of the sample series often variations in the % occupations in the '6h' and '4f' sites as a function of the amount of potassium (x) and strontium (y&z) (Tables .4&5). The effects of cations substitution indicate clearly that there is a complete solubility and thus a continuous series of solid solutions, in which a given proportion of $\text{K}^+/\text{Sr}^{2+}$ replaces an equal proportion of $\text{Na}^+/\text{Pb}^{2+}$. The progressive substitution is the most important cause for the increase of $\text{Sr}^{2+}(1)$ and a decrease of $\text{Pb}^{2+}(1)$ in the 6h sites. This situation is inversely proportional to the 4f sites, the results are shown in Tables .4&5 and Fig.8. Rietveld refinements showed that more than 68% of Pb^{2+} cations are located in the 6h sites.

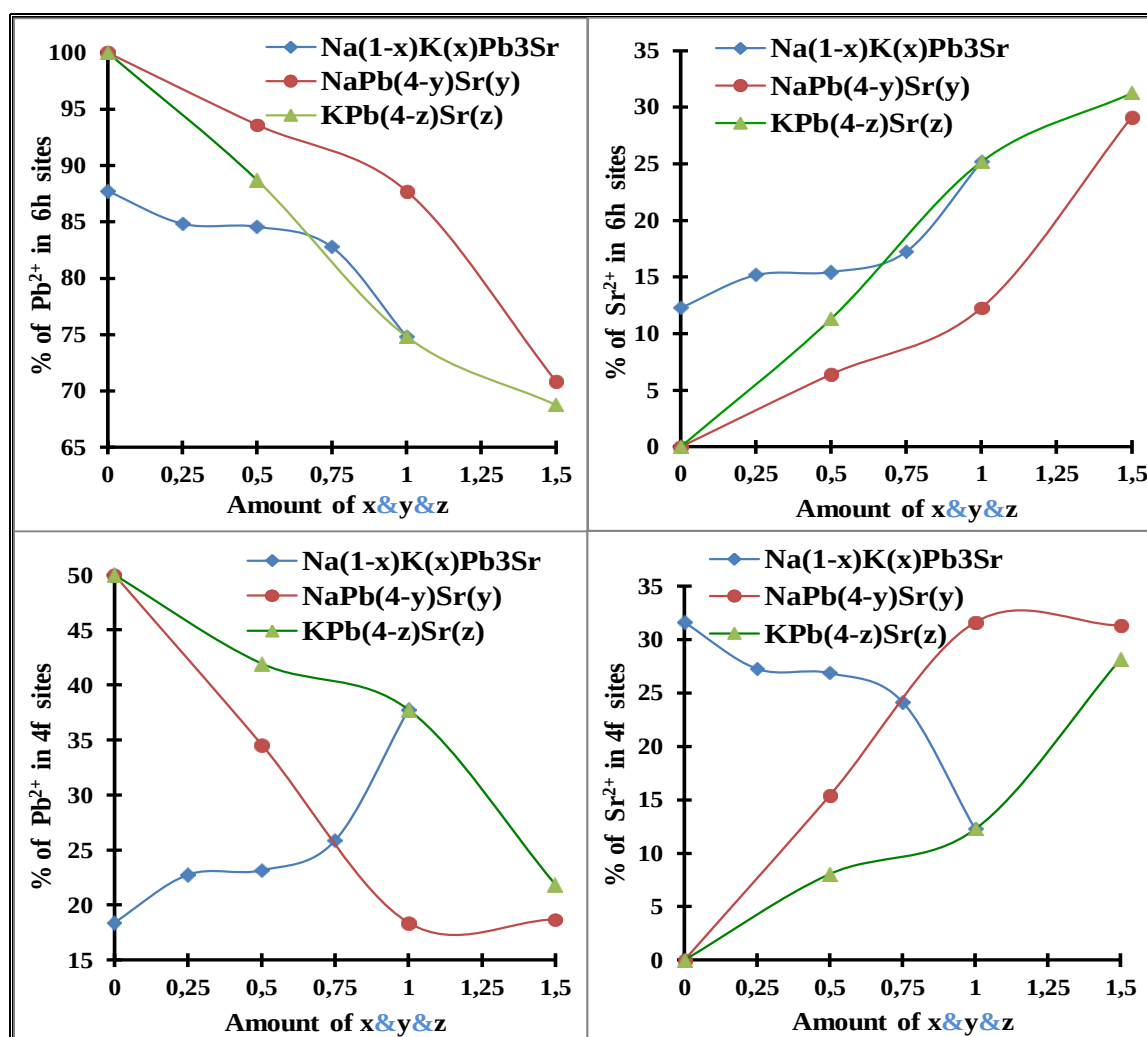


Fig.8: % Occupation in the M (6h) and M (4f) sites as a function of the amount of potassium, sodium, and strontium (x&y&z) in $\text{Na}_{1-x}\text{K}_x\text{Pb}_{4-y/2}\{\text{Sr}_y/\text{CaCd}/\text{CaSr}\}(\text{PO}_4)_3$.

Figs.9&10 and Tables.1&2 show the unit cell parameter variation as a function of (x&y&z). For $\text{Na}_{1-x}\text{K}_x\text{Pb}_3\text{Sr}(\text{PO}_4)_3$ where progressive substitution of sodium by potassium provokes an increase of the unit cell parameters (a), (c), and (V). The increase is due to the substitution of Na^+ ($r_i=1.24\text{\AA}$) by K^+ ($r_i=1.55\text{\AA}$) [18] with larger-radius. But for $\text{NaPb}_{4-y}\text{Sr}_y(\text{PO}_4)_3$, where progressive substitution of lead by strontium with small-radius Pb^{2+} ($r_i=1.19\text{\AA}$) by Sr^{2+} ($r_i=1.18\text{\AA}$) [18] provokes a decrease of the unit cell parameters (a), (c), and (V). Unlike the series of $\text{KPb}_{4-z}\text{Sr}_z(\text{PO}_4)_3$ for the unit cell parameters (a) decrease and (c) and (V) an increase.

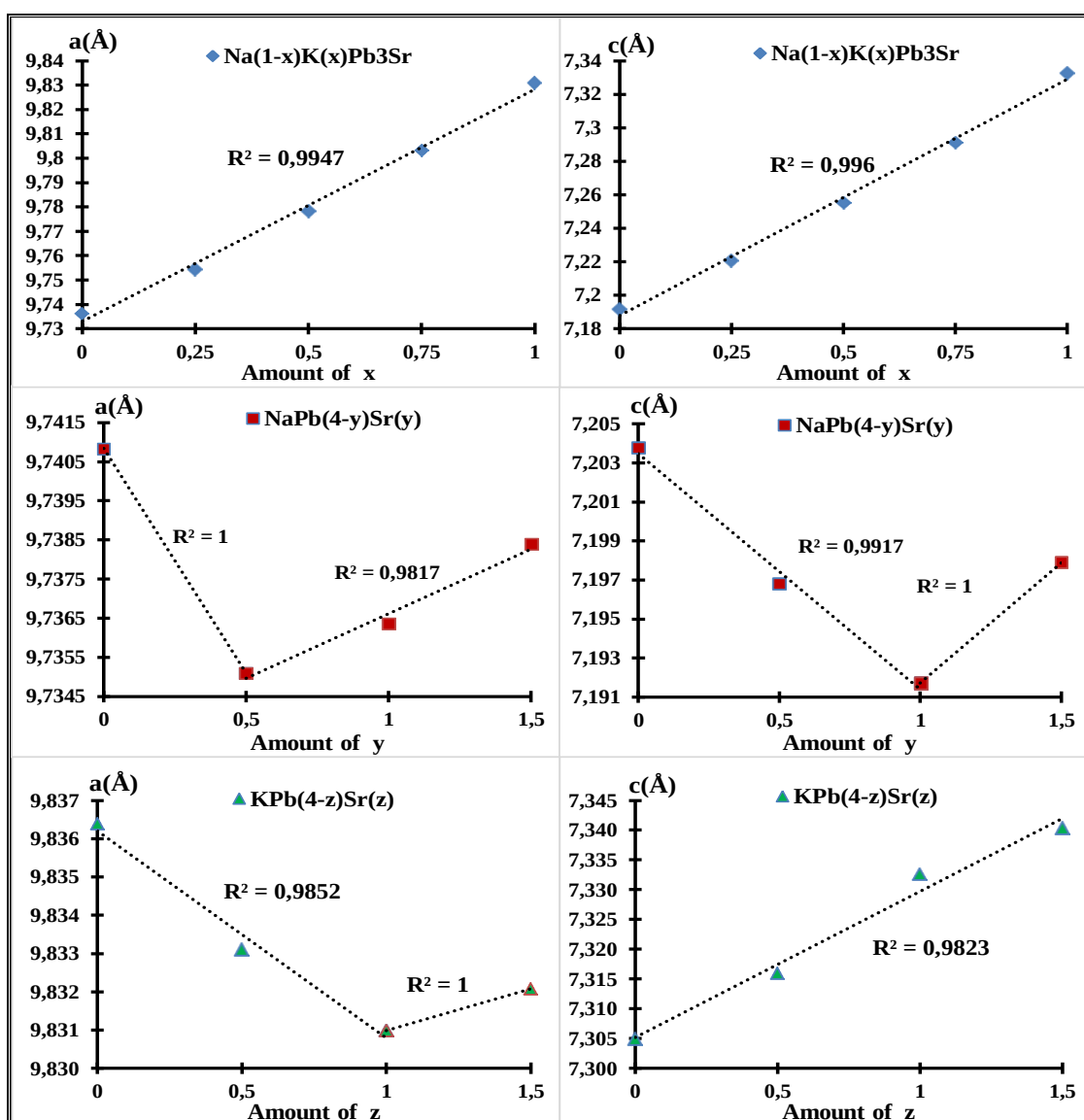


Fig.9: Unit cell parameters variation, as a function of x&y&z in $\text{Na}_{1-x}\text{K}_x\text{Pb}_{4-y/2}\text{Sr}_y\text{Sr}_z(\text{PO}_4)_3$.

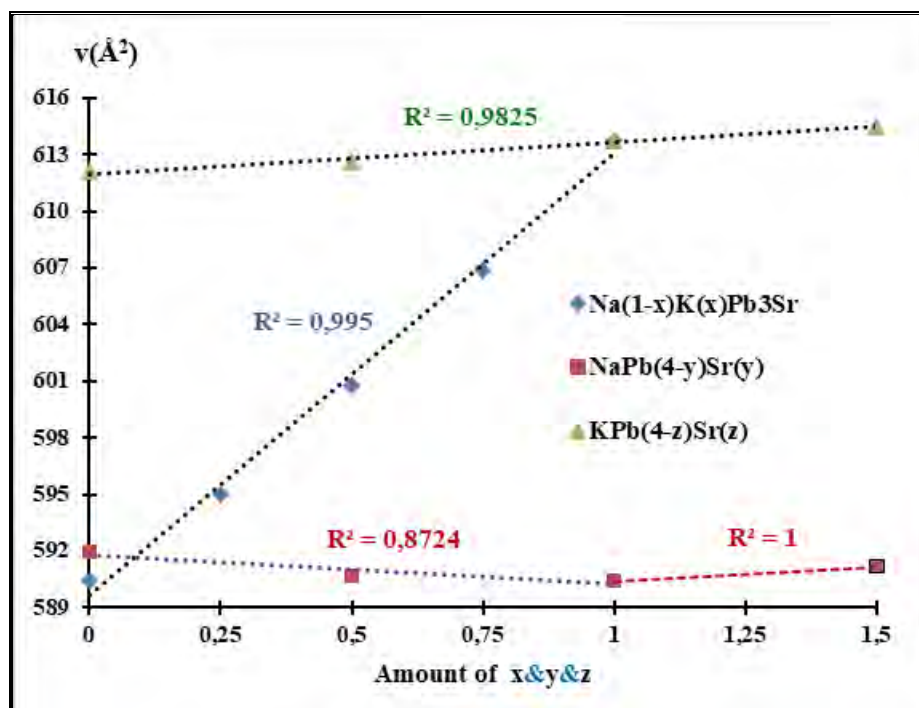
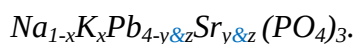


Fig.10: Variation of the unit cell volume as a function of x, y, z in



According to the X-ray diffraction results of Fig.4, all the diffractograms have the same shape with two notable differences; the intensity and the orientations or the shift of diffractogram concerning each other. The results of Rietveld refinements showed in the Table.5 reflect of shift and difference between intensity for the lattice spacings (d values) as a function of (x, y, z) in $Na_{1-x}K_xPb_{4-y/2}Sr_{y/2}(PO_4)_3$. Fig.11 shows a shift on the Lattice planes concerning each other is schematized online for two planes $d(1\ 2\ 1)$ and $d(1\ 1\ 2)$. This is based on Bragg's equation: $n\lambda = 2d\sin(\theta)$, because potassium and lead are larger ionic radius respectively when compared with sodium and strontium. We observe that the lattice planes vary in the same way of unit cell parameters variation as a function of (x, y), for $Na_{1-x}K_xPb_3Sr(PO_4)_3$ and $NaPb_{4-y}Sr_y(PO_4)_3$. Unlike the series of $KPb_{4-y}Sr_y(PO_4)_3$, the parameter (c) in vary in the same way of $d(1\ 1\ 2)$, but the parameter (a) varies in the opposite way of $d(1\ 2\ 1)$. For all, the distances $d(1\ 2\ 1)$ are more intense than $d(1\ 1\ 2)$, except that material $KPb_3Sr(PO_4)_3$. Fig.12 show that the reticular plane, $d(1\ 2\ 1)$ chopped off the crystal structure of $Na_{1-x}K_xPb_{4-y/2}Sr_{y/2}(PO_4)_3$.

$\text{xK}_x\text{Pb}_{4-y/2}\text{Sr}_{y/2}(\text{PO}_4)_3$ in the ‘P-O₂; P-O₃; O₁-P-O₂; P; M(1); M(2) and O₃’, and that the d(1 1 2) a chopped off the crystal structure in the ‘P; M(1); M(2) and O₁’.

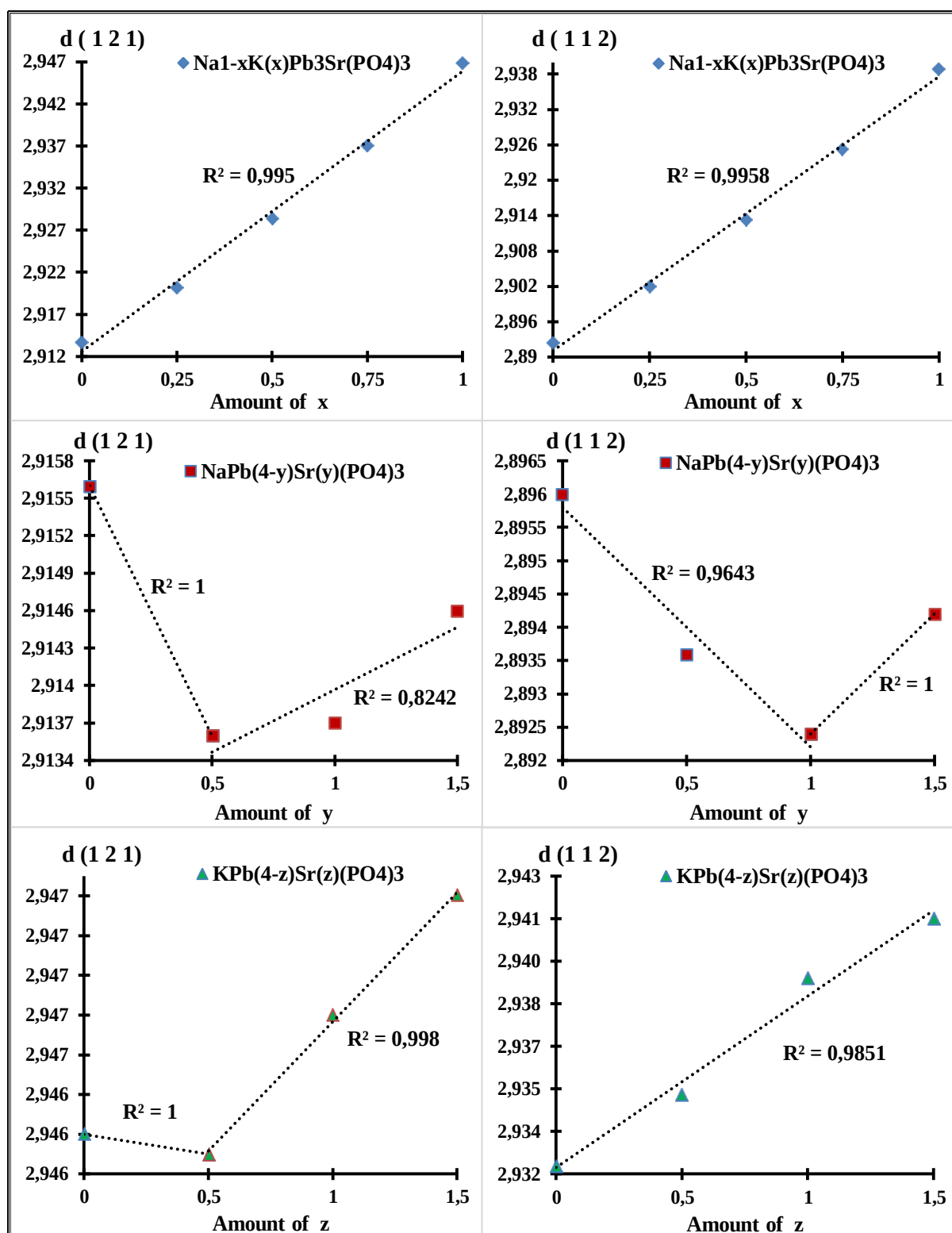


Fig.11: Variation of the reticular planes $d(1\ 2\ 1)$ and $d(1\ 1\ 2)$ as a function of x , y and z in $\text{Na}_{1-x}\text{K}_x\text{Pb}_{4-y/2}\{\text{Sr}_y/\text{CaCd}/\text{CaSr}\}(\text{PO}_4)_3$.

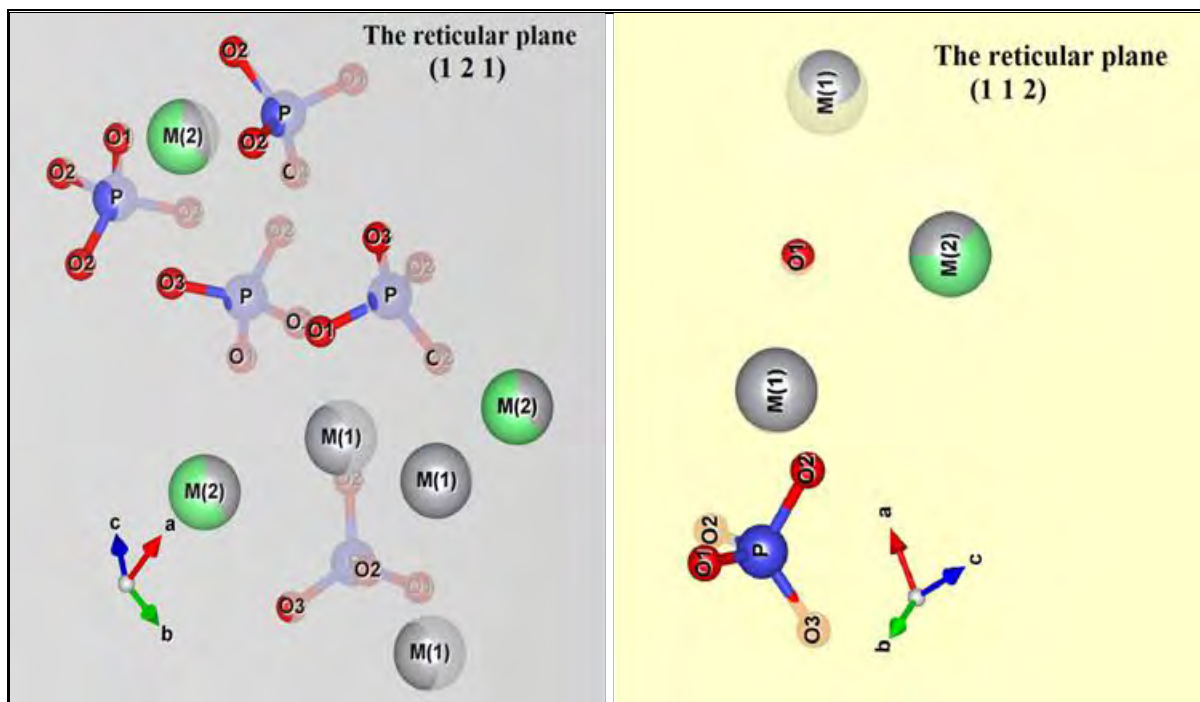


Fig.12: The reticular planes $d(1\ 2\ 1)$ and $d(1\ 1\ 2)$ chopped off the crystal structure of $Na_{1-x}K_xPb_{4-y/2}\{Sr_y/CaCd/CaSr\}(PO_4)_3$.

II.2. Vibrational Spectra Analysis.

a) Infrared and Raman at Room Temperature.

Figs.13&14 show the results of Infrared and Raman measurement at room temperature, respectively. The wavenumbers and the corresponding assignments are listed in Tables.6&7. The Lattice Modes (M(2)-O₉ and M(1)-O₆), this mode is observed at frequencies below 300 cm⁻¹. A pattern of bands was observed in the 350-800cm⁻¹ region is attributed to ‘O-P-O’ bending vibrations [V_2 (from 386cm⁻¹ to 455cm⁻¹) and V_4 (from 415cm⁻¹ to 593cm⁻¹)], and the series of high-frequency bands observed above 900cm⁻¹ is assigned to ‘P-O’ stretching vibrations [V_1 (observed around 925cm⁻¹ and 959cm⁻¹ as a strong band in the Raman spectra and as shoulder in the IR spectra) and V_3 (from 953cm⁻¹ to 1097cm⁻¹)].

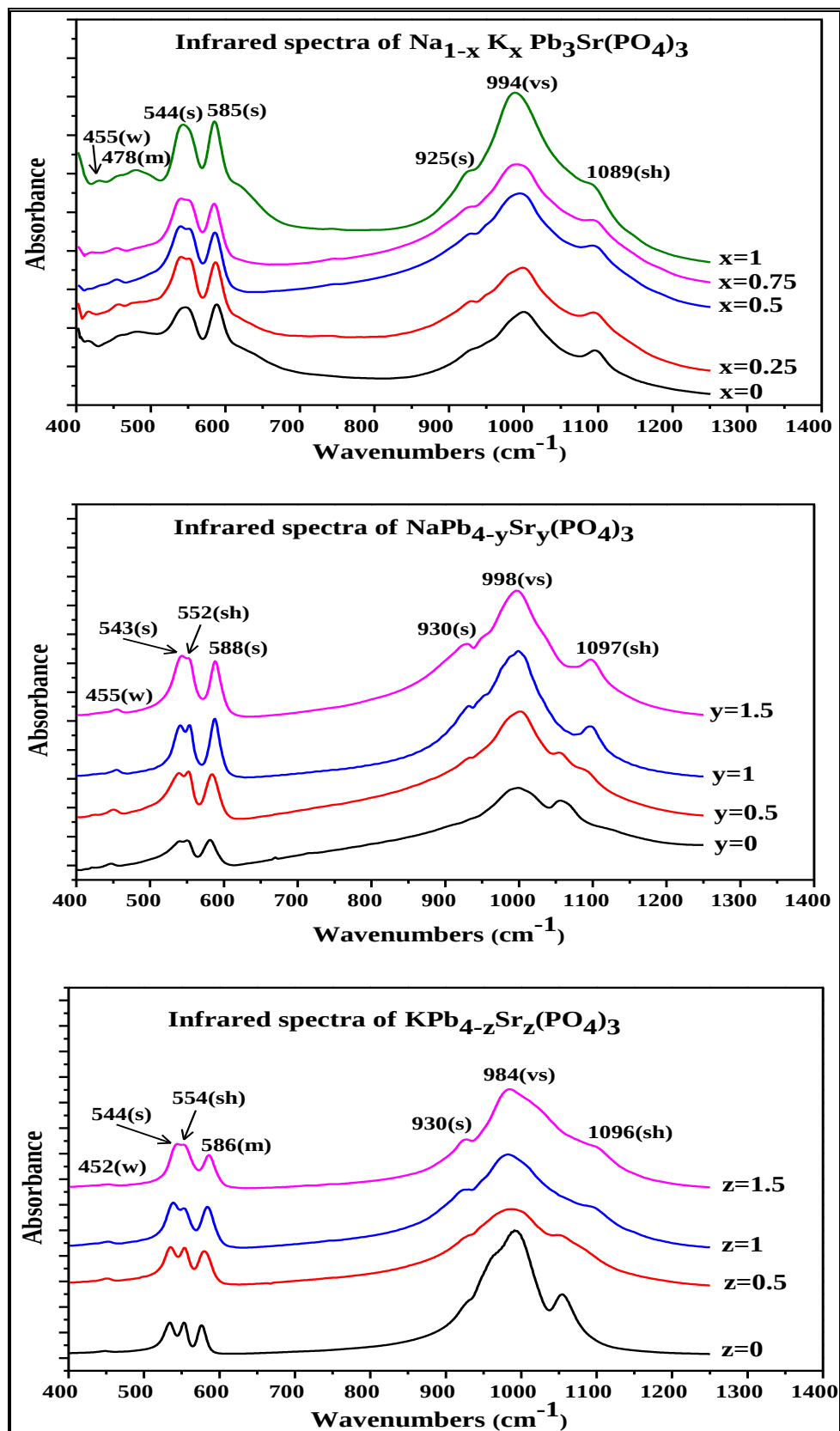


Fig.13: Infrared spectrum measurements at room temperature for $\text{Na}_{1-x}\text{K}_x\text{Pb}_{4-y\&z}\text{Sr}_{y\&z}(\text{PO}_4)_3$, in the spectral range between 400 and 1250 cm^{-1} .

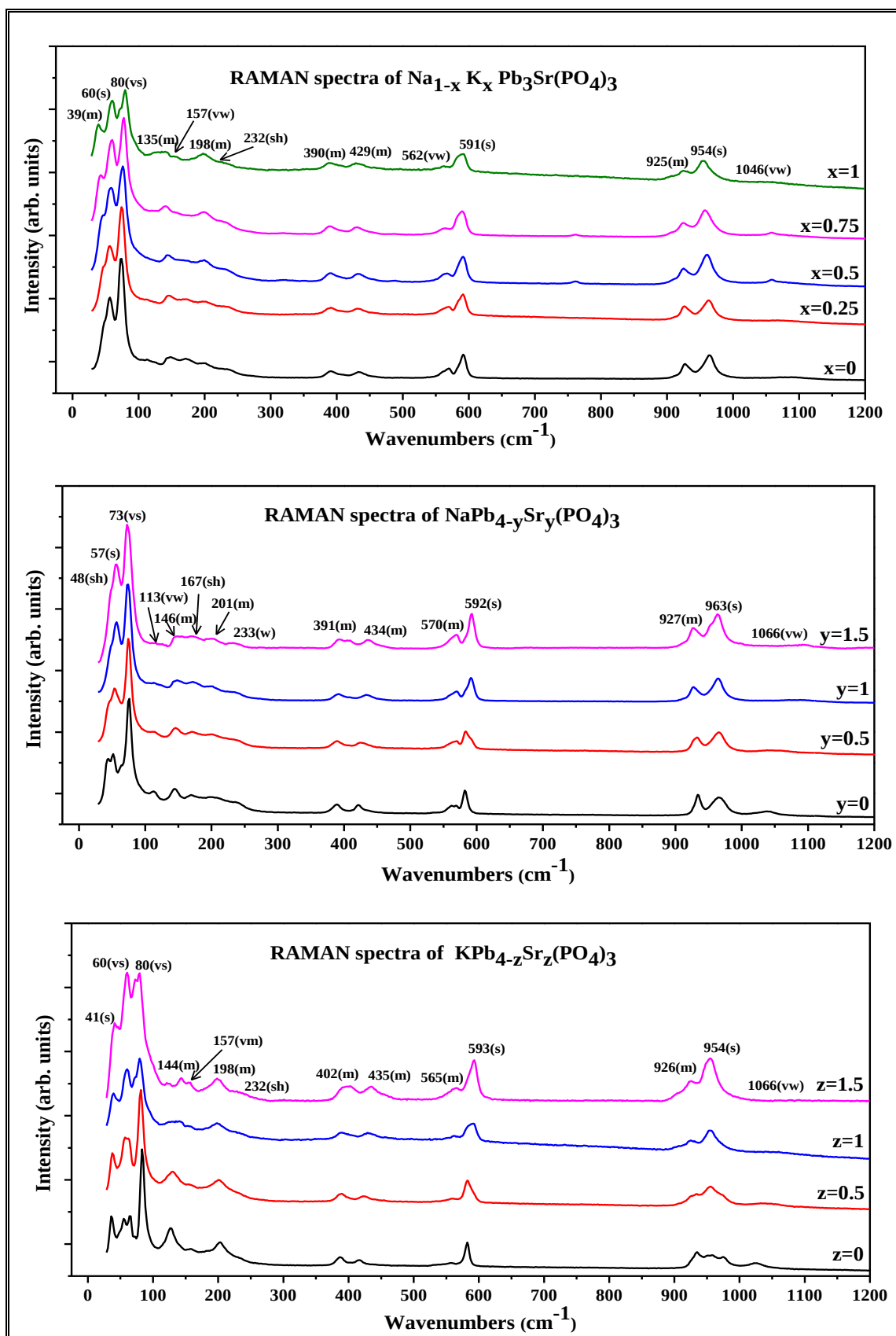


Fig.14: Raman spectra of $\text{Na}_{1-x}\text{K}_x\text{Pb}_{4-y/2}\{\text{Sr}_y/\text{CaCd}/\text{CaSr}\}(\text{PO}_4)_3$ at room temperature, in the spectral range between 30 and 1200 cm^{-1} .

Table 6: Assignments of observed Infrared bands of synthetics $\text{Na}_{1-x}\text{K}_x\text{Pb}_{4-y/2}\text{Sr}_y(\text{PO}_4)_3$.

$x\&y\&z$	Bending modes				Stretching modes		
	V_2	V_4	V_1	V_3	V_1	V_3	V_3
x	$\text{Na}_{1-x}\text{K}_x\text{Pb}_3\text{Sr}(\text{PO}_4)_3$						
0	453(m)	540(s)	554(sh)	587(s)	929(sh)	998(vs)	1096(m)
0.25	454(m)	539(s)	549(sh)	585(s)	925(s)	990(vs)	1093(m)
0.50	453(m)	538(s)	551(sh)	586(s)	928(s)	993(vs)	1093(sh)
0.75	455(m)	537(s)	551(sh)	587(s)	929(s)	997(vs)	1093(sh)
1	455(w)	478(m)	544(s)	585(s)	925(s)	994(vs)	1089(sh)
y	$\text{NaPb}_{4-y}\text{Sr}_y(\text{PO}_4)_3$						
0	446(w)	538(s)	550(s)	582(s)	934(sh)	998(vs)	1055(s)
0.5	450(w)	537(s)	552(s)	585(s)	929(s)	998(vs)	1053(sh)
1.5	455(w)	543(s)	552(sh)	588(s)	930(s)	998(vs)	1097(m)
z	$\text{KPb}_{4-z}\text{Sr}_z(\text{PO}_4)_3$						
0	448(w)	533(s)	553(s)	576(s)	959(sh)	994(vs)	1053(s)
0.5	449(w)	534(s)	554(s)	580(s)	929(sh)	986(vs)	1047(sh)
1.5	452(w)	544(s)	554(sh)	586(m)	930(s)	984(vs)	1096(sh)

Table 7: Assignments of observed Raman bands of synthetics $\text{Na}_{1-x}\text{K}_x\text{Pb}_{4-y/2}\text{Sr}_y(\text{PO}_4)_3$.

x&y&z	Lattice Modes								Bending modes				Stretching modes		
									V_2		V_4		V_1	V_3	
x	Na _{1-x} K _x Pb ₃ Sr(PO ₄) ₃														
0	48.6(sh)	56.9(s)	74.4(vs)	112.7(vm)	148.7(m)	171.1(vm)	201.8(sh)	234.2(vw)	391.2(m)	433.9(m)	570.1(m)	591.52(s)	926.8(m)	964.6(s)	1065.5(vw)
0.25	46.8(sh)	57.2(s)	75.4(vs)	114.0(m)	145.5(vm)	172.1(vm)	201.7(sh)	235.4(vw)	390.7(m)	431.9(m)	569.8(m)	591.51(s)	926.5(m)	963.5(s)	1064.5(vw)
0.5	46.5(sh)	58.8(s)	76.2(vs)	119.4(m)	144.5(vm)		199.9(sh)	232.7(vw)	390.3(m)	431.4(m)	567.1(m)	591.49(s)	925.6(m)	960.9(s)	1059.6(vw)
0.75	43.2(sh)	60.2(s)	77.9(vs)	121.5(m)	141(vm)	178.5(vm)	198.4(sh)	231.5(vw)	390.2(m)	430.2(m)	562.3(m)	591.44(s)	925.4(m)	957.9(s)	1058.6(vw)
1	39.4(m)	60.4(s)	79.6(vs)	135.1(m)	156.9(vw)		198.4(m)	232.0(sh)	389.8(m)	429.2(m)	561.8(w)	591.42(s)	925.3(m)	953.5(s)	1046.2(vw)
y	NaPb _{4-y} Sr _y (PO ₄) ₃														
0	44.4(s)	51.7(s)	74.36(vs)	112.5(vm)	143.6(m)	169.0(vm)	198.4(m)	233.2(vw)	388.2(m)	420.7(m)	569.4(m)	582.1(s)	933.5(s)	964.7(s)	1037.9(vw)
0.5	46.6(sh)	53.4(s)	74.39(vs)	112.6(w)	145.4(m)	170.7(vm)	199.6(m)	233.7(vw))	389.3(m)	423.5(vm)	569.7(m)	583.7(s)	933.6(m)	964.9(s)	1040.9(vw)
1.5	48.1(sh)	56.7(s)	72.65(vs)	112.5(vw)	146.3(m)	167.3(sh)	201.4(m)	232.6(w)	390.7(m)	433.6(m)	569.5(m)	591.50(s)	926.7(m)	963.3(s)	1065.6(vw)
z	KPb _{4-z} Sr _z (PO ₄) ₃														
0	35.9(m)	55.2(vm)	63.9(m)	83.1(vs)	126.8(m)	157.1(vw)	203.4(m)	230.4(sh)	386.5(m)	415.9(vm)	556.2(vw)	582.1(s)	935.0(s)	974.6(s)	1024.5(w)
0.5	37.6(m)	56.9(s)	63.9(sh)	81.4(vs)	129.8(m)	155.9(vw)	200.5(m)	230.8(sh)	389.6(m)	422.2(vm)	558.2(w)	582.2(s)	933.8(sh)	956.3(s)	1034.1(w)
1.5	41.1(s)	60.4(vs)	72.7(sh)	79.6(vs)	143.6(m)	157.3(vm)	198.3(m)	232.5(sh)	402.2(m)	435.1(m)	565.4(m)	592.9(s)	926.1(m)	954.4(s)	1066(vw)

The effect of the larger size and mass of the $\text{K}^+/\text{Pb}^{2+}$ ion is evident from the Raman spectra and it was shown in previous works [5-9]. For all Raman spectra, in the different modes (Lattice, Bending, and Stretching modes), the frequencies of vibration of the substituent (Amount of potassium and strontium) between two extremities ($0 \leq x \leq 1$), and ($0 \leq y \& z \leq 1.5$) are presented in Table.7. Fig.15 shows the variation of the fundamental frequencies of the different modes (Lattice, Bending, and Stretching modes) for $\text{Na}_{1-x}\text{K}_x\text{Pb}_{4-y/2}\text{Sr}_y(\text{PO}_4)_3$ as a function of potassium and strontium amount ($x\&y\&z$).

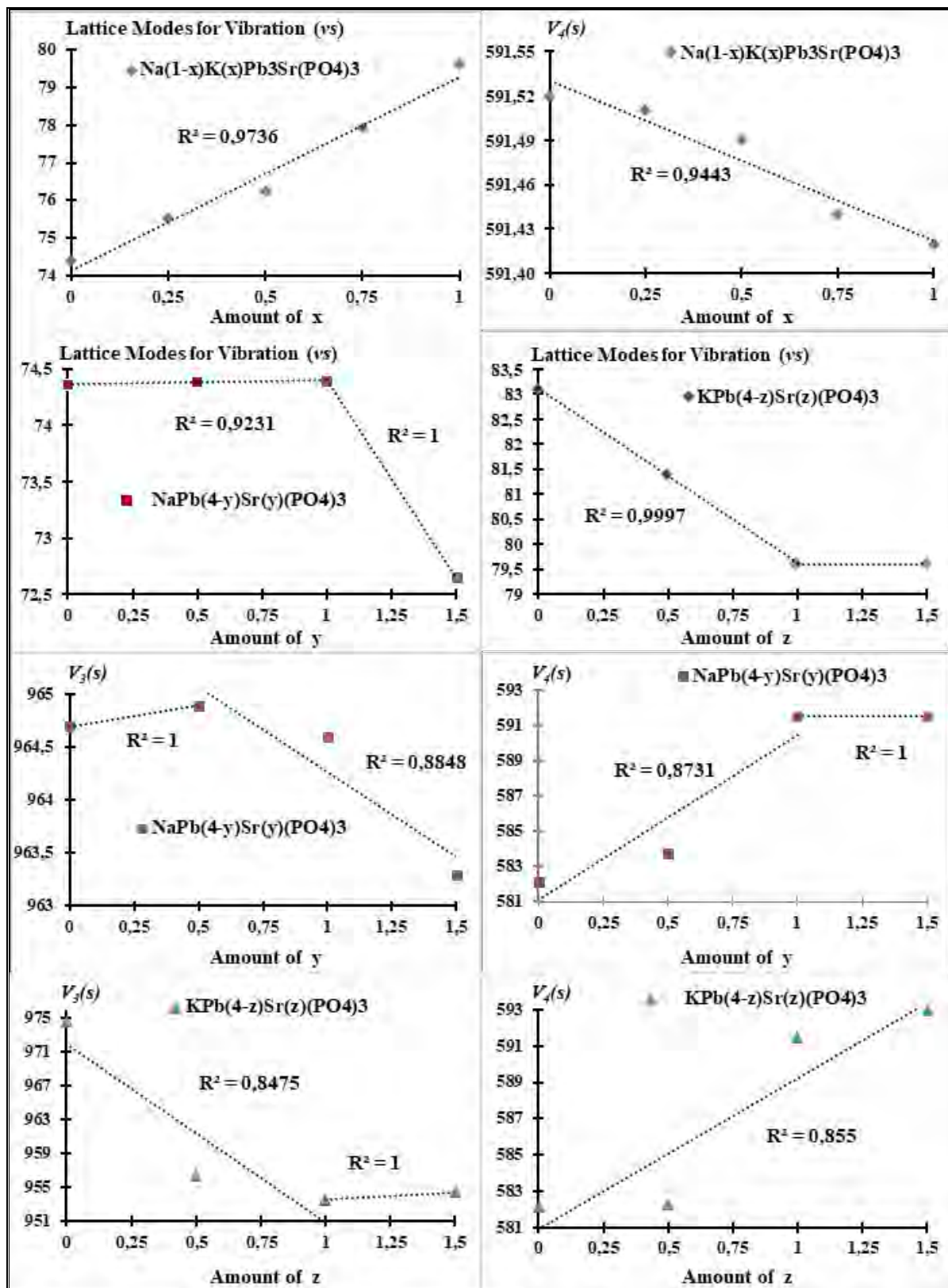


Fig.15: Variation of the fundamental frequencies of the different modes (Lattice, Bending, and Stretching modes) for $\text{Na}_{1-x}\text{K}_x\text{Pb}_{4-y/2}\{\text{Sr}_y/\text{CaCd}/\text{CaSr}\}(\text{PO}_4)_3$ as a function of potassium and strontium amount (x&y&z).

As found in of $\text{Na}_{1-x}\text{K}_x\text{Pb}_3\text{Sr}(\text{PO}_4)_3$, we noted that once the sodium is substituted by potassium, the frequencies of the modes bending and stretching observed shift towards lower frequencies. These modes are varied as well depending on (x) in contrary of unit cells (a) and (c) and the reticular planes d(1 2 1) and d(1 1 2). According to (x) for lattice mode, for two frequencies decrease and of the four frequencies increase, with the increase of the (x), and the other two frequencies decrease and increase according to (x).

As found in $\text{NaPb}_{4-y}\text{Sr}_y(\text{PO}_4)_3$ the all frequencies of lattice mode and for bending mode, vary oppositely with the unit cell (c) and the reticular plane, d(1 1 2). As well, frequencies of stretching mode are varied oppositely with the unit cell (a) and the reticular plane, d(1 2 1).

As well depending in (z) for $\text{KPb}_{4-z}\text{Sr}_z(\text{PO}_4)_3$, the frequencies of bending mode vary as way as the unit cell (c) and the reticular plane, d (1 1 2), and for frequencies of stretching, mode varies as the way the unit cell (a). For lattice mode, two frequencies vary as way as the unit cell (a) and of four frequencies vary as way as the unit cell (c) and the reticular plane, d (1 1 2) linearly with the increase on (z). Two other frequencies vary as the way the reticular plane, d (1 2 1). For more information shows [Fig.15](#).

b) High-Temperature Raman Study of $\text{NaPb}_3\text{Sr}(\text{PO}_4)_3$.

The structural stability of the $\text{NaPb}_3\text{Sr}(\text{PO}_4)_3$ compound, is tested as a function of temperature. The experimental Raman spectra were collected in situ at room-pressure and elevated temperatures, up to 773K; the Raman spectra obtained at several temperatures are shown in [Fig.16](#). The results obtained at several temperatures are presented in [Table.8](#). The temperature dependence of all modes (Lattice, Bending, and Stretching modes), show a monotonous decrease in changes in wavenumbers while the temperature is increased.

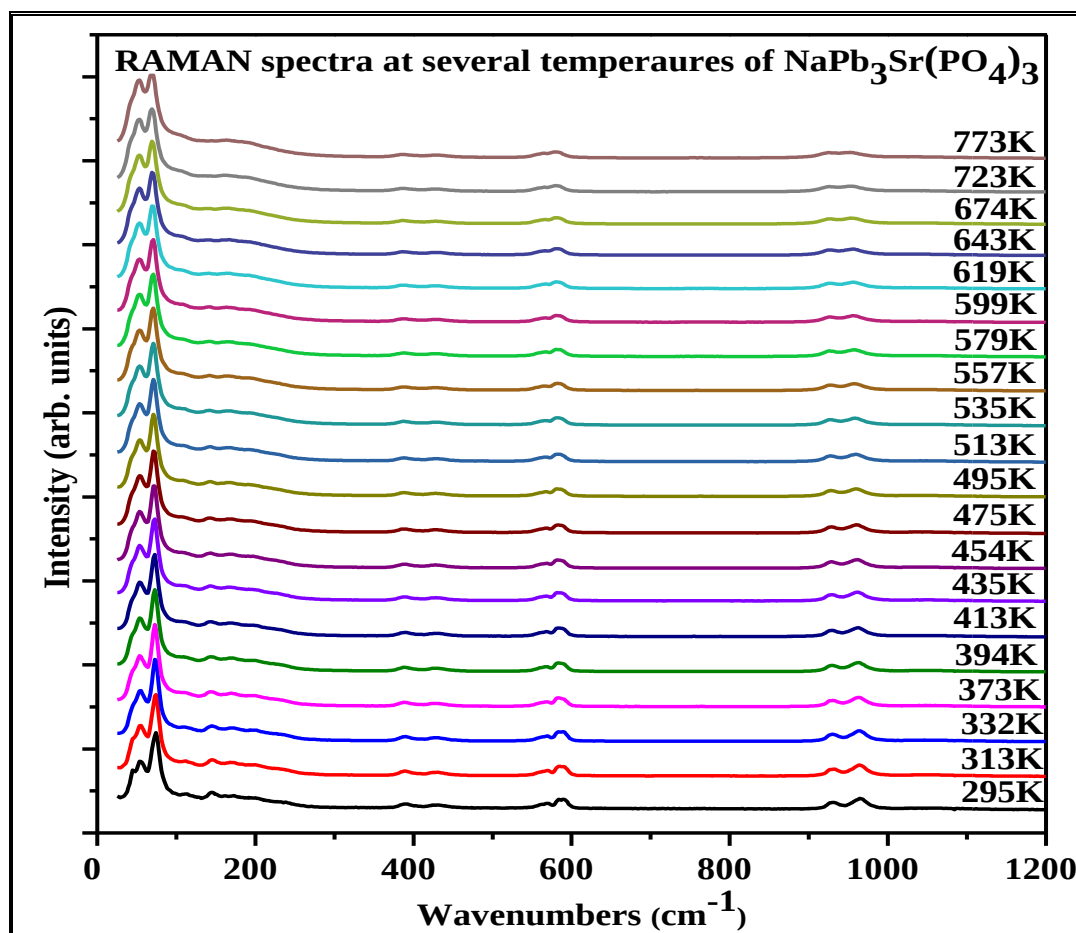


Fig.16: Raman spectra of $\text{NaPb}_3\text{Sr}(\text{PO}_4)_3$ obtained for selected temperatures.

Table 8: Raman spectra obtained at several temperatures of $\text{NaPb}_3\text{Sr}(\text{PO}_4)_3$.

T(K)	Lattice Modes				Bending modes				Stretching modes		
					V_2		V_4		V_1	V_3	
295	44.65(m)	53.42(s)	74.39(vs)		388.17(m)	431.37(m)	570.17(m)	589.60(s)	932.20(m)	964.94(s)	1065.54(vw)
313	44.61(sh)	53.41(s)	74.38(vs)		388.07(m)	430.90(m)	569.66(m)	589.40(s)	932.06(m)	964.55(s)	1065.50(vw)
332	44.54(sh)	53.40(s)	72.68(vs)		387.80(m)	427.62(m)	569.65(m)	589.16(s)	930.07(m)	964.37(s)	1065.50(vw)
353	44.10(sh)	53.41(s)	72.67(vs)		387.68(m)	427.57(m)	568.73(m)	588.76(s)	929.71(m)	964.19(s)	1065.48(vw)
394	42.89(sh)	53.43(s)	72.65(vs)		387.62(m)	427.28(m)	568.69(m)	588.71(s)	929.56(m)	963.77(s)	1065.44(vw)
413	42.87(sh)	53.41(s)	72.64(vs)		387.48(m)	427.13(m)	568.25(m)	588.68(s)	929.21(m)	963.60(s)	1065.37(vw)
435	42.85(sh)	53.37(s)	72.63(vs)		387.13(m)	426.95(m)	568.11(m)	588.30(s)	928.68(m)	963.15(s)	1065.34(vw)
454	42.84(sh)	53.36(s)	72.58(vs)		387.10(m)	426.89(m)	567.80(m)	588.21(s)	928.55(m)	963.08(s)	1065.28(vw)
475	42.67(sh)	53.33(s)	71.90(vs)		387.02(m)	426.75(m)	567.43(m)	588.02(s)	928.32(m)	961.23(s)	1065.23(vw)
495	42.40(sh)	53.32(s)	71.89(vs)		387.12(m)	426.70(m)	567.40(m)	587.68(s)	927.55(m)	960.20(s)	1065.21(vw)
513	42.32(sh)	53.30(s)	71.89(vs)		387.01(m)	426.59(m)	567.34(m)	587.16(s)	927.80(m)	960.21(s)	1065.18(vw)
535	42.25(sh)	53.27(s)	70.90(vs)		386.86(m)	426.47(m)	567.24(m)	587.08(s)	927.65(m)	959.49(s)	1065.16(vw)
557	41.15(sh)	53.21(s)	70.89(vs)		386.66(m)	426.22(m)	567.14(m)	586.80(s)	927.26(m)	959.39(s)	1065.10(vw)
579	41.05(sh)	51.84(s)	70.85(vs)		386.46(m)	426.10(m)	566.85(m)	586.76(s)	926.49(s)	958.35(s)	1065.07(vw)
599	40.75(sh)	51.69(s)	70.83(vs)		385.54(m)	425.89(m)	566.18(m)	586.65(s)	926.32(s)	958.01(s)	1065.03(vw)
619	40.62(sh)	51.54(s)	69.74(vs)		384.79(m)	425.53(m)	566.05(m)	586.60(s)	925.88(s)	956.79(s)	1064.89(vw)
643	39.30(sh)	51.50(s)	69.21(vs)		384.56(m)	425.43(m)	565.87(m)	586.54(s)	925.58(s)	956.11(s)	1064.87(vw)
674	39.22(sh)	49.91(s)	69.16(vs)		384.11(m)	425.15(m)	565.43(m)	586.49(s)	925.36(s)	953.37(s)	1064.84(vw)
723	38.68(sh)	49.88(s)	69.11(vs)		384.06(m)	424.89(m)	564.09(m)	586.41(s)	923.75(s)	951.94(s)	1064.80(vw)
773	37.11(sh)	49.59(s)	67.49(vs)		383.82(m)	424.31(m)	563.47(m)	586.36(s)	923.23(s)	949.81(s)	1064.77(vw)

Fig.17 shows a linear large decrease in wavenumbers with an increase in temperature. As an example, the lattice model of the frequencies strong (s) and very strong (vs) observed in the full spectral range between 40.59 and 74.39cm^{-1} , and with the two principal vibrational modes of the $[\text{PO}_4]^{3-}$ the triply degenerate asymmetric ‘P-O’ between 949.81 and 964.94cm^{-1} as well as the triply degenerate ‘O-P-O’ bending mode between 586.36 and 589.6cm^{-1} (MANOUN and al.). No considerable changes in the temperature dependence of the modes and the corresponding intensity are observed and thus no temperature-induced phase transition is observed in $\text{NaPb}_3\text{Sr}(\text{PO}_4)_3$ in the temperature range studied here.

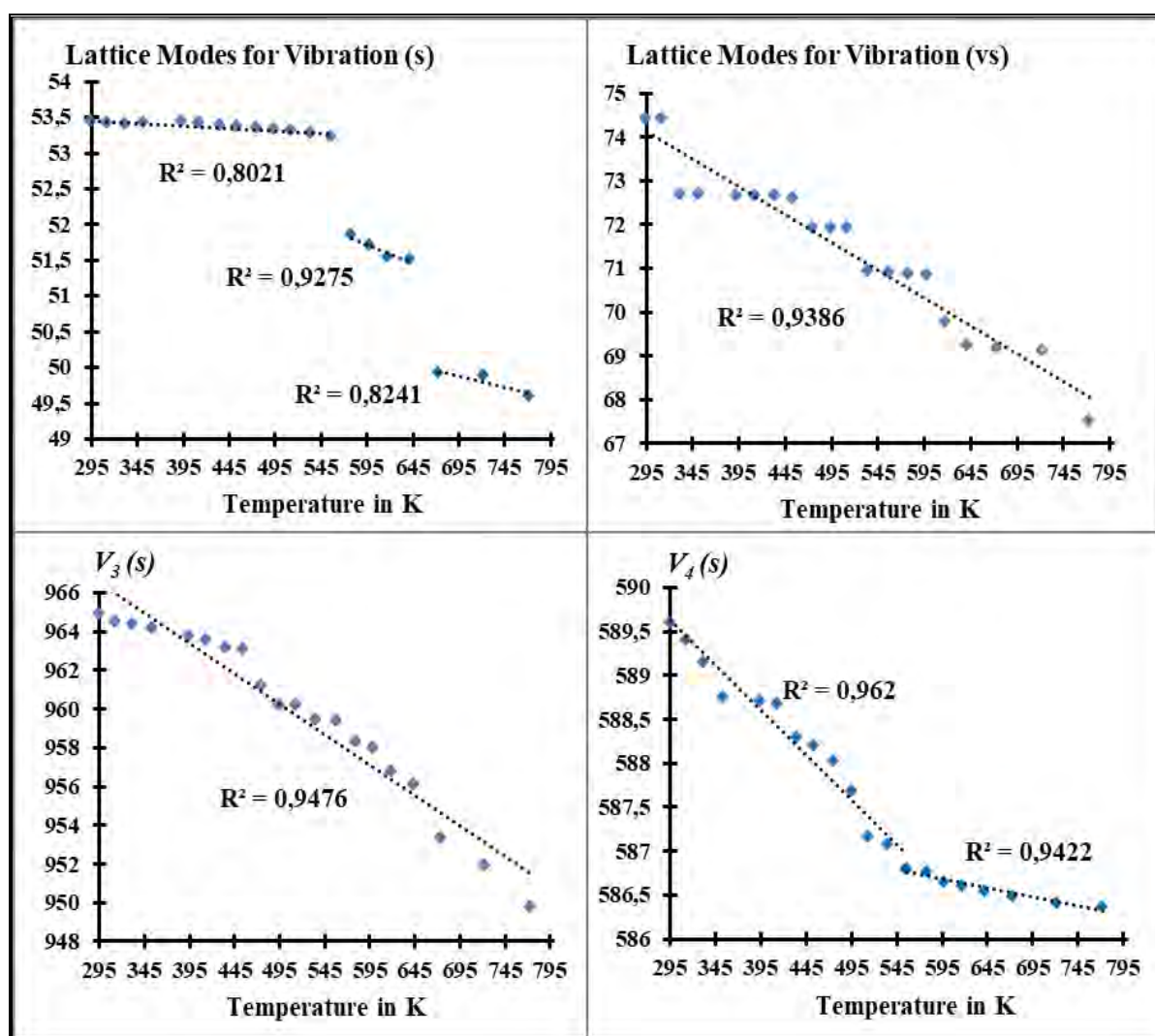


Fig.17: Variation of the fundamental frequencies of the different modes (Lattice, Bending, and Stretching modes) for $\text{NaPb}_3\text{Sr}(\text{PO}_4)_3$ as a function of temperature.

II.3. Optoelectronic Properties.

Fig.18 shows the converted reflectance data to absorbance using the Kubelka-Mank function (For more details; see Chapter. I), which will be used in the optical band calculation. The solid UV visible /far-ultraviolet spectra of the compound's series described in $\text{Na}_{1-x}\text{K}_x\text{Pb}_{4-y/2}\text{Sr}_{y/2}\text{Sr}_{y/2}(\text{PO}_4)_3$ ($0 \leq x \leq 1$) and ($0 \leq y \leq 1.5$) were measured in the range 250 nm to 800 nm at room temperature.

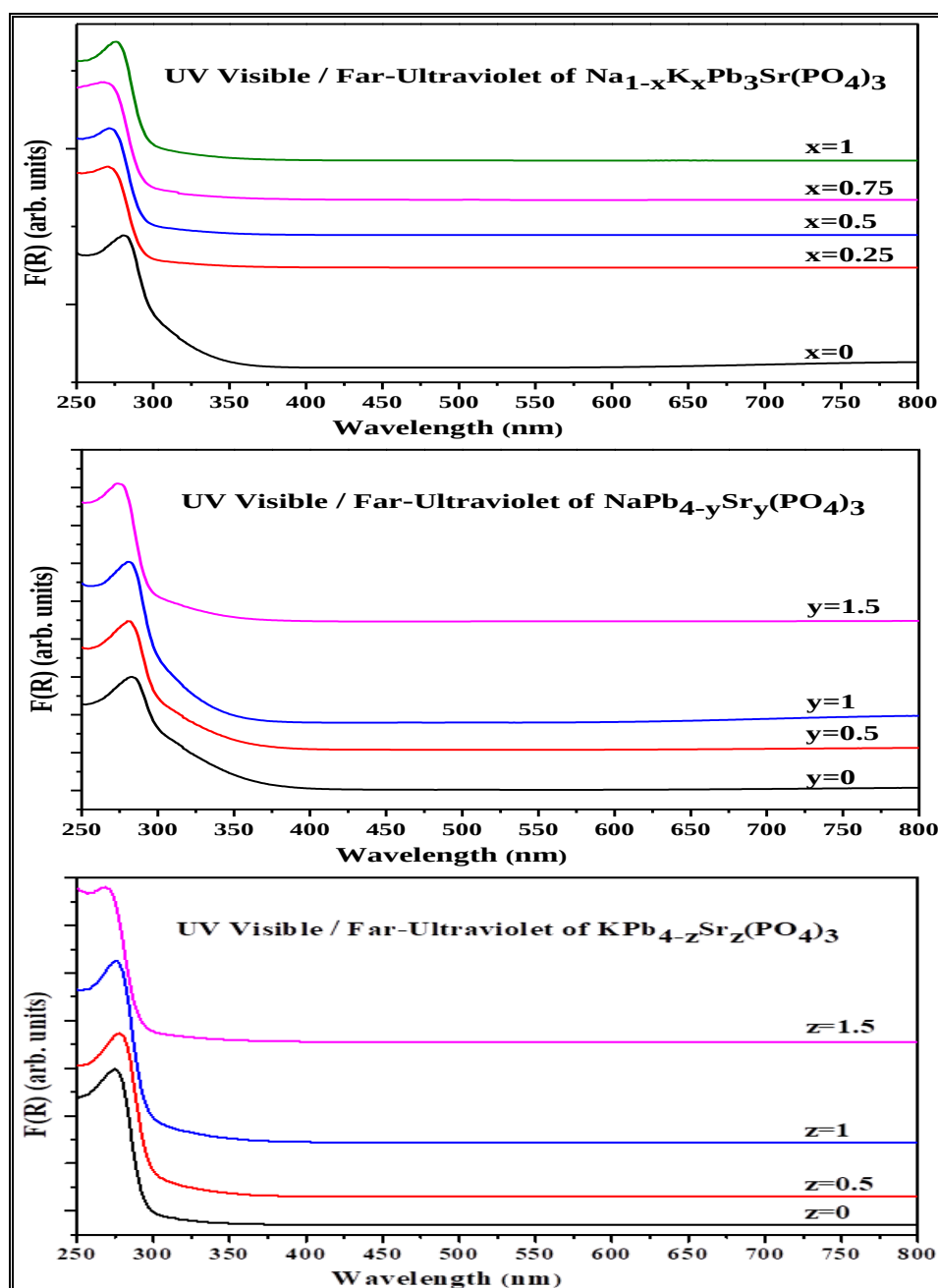


Fig.18: UV visible / Far-Ultraviolet of the series $\text{Na}_{1-x}\text{K}_x\text{Pb}_{4-y/2}\text{Sr}_{y/2}(\text{PO}_4)_3$.

Table.9 shows the evolution of the absorption coefficient of reflectance $F(R)$ as a function of the wavelength in the range (250-800nm) at room temperature, for example, Fig.19(A) shows the intense band (λ_{Max}) determined by LabSpec® software at 273nm and 269nm for $NaPb_{2.5}Sr_{1.5}(PO_4)_3$ and $KPb_{2.5}Sr_{1.5}(PO_4)_3$ respectively, were of Reflectance spectra recorded from powder materials. The Band-Gap Energy (eV) determined by OriginePro® software at 4.28ev and 4.35056ev for $NaPb_{2.5}Sr_{1.5}(PO_4)_3$ and $KPb_{2.5}Sr_{1.5}(PO_4)_3$ respectively.

Table.9: Lamda Max of peaks absorption in the UV-Visible and the calculated optical indirect allowed energy gap using Tauc's relationship of the series $Na_{1-x}K_xPb_{4-y/2}Sr_{y/2}(PO_4)_3$.

x&y&z	Lamda Max			Bandgap Energy (ev)		
	$Na_{1-x}K_xPb_3Sr$	$NaPb_{4-y}Sr_y$	$KPb_{4-z}Sr_z$	$Na_{1-x}K_xPb_3Sr$	$NaPb_{4-y}Sr_y$	$KPb_{4-z}Sr_z$
0	280	283	275	4.16931	4.10204	4.29423
0.25	266	--	--	4.30541	--	--
0.5	271	280	278	4.30565	4.1728	4.23818
0.75	271	--	--	4.31456	--	--
1	276	280	276	4.27333	4.16931	4.27333
1.25	--	--	--	--	--	--
1.5	--	273	269	--	4.28000	4.35056

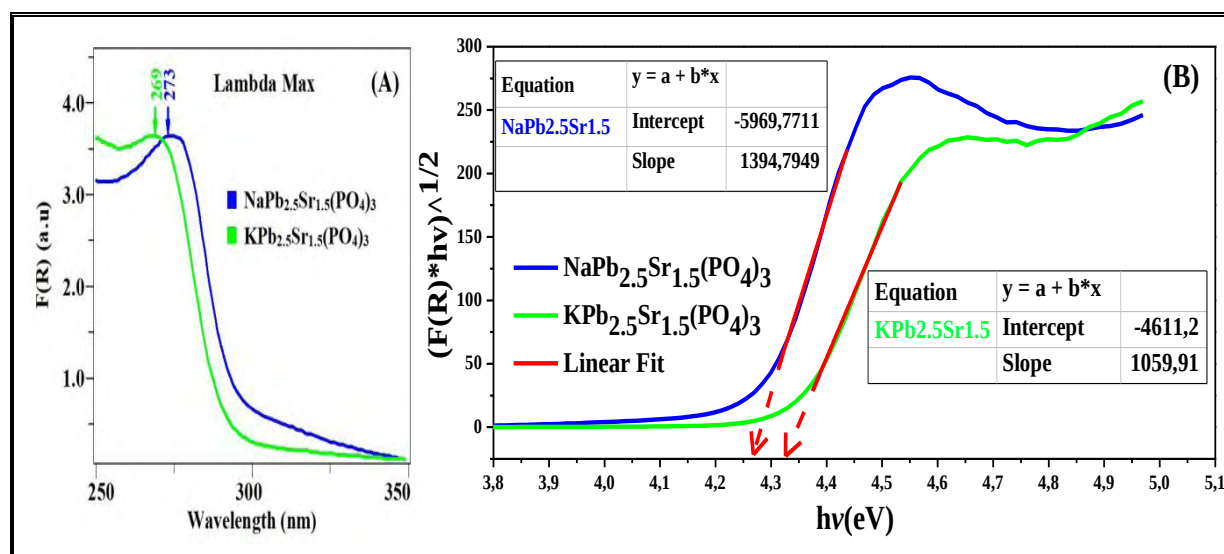


Fig.19: Figure (A) shows the optical absorption as a function of the wavelength, and Figure (B) illustrates the Tauc plots for $NaPb_{2.5}Sr_{1.5}(PO_4)_3$ and $KPb_{2.5}Sr_{1.5}(PO_4)_3$.

Fig.20 shows the variation of the wavelengths of Lamda Max absorbance. As found in $Na_{1-x}K_xPb_3Sr(PO_4)_3$ $0 \leq x \leq 1$, we noted that once the sodium is substituted by potassium, the wavelength of Lamda Max is decreased toward $x=0.25$ and increases according to (x) . For

$\text{NaPb}_{4-y}\text{Sr}_y(\text{PO}_4)_3$ $0 \leq y \leq 1.5$, all wavelength of Lamda Max shift towards lower frequencies according to (y). $\text{KPb}_{4-z}\text{Sr}_z(\text{PO}_4)_3$ $0 \leq z \leq 1.5$, are very oppositely with the reticular plane, d(1 2 1) according to (z).

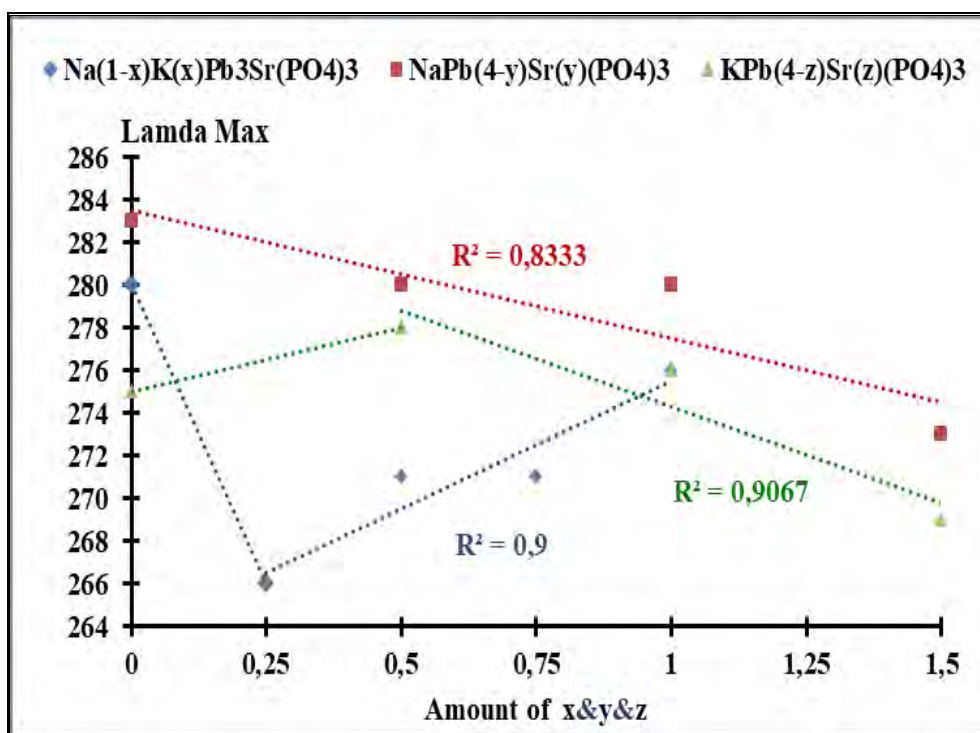


Fig.20: The effect of Potassium and Strontium substitutions for the crystal structure of $\text{Na}_{1-x}\text{K}_x\text{Pb}_{4-y/2}\text{Sr}_y(\text{PO}_4)_3$ depending on the wavelengths for Lamda Max absorption shift as a function of x&y&z.

The values of the indirectly allowed energy gap of the crystal structure of apatites $\text{Na}_{1-x}\text{K}_x\text{Pb}_{4-y/2}\text{Sr}_y(\text{PO}_4)_3$ depending on the effect of potassium and strontium substitutions as a function of x&y&z, are tabulated in Table.9. Fig.21 shows the Bandgaps Energy, determined using Tauc's relationship in the high absorption. As found in $\text{Na}_{1-x}\text{K}_x\text{Pb}_3\text{Sr}(\text{PO}_4)_3$, we noted that once sodium is substituted by potassium (x), the band gaps energy increases toward $x=0.75$ and decreases then toward $x=1$. For $\text{NaPb}_{4-y}\text{Sr}_y(\text{PO}_4)_3$ the all the band gaps energy shift towards upper values according to (y). The band gaps energy of $\text{KPb}_{4-z}\text{Sr}_z(\text{PO}_4)_3$ are varied in the opposite of Lamda Max, according to (z), but vary in the same way of the reticular plane, d(1 2 1).

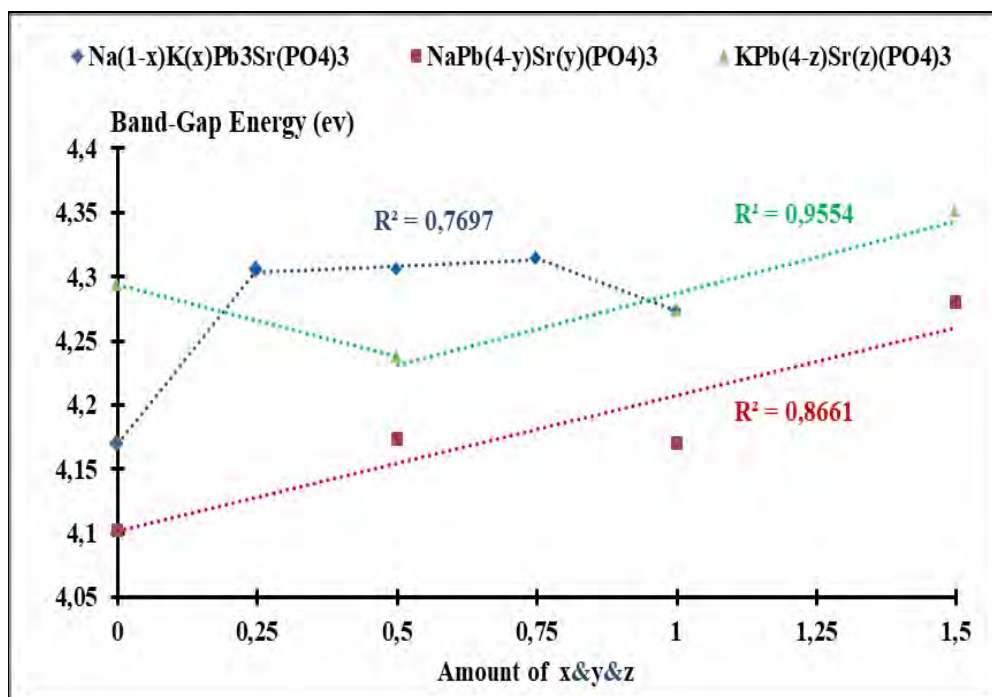


Fig.21: the Band-Gap Energy depending on the effect of potassium and strontium substitutions for the crystal structure of apatite $\text{Na}_{1-x}\text{K}_x\text{Pb}_{4-y/2}\text{Sr}_{y/2}(\text{PO}_4)_3$ as a function of $x, y, \& z$.

III. New Serie of $\text{Na}_{1-x}\text{K}_x\text{Pb}_2\text{CdCa}(\text{PO}_4)_3$.

III.1. Structural Analysis.

Fig.22 shows the X-ray powder diffraction patterns of $\text{Na}_{1-x}\text{K}_x\text{Pb}_2\text{CaCd}(\text{PO}_4)_3$. The Rietveld plot of the final phase refinement is shown in Fig.23. Details of the final refinement conditions, cell parameters, and reliability factors are given in Table.10. Interatomic bond distances and angles are given in Table.11. The resulting data for atomic coordinates, isotropic temperature factors, and occupation in the 6h and 4f sites as a function of the amount of potassium (x) in $\text{Na}_{1-x}\text{K}_x\text{Pb}_2\text{CaCd}(\text{PO}_4)_3$ are listed in Table.12. For all, with their estimated deviations in parentheses.

It should be noted that the refinements of $\text{Na}_{1-x}\text{K}_x\text{Pb}_2\text{CaCd}(\text{PO}_4)_3$ show that there are two symmetrically non-equivalent sites; labelled M(1) and M(2), residing respectively in two sites 6h and 4f.

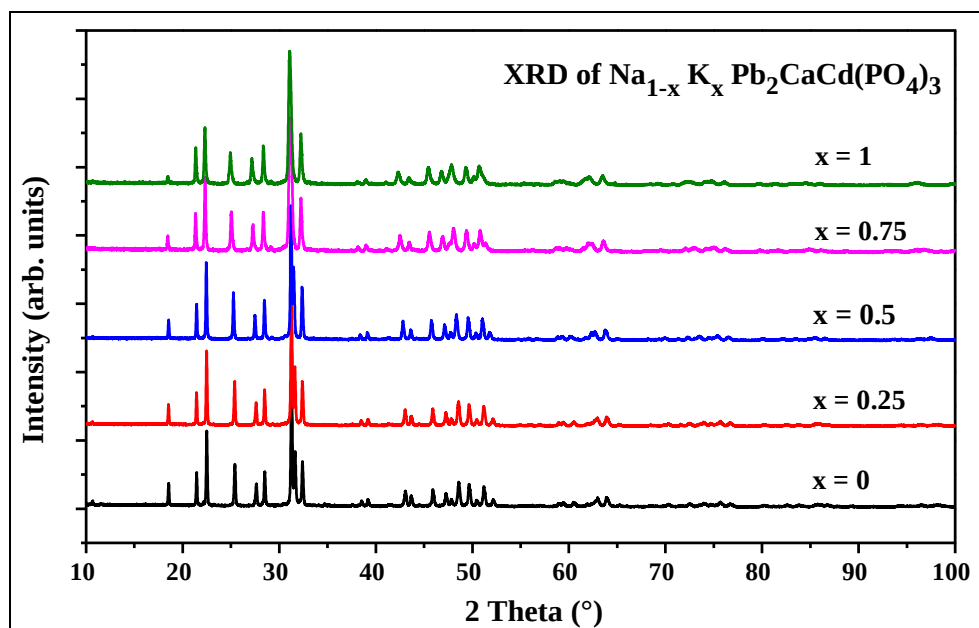


Fig.22: Powder diffraction patterns of $\text{Na}_{1-x}\text{K}_x\text{Pb}_2\text{CaCd}(\text{PO}_4)_3$.

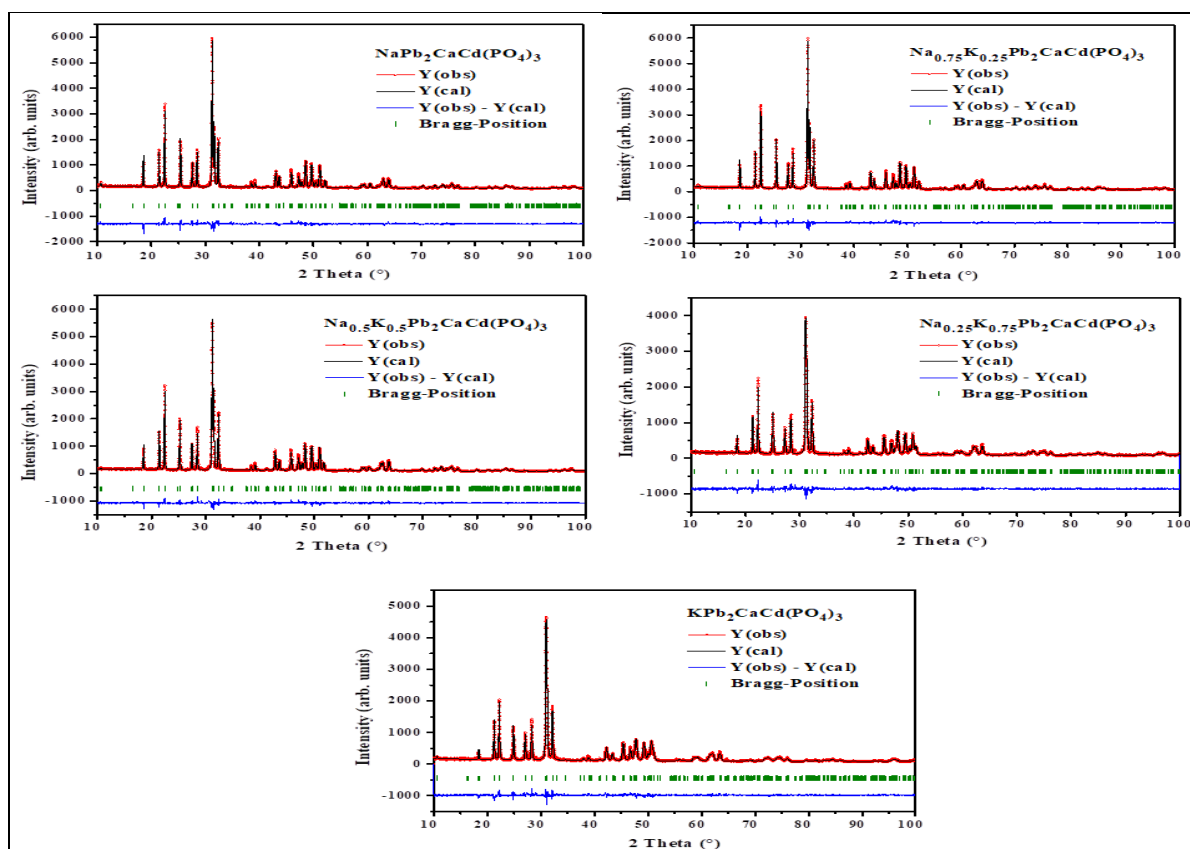


Fig.23: Final Rietveld plot for $\text{Na}_{1-x}\text{K}_x\text{Pb}_2\text{CaCd}(\text{PO}_4)_3$; with upper symbols illustrate: the observed data $N^\circ 1$, and the calculated pattern (solid line) for $N^\circ 2$, the lower curve is the difference diagram schematize in the $N^\circ 3$ and the vertical markers show calculated positions of Bragg reflections in $N^\circ 4$.

Table.10: Results for Rietveld Refinement for X-ray powders data of $\text{Na}_{1-x}\text{K}_x\text{Pb}_2\text{CaCd}(\text{PO}_4)_3$.

x		0	0.25	0.5	0.75	1
Zero-point (deg.2 θ)		-0.004(2)	-0.015(2)	0.038(2)	-0.014(4)	0.078(4)
Pseudo-Voigt function $\text{PV}=\eta\text{L} + (1-\eta)\text{G}$	η	0.663(9)	0.591(8)	0.578(3)	0.505(3)	0.458(3)
Caglioti parameters	U	0.154(11)	0.201(11)	0.200(11)	0.381(31)	0.563(41)
	V	0.003(7)	-0.019(6)	-0.020(6)	-0.002(2)	-0.028(2)
	W	0.004(1)	0.006(1)	0.008(1)	0.007(2)	0.015(3)
No. of reflections		510/2	588/2	596/2	496/2	507/2
No. of refined parameters		33				
Space group		$P 6_3/m$				
a (Å)		9.5669(3)	9.5670(2)	9.5896(2)	9.6113(4)	9.6340(4)
c (Å)		7.0115(2)	7.0164(2)	7.0628(2)	7.1088(3)	7.1554(3)
V (Å ³)		555.75(3)	556.15(2)	562.48(3)	568.72(4)	575.14(4)
Density		7.84	7.87	7.82	7.77	7.72
Z		2				
Atom Number		10	11			10
User-weighted Chi2		1.83	1.55	1.48	1.69	1.72
%*R _F		4.78	4.29	3.97	3.34	3.63
%*R _B		5.48	4.71	4.75	5.19	4.73
%*R _p		7.29	6.96	6.80	7.31	7.18
%*R _{wp}		9.53	8.97	8.77	9.45	9.24
%*cR _p		16.0	15.7	15.4	16.5	15.6
%*cR _{wp}		16.6	15.8	15.5	17.0	16.3

Table.11: Interatomic distances in (Å) and O-P-O angles in (°) of $\text{Na}_{1-x}\text{K}_x\text{Pb}_2\text{CaCd}(\text{PO}_4)_3$.

x	0	0.25	0.5	0.75	1
M(I)-O ₁	2.727(3)	2.719(2)	2.722(2)	2.777(3)	2.768(3)
2*M(I)-O ₂	2.348(10)	2.380(8)	2.423(8)	2.430(10)	2.456(10)
2*M(I)-O ₂	2.638(13)	2.629(11)	2.625(11)	2.620(14)	2.552(14)
M(I)-O ₃	2.191(15)	2.210(14)	2.179(13)	2.206(16)	2.192(15)
<M(I)-O>	2.476	2.485	2.487	2.508	2.492
3*M(II)-O ₁	2.397(8)	2.393(6)	2.416(6)	2.427(6)	2.429(6)
3*M(II)-O ₂	2.863(12)	2.822(10)	2.811(10)	2.836(12)	2.878(11)
3*M(II)-O ₃	2.667(13)	2.650(11)	2.667(11)	2.682(12)	2.723(12)
<M(II)-O>	2.642	2.622	2.631	2.648	2.677
P-O ₁	1.528(13)	1.539(11)	1.540(12)	1.509(13)	1.538(15)
2*P-O ₂	1.550(11)	1.542(9)	1.530(10)	1.535(12)	1.557(13)
P-O ₃	1.576(8)	1.549(7)	1.554(8)	1.569(9)	1.591(10)
<P-O>	1.551	1.543	1.541	1.538	1.562
2*O ₁ -P-O ₂	110.3(10)	111.1(9)	112.1(9)	112.4(11)	114.0(12)
O ₁ -P-O ₃	107.5(8)	109.4(7)	108.7(7)	106.5(8)	104.4(9)
O ₂ -P-O ₂	113.1(10)	111.7(8)	110.5(9)	111.5(10)	108.3(10)
2*O ₂ -P-O ₃	107.7(8)	106.6(7)	106.6(7)	106.8(9)	107.9(9)
<O-P-O>	109.65	109.7	109.48	109.3	108.65

Table.12: Refined structural parameters for $Na_{1-x}K_xPb_2CaCd(PO_4)_3$.

Atom	Wyckoff	Sym	x/a	y/b	z/c	B ($\text{\AA}^2$)	Occupancy	x
M(I) = Pb(1)/Ca(1)/Cd	6h	M	0.2542(2)	0.2570(2)	0.25	1.55(4)	1.598(2)/0.402(2)/1	0
			0.2550(2)	0.2583(2)		1.32(3)	1.585(4)/0.415(4)/1	0.25
			0.2568(2)	0.2601(2)		1.18(3)	1.534(4)/ 0.466(4)/1	0.5
			0.2565(3)	0.2598(2)		2.53(4)	1.507(5)/0.493(5)/1	0.75
			0.2569(3)	0.2580(3)		1.05(4)	1.418(5)/0.582(5)/1	1
M(II) = Pb(2)/Ca(2)/Na/K	4f	3	0.6667	0.3333	0.5083(16)	1.31(13)	0.402(2)/0.598(2)/1	0
					0.5094(12)	1.02(11)	0.415(4)/0.585(4)/0.75/0.25	0.25
					0.5070(11)	1.15(10)	0.466(4)/0.534(4)/0.5/0.5	0.5
					0.5114(12)	2.05(12)	0.493(5)/0.507(5)/0.25/0.75	0.75
					0.5092(12)	0.65(12)	0.582(5)/0.418(5)/1	1
P	6h	M	0.3731(12)	0.3943(10)	0.75	1.49(19)	3	0
			0.3744(10)	0.3972(9)		1.86(17)		0.25
			0.3748(10)	0.3973(9)		1.95(17)		0.5
			0.3715(11)	0.3961(11)		1.77(22)		0.75
			0.3688(13)	0.3907(12)		1.79(23)		1
O(1)	6h	M	0.4842(10)	0.3224(11)	0.75	7.98(36)	3	0
			0.3744(10)	0.3972(9)		1.86(17)		0.25
			0.4842(2)	0.3224(2)		4.89(26)		0.5
			0.4841(1)	0.3293(1)		8.58(38)		0.75
			0.4846(1)	0.3243(1)		6.97(37)		1
O(2)	12i	1	0.2701(12)	0.3459(12)	0.5655(13)	7.98(36)	6	0
			0.2701(11)	0.3509(10)	0.5682(10)	6.26(31)		0.25
			0.2702(11)	0.3532(10)	0.5720(11)	4.89(26)		0.5
			0.2680(15)	0.3510(12)	0.5715(13)	8.58(38)		0.75
			0.2600(16)	0.3447(11)	0.5736(13)	6.97(37)		1
O(3)	6h	M	0.4834(20)	0.5837(11)	0.75	7.98(36)	3	0
			0.4799(18)	0.5837(1)		6.26(31)		0.25
			0.4825(17)	0.5837(1)		4.89(26)		0.5
			0.4801(23)	0.5839(1)		8.58(38)		0.75
			0.4827(23)	0.5801(1)		6.97(37)		1

The occupation of monovalent and divalent cations, in the non-equivalent sites, behind the variation of the structural parameters for structure hexagonal is established. For that, we have illustrated the simulation results on a particular case of percentages of the occupation rate (%) of these cations Pb^{2+} and Ca^{2+} in Table.13. We noted ($[M(1) / 3] * 100$) for 6h site, and ($[M(2)/2] * 100$) for 4f site. It should be noted, however, that two principal prerequisites information supplied by the references [6,19], that according to 50% the percentage of occupation for monovalent cations is fixed in the site 4f, and Cd^{2+} residing entirely in the sites 6h.

[19] Lahrich. S.; Manoun. B.; El Mhammedi. M. A. Catalytic Effect of Potassium in $Na_{1-x}K_xCdPb_3(PO_4)_3$ to Detect Mercury (II) in Fish and Seawater Using a Carbon Paste Electrode. Talanta 2016. 149. 158–167.

Table.13: The occupancy rate in (%) as a function of x for $\text{Na}_{1-x}\text{K}_x\text{Pb}_2\text{CaCd}(\text{PO}_4)_3$. $0 \leq x \leq 1$.

x	% M(I)		% M (II)	
	$\text{Pb}^{2+}(1)$	$\text{Ca}^{2+}(1)$	$\text{Pb}^{2+}(2)$	$\text{Ca}^{2+}(2)$
0	53.27	13.40	20.10	29.90
0.25	52.83	13.83	20.75	29.25
0.5	51.13	15.53	23.30	26.70
0.75	50.23	16.43	24.65	25.35
1	47.27	19.40	29.10	20.90

The Rietveld simulations for $\text{Na}_{1-x}\text{K}_x\text{Pb}_2\text{CaCd}(\text{PO}_4)_3$ ($0 \leq x \leq 1$), showed that this solid solution is continuously adopting the $P6_3/m$ space group. The results given in Table.10 and Fig.24 show the cell parameter variation as a function of (x). The progressive substitution of sodium by potassium provokes an increase of the unit cell parameters (a), (c), and (V). The increase is due to the substitution of Na^+ ($r_i=1.24 \text{ \AA}$) by K^+ ($r_i=1.55 \text{ \AA}$) [18] with larger-radius.

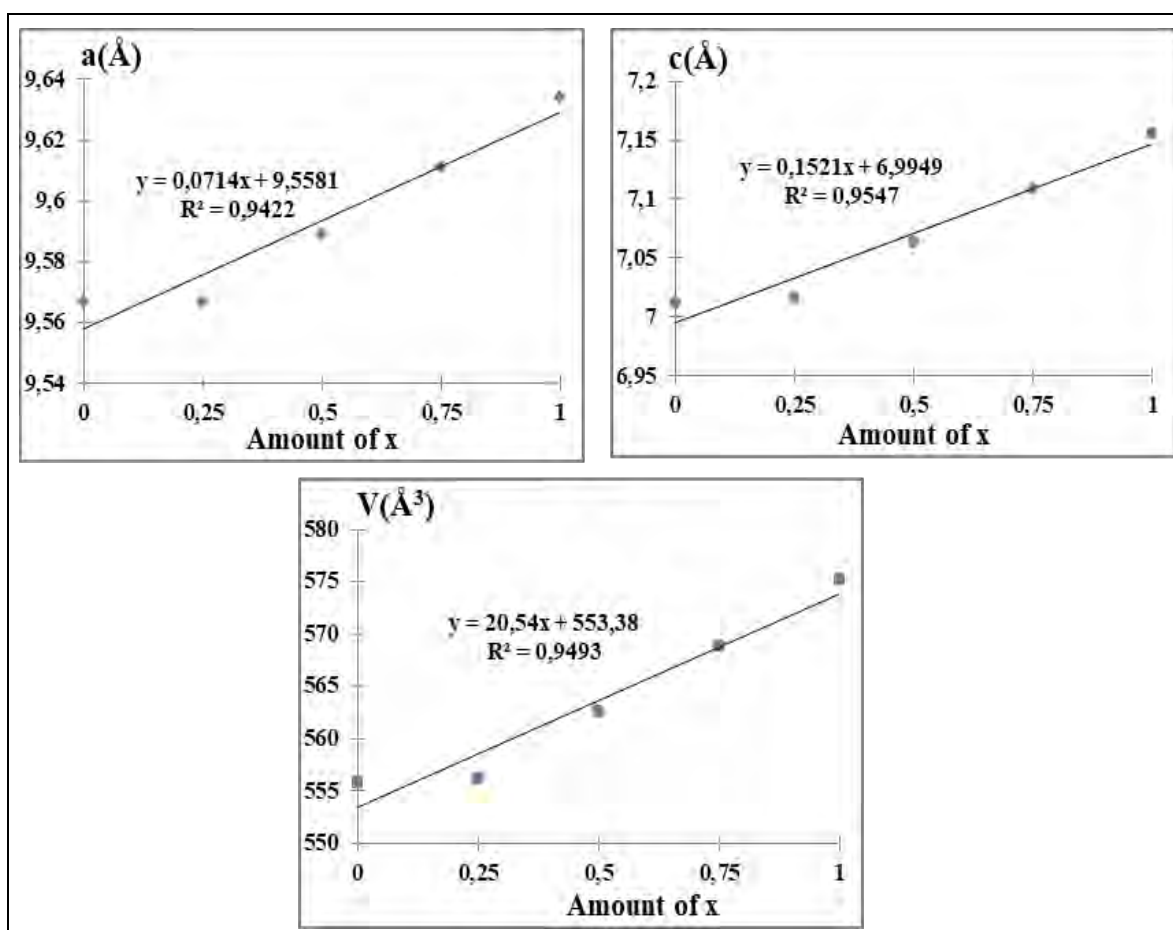


Fig.24: Unit cell parameters variation as a function of x for $\text{Na}_{1-x}\text{K}_x\text{Pb}_2\text{CaCd}(\text{PO}_4)_3$ ($0 \leq x \leq 1$), where progressive substitution of sodium by potassium provokes an increase of the unit cell parameters $a(\text{\AA})$, $c(\text{\AA})$, and $V(\text{\AA}^3)$.

These variations indicate clearly that there is a complete solubility and thus a continuous series of solid solutions, in which a given proportion of ' K^+ ' replaces an equal proportion of ' Na^+ '. The progressive substitution is the most important cause for the increase of ' $Ca^{2+}(1)$ ' and a decrease of ' $Pb^{2+}(1)$ ' in the '6h' sites. This situation is inversely proportional to the '4f' sites, the results are shown in Tables.12 and 13 and Fig.25.

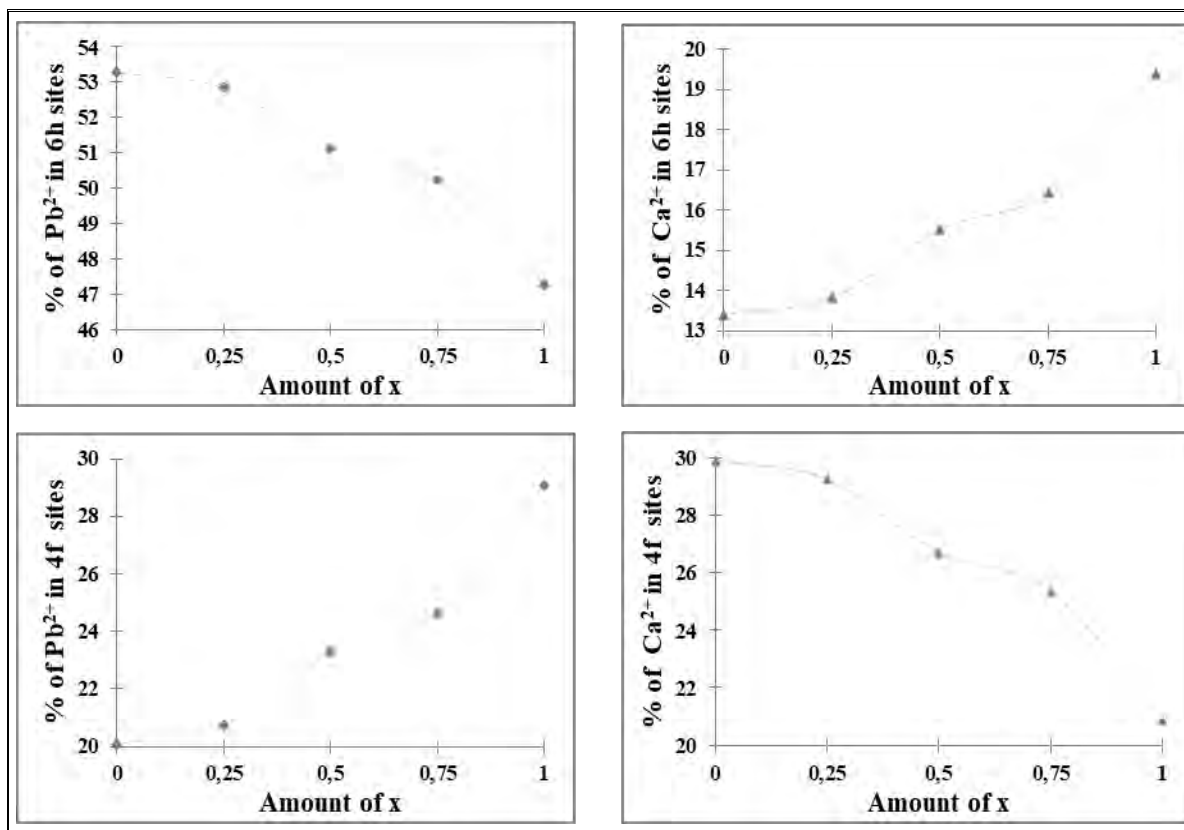


Fig.25: % occupation in the 6h and 4f sites as a function of the amount of potassium (x) in $Na_{1-x}K_xPb_2CaCd(PO_4)_3$ ($0 \leq x \leq 1$).

The interatomic distances and angles are reasonable, this is similar and agrees well with those found in $Na_{1-x}K_xPb_4(PO_4)_3$ [6]. Where the ' $M(1)-O_6$ ' in the site (6h) distances vary from 2.17 Å to 2.78 Å for $Pb^{2+}(1)/Ca^{2+}(1)/Cd-O_6$. $M(2)-O_9$ in the mixed site (4f) and from 2.39 Å to 2.88 Å for ' $Pb^{2+}(2)/Ca^{2+}(2)/Na^+/K^+-O_9$ '. ' $P-O$ ' is with an average value of 1.5 Å and the ' $O-P-O$ ' angles are between 104.4° and 114°.

III.2. Vibrational Spectra Analysis.

a) Infrared and Raman at Room-Temperature.

Figs.26&27 show the Infrared and Raman spectra results recorded at ambient conditions of $\text{Na}_{1-x}\text{K}_x\text{Pb}_2\text{CaCd}(\text{PO}_4)_3$; ($0 \leq x \leq 1$). The wavenumbers and the corresponding assignments are listed in Table.14. The bands observed in the infrared and Raman spectra of these compounds do not differ significantly from those observed for silver-lead apatite [20]. A pattern of bands was observed in the $350\text{-}800\text{cm}^{-1}$ region is attributed to ‘O-P-O’ bending vibrations [V_2 (from 380cm^{-1} to 420cm^{-1}) and V_4 (from 430cm^{-1} to 800cm^{-1})], and the series of high-frequency bands observed above 900cm^{-1} are assigned to ‘P-O’ stretching vibrations [V_1 (observed around 930cm^{-1} and 955cm^{-1} as a strong band in the Raman spectra and as shoulder in the IR spectra) and V_3 (from 960cm^{-1} to 1100cm^{-1})]. The lattice vibrations: ‘ $\text{Pb}^{2+}/\text{Ca}^{2+}/\text{Cd}^{2+}/\text{Na}^+/\text{K}^+ \text{-O}$ ’, this mode is observed at frequencies below 300cm^{-1} .

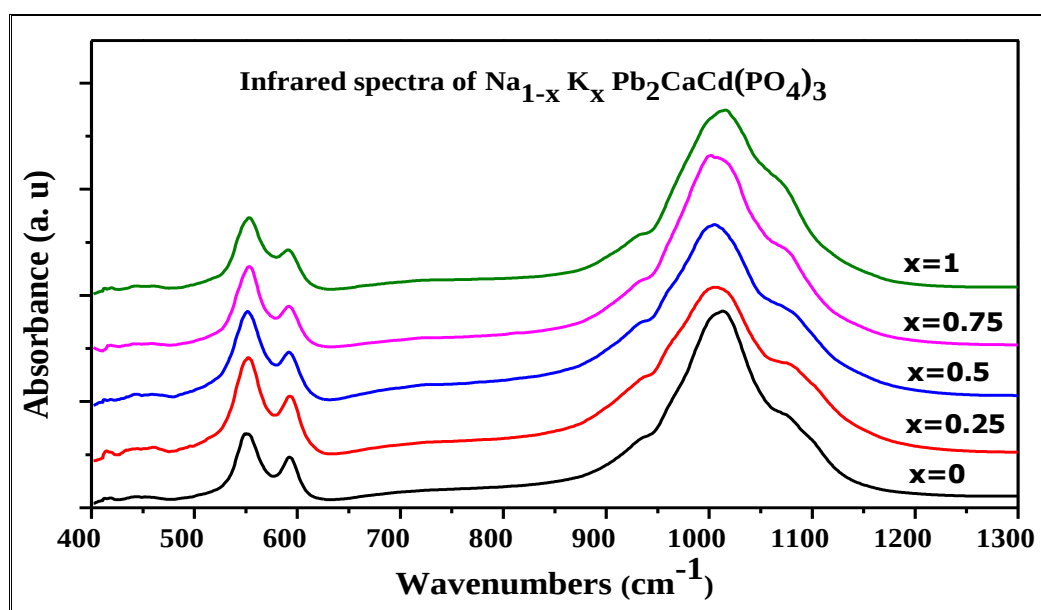


Fig.26: Infrared spectra of $\text{Na}_{1-x}\text{K}_x\text{Pb}_2\text{CaCd}(\text{PO}_4)_3$, with ($0 \leq x \leq 1$) recorded at ambient conditions.

[20] M. Querton, M.T. Oumba, W. Freundlich and A.W. Kolsi. Mat. Res. Bull.. 19 (1984) 1063.

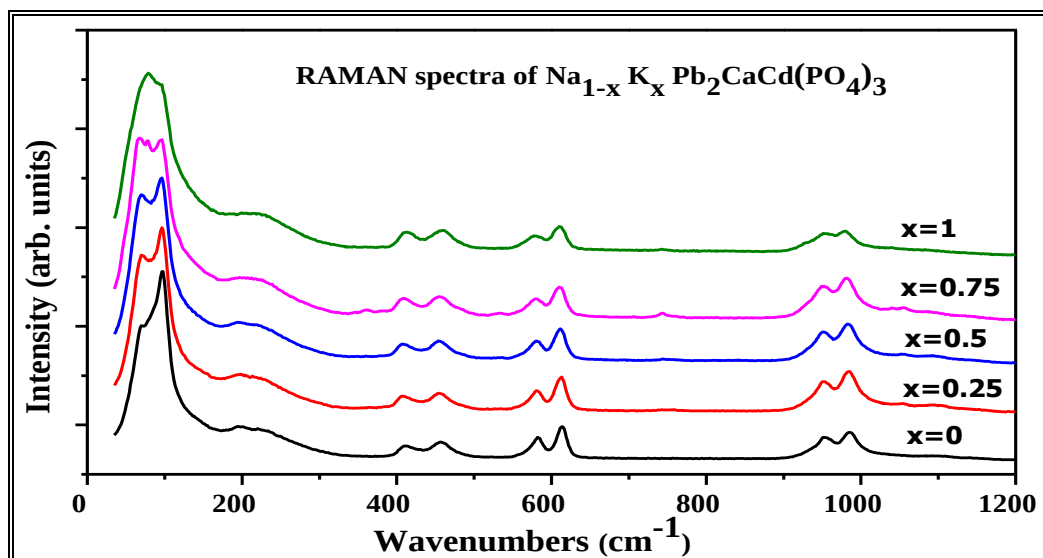


Fig.27: Raman spectra of $\text{Na}_{1-x}\text{K}_x\text{Pb}_2\text{CaCd}(\text{PO}_4)_3$, with $(0 \leq x \leq 1)$ recorded at ambient conditions.

Table.14: Assignments of observed Raman and Infrared bands at ambient temperature.

x	Lattice Mode					Bending Mode				Stretching Mode		
						V_2		V_4		V_1	V_3	
0	70.24(s)	87.08(sh)	96.28(vs)	201.46(m)	220.40(sh)	411.10(w)	456.98(vm)	582.63(m)	613.03(s)	952.47(m)	984.72(s)	1080.97(vw)
0.25	70.12(s)	86.94(sh)	96.25(vs)	201.32(m)	219.83(sh)	408.62(w)	454.78(vm)	580.80(m)	612.11(s)	951.61(m)	984.40(s)	1072.80(vw)
0.50	70.11(s)	84.31(sh)	96.22(vs)	195.77(m)	218.54(sh)	407.19(w)	454.19(vm)	580.42(m)	611.41(s)	951.46(m)	983.72(s)	1058.03(vw)
0.75	68.15(vs)	78.47(s)	96.19(vs)	195.60(m)	216.96(sh)	406.47(w)	453.78(vm)	580.11(m)	610.30(s)	950.53(s)	981.83(vs)	1043.25(w)
1	78.74(vs)	87.17(sh)	96.32(sh)	203.20(m)	222.41(sh)	411.32(m)	461.38(m)	582.75(vm)	613.14(s)	952.61(s)	982.43(vs)	1055.54(w)
0	Infrared					419.19(vw)	444.41(w)	552.02(s)	592.76(m)	939.19(sh)	1014.36(vs)	1076.95(s)
0.25						419.02(vw)	444.24(w)	552.40(s)	593.26(m)	935.72(sh)	1007.34(vs)	1076.76(s)
0.50						419.54(vw)	444.07(w)	592.27(s)	552.18(m)	933.99(sh)	1005.84(vs)	1077.28(s)
0.75						419.02(vw)	440.61(w)	553.32(s)	591.83(m)	933.05(sh)	1002.03(vs)	1072.10(s)
1						419.67(vw)	444.58(w)	553.49(s)	591.52(m)	931.19(sh)	1017.04(vs)	1065.23(s)

The effect of the larger size and mass of the K^+ ion is evident from the Raman spectra it was shown in previous works [6,21]. For all Raman spectra in the different modes (Lattice, Bending and Stretching modes), the frequencies of vibration between two extremities ($x = 0$ and $x = 1$) in $\text{Na}_{1-x}\text{K}_x\text{Pb}_2\text{CaCd}(\text{PO}_4)_3$, we noted that once the sodium is substituted by potassium, the frequencies of the modes observed shift towards lower frequencies and then increase for ' $x = 1$ '. Except for the antisymmetric vibrations V_3 (P-O), the frequencies remain below the extremity ' $x = 0$ '. The results of variations of the strong and very strong frequencies of the vibrations, as an example we show in Fig.28.

[21] A.Laghzizil. P.Barboux. A. Bouhaouss, Solid State Ionics128(2000)177.

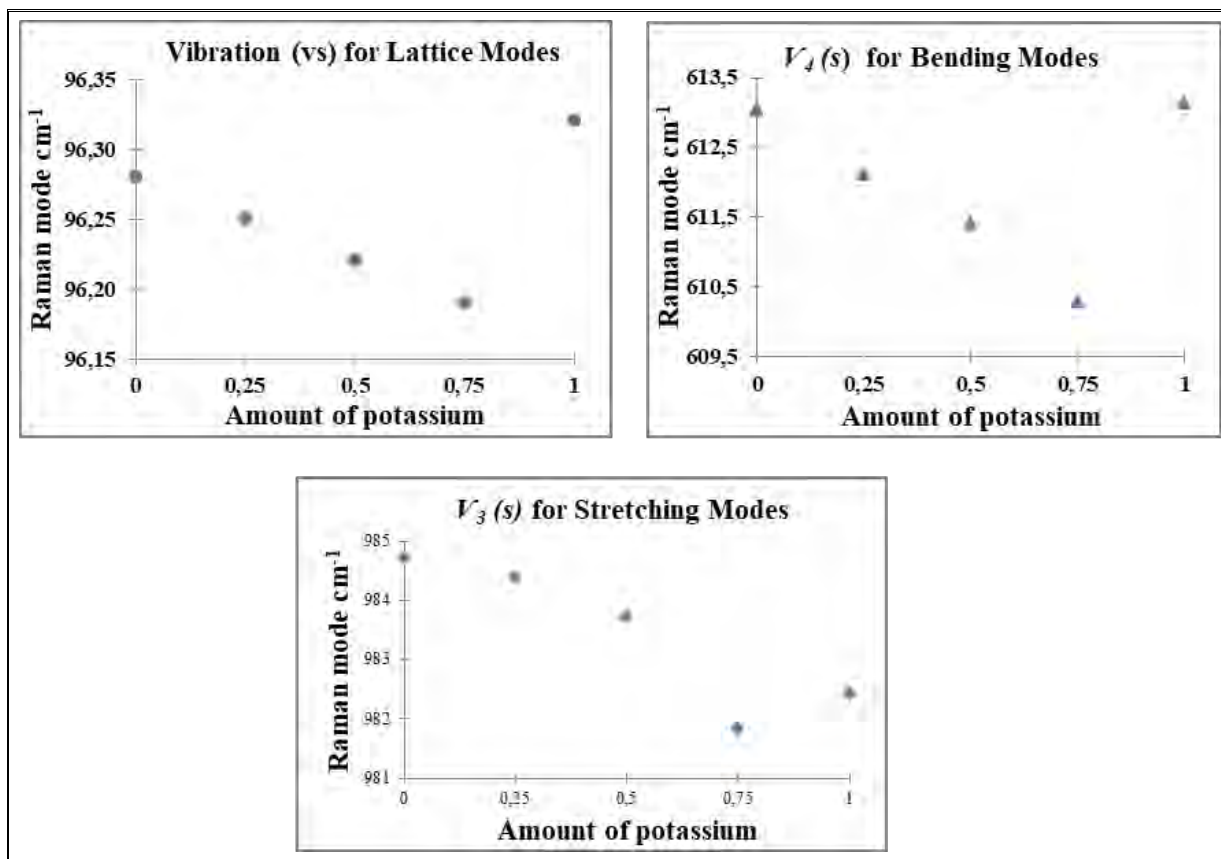


Fig.28: Variation of different modes (Lattice, Bending, and Stretching modes) for $\text{Na}_{1-x}\text{K}_x\text{Pb}_2\text{CaCd}(\text{PO}_4)_3$ ($0 \leq x \leq 1$) as a function of potassium amount.

b) High-Temperature Raman Study of $\text{NaPb}_2\text{CaCd}(\text{PO}_4)_3$.

The structural stability of the $\text{NaPb}_2\text{CaCd}(\text{PO}_4)_3$ compound, is tested as a function of temperature. The Raman spectra obtained at several temperatures are shown in Fig.29. The experimental Raman spectra were collected in situ at room-pressure and elevated temperatures; up to 773K. The results obtained at several temperatures are presented in Table.15. The temperature dependence of all lattice modes (Lattice, Bending, and Stretching modes), show monotonous changes, in wavenumbers while the temperature is increased. As an example, the lattice modes observed in the full spectral range between 384 and 1040 cm^{-1} with the two principal vibrational modes of the “ PO_4^{3-} ” the triply degenerate asymmetric ‘P-O’ stretching mode of V_3 at 1040 cm^{-1} as well as the triply degenerate ‘O-P-O’ bending mode of ‘ V_4 ’ at 600 cm^{-1} (MANOUN and al.).

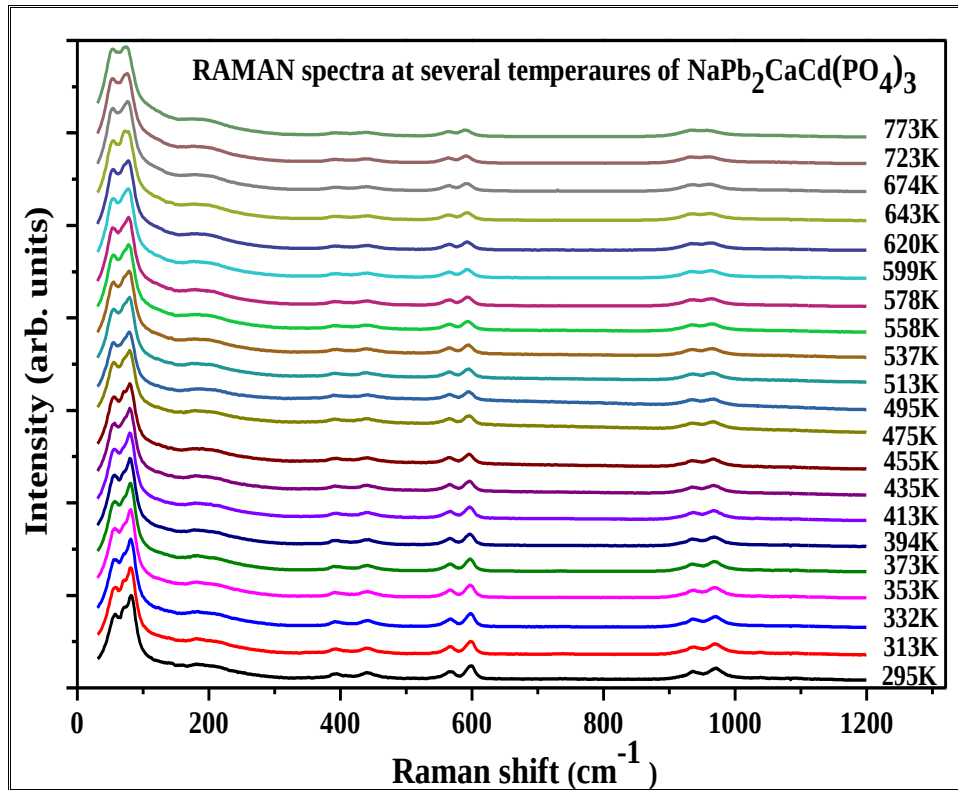


Fig.29: Raman spectra of $\text{NaPb}_2\text{CaCd}(\text{PO}_4)_3$ obtained for selected temperatures as indicated.

Table.15: Assignments of observed Raman at several temperatures of $\text{NaPb}_2\text{CaCd}(\text{PO}_4)_3$.

Temperature	Lattice Modes					Bending modes				Stretching modes		
						V_2	V_4			V_1	V_3	
295K	58.66(s)	71.83(sh)	81.43(vs)	191.73(m)	215.43(sh)	393.92(w)	442.82(vm)	569.10(m)	599.28(s)	936.18(m)	969.32(s)	1039.90(vw)
313K	58.60(s)	70.94(sh)	81.42(vs)	186.35(m)	215.23(sh)	393.12(w)	441.68(vm)	568.45(m)	599.12(s)	936.13(m)	969.18(s)	1039.08(vw)
332K	58.43(s)	70.88(sh)	81.41(vs)	184.13(m)	215.07(sh)	392.71(w)	441.30(vm)	568.33(m)	598.50(s)	935.89(m)	969.04(s)	1038.63(vw)
353K	56.98(s)	70.88(sh)	81.35(vs)	183.50(m)	213.46(sh)	392.42(w)	440.17(vm)	568.20(m)	598.07(s)	935.78(m)	968.90(s)	1038.52(vw)
373K	56.92(s)	70.72(sh)	81.29(vs)	182.23(m)	210.09(sh)	390.15(w)	440.10(vm)	568.08(m)	598.00(s)	935.57(m)	968.48(s)	1038.24(vw)
413K	56.91(s)	70.40(sh)	79.67(vs)	179.49(m)	209.13(sh)	390.14(w)	439.79(vm)	567.33(m)	597.37(s)	935.43(m)	968.34(s)	1037.97(vw)
435K	56.79(s)	70.24(sh)	79.63(vs)	178.75(m)	208.17(sh)	389.77(w)	438.88(vm)	567.08(m)	595.64(s)	935.01(m)	968.20(s)	1037.41(vw)
455K	55.40(s)	70.08(sh)	79.62(vs)	178.46(m)	208.01(sh)	389.39(w)	438.65(vm)	566.83(m)	595.49(s)	934.87(m)	967.92(s)	1037.13(vw)
475K	55.20(s)	69.76(sh)	79.58(vs)	178.30(m)	207.85(sh)	388.25(w)	438.27(vm)	566.70(m)	595.12(s)	934.73(m)	967.78(s)	1036.85(vw)
513K	55.16(s)	69.44(sh)	79.54(vs)	178.11(m)	207.04(sh)	387.87(w)	437.67(vm)	566.58(m)	594.99(s)	934.59(m)	967.64(s)	1036.57(vw)
537K	55.12(s)	69.43(sh)	78.01(vs)	177.77(m)	206.88(sh)	387.49(w)	437.51(vm)	566.08(m)	594.42(s)	934.45(m)	967.50(s)	1036.29(vw)
558K	55.06(s)	69.42(sh)	77.90(vs)	177.25(m)	205.76(sh)	387.12(w)	437.14(vm)	565.83(m)	594.37(s)	934.17(m)	967.36(s)	1036.01(vw)
578K	53.46(s)	69.41(sh)	77.87(vs)	177.08(m)	205.60(sh)	386.74(w)	436.76(vm)	565.70(m)	594.12(s)	934.03(m)	967.08(s)	1035.73(vw)
599K	53.43(s)	69.13(sh)	77.74(vs)	176.91(m)	205.44(sh)	386.36(w)	436.38(vm)	565.58(m)	593.74(s)	933.89(m)	966.94(s)	1035.45(vw)
620K	53.42(s)	69.11(sh)	77.66(vs)	176.56(m)	205.12(sh)	385.98(w)	436.00(vm)	565.45(m)	593.21(s)	933.75(m)	966.66(s)	1035.17(vw)
643K	53.41(s)	69.05(sh)	77.48(vs)	176.41(m)	204.96(sh)	385.60(w)	435.62(vm)	565.32(m)	593.12(s)	933.61(m)	966.10(s)	1034.89(vw)
674K	53.38(s)	69.00(sh)	76.24(vs)	176.22(m)	202.23(sh)	385.22(w)	435.24(vm)	565.20(m)	592.86(s)	933.47(m)	965.96(s)	1034.34(vw)
723K	53.32(s)	68.93(sh)	76.05(vs)	175.87(m)	201.90(sh)	384.84(w)	434.86(vm)	565.07(m)	592.61(s)	933.33(m)	965.68(s)	1033.95(vw)
773K	53.30(s)	68.88(sh)	74.38(vs)	175.36(m)	201.10(sh)	384.46(w)	434.48(vm)	564.95(m)	591.74(s)	933.19(m)	964.00(s)	1033.79(vw)

Fig.30 shows a linear large decrease in wavenumbers with an increase in temperature. No considerable changes in the temperature dependence of the modes and the corresponding intensity are observed and thus no temperature-induced phase transition is observed in $\text{NaPb}_2\text{CaCd}(\text{PO}_4)_3$ in the temperature range studied here.

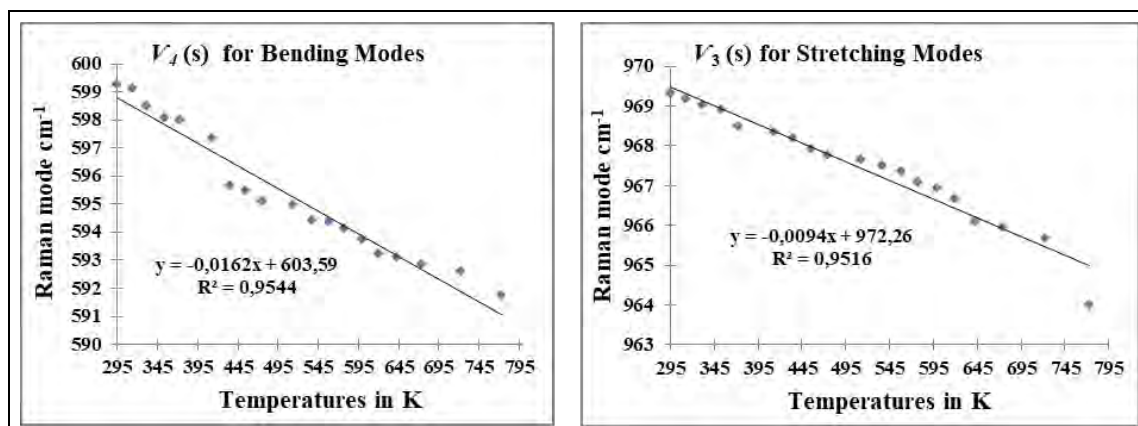


Fig.30: Showing a linear large decrease with the increase in temperature for two principal vibrational modes of the ' PO_4^{3-} '; V_3 and V_4 .

III.3. Optoelectronic Properties.

Fig.31 shows the converted reflectance data to absorbance using the kubelka-Mank function which will be used in the optical band calculation. The solid UV-visible/far-ultraviolet spectra of the compound's series described in $\text{Na}_{1-x}\text{K}_x\text{Pb}_2\text{CaCd}(\text{PO}_4)_3$ ($0 \leq x \leq 1$) were measured in the range 250 nm to 800 nm at room temperature.

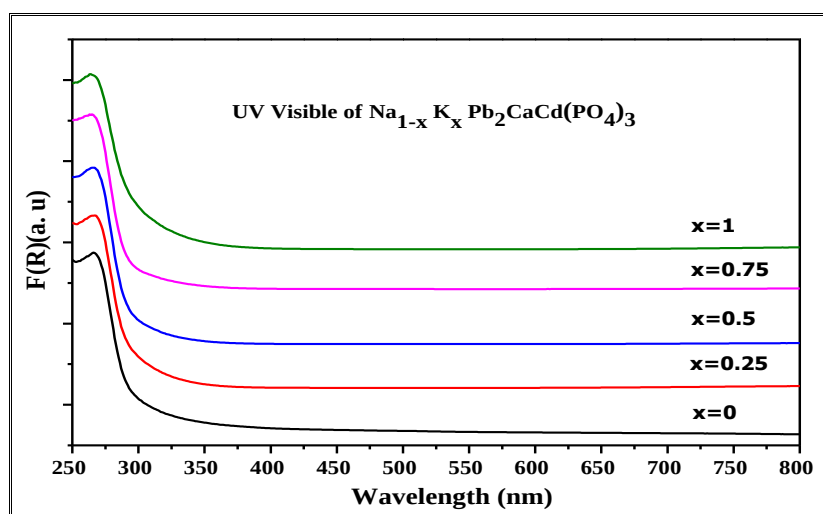


Fig.31: UV visible / Far-Ultraviolet of the series $\text{Na}_{1-x}\text{K}_x\text{Pb}_2\text{CaCd}(\text{PO}_4)_3$.

The results of example $\text{KPb}_2\text{CaCd}(\text{PO}_4)_3$ as tabulated in Fig.32 we can extend the straight line to intercept $(h\nu)$ -axis at $[\text{F(R)}*h\nu]^{1/2} = 0$ and for $\text{F(R)} = 0$. To estimate the values of the indirect allowed gap energy and cut-off absorption shift of the series $\text{Na}_{1-x}\text{K}_x\text{Pb}_2\text{CaCd}(\text{PO}_4)_3$ ($0 \leq x \leq 1$), for example, $\text{KPb}_2\text{CaCd}(\text{PO}_4)_3$ as shown in Fig.32.

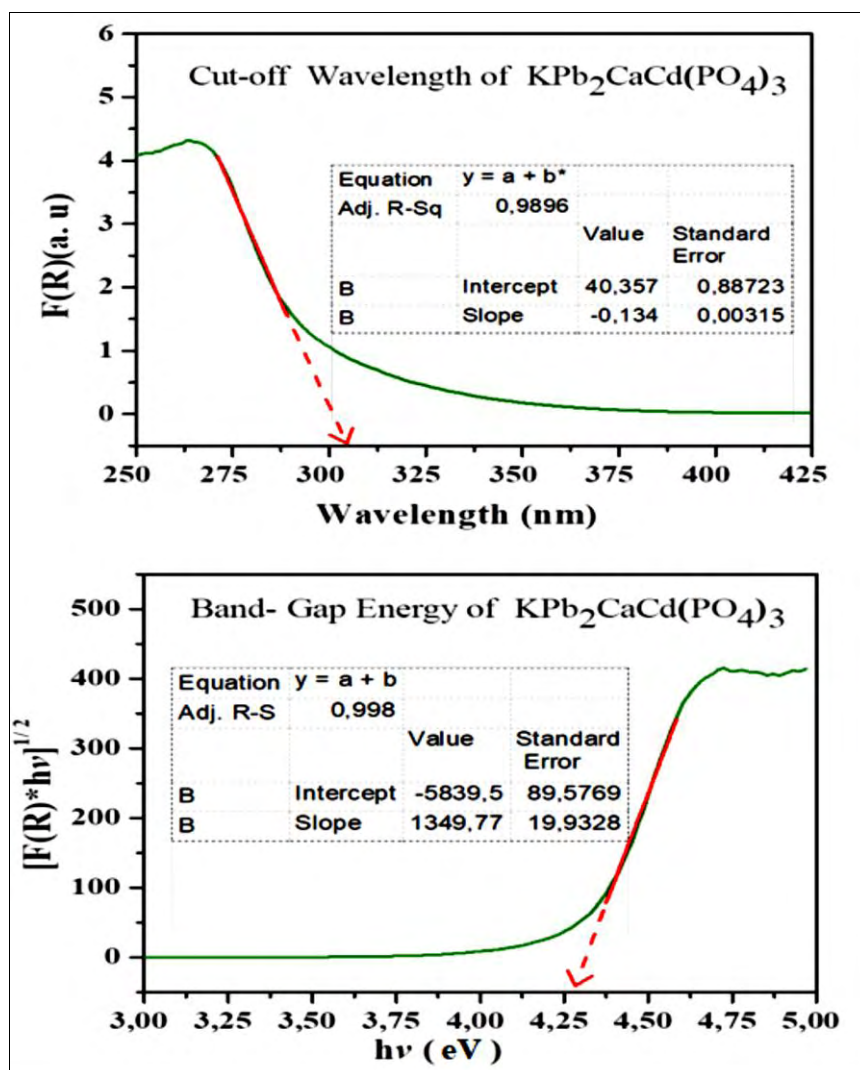


Fig.32: $[\text{F(R)}*h\nu]^{1/2}$ and of F(R) for $\text{KPb}_2\text{CaCd}(\text{PO}_4)_3$ lacunar apatites, depending upon the incident photon energy ($h\nu$) and the optical absorption.

Table.16 summarizes the main peak absorption in the UV visible / Far-Ultraviolet ($250 \text{ nm} < \lambda < 350 \text{ nm}$). These measurements in the ultraviolet/visible region (UV-VIS) cover wavelengths from about 250 nm to 800 nm. Fig.33 shows the variation of the absorbance using the Kubelka-Munk function which will be used in the optical band calculation.

Table.16: A cut-off edge of peaks absorption, and the calculated optical indirect allowed energy gap using Tauc's relationship of the series $Na_{1-x}K_xPb_2CaCd(PO_4)_3$ ($0 \leq x \leq 1$).

x	0	0.25	0.5	0.75	1
Cut-off Wavelength (nm)	296.67	295.54	294.59	292.10	301.17
Band-Gap Energy (eV)	4.3424	4.3460	4.3533	4.3693	4.3263

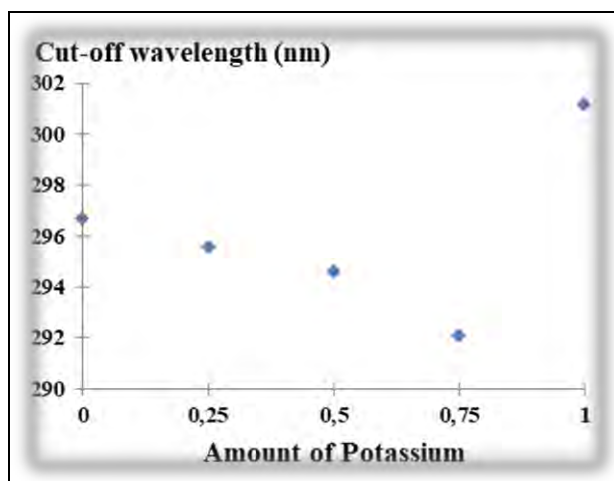


Fig.33: The effect of Potassium substitution for the crystal structure of apatite $Na_{1-x}K_xPb_2CaCd(PO_4)_3$ depending on the cut-off absorption shift.

The results by X-Ray diffraction, using $CuK\alpha$ radiation: emissions associated with electronic transitions from the heart Electrons (Electron-Electron Interactions) proved the sequential substitution of Na^+ by K^+ in the series of apatite $Na_{1-x}K_xPb_2CaCd(PO_4)_3$, behind the distortion of the connection between 'P-O' Fig.34. However, the observed Raman modes (Electron-Phonon Interaction), in Fig.28, for the lattice vibrations: ' $Pb^{2+}(2)/Ca^{2+}(2)/Na^+/K^+-O$ ' (M (2)-O) and ' $Pb^{2+}(1)/Ca^{2+}(1)/Cd^{2+}-O$ ' (M(1)-O) of external mode, are observed at frequencies below $300cm^{-1}$. It follows the same variation in the emission intensity of the UV band (Fig.33) and distortion of 'P-O' (Fig.34) studied by X-Ray diffraction.

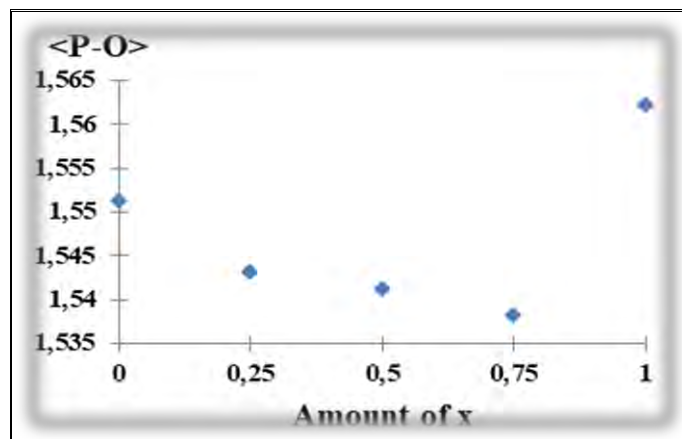


Fig.34: The sequential substitution of Na^+ by K^+ in the series of apatite $\text{Na}_{1-x}\text{K}_x\text{Pb}_2\text{CaCd}(\text{PO}_4)_3$, behind the distortion of the connection between $\langle\text{P-O}\rangle$.

The atomic percentage of substitution K^+ and the degree of distortion of 'P-O' are directly linked with optical absorption and thus the bandgap energy. The values of the indirectly allowed energy gap of the series $\text{Na}_{1-x}\text{K}_x\text{Pb}_2\text{CaCd}(\text{PO}_4)_3$ ($0 \leq x \leq 1$) are tabulated in [Table.16](#) and in [Fig.35](#), this shift was suggested to be in relation with the crystal structure and electronic structure stability and the effect of distortion degree.

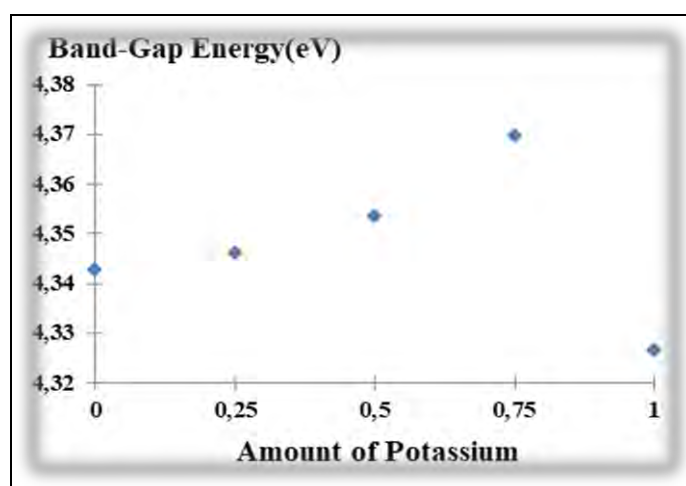


Fig.35: The Bandgap Energy depending on the effect of potassium substitution for the crystal structure of apatite $\text{Na}_{1-x}\text{K}_x\text{Pb}_2\text{CaCd}(\text{PO}_4)_3$.

According to the results obtained, oxygen radicals react mainly with $\text{M}(2)\text{-O}_9$ site, where there are monovalent cations Na^+/K^+ . Because the low-energy-loss region reflects the valence and conduction band structures of solids. This indicates that the electron carrier

concentration is decreased by the existence of K^+/Na^+ , increasing 'Eg'. This agrees with the variation of the distance 'P-O'. As the ' K^+ ' content increased, the gap between the conduction band {Ec} and Fermi level {EF} has slightly increased. The electrical properties of the lacunar apatite confirmed that the field-effect mobility decreased with increasing concentration of potassium, indicating that K^+/Na^+ was indeed acting as a carrier suppressor by reducing the number of oxygen donor in the apatitic system.

IV. New Serie of $\text{Na}_{1-x}\text{K}_x\text{Pb}_2\text{SrCa}(\text{PO}_4)_3$.

IV.1. Structural Analysis.

Fig.36 shows the X-ray powder diffraction patterns of $\text{Na}_{1-x}\text{K}_x\text{Pb}_2\text{SrCa}(\text{PO}_4)_3$. Unlike the previous series, this series presents several cases of refinement. Indeed, as we have shown that the M(1) and M(2) sites are occupied by divalent cations and since we have three cations, the study of the cases is essential. In case-1 we fix the Pb^{2+} cations in the 6h site (M(1)), then we refine the $\text{Sr}^{2+}/\text{Ca}^{2+}$ cations in the two sites M(1) and M(2). For case-2, the cationic percentage of Ca^{2+} is fixed {0.75% in M(1) and 0.25% in M(2)}, then the occupation of the $\text{Pb}^{2+}/\text{Sr}^{2+}$ cations in the two sites is refined. Concerning case-3, the cationic percentage of Sr^{2+} is fixed {0.75% in M(1) and 0.25 in M(2)} and the occupation of $\text{Pb}^{2+}/\text{Ca}^{2+}$ cations is refined in the two sites. Concerning case-4(2), the refinement results obtained in case-2 are exploited, such that the occupation of the Sr^{2+} cations in the two sites is determined and the $\text{Pb}^{2+}/\text{Ca}^{2+}$ cations in the sites M(1) and M(2) are refined. Concerning case-5(3), the refinement results obtained in case-3 are exploited, such that the Ca^{2+} cation occupancy is determined at both sites and the $\text{Pb}^{2+}/\text{Sr}^{2+}$ cations at sites M(1) and M(2) are refined. For a good choice among the proposed cases, one is interested in case-5(3), because of the good values of the obtained reliability factors. For example, $\text{NaPb}_2\text{SrCa}(\text{PO}_4)_3$ ($x=0$) for the different proposed cases are justified in [Annex. II, Table. II.1](#).

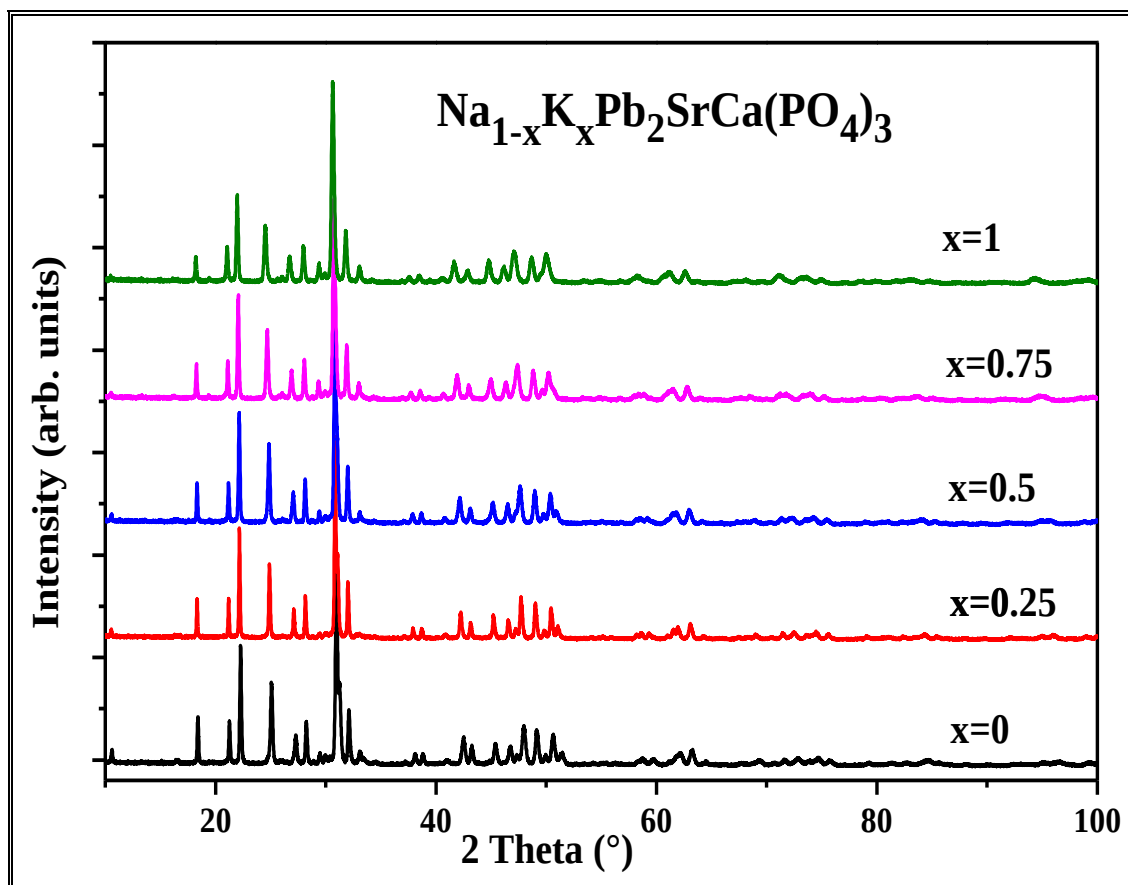


Fig.36: Powder diffraction patterns of $\text{Na}_{1-x}\text{K}_x\text{Pb}_2\text{SrCa}(\text{PO}_4)_3$.

Rietveld refinements, watched in Fig.37, to justify all the observed reflections for the compositions ($0 \leq x \leq 1$), could be indexed in the space group $P6_3/m$ (N°176), except for reflections indicated at ' 2θ ' successively, between 29° and 34° for all sample. The additional peaks have been detected by the HighScore program (PANalytical. 2003), they were assigned to the compound $\text{Pb}_3(\text{PO}_4)_2$ [16,17]. The results indicate that the formation of the minor phase is of low intensity. The results of the first refinements are shown in Annex. II; Figure. II.1, Table. II.2, Table. II.3 and Table. II.4.

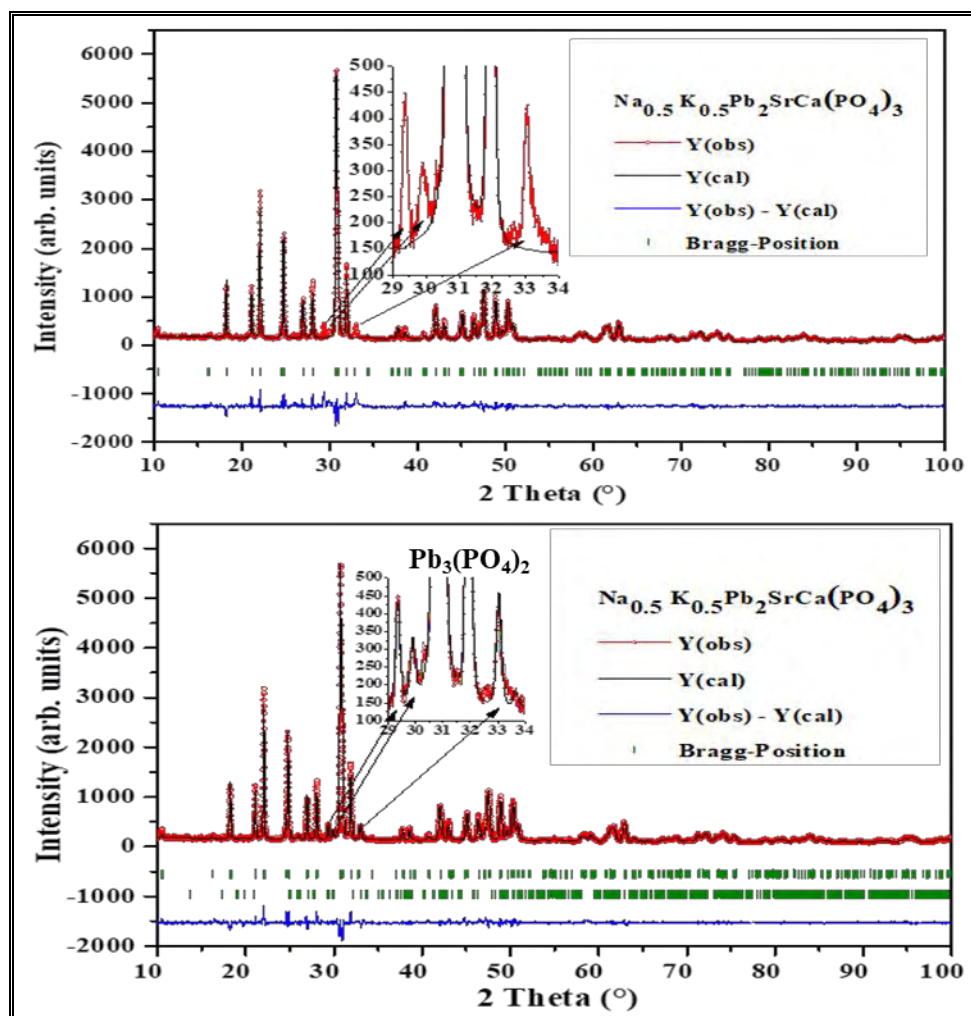


Fig.37: Rietveld first and second refinement of the two phases $\text{Na}_{0.5}\text{K}_{0.5}\text{Pb}_2\text{SrCa}(\text{PO}_4)_3$ and $\text{Pb}_3(\text{PO}_4)_2$ of the sample; $x=0.5$.

Two phases presented in Fig.38 illustrate how perceptual indicators of the quality of the structural models respectively for $\text{Na}_{1-x}\text{K}_x\text{Pb}_2\text{SrCa}(\text{PO}_4)_3$ and $\text{Pb}_3(\text{PO}_4)_2$ carried out in the $P6_3/m$ and C_2/c space groups respectively. The results of the reliability factors, the judges to be a very satisfactory result, displays the agreement obtained between observed and calculated diffraction profiles. For more details of final phases, refinements see Table.17, the finals resulting data, interatomic bond distances, and angles are given in Table.18. The atomic coordinates, isotropic temperature factors, and occupation in the 6h and 4f sites as a function of the amount of potassium (x) are listed in Table.19. For all with; their estimated deviations in parentheses.

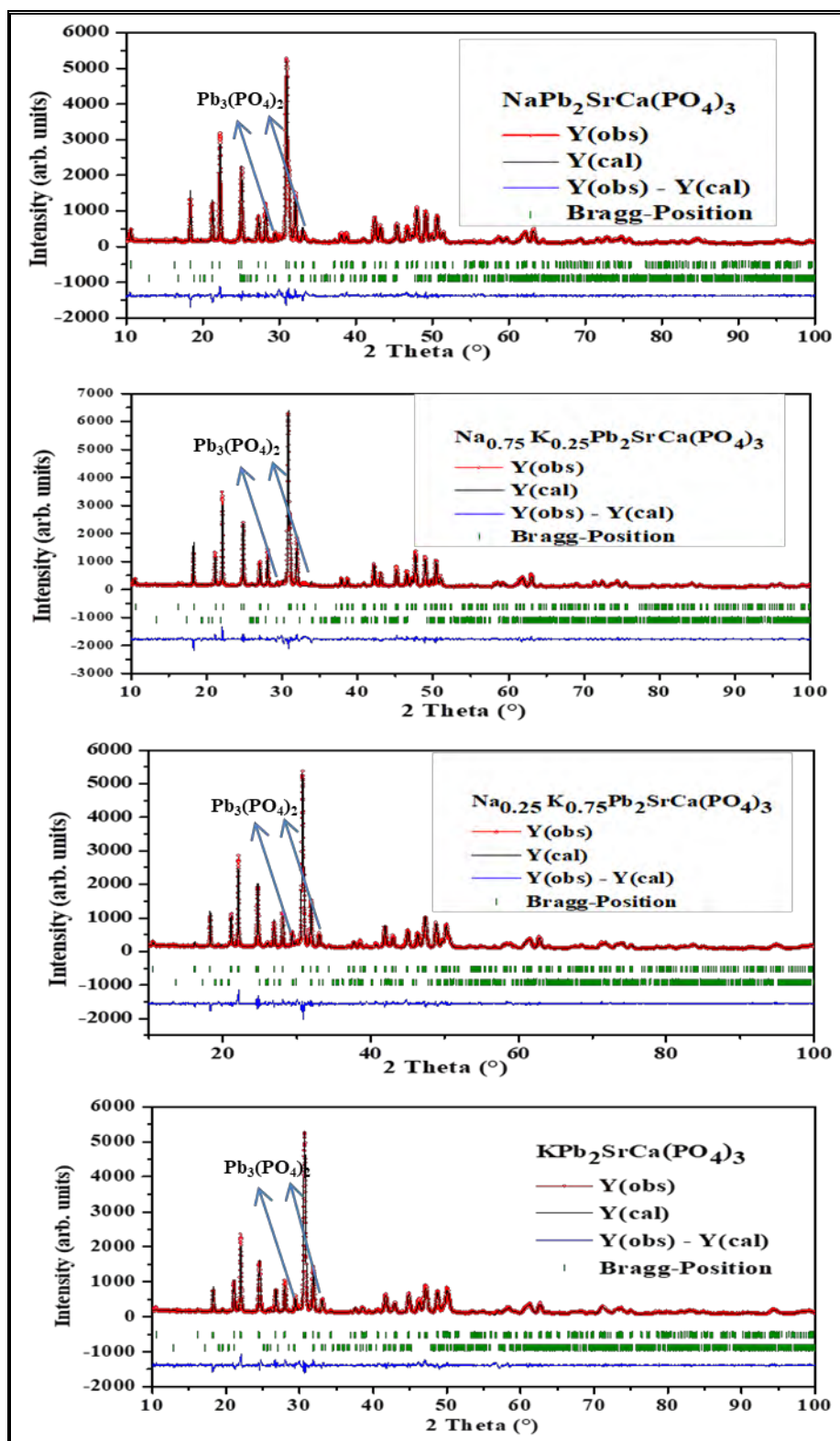


Fig.38: Final Rietveld plot for $\text{Na}_{1-x}\text{K}_x\text{Pb}_2\text{SrCa}(\text{PO}_4)_3$ and $\text{Pb}_3(\text{PO}_4)_2$; with upper symbols illustrate the observed data $N^\circ 1$, and the calculated pattern (solid line) for $N^\circ 2$, the lower curve is the difference diagram schematize in the $N^\circ 3$ and the vertical markers show calculated positions of Bragg reflections in $N^\circ 4$.

Table.17: Details of second refinement plot of $Na_{1-x}K_xPb_2SrCa(PO_4)_3$ and $Pb_3(PO_4)_2$.

		$Na_{1-x}K_xPb_2CaSr(PO_4)_3$				
x		0	0.25	0.5	0.75	1
Zero-point (deg.20)		0.0112(14)	0.0506(17)	0.0738(41)	-0.0314(15)	-0.0445(9)
Pseudo-Voigt function $PV=\eta L + (1-\eta) G$	η	0.4291(86)	0.4305(106)	0.4212(75)	0.4436(79)	0.4704(79)
Caglioti parameters	U	0.5900(200)	0.4357(213)	0.7213(204)	0.7402(255)	2.4876(400)
	V	-0.0978(122)	-0.1923(123)	-0.2066(130)	-0.1443(157)	-0.8799(246)
	W	0.0246(18)	0.0408(32)	0.0414(20)	0.0301(23)	0.1215(37)
No. of reflections		504/2	484/2	511/2	524/2	559/2
No. of refined parameters		33				
Space group		$P 6_3/m$				
a (Å)		9.6669(3)	9.6877(3)	9.7011(3)	9.7160(3)	9.7415(4)
c (Å)		7.1104(2)	7.1573(2)	7.1779(2)	7.2124(3)	7.2573(4)
V (Å ³)		575.44(3)	581.73(3)	585.02(3)	589.63(3)	596.43(5)
Density(g/cm ³)		6.560	6.571	6.756	6.689	6.172
Z		2				
Atom Number		11	12			11
User-weighted Chi2		2.36	2.90	1.97	2.11	2.38
%*R _F		1.47	2.35	2.15	1.78	1.40
%*R _B		3.34	5.72	4.99	4.76	4.32
%*R _p		7.58	8.75	7.32	7.63	7.84
%*R _w p		10.4	12.1	9.53	9.97	10.7
%*cR _p		11.1	13.7	13.6	13.3	12.3
%*cR _w p		13.7	16.6	15.3	15.4	15.0
$Pb_3(PO_4)_2$						
Caglioti parameters	U	0.4642(199)	0.2758(149)	0.7213(204)	0.8544(255)	0.9199(400)
	V	-0.0099(122)	-0.1104(98)	-0.2066(130)	-0.2238(157)	-0.1142(246)
	W	0.0109(18)	0.0415(16)	0.0414(20)	0.0420(23)	0.0236(37)
No. of reflections		743/2	688/2	686/2	690/2	740/2
No. of refined parameters		7				
Space group		$C 2/c$				
a (Å)		13.8890(11)	13.5444(10)	13.4164(15)	13.4280(13)	13.9987(14)
b(Å)		5.7114(5)	5.5402(4)	5.5723(7)	5.6033(7)	5.6108(7)
c(Å)		9.2355(6)	8.9569(7)	9.3041(9)	9.3076(8)	9.2927(7)
beta		102.0723(61)	101.9930(50)	105.4273(89)	105.2669(80)	101.9289(82)
V (Å ³)		716.41(10)	657.44(8)	670.51(13)	675.60(12)	714.13(12)
Z		4				
Atom Number		7				
%*R _F		0.279	1.14	0.746	0.496	0.454
%*R _B		0.806	2.47	1.39	1.22	1.19

Table.18: Interatomic distances in (Å) and 'O-P-O' angles in (°) of $Na_{1-x}K_xPb_2SrCa(PO_4)_3$.

x	0	0.25	0.5	0.75	1
M(1)-O ₁	2.808(2)	2.825(4)	2.898(2)	2.974(2)	2.957(2)
2*M(1)-O ₂	2.3779(8)	2.461(4)	2.4634(8)	2.450(4)	2.5006(9)
2*M(1)-O ₂	2.604(2)	2.637(13)	2.6136(19)	2.646(12)	2.659(2)
M(1)-O ₃	2.3312(16)	2.202(16)	2.2719(14)	2.2860(16)	2.5006(9)
<M(2)-O>	2.5303	2.5313	2.5617	2.589	2.6543
3*M(2)-O ₁	2.529(7)	2.502(10)	2.478(5)	2.556(6)	2.526(3)
3*M(2)-O ₂	2.8271(17)	2.893(12)	2.7723(14)	2.874(10)	2.7338(12)
3*M(2)-O ₃	2.531(8)	2.684(15)	2.673(5)	2.588(6)	2.722(4)
<M(II)-O>	2.6290	2.693	2.6411	2.6727	2.6606
P-O ₁	1.579(11)	1.550(16)	1.591(8)	1.574(10)	1.5761(5)
2*P-O ₂	1.583(4)	1.538(9)	1.546(3)	1.510(6)	1.510(7)
P-O ₃	1.563(8)	1.504(10)	1.531(5)	1.576(7)	1.583(6)
<P-O>	1.575	1.5307	1.556	1.5533	1.5563
2*O ₁ -P-O ₂	106.6(4)	105.5(1)	111.4(3)	106.8(8)	106.87(6)
O ₁ -P-O ₃	110.9(5)	108.5(9)	102.7(4)	101.6(4)	100.6(6)
O ₂ -P-O ₂	117.1(2)	110.3(5)	117.7(2)	121.1(3)	129.6(1)
2*O ₂ -P-O ₃	107.8(3)	113.2(8)	106.1(2)	109.4(5)	104.7(5)
<O-P-O>	110.593	109.375	109.47	109.725	110.4235

Table.19: Refined structural parameters for $\text{Na}_{1-x}\text{K}_x\text{Pb}_2\text{SrCa}(\text{PO}_4)_3$.

Atom	Wyckoff	Sym	x/a	y/b	z/c	B ($\text{\AA}^2$)	Occupancy	x
M(1) = Pb(1)/Ca(1)/Sr(1)	6h	M	0.2566(2)	0.25396(2)	0.25	0.79(7)	1.882(3)/0.361(3)/0.757(3)	0
			0.2553(3)	0.2553(3)		1.07(4)	1.865(5)/0.361(5)/0.774(5)	0.25
			0.2577(2)	0.2550(2)		1.36(5)	1.829(4)/0.334(4)/0.837(4)	0.5
			0.2580(2)	0.2540(2)		1.38(4)	1.844(4)/0.334(4)/0.822(4)	0.75
			0.2604(2)	0.2533(2)		1.08(9)	1.831(7)/0.513(7)/0.656(7)	1
M(2) = Pb(2)/Ca(2)/Sr(2)/Na/K	4f	3	0.6667	0.3333	0.5042(15)	0.063(5)	0.118(4)/0.639(4)/0.243(4)/1/0	0
					0.5068(20)	0.73(2)	0.135(2)/0.639(2)/0.226(2)/0.75/0.25	0.25
					0.5085(6)	0.10(4)	0.171(4)/0.666(4)/0.163(4)/0.5/0.5	0.5
					0.5004(11)	0.42(2)	0.156(5)/0.666(5)/0.178(5)/0.25/0.75	0.75
					0.5255(7)	0.81(5)	0.169(3)/0.487(3)/0.344(3)/0/1	1
P	6h	M	0.3636(9)	0.4034(10)	0.75	4.99(1)	3	0
			0.3755(14)	0.4100(12)		2.88(26)		0.25
			0.3635(7)	0.3998(7)		1.42(8)		0.5
			0.3601(8)	0.4013(9)		1.58(7)		0.75
			0.3520(8)	0.4039(4)		1.59(6)		1
O(1)	6h	M	0.4743(6)	0.3265(5)	0.75	9.80(9)	3	0
			0.4794(3)	0.3296(4)		7.05(8)		0.25
			0.4850(1)	0.3349(2)		7.21(2)		0.5
			0.4850(1)	0.3431(3)		7.43(5)		0.75
			0.4716(5)	0.3394(7)		6.15(7)		1
O(2)	12i	1	0.2650(1)	0.3500(4)	0.5601(9)	9.80(9)	6	0
			0.2714(14)	0.3480(11)	0.5736(14)	7.05(8)		0.25
			0.2686(4)	0.3596(7)	0.5657(9)	7.21(2)		0.5
			0.2724(13)	0.3496(10)	0.5677(6)	7.43(5)		0.75
			0.2759(3)	0.3695(3)	0.5618(7)	6.15(7)		1
O(3)	6h	M	0.4657(6)	0.5899(7)	0.75	9.80(9)	3	0
			0.4836(23)	0.5879(25)		7.05(8)		0.25
			0.4741(3)	0.5806(5)		7.21(2)		0.5
			0.4717(9)	0.5874(8)		7.43(5)		0.75
			0.4717(8)	0.5889(4)		6.15(7)		1

The Rietveld simulations for $\text{Na}_{1-x}\text{K}_x\text{Pb}_2\text{SrCa}(\text{PO}_4)_3$ ($0 \leq x \leq 1$), showed that this solid solution is continuously adopting the ***P6₃/m*** space group. The results given in [Table.17](#) and [Fig.39](#) show the cell parameters variation as a function of (x), where progressive substitution of sodium by potassium provokes an increase of the unit cell parameters (a), (c) and (V) and of the average distances $\langle \text{M}(1)\text{-O}_6 \rangle$. The increase is due to the substitution of Na^+ ($r_i=1.24 \text{ \AA}$) by K^+ ($r_i=1.55 \text{ \AA}$) [18] with larger-radius.

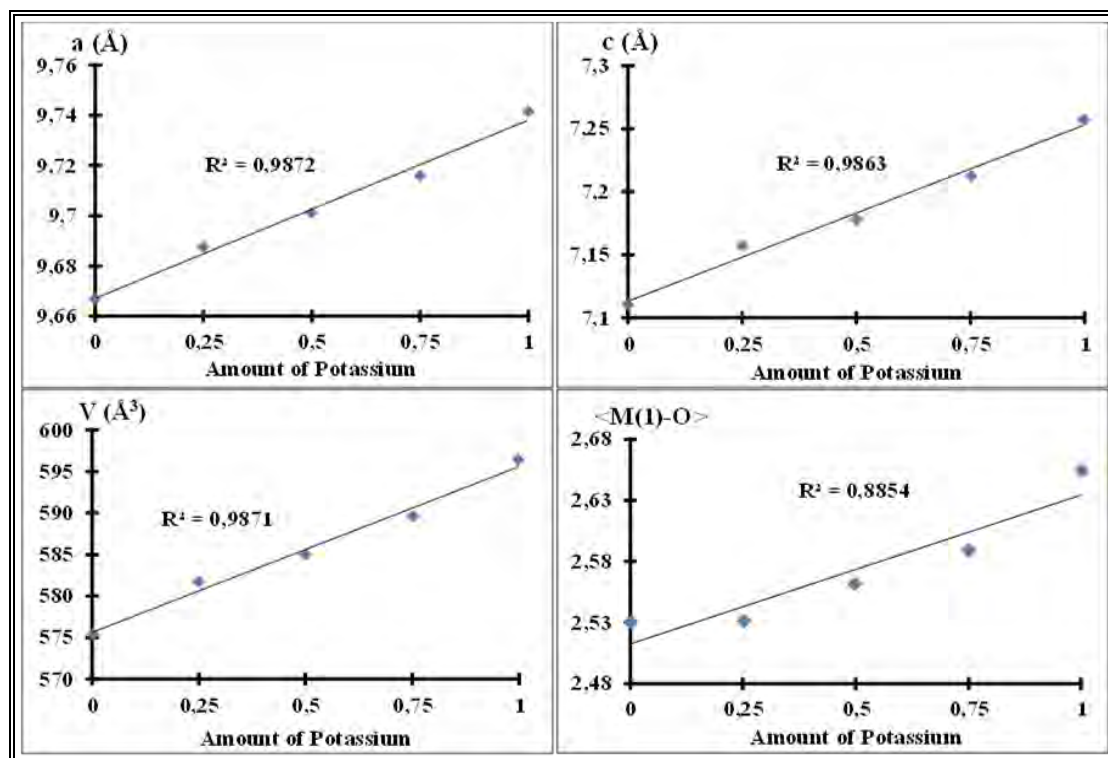


Fig.39: Unit cell parameters variation as a function of 'x' for $\text{Na}_{1-x}\text{K}_x\text{Pb}_2\text{SrCa}(\text{PO}_4)_3$ ($0 \leq x \leq 1$), where progressive substitution of sodium by potassium provokes an increase of the unit cell parameters $a(\text{\AA})$, $c(\text{\AA})$, $V(\text{\AA}^3)$ and $\langle M(1)-O_6 \rangle$.

The progressive substitution of Na^+ by K^+ is the most important cause influencing the per cent occupancy of the divalent cations Pb^{2+} , Ca^{2+} , and Sr^{2+} in the two sites M(1) and M(2), the results are presented in Table.20.

Table.20: % occupation of Pb^{2+} , Ca^{2+} and Sr^{2+} in the 6h and 4f sites as a function of the amount of potassium (x) in $\text{Na}_{1-x}\text{K}_x\text{Pb}_2\text{SrCa}(\text{PO}_4)_3$; ($0 \leq x \leq 1$).

x	% M(1)			% M (2)				
	$\text{Pb}^{2+}(1)$	$\text{Ca}^{2+}(1)$	$\text{Sr}^{2+}(1)$	$\text{Pb}^{2+}(2)$	$\text{Ca}^{2+}(2)$	$\text{Sr}^{2+}(2)$	Na^+	K^+
0	62.73	12.03	25.24	5.90	31.95	12.15	50.00	0.00
0.25	62.17	12.03	25.80	6.75	31.95	11.30	37.50	12.50
0.5	60.97	11.13	27.90	8.55	33.30	8.15	25.00	25.00
0.75	61.47	11.13	27.40	7.80	33.30	8.90	12.50	37.50
1	61.03	17.10	21.87	8.45	24.35	17.20	0.00	50.00

Fig.40 shows the variation in % occupancy of divalent cations at the two crystallographic sites. It can be seen that the majority of Pb^{2+} cations reside in size M(1), followed by Sr^{2+} cations. On the contrary, the majority of Ca^{2+} cations reside in the M(2) site.

According to $0 \leq x \leq 0.75$, when the percentage (%) occupancy of $Pb^{2+}(1)$ cations decreases, $Sr^{2+}(1)$ cations increase, and vice versa, as well $Ca^{2+}(1)$ cations decrease. Except for the $x=1$ extremity, where the cationic percentage of $Pb^{2+}(1)$ and $Sr^{2+}(1)$ decreases, on the contrary $Ca^{2+}(1)$ increases. The occupation results of the divalent cations in the site M(2), are inversely proportional to the case M(1). Indeed, according to $0 \leq x \leq 0.75$ when the cationic percentage of $Pb^{2+}(2)$ increases for $Sr^{2+}(2)$ is decreases and vice versa, and the cationic percentage of Ca^{2+} is increased. Except for the $x=1$ extremity, where the cationic percentage of $Pb^{2+}(2)$ and $Sr^{2+}(2)$ increases and the cationic percentage of $Ca^{2+}(2)$ are decreased.

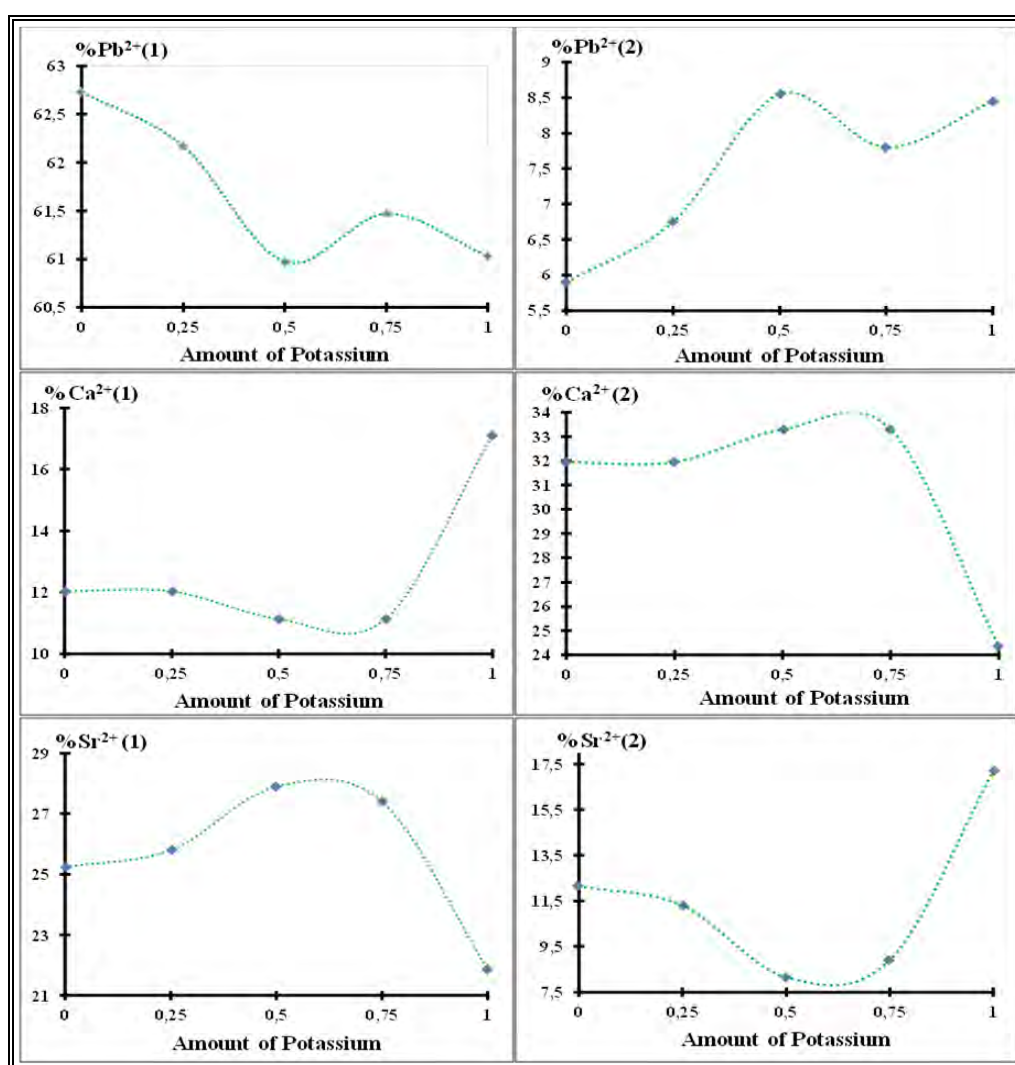


Fig.40: Variations % occupation of Pb^{2+} , Ca^{2+} and Sr^{2+} in the 6h and 4f sites as a function of the amount of potassium (x) in $Na_{1-x}K_xPb_2SrCa(PO_4)_3$; ($0 \leq x \leq 1$).

The interatomic distances and angles are reasonable; these are similar and agree well with those found previously. Where the ‘M(1)–O₆’ in the site (6h) distances vary from 2.202 Å to 2.974 Å for ‘Pb²⁺(1)/Ca²⁺(1)/Sr²⁺(1)–O₆’. ‘M(2)–O₉’ in the mixed site (4f), and from 2.502 Å to 2.893 Å for ‘Pb²⁺(2)/Ca²⁺(2)/Na⁺/K⁺–O₉’. ‘P–O’ is with an average value of 1.5 Å, and the ‘O–P–O’ angles are between 100.6° and 129.6°.

IV.2 Vibrational Spectra Analysis.

a) Infrared and Raman at Room-Temperature.

Figs.41&42 show the Infrared and Raman spectra results recorded at ambient conditions of $\text{Na}_{1-x}\text{K}_x\text{Pb}_2\text{SrCa}(\text{PO}_4)_3$, ($0 \leq x \leq 1$). The wavenumbers and the corresponding assignments are listed in Tables.21&22. The bands observed in the infrared and Raman spectra of these compounds do not differ significantly from those observed for previously apatite. A pattern of bands was observed in the 350-800cm⁻¹ region and is attributed to ‘O-P-O’ bending vibrations [V_2 (from 400cm⁻¹ to 500cm⁻¹) and V_4 (from 550cm⁻¹ to 600cm⁻¹)], and the series of high-frequency bands observed above 900 cm⁻¹ are assigned to ‘P-O’ stretching vibrations [V_1 (observed around 930cm⁻¹ and 955cm⁻¹ as a strong band in the Raman spectra and as shoulder in the IR spectra) and V_3 (from 960cm⁻¹ to 1150cm⁻¹)]. The lattice vibrations: ‘Pb²⁺/Ca²⁺/Cd²⁺/Na⁺/K⁺-O’. this mode is observed at frequencies below 300cm⁻¹.

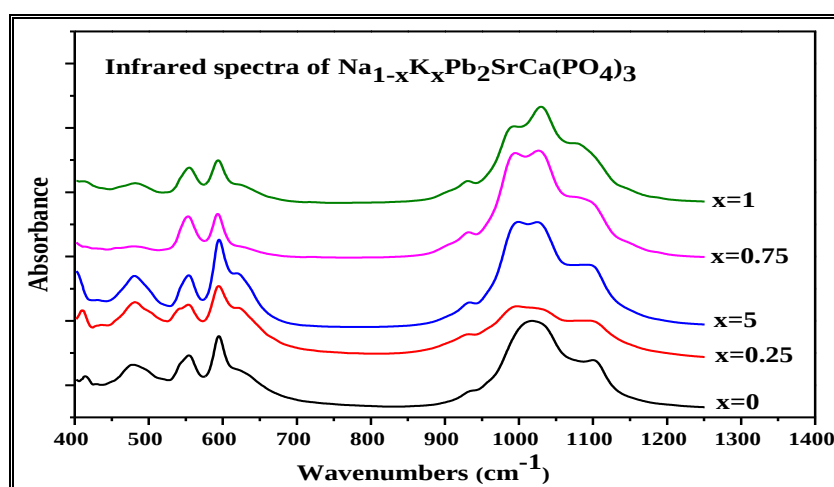


Fig.41: Infrared spectra of $\text{Na}_{1-x}\text{K}_x\text{Pb}_2\text{SrCa}(\text{PO}_4)_3$, recorded at ambient conditions.

Table.21: Assignments of observed Infrared bands of synthetics $\text{Na}_{1-x}\text{K}_x\text{Pb}_2\text{SrCa}(\text{PO}_4)_3$.

x	Bending modes				Stretching modes		
	V_2		V_4		V_1	V_3	
0	415.04(vm)	478.73(m)	555.38(m)	595.32(s)	937.54(sh)	1016.35(vs)	1101.63(vw)
0.25	410.72(vm)	480.89(m)	554.30(m)	593.16(s)	931.06(sh)	995.83(vs)	1099.47(vw)
0.50	433.39(vw)	480.89(m)	554.30(m)	595.32(s)	999.07(vs)	1027.14(vs)	1095.16(vw)
0.75	417.51(vw)	478.12(w)	553.05(s)	592.72(s)	995.83(s)	1027.14(vs)	1087.60(vw)
1	416.12(m)	481.97(vm)	554.30(m)	593.16(s)	990.44(sh)	1028.22(vs)	1080.04(vw)

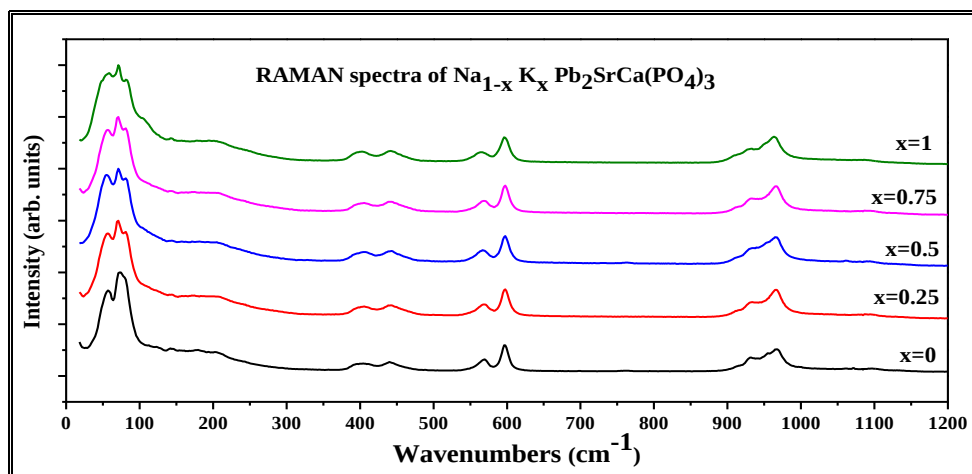


Fig.42: Raman spectra of $\text{Na}_{1-x}\text{K}_x\text{Pb}_2\text{SrCa}(\text{PO}_4)_3$, recorded at ambient conditions.

Table.22: Assignments of observed Raman bands of synthetics $\text{Na}_{1-x}\text{K}_x\text{Pb}_2\text{SrCa}(\text{PO}_4)_3$.

x	Lattice Modes								Bending modes				Stretching modes		
									V_2		V_4		V_1	V_3	
0	53.95(s)	75.47(vs)		122.74(w)	142.03(w)	157.89(vw)	176.05(vw)	193.43(vw)	402.01(m)	440.98(m)	566.66(m)	596.67(s)	934.60(m)	964.61(s)	1094.57(vw)
0.25	56.91(s)	70.74(vs)	81.41(sh)	123.81(w)	143.54(w)	157.53(vw)	174.03(vw)	183.36(vw)	405.50(m)	441.66(m)	568.48(m)	597.68(s)	932.82(m)	967.01(s)	1092.33(vw)
0.5	55.21(s)	70.82(vs)	81.38(sh)	124.67(w)	143.85(w)	157.51(vw)	171.80(vw)	192.66(vw)	406.65(m)	443.05(m)	566.89(m)	597.68(s)	933.19(m)	964.83(s)	1094.07(vw)
0.75	56.87(s)	70.86(vs)	81.42(sh)	125.44(w)	142.14(w)	155.66(vw)	177.86(vw)	193.01(vw)	404.35(m)	440.02(m)	567.96(m)	596.11(s)	929.48(m)	964.93(s)	1094.77(vw)
1	58.74(s)	70.95(vs)	81.41(sh)	125.44(w)	142.09(w)	157.47(vw)	177.65(vw)	194.20(vw)	402.37(m)	441.42(m)	565.06(m)	596.15(s)	931.60(m)	962.84(s)	1093.11(vw)

b) High-Temperature Raman Study of $\text{KPb}_2\text{SrCa}(\text{PO}_4)_3$.

The structural stability of the $\text{KPb}_2\text{SrCa}(\text{PO}_4)_3$ compound, is tested as a function of temperature. The experimental Raman spectra were collected in situ at room-pressure and elevated temperatures; up to 773K, the Raman spectra obtained at several temperatures are shown in Fig.43. The results obtained at several temperatures are presented in Table.23. Like the series presented previously, the temperature dependence of all lattice modes (Lattice, Bending, and Stretching modes), show a monotonous decrease in changes in wavenumbers while the temperature is increased.

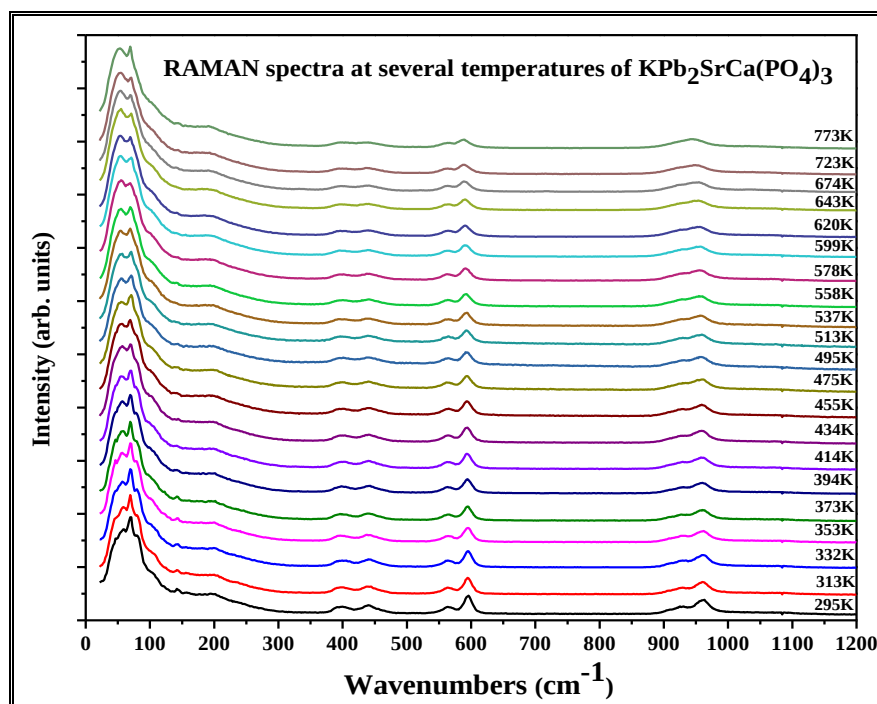


Fig.43: Raman spectra of $\text{KPb}_2\text{SrCa}(\text{PO}_4)_3$ obtained for selected temperatures as indicated.

Table.23: Assignments of observed Raman at several temperatures of $\text{KPb}_2\text{SrCa}(\text{PO}_4)_3$.

T(K)	Lattice Modes	Bending modes				Stretching modes		
		V_2		V_4		V_1	V_3	
295	59.55(s) 70.15(vs) 79.69(sh)	398.06(m)	440.91(m)	564.12(m)	596.15(s)	931(m)	963.64(s)	1092.46(vw)
313	59.44(s) 69.45(vs) 79.61(sh)	397.63(m)	440.62(m)	563.25(m)	595.85(s)	930.14(m)	962.77(s)	1090.9(vw)
332	57.77(s) 69.28(vs) 79.52(sh)	397.06(m)	440.48(m)	563.05(m)	595.28(s)	930.1(m)	961.91(s)	1088.73(vw)
353	56.27(s) 69.15(vs) 78.64(sh)	396.76(m)	439.75(m)	562.82(m)	595.2(s)	929.27(m)	961.44(s)	1088.7(vw)
373	56.17(s) 69.08(vs) 78.19(sh)	396.33(m)	439.18(m)	562.02(m)	594.42(s)	927.11(m)	961.37(s)	1086.57(vw)
394	56.01(s) 68.94(vs) 78.10(sh)	395.47(m)	438.75(m)	561.95(m)	593.98(s)	925.81(m)	960.61(s)	1086.14(vw)
414	55.42(s) 68.86(vs) 77.56(sh)	395.2(m)	437.88(m)	561.75(m)	593.12(s)	925.64(m)	959.74(s)	1085.27(vw)
434	55.31(s) 68.68(vs) 77.35(sh)	395.03(m)	437.32(m)	561.52(m)	593.02(s)	925.38(m)	959.31(s)	1084.84(vw)
455	54.81(s) 68.51(vs) 77.12(sh)	394.17(m)	437.15(m)	561.35(m)	592.72(s)	925.33(m)	959.27(s)	1083.54(vw)
475	54.62(s) 68.29(vs) 77(sh)	393.73(m)	436.15(m)	561.09(m)	592.12(s)	924.65(m)	958.44(s)	1083.5(vw)
495	54.42(s) 68.15(vs) 76.86(sh)	393.3(m)	436.05(m)	560.65(m)	591.82(s)	924.08(m)	957.71(s)	1082.24(vw)
513	54.14(s) 68.09(vs) 76.19(sh)	390.7(m)	435.29(m)	560.22(m)	591.62(s)	923.65(m)	957.14(s)	1081.81(vw)
537	53.84(s) 68.01(vs) 76.15(sh)	390.27(m)	434.85(m)	559.79(m)	590.52(s)	923.45(m)	956.28(s)	1081.37(vw)
558	53.63(s) 67.87(vs)	389.84(m)	433.56(m)	559.62(m)	590.35(s)	922.78(m)	955.98(s)	1080.94(vw)
578	53.62(s) 67.57(vs)	389.82(m)	433.42(m)	559.35(m)	590.09(s)	922.35(m)	955.41(s)	1079.21(vw)
599	53.53(s) 66.89(vs)	389.41(m)	433.12(m)	558.92(m)	589.22(s)	922.21(m)	954.55(s)	1078.78(vw)
620	53.44(s) 66.18(vs)	389.31(m)	433.08(m)	558.49(m)	588.79(s)	921.91(m)	952.38(s)	1077.91(vw)
643	53.32(s) 65.95(vs)	388.97(m)	432.69(m)	558.06(m)	588.6(s)	921.08(sh)	950.22(s)	1077.48(vw)
674	53.24(s) 65.84(vs)	388.11(m)	431.82(m)	557.49(m)	587.92(s)	919.92(sh)	948.92(s)	1077.05(vw)
723	53.14(s) 65.69(vs)	386.81(m)	431.26(m)	557.19(m)	587.06(s)	919.82(sh)	947.62(s)	1076.61(vw)
773	53.05(s) 64.98(vs)	386.57(m)	430.82(m)	555.89(m)	585.33(s)	919.08(sh)	944.16(s)	1076.18(vw)

Fig.44 presents the variation of the fundamental frequencies of the different modes (Lattice, Bending and Stretching modes) for $\text{KPb}_2\text{SrCa}(\text{PO}_4)_3$ as a function of temperature. Shows a linear large decrease in wavenumbers with the increase of temperature. No considerable changes in the temperature dependence of the modes and the corresponding intensity are observed and thus no temperature-induced phase transition is observed in $\text{Na}_{1-x}\text{K}_x\text{Pb}_2\text{SrCa}(\text{PO}_4)_3$ in the temperature range studied here.

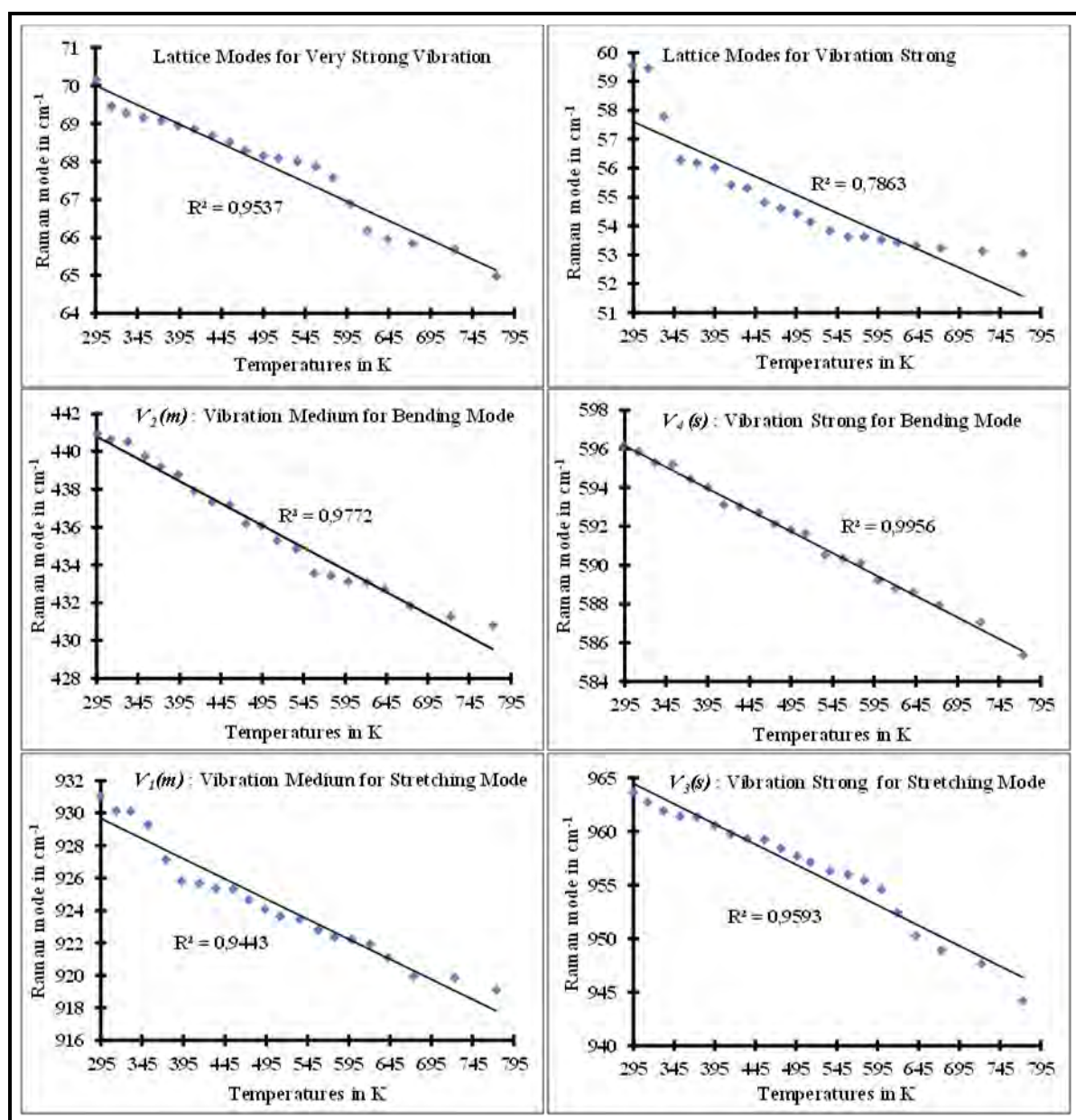


Fig.44: Variation of the fundamental frequencies of the different modes (Lattice, Bending and Stretching modes) for $\text{KPb}_2\text{SrCa}(\text{PO}_4)_3$ as a function of temperature.

IV.3. Optoelectronic Properties.

The solid UV-visible/far-ultraviolet spectra of the compound's series described in $\text{Na}_{1-x}\text{K}_x\text{Pb}_2\text{CaCd}(\text{PO}_4)_3$ ($0 \leq x \leq 1$) were measured in the range 250nm to 800nm at room temperature. Fig.45 shows the converted reflectance data to absorbance using the Kubelka-Munk $\{F(R)\}$, a function that will be used in the optical band calculation $\{E_g\}$. To Experimentally, to determine the optical band gap $\{E_g\}$, we can plot $[F(R)*hv]^{1/2}$ versus the photon energy (hv) using the data obtained from the optical absorption spectra. It reveals that the obtained two plots give two straight lines in the region $\{hv\}$ between 3-4.5eV (for example in Chapter. I show the Bandgap Energies (eV) determined by OriginPro® software at 3.1516eV and 4.0882eV for $\text{NaPb}_2\text{SrCa}(\text{PO}_4)_3$).

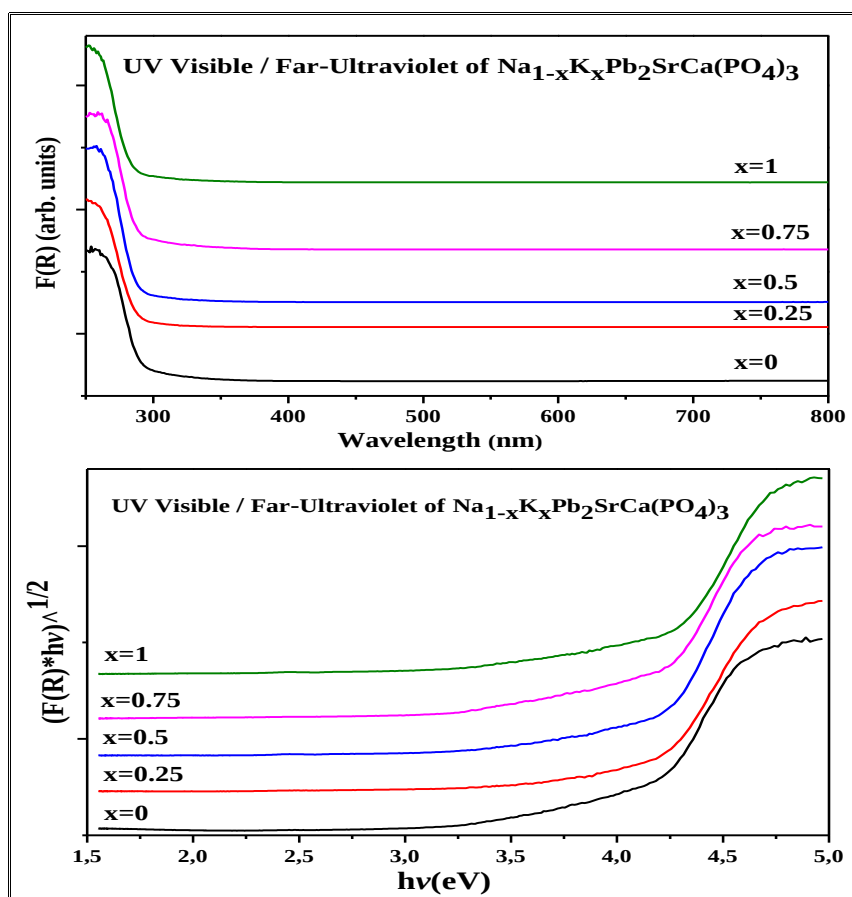


Fig.45: $F(R)$ and $[F(R)*hv]^{1/2}$ for $\text{Na}_{1-x}\text{K}_x\text{Pb}_2\text{SrCa}(\text{PO}_4)_3$ lacunar apatites, respectively depending upon the optical absorption and the incident photon energy (hv).

The values of the indirectly allowed energy gap for Gap(1) and Gap(2), of the crystal structure of apatites $Na_{1-x}K_xPb_2SrCa(PO_4)_3$ ($0 \leq x \leq 1$) depending on the effect by potassium substitution as a function of (x) are tabulated in Table.24. The wavelength values corresponding to the maximum absorbance of the compounds as a function of (x) are λ_{Max} , also presented in the same Table.24. This condition allows working at the highest absorption sensitivity of the deficient materials (for example of sample $NaPb_2SrCa(PO_4)_3$, the results of calculations of $F(R)$ and $[F(R)*hv]^{1/2}$ depending on the wavelength (λ), ' hv ' and the diffuse reflectance are shown in Annex. II; Table. II.5).

Table.24: Lamda Max of peaks absorption in the UV-Visible and the calculated optical indirect allowed energy gap using Tauc's relationship of the series $Na_{1-x}K_xPb_2SrCa(PO_4)_3$.

x		0	0.25	0.5	0.75	1
Lambda Max (nm)	λ_{Max}	254	256	257	258	259
Band-Gap Energy (eV)	Gap(1)	4.0882	4.1538	4.1639	4.1888	4.2156
	Gap(2)	3.1516	3.2829	3.3045	3.3122	3.3429

Fig.46 shows the variation of the wavelength of Lamda Max absorbance and the Bandgap Energies, as a function of (x) in $Na_{1-x}K_xPb_2SrCa(PO_4)_3$. We noted that once sodium is substituted by potassium, the wavelength of Lamda Max is towards the higher values of the right-hand side, according to (x). The Bandgap Energies shift towards upper values once the sodium is substituted by potassium (x). These variations are proportional to the parameters of cellular materials.

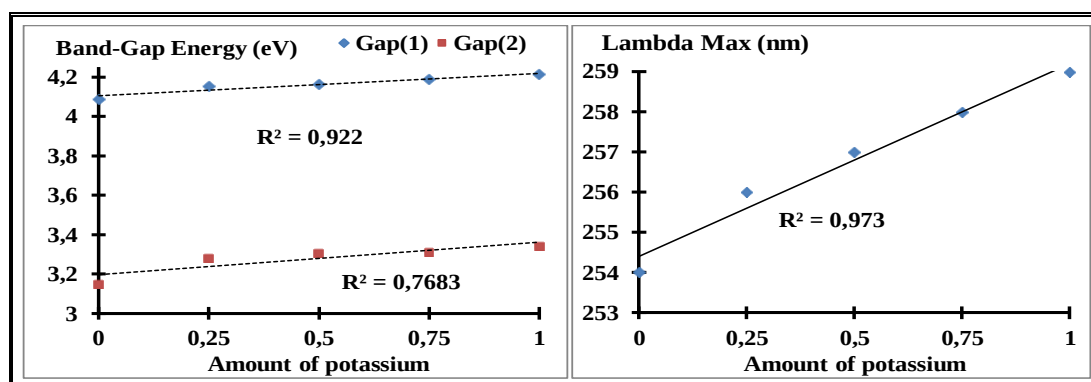


Fig.46: The effect of Potassium substitution depending on the wavelengths for Lamda Max absorption shift, and the Band-Gap Energy as a function of x for $Na_{1-x}K_xPb_2SrCa(PO_4)_3$.

V. Conclusion.

The solid Specimens $\text{Na}_{1-x}\text{K}_x\text{Pb}_{4-y/2}\{\text{Sr}/\text{Ca}/\text{Cd}\}_y(\text{PO}_4)_3$ ($0 \leq x \leq 1$) and ($0 \leq y \leq 1.5$), in the system of $\text{Na}_2\text{O}-\text{K}_2\text{O}-\{\text{Sr}/\text{Ca}/\text{Cd}\}\text{O}-\text{PbO}-\text{P}_2\text{O}_5$, were successfully synthesized using a solid-state chemical reaction. The solid solutions were characterized by X-ray diffraction, Raman and infrared spectroscopies as well as UV-vis spectroscopy. Using the Rietveld refinements method we showed that this solid solution is continuous and adopts ***P6₃/m*** as a space group. The site, of the metal ions in the solid solutions, was also analyzed by the Rietveld method.

The lattice constants of the crystal structure of apatites $\text{Na}_{1-x}\text{K}_x\text{Pb}_{4-y/2}\{\text{Sr}/\text{Ca}/\text{Cd}\}_y(\text{PO}_4)_3$ depending on the effect of {Strontium/Calcium/Cadmium} and of potassium substitutions as a function of x & y , are discussed. The lattice constants of the solid solutions varied linearly with (x) and with (y). It was found that $\{\text{Sr}/\text{Ca}/\text{Cd}\}^{2+}(1)$ and $\text{Pb}^{2+}(1)$ ions occupied M (1), and $\text{Pb}^{2+}(2)/\{\text{Sr}/\text{Ca}\}^{2+}(2)/\text{Na}^+/\text{K}^+$ occupied the M(2) sites. The structure was described as built up of $[\text{PO}_4]^{3-}$ tetrahedra and M (1) of sixfold coordination cavities (6h positions), which delimit void hexagonal tunnels running along (0 0 1). The tunnels are connected by cations of mixed sites (4f) half occupied by $\text{Pb}^{2+}(2)/\{\text{Sr}/\text{Ca}\}^{2+}$ and a half by Na^+/K^+ mixed alkali cations.

The results of vibrational spectroscopy were in good agreements with the XRD measurement. The assignment of internal modes of $(\text{PO}_4)^{3-}$ tetrahedra have been made. Raman and Infrared spectra of all the compositions are similar and show some shifts of the wavenumbers as a function x & y , due to the substitution of Na^+ by K^+ and of Pb^{2+} by Sr^{2+} , Ca^{2+} , and Cd^{2+} with a larger or small radius resulting in an increase or decrease of the unit cell parameters. However, the observed Infrared and Raman modes can be classified into two for IR and three for RAMAN. These general families of lattice vibrations; Lattice Mode (M(2)-O₉ and M(1)-O₆), are observed at frequencies below 300cm^{-1} , as well as translational and rotational modes of $[\text{PO}_4]^{3-}$ tetrahedra, greater than of 400cm^{-1} . No considerable changes in

the temperature dependence of the Raman modes and the corresponding intensity are observed and thus no temperature-induced phase transition is observed up to 773K.

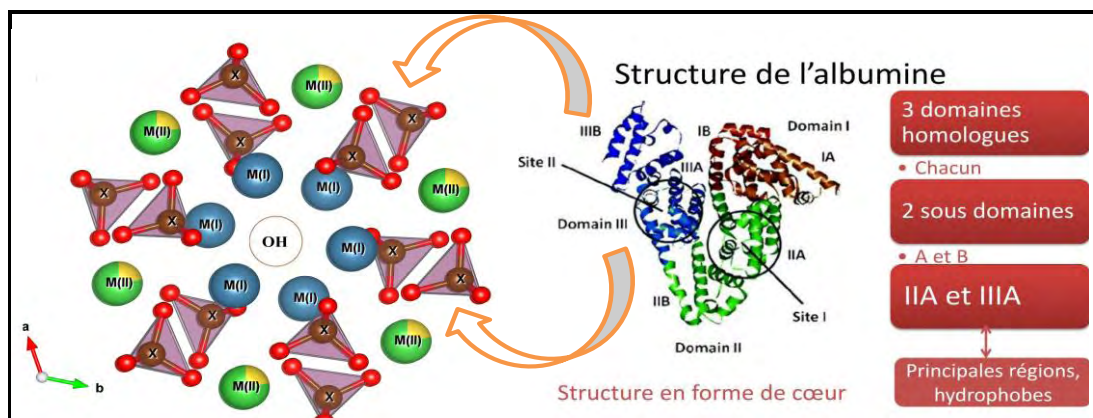
The lacunar apatite is composed of an optical material exhibiting light transmission characteristics in the far-ultraviolet region. The electrical properties of the lacunar apatite confirmed that the field-effect mobility decreased or increase with increasing concentration for K^+ ($0 \leq x \leq 1$) and $\{Sr/Ca/Cd\}^{2+}$ ($0 \leq y \leq 1.5$), indicating that K^+/Na^+ and $Pb^{2+}/\{Sr/Ca/Cd\}^{2+}$ was indeed acting as a carrier suppressor through reducing or increasing the number of oxygen donor in the apatitic system.

Chapter. III: Adsorption of Bovin Serum Albumin Protein by Synthetic Apatites and Structural Properties of Hydroxy- and New Lacunar Apatites.

Abstract;

Design of novel phosphorus apatites, $K_2Pb_6Zn_2(PO_4)_6$ and $K_2Pb_4Ca_4(PO_4)_6$, zinc hydroxyapatite $Ca_8Zn_2(PO_4)_6(OH)_2$, as well as hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$, and its corresponding calcined powder were conducted using two different synthesis protocols, i.e. solid-state and wet chemical methods. The prepared materials adopt $P6_3/m$ (No 176) as a space group. Structural refinements for $K_2Pb_6Zn_2(PO_4)_6$ and $K_2Pb_4Ca_4(PO_4)_6$ lacunar apatites, and that for the calcined hydroxyapatite, were performed using the Rietveld method. For $K_2Pb_6Zn_2(PO_4)_6$, the refinement results showed that the majority of Pb^{2+} cations occupy (6h) sites.

This study examines the impact of the synthesis conditions on the Physico-chemical properties and the surface reactivity of the prepared materials. The analysis of the interactions of the samples concerning a protein model (Bovin Serum Albumin), evaluated under the same experimental conditions, revealed a fast-kinetic process for the precipitated samples, compared to the crystals obtained by solid chemical reaction (Abstract Fig. III Style). Thus, the equilibrium conditions were reached in less than 20min for the former while 6hours of contact were requested for the latter. However, all the obtained isotherms show a Langmuirian shape. The difference in the adsorption parameters of the materials, i.e. constant affinity and amount adsorbed at saturation, is discussed in terms of surface characteristics, chemical composition, crystals size, and specific surface area. It is concluded that the interaction with the Bovin Serum Albumin (BSA) molecules is highly sensitive to the microstructure of the crystals.



Abstract Fig. III Style: The Structures of Bovine Serum Albumin BSA and Apatite $M_{10}(\{XO_4\}_5(OH))$.

I. Introduction.

Apatites materials are very abundant in nature and living organisms, that is why researchers have reported on their design, structure, chemical composition doping and surface properties [1-3]. The intrinsic characteristics of apatites compounds allow them to have a wide range of applications in various fields and these can be controlled by adapting the synthesis conditions. That fact is the main motivation of the present work, which deals with the structural characterization of lacunar lead phosphate apatites of potassium without anions $\{K_2Pb_4Ca_4(PO_4)_6$ and $K_2Pb_6Zn_2(PO_4)_6$ respectively labelled; Ap-Ca and Ap-Zn} and a calcium zinc hydroxyapatite $\{Ca_8Zn_2(PO_4)_6(OH)_2$ labelled; Zn-HA}, together with the reference hydroxyapatite $\{Ca_{10}(PO_4)_6(OH)_2$ labelled; HA and HA₉₀₀}. The specimens were prepared by solid-state reaction and by aqueous solution precipitation to examine the effect of the synthesis routes on the final structural and microstructural properties of phosphorus apatites as well as their surface reactivity concerning a biological medium.

Studying the interaction between proteins and calcium phosphate implants is one of the basic subjects in biomaterials science and engineering. Extensive research has focused on the adsorption of proteins by various calcium phosphates during the last two decades. The interaction between macromolecules and hydroxyapatite has received special attention because of the physicochemical properties of this material, which is similar to bone mineral, as well as its biocompatibility, osteoconduction, and biosorption properties [4,5]. Calcium phosphates, especially apatites, are widely used for chromatographic purposes [6,7] and are suitable for several biomedical applications, e.g., artificial bone and roofs of teeth as well as a carrier for drug delivery [8–10].

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Biological apatites are exposed to the numerous proteins present in body fluids (bone mineral) or saliva (tooth enamel). Because of the complex structure and the heterogeneity of natural systems, synthetic apatites are generally used to throw light on the surface reactivity of bone mineral. Despite the wealth of information in the literature on the adsorptive properties of well-crystallized apatites [11–15], investigations of the surface reactivity of poorly crystalline calcium phosphates, the major constituent of mineralized tissues of vertebrates, are scarce [16,17]. The present work reports on the changes of crystallinity and composition of poorly crystalline apatites upon maturation as well as their consequences on the adsorptive properties of these materials. This study may contribute to a further understanding of the relative importance of nonapatitic environments in the behaviour of proteins at the bone surface and several biological processes. To acquire knowledge of protein interaction, it is necessary to study well-defined model proteins as well as characterized adsorbents. For this purpose, bovine serum albumin (BSA), the main blood protein and one of the most important components of saliva [18], has been taken as an adsorbate.

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The targeted apatite specimens were synthesized under fixed conditions to evaluate the role of the physicochemical factors on their structural and surface properties, for a detailed synthesis of the apatite materials see [Chapter. I](#) in reactions N°6&7&8&9 and 10. The structural characterization of the prepared specimens was carried out by X-ray powder diffraction, infrared spectroscopy, and chemical analyses, while the surface area of the crystals was determined by the {BET} method.

II. Materials and Methods.

II.1. Physico-Chemical Characterization.

The structural refinements of the final products (Ap-Ca, Ap-Zn, HA, HA₉₀₀, and Zn-HA) were undertaken using the powder data. Diffraction data were collected at room temperature on a D2 PHASER diffractometer, having the Bragg-Brentano geometry, see page 74. Rietveld's profile analysis method was employed for refinements using the FULLPROF program [19]. The infrared spectra were recorded over the 400-4000cm⁻¹ range using a Perkin Elmer frontier Fourier-transform infrared (FTIR) spectrometer. The surface-specific area (SSA) of the crystals was determined by the BET method, using N₂ adsorption (Micromeritics Gemini VII 1014 Instrument). The concentration of calcium-zinc ions and phosphate species in the hydroxyapatites obtained by the wet method (HA, HA₉₀₀, and Zn-HA) were determined, respectively, by complexometry with EDTA and spectrophotometry using the phosphovanadomolybdic complex at $\lambda = 460\text{nm}$ [20]. The content of the elements in the samples obtained by the dry method (Ap-Ca and Ap-Zn) was determined using the refinement of the occupation parameters. For more details of equipment, see [Chapter. I](#).

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Bovine Serum Albumin (BSA) was purchased from Sigma (fraction V powder). This protein exhibits a molecular weight of 67000, a size of 11.6x2.7x2.7nm, and has an isoelectric point around 4.7 [21].

II.2. Adsorption experiments.

The adsorption experiments are carried out in the laboratory LPCME, Marrakech, in collaboration with the CIAM and MSN, Benguerir departments.

The interaction of the protein with the apatite samples was carried out at room temperature (25 ± 1 °C) by dispersing the adsorbent (25mg) into 5mL of the adsorption solution in a polyethene tube. The adsorbate was dissolved in 1mM potassium nitrate solution with a concentration varying from 0 to 3.5mg/mL. The pH of the prepared solutions was adjusted to a value close to 7.4 by adding potassium hydroxide and hydrochloric acid. After sonication for 1-2min, the suspensions were incubated for a period of 2h to 8h without stirring and centrifuged for 10min at 4000rpm. This equilibration time was previously determined from kinetic experiments using BSA concentrations of 2.5mg/ml. Blanks without apatite solid, containing only the protein, were incubated similarly to the adsorption tests and used as control.

The resulting supernatants were filtered through Millipore filters (pore size 0.2 μ m) and the BSA concentration in the filtrates was determined using UV spectrophotometric absorption at $\lambda=280$ nm (BECKMAN type 24 with dual-beam), that corresponds to the maximum absorbance of the BSA molecules. The calibration curve ranged from 0 to 2 mg/mL. The molar absorption coefficient deduced from all calibration curves was 0.66 ± 0.02 L.g⁻¹.cm⁻¹ at pH 7.4. This value is close to that reported (0.65 ± 0.04 .L.g⁻¹.cm⁻¹ at pH 7) in the literature [21].

[21] S. Ouizat, A. Barroug, A. Legrouiri, C. Rey, Adsorption of bovine serum albumin on poorly crystalline apatite: influence of maturation, Mater. Res. Bull. 34 (1999) 2279 -2289. doi:10.1016/S0025-5408(00)00167-7.

The quantity of BSA adsorbed Q (mg/g) was then determined following the relationship: $Q = (C_i - C_e) \cdot V / W$. where C_i and C_e (mg/L) are BSA solution concentration at initial and equilibrium time, V (L) is the volume of the solution in contact with W (g) of apatite. The reproducibility of the adsorbed BSA, as the average of 3 measurements, is 7 %.

III. Results and Discussion.

III.1. X-ray Diffraction Study.

Fig.1 shows the X-ray powder diffraction patterns of the synthesized apatites, that are comparable to those reported earlier [23,3]. Indexing of the X-ray powder patterns was performed using the software DICVOL [23]. The first 20 peak positions, with a maximal absolute error of $0.03^\circ(2\theta)$, were used as input data. The data were calibrated externally using the zero shift of the Rietveld refinement. All the found compositions were assigned to a hexagonal apatite structure.

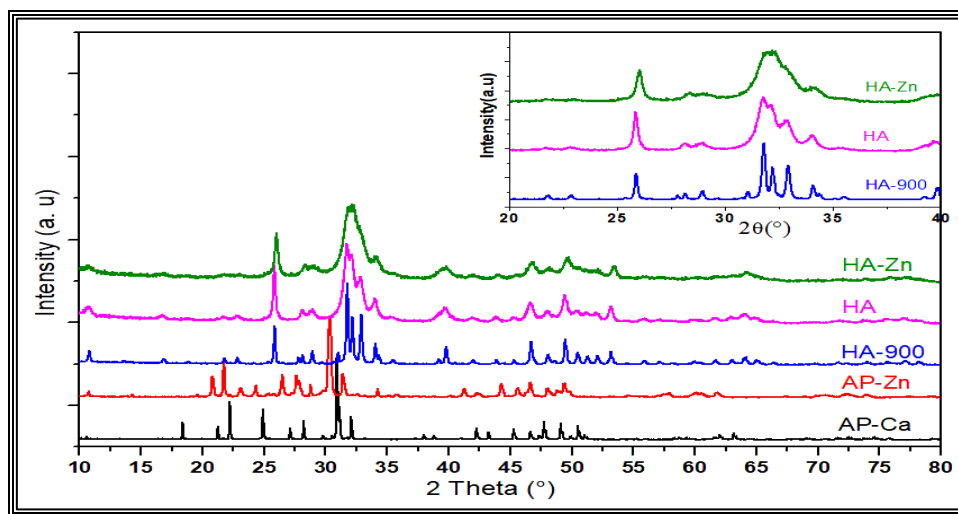


Fig.1: X-ray powder diffraction patterns of the synthesized apatites Ap-Ca, Ap-Zn, HA, HA₉₀₀, and Zn-HA. The inset shows a comparison of the crystallinity in the hydroxyapatites prepared under different conditions.

[22] M. Azrour, M. Azdouz, B. Manoun, R. Essehli, S. Benmokhtar, L. Bih, L. El Ammari, A. Ezzahi, A. Ider, A.A. Hou, Rietveld refinements and vibrational spectroscopic studies of $Na_{1-x}K_xPb_4(PO_4)_3$ lacunar apatites ($0 \leq x \leq 1$), J. Phys. Chem. Solids. 72.

[23] A. Boultif, D. Loueer, D. Louër, Indexing of powder diffraction patterns for low-symmetry lattices by the successive dichotomy method, J. Appl. Crystallogr. 24 (1991) 987–993. doi:10.1107/S0021889891006441.

The diffraction peaks of the precipitated calcium phosphate powders are typical of hydroxyapatites. As can be seen in Fig.1, the peaks of the calcined sample (HA₉₀₀) are sharper and more defined which reflect a well-crystallized apatitic phase. The pattern indicates the presence of a small quantity of beta-Tricalcium phosphate (less than 5%), due to the slight calcium deficiency of the reference HA. The calcination of the powder HA results in a significant increase in the intensity of peaks and a decrease in the width compared to the phase HA. However, an opposite tendency occurred upon substitution of calcium ions by zinc species in the lattice of the mother sample HA.

The unit cell parameters obtained for the prepared compositions (Ap-Ca, Ap-Zn, HA, HA₉₀₀, and Zn-HA) are given in Table.1 and they are close to those reported in the literature [24,25]. The unit cell parameters of the lacunar apatites (Ap-Ca and Ap-Zn) are much bigger than those of the precipitated samples (HA, HA₉₀₀, and Zn-HA); this fact can be simply explained by the size of the lead, and potassium atoms which have bigger radii compared to that of calcium species.

Table.1: Main characteristics of the prepared apatites: structural parameters, chemical composition, crystals size, and specific surface area.

Sample	Unit cell parameters		Volume (Å ³)	Me/P (± 0.02)	Crystals Dimension (nm)		SSA (m ² /g) (± 3 %)
	a(Å)	c (Å)			Length	Width	
HA ₉₀₀	9.435	6.890	531.12	1.67	54.2	42.2	8.00
HA	9.419	6.875	528.22	1.65	36.9	9.9	79.00
Zn-HA	9.431	6.853	527.89	1.66	27.6	7.6	120.00
Ap-Ca	9.671	7.159	579.89	1.67	117.0	126.4	0.69
Ap-Zn	9.853	7.319	615.40	1.67	62.6	-	0.62

Me: Ca or (Ca +Zn)

[24] S. Lahrich, B. Manoun, M.A. El Mhammedi, Synthesis, characterization and electrochemical investigation of NaPb_{4-x}Cax(PO₄)₃ (0 ≤ x ≤ 1.5) in capturing cadmium (II), South African J. Chem. Eng. 23 (2017) 98–106. doi:10.1016/J.SAJCE.2017.04.001.

[25] C. Rey, C. Combes, C. Drouet, D. Grossin, G. Bertrand, J. Soulié, Bioactive Calcium Phosphate Compounds: Physical Chemistry, in P. Ducheyne (Ed), Comprehensive Biomaterials II, Elsevier, Oxford, 2017, pp. 244–290. doi:10.1016/B978-0-12-803581-8.10171-7.

The mean crystallite size derived from Scherrer's formula applied to the apatitic diffraction lines (002) and (310) was calculated, after deconvolution of the peaks (λ_{ka_1} and λ_{ka_2}) (Table.1), for more details see Annex. III, Table. III.1. The values of the crystals length (L_{002}) and width (L_{310}) obtained for the specimen HA are respectively 36.9 nm and 9.9 nm. Substituting calcium with zinc in the apatite lattice slightly decreases the crystallite dimensions (27.6nm and 7.6nm). However, an increase in crystallite sizes (54.2nm and 42.2nm) was observed for the sample 'HA' calcined at 900°C, in good agreement with the evolution of the XRD patterns. A comparison of the length and the width values suggests that the precipitated crystals are elongated along the axis ($L_{(002)} > L_{(310)}$). A similar tendency was observed for compounds synthesized in similar conditions [26,27]. Contrarily, the lacunar apatites prepared by the dry method reveal a different behaviour: the specimen Ap-Ca exhibits high values as well as an anisotropic attitude concerning the crystallite dimensions ($L_{(002)} = 117.0\text{nm}$ and $L_{(310)} = 126.4\text{nm}$). Besides, an important drop in the length of the crystal (62.6nm) happened when zinc species were incorporated in the apatite lattice.

The structural refinements were done using the Rietveld method with the Fullprof program integrated into WINPLOTR software [23,28]. The starting model for Rietveld refinement was taken from [24]. 40 structural and non-structural parameters were allowed to vary to adjust the refinement. Fig.2(A)&(B) shows the Rietveld refinement patterns for (A) $K_2Pb_4Ca_4(PO_4)_6$ and of the calcined hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), for (B) $K_2Pb_4Zn_4(PO_4)_6$.

[26] F. Errassifi, S. Sarda, A. Barroug, A. Legrouri, H. Sfihi, C. Rey, Infrared, Raman and NMR investigations of risedronate adsorption on nanocrystalline apatites, J. Colloid Interface Sci. 420 (2014) 101–111. doi:10.1016/j.jcis.2014.01.017.

[27] J. Gómez-Morales, M. Iafisco, J.M. Delgado-López, S. Sarda, C. Drouet, Progress on the preparation of nanocrystalline apatites and surface characterization: Overview of fundamental and applied aspects, Prog. Cryst. Growth Charact. Mater. 59 (2013) 1–46. doi:10.1016/J.PCRYSGROW.2012.11.001.

[28] T. Roisnel, J. Rodríguez-Carvajal, WinPLOTR: A Windows Tool for Powder Diffraction Pattern Analysis, Mater. Sci. Forum. 378–381 (2001) 118–123. doi:10.4028/www.scientific.net/MSF.378-381.118.

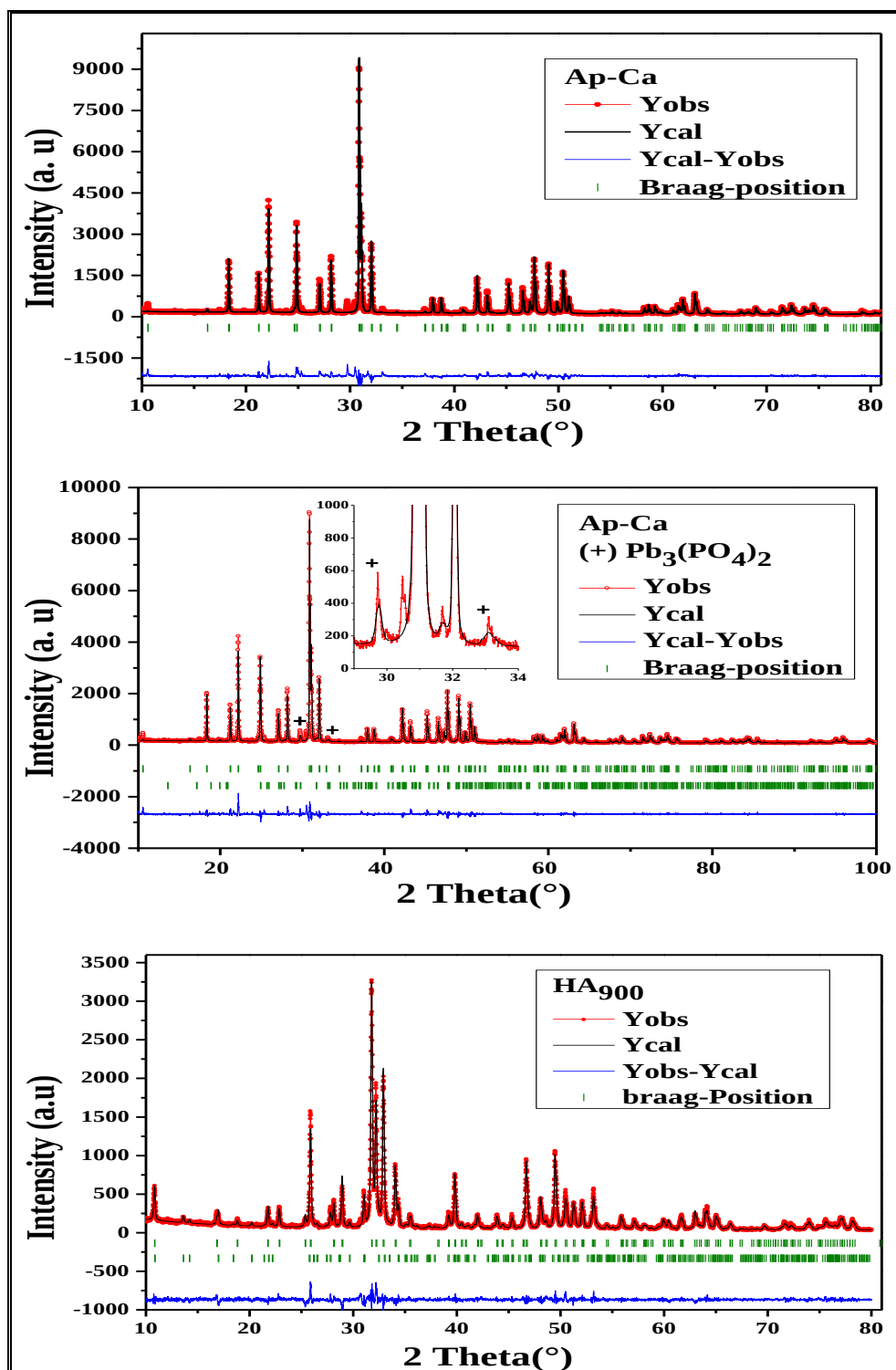


Fig.2(A): Final Rietveld plot of lacunar apatite $Ap-Ca \{K_2Pb_4Ca_4(PO_4)_6 \text{ and } Pb_3(PO_4)_2\}$ and calcined hydroxyapatite $HA_{900} (Ca_{10}(PO_4)_6(OH)_2)$. The solid line with dots illustrates the observed data and the calculated pattern (solid line). The vertical markers show calculated positions of Bragg reflections. The lower curve is the difference diagram.

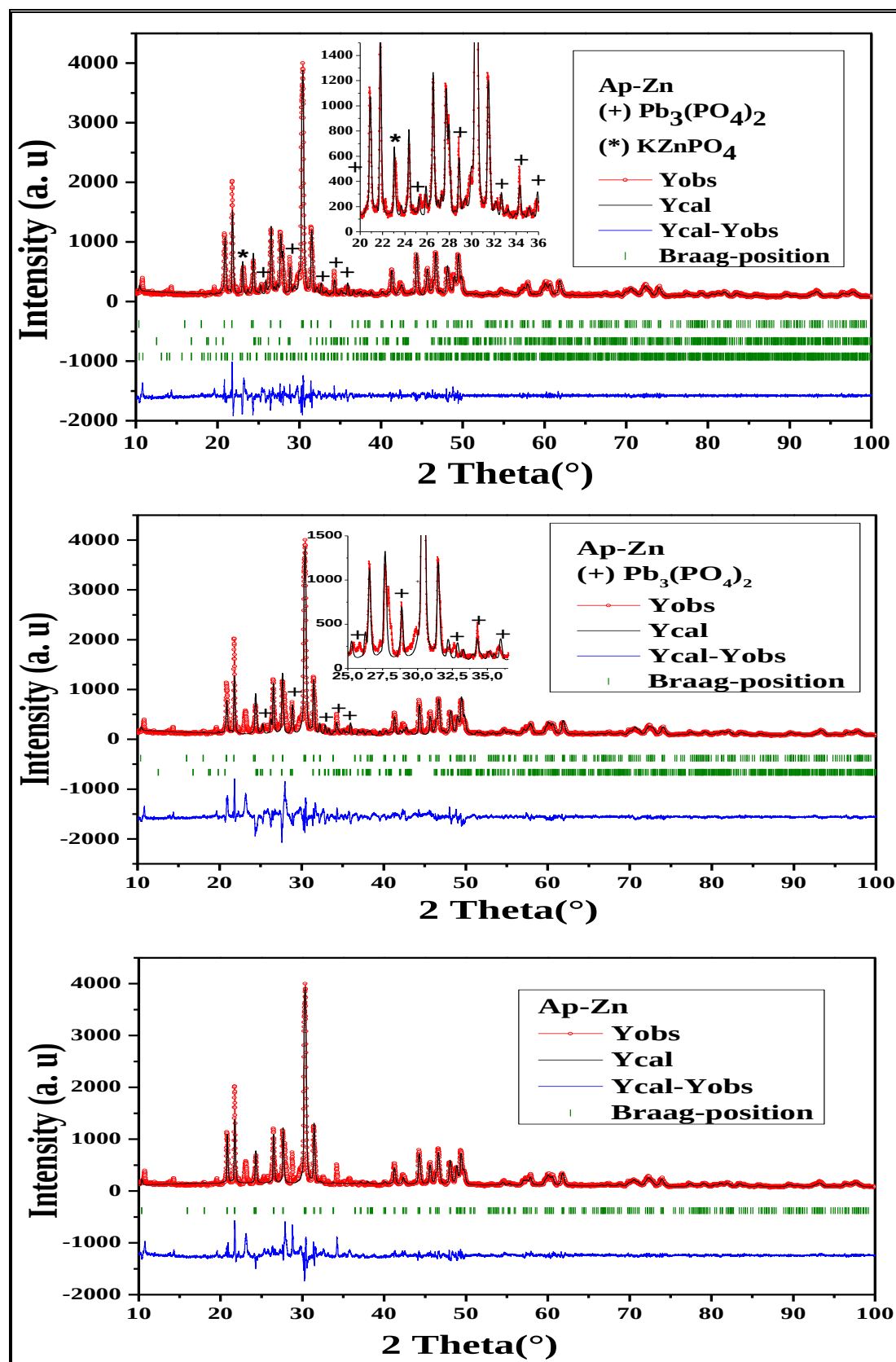


Fig.2(B): Final Rietveld plot of lacunar apatite Ap-Zn ($K_2Pb_4Zn_4(PO_4)_6$), $Pb_3(PO_4)_2$ and $KZnPO_4$.

The structural parameters and their estimated standard deviations for $K_2Pb_4Ca_4(PO_4)_6$, and $K_2Pb_6Zn_2(PO_4)_6$ are given in Table.2; a list of selected bond lengths and angles is given in Annex. III, Table. III.2.

Table.2: Crystallographic characteristics obtained from Rietveld refinements of lacunar apatite Ap-Ca, Ap-Zn, and calcined hydroxyapatite HA₉₀₀.

	Site	x	y	z	Occupancy
Formula	$K_2Pb_4Ca_4(PO_4)_6$				
Lattice parameters	Space group: $P 6_3/m$ a (Å) = 9.67104(13), c (Å) = 7.15931(10), V (Å³) = 579.89(1)				
R-Factors	%R_F = 3.66, %R_B = 5.83, χ = 3.25				
Pb(1)/Ca(1)	6h	0.2563(2)	0.2566(2)	0.25	1.81/1.19
Pb(2)/Ca(2)/K	4f	0.6667	0.3333	0.4995(11)	0.19/0.81/1
P	6h	0.3771(12)	0.4089(10)	0.75	3
O(1)	6h	0.4954(13)	0.3476(13)	0.75	3
O(2)	12i	0.2681(12)	0.3576(9)	0.5708(11)	6
O(3)	6h	0.4910(15)	0.5914(16)	0.75	3
Formula	$K_2Pb_6Zn_2(PO_4)_6$				
Lattice parameters	Space group: $P 6_3/m$ a (Å) = 9.85313(61) c (Å) = 7.31939(53), V (Å³) = 615.395(70)				
R-Factors	%R_F = 1.81, %R_B = 3.99, χ = 4.50				
Pb(1)/Zn(1)	6h	0.2517(39)	0.2499(12)	0.25	2.058/0.942
Pb(2)/Zn(2)/K	4f	0.66667	0.33333	0.5145(18)	0.942/0.058/1
P	6h	0.3763(12)	0.4083(18)	0.75	3
O(1)	6h	0.4765(11)	0.3276(13)	0.75	3
O(2)	12i	0.2734(10)	0.3680(15)	0.5756(24)	6
O(3)	6h	0.4763(21)	0.5841(15)	0.75	3
Formula	$Ca_{10}(PO_4)_6(OH)_2$				
Lattice parameters	Space group: $P 6_3/m$ a (Å) = 9.42281 (36) c (Å) = 6.88275 (28), V (Å³) = 529.241(36)				
R-Factors	%R_F = 2.5, %R_B = 4.68, χ = 1.86				
Ca₁	4f	0.33333	0.66667	0	4
Ca₂	6h	0.25	0	0.25	6
P	6h	0.3913(31)	0.3740(31)	0.25	6
O(1)	6h	0.3352(60)	0.5	0.25	6
O(2)	6h	0.5780(71)	0.4566(66)	0.25	6
O(3)	12i	0.3333	0.25	0.0733(58)	12
O(4)	2a	0.0000	0.0000	0.25000	2

The $P6_3/m$ space group was adopted by the lacunar apatites (Ap-Ca, Ap-Zn) as well as the calcined hydroxyapatite (HA₉₀₀). As an example, the structure of $K_2Pb_6Zn_2(PO_4)_6$ is built up from $[PO_4]^{3-}$ tetrahedra and $Pb(1)^{2+}/Zn(1)^{2+}$ of sixfold coordination cavities (6h positions) creating tunnels along the c-axis. The tunnels are connected by cations of mixed sites (4f), half occupied by $Pb(2)^{2+}/Zn(2)^{2+}$, and half by K^+ alkali cations. Fig.3 shows a structural view

comparing the lacunar apatite (Ap-Zn) and the calcined hydroxyapatite (HA_{900}). While the tunnels are empty along the c-axis for Ap-Zn, they are fully occupied by the anions OH^- in HA_{900} .

The $Pb^{2+}(2)/Zn^{2+}(2)/K^+-O$ bonds in the mixed site Me(4f) are ionic, the average distances of Me(2)-O₉ vary from 2.581 to 2.679Å. $Pb^{2+}(1)/Zn^{2+}(1)-O$ in the mixed site Me(6h) shows a more covalent character and the average distances of Me(1)-O₆, varies from 2.23 to 2.79Å (Annex. III, Table. III.2), this can be explained by the distorting effect of the lone pair $6s^2$ of lead cations are studied in electron densities.

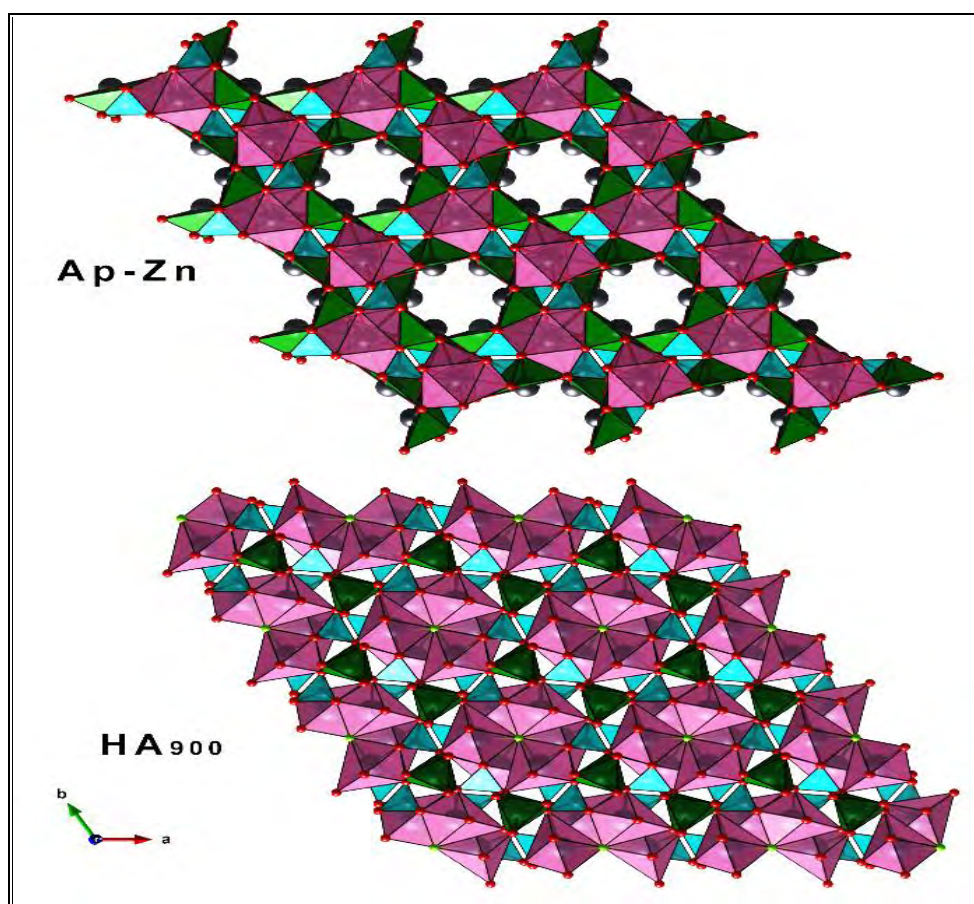


Fig.3: Polyhedral view in the *ab*-plane of the crystal structure of lacunar apatite Ap-Zn and calcined hydroxyapatite HA_{900} . The large tunnel in the case of the lacunar specimen illustrates the metal and oxygen arrangement around (6h) sites connected to the $5[PO_4]^{3-}$ tetrahedra. In the case of simple HA_{900} , this tunnel is occupied by OH^- anions.

The small tunnel (mixed site Me(2)) is occupied half by K^+ and half by $Pb^{2+}(2)/Zn^{2+}(2)$ cations forming $(K/Pb/Zn)O_9$ polyhedra. Each polyhedron is linked to $3[PO_4]^{3-}$ tetrahedra via corners and three others via edges (Fig.3). The bigger tunnel on the other side is surrounded by lead-zinc cations Me(1). These cations are inserted into six-fold sites that constitute the walls of the tunnels; each polyhedron is linked to $4[PO_4]^{3-}$ tetrahedra via corners and to one $[PO_4]^{3-}$ via edge. Mathew et al. [29] and Engel et al. [30] showed that the stabilization of the structural apatite seems to be directly related to the presence of a minimum electronic density within its large tunnels. In the normal apatites these negative charges could be provided by the Y- (F^- , Cl^- , OH^-) anions that occupy the large tunnels encompassing 6_3 axes. Whenever the Y anions are removed from the lattice, the apatite network collapses and rises a mixture of phases or a new structural type, except in the cases where the host channels are occupied by cations having lone pairs such as Pb^{2+} , or Bi^{3+} . This structural stabilization has been attributed to the orientation of the lone pairs $6s^2$ of lead within the tunnels.

The stability of $Me_{10}(XO_4)_6 \square_2$ lacunar apatites is linked to the lone pair ns^2 like in Tl^+ , Pb^{2+} or Bi^{3+} [31-33]. This stabilization is due to the orientation of the lone pairs $6s^2$ within the tunnels. In the lead lacunar apatites, the stereo activity of Pb^{2+} cations is manifested only in the 6h sites but not in the mixed sites (K^+ , Pb^{2+} , and Ca^{2+}). The interatomic distances for P-O vary between 1.51Å and 1.55Å and the average of O-P-O angles is 108.5°, as indicated in supplemental files (Annex. III, Table. III.2). The average distances are similar and agree well with those reported previously [24,30].

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- [29] M. Mathew, W.E. Brown, M. Austin, T. Negas, Lead alkali apatites without hexad anion: The crystal structure of $Pb_8K_2(PO_4)_6$, J. Solid State Chem. 35 (1980) 69–76. doi:10.1016/0022-4596(80)90464-8.
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- [33] C. Colbeau-Justin, G. Wallez, A.M. Xuriguera, A. Elfakir, S. Jaulmes, M. Querton, Structure determination of $Tl_3Li(MoO_4)_2$. Stereochemical activity of $Tl(I)$ lone pair, Eur.J. Solid State Inorg.Chem. 34 (1997)1097-1106.

III.2. Infrared Spectroscopy and Chemical Analysis.

The synthesized samples were examined by FTIR spectroscopy (Fig.4). The precipitated powders showed spectra characteristics of hydroxyapatite environments, as it can be observed by the main vibration bands of $[PO_4]^{3-}$ species ν_3 ($1000-1100\text{cm}^{-1}$), ν_1 (961cm^{-1}), ν_4 ($550-600\text{cm}^{-1}$), ν_2 (472cm^{-1}) as well as the ‘O-H’ sharp bands (Elongation mode centred at 3570cm^{-1} and libration mode centred at 632cm^{-1}). The ‘OH’ bands are well illustrated in the calcined apatite HA_{900} . The samples Ap-Ca and Ap-Zn obtained by the dry method indicated also the typical apatitic bands. However, we noticed the absence of the ‘OH’ vibrations, attesting to the lacunar character of the Ap-Ca and Ap-Zn specimens. Besides, there was a shift of $[PO_4]^{3-}$ bands towards low wavenumbers for the lacunar apatites compared to those of precipitated samples. This shift is due to the difference in P-O distances. Not only that, but we also noticed that the unit cells parameter of the hydroxyapatites are much smaller than those of the lacunar ones (Table.2).

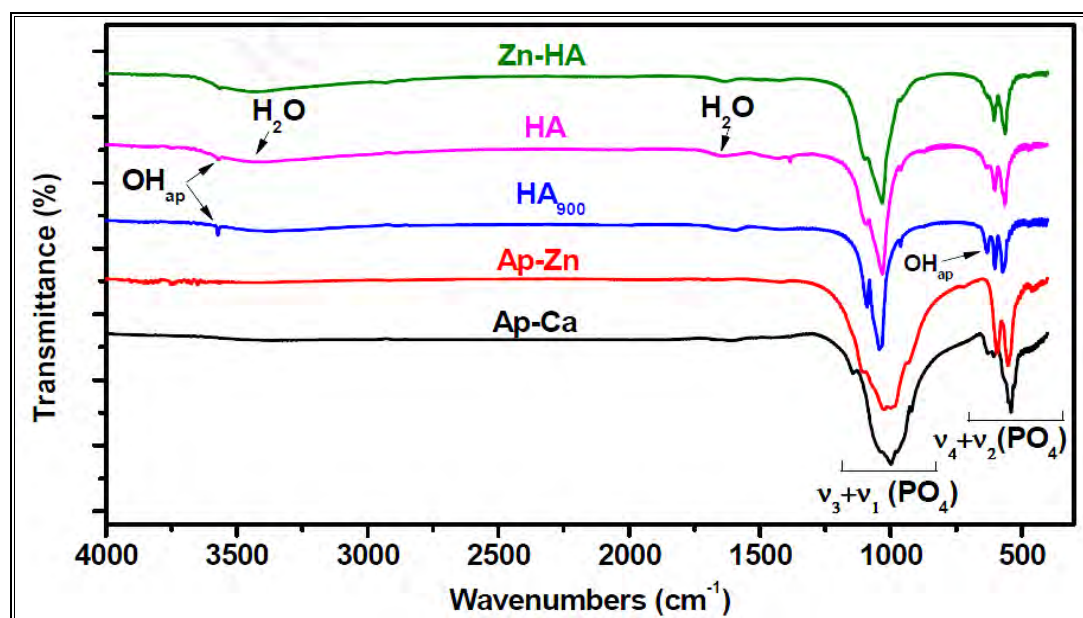


Fig.4: FTIR spectra of lacunar apatites Ap-Ca and Ap-Zn and the hydroxyapatites HA, Zn-HA, and HA_{900} .

The chemical analyses (Table.1) show that the sample HA is slightly calcium-deficient hydroxyapatite and that fact agrees with FTIR results, while Zn-HA exhibits an atomic ratio

([Me]/[P] close to stoichiometry. The content of the elements in the samples obtained by the dry method (Ap-Ca and Ap-Zn) was determined using the Rietveld refinement of the occupation parameters, leading to a stoichiometric composition (atomic ratio [Me]/[P] of 1.67).

The powders synthesized by double decomposition exhibit specific surface area (SSA) values within the range of 8-120m²/g, as shown for samples prepared under similar experimental conditions [2,34]. Zinc incorporation in the apatite matrix lowered the dimension of the crystal and raised the SSA value of the yield sample (Zn-HA), compared to the mother phase (HA). However, the calcination of HA powder drastically decreased the SSA (down to 90%), without destroying the original framework. These findings agree with the evolution of the crystallinity degree with operative conditions, as confirmed by XRD diagrams (Fig.1). The influence of calcination temperature on the surface area is more pronounced in the samples Ap-Ca and Ap-Zn prepared by dry method; the values found are less than 1m²/g.

III.3. Adsorption

The kinetic study aimed at determining the contact time needed to reach the thermodynamic equilibrium conditions. Fig.5 shows the variation of the amount of BSA adsorbed per unit of mass of the apatite as a function of contact time. Examination of the data indicated that a contact time of 20min was sufficient to attain a stationary concentration for the sample HA, while the yield plateau was reached after 6h for the specimen Ap-Ca. Therefore, the adsorption tests were conducted using incubation periods of 2h and 8h for the powders prepared by the wet and dry methods, respectively.

[34] A. Barroug, J. Lemaître, P.G. Rouxhet, Influence of crystallite size on the surface properties of calcium-deficient hydroxyapatites, J. Alloys Compd. 188 (1992) 152–156. doi:10.1016/0925-8388(92)90664-U.

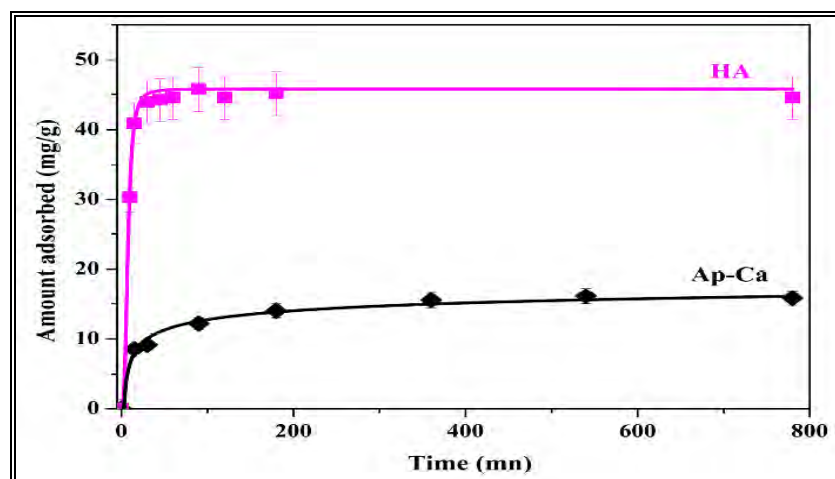


Fig.5: Adsorption kinetics of BSA onto apatite samples HA and Ap-Ca: 1mM potassium nitrate, initial concentration $C_o = 2.5$ mg/mL, $pH_{ads} = 7.1$ and temperature $T = 25^\circ C$.

Those times ensure a constant concentration of the adsorbate in the liquid phase even after 24h of incubation. The obtained results indicate a rapid kinetic for the precipitated hydroxyapatite (HA) and a relatively slow process for the sample obtained by solid reaction (Ap-Ca). The quick adsorption of the former indicates a strong surface affinity for the biomolecules, compared to the sample Ap-Ca. Slow kinetic processes reported for phosphate materials tested with a variety of adsorbates were assigned to the existence of repulsive electrostatic interactions between the adsorbent and the adsorbate as confirmed by electrokinetic measurement [35].

The adsorption experiments conducted by varying the adsorbate initial concentration (0 to 3.5mg/mL) reveal that the uptake rate ranged from 5 to 95% for the precipitated samples, while the apatites formed through solid-state reaction had a lower loading capacity (1-24%). This fact suggests that the latter specimens are less reactive toward BSA molecules. The experimental data of the compounds investigated under similar experimental conditions (concentration 0 - 3.5mg/mL, room temperature, $pH=7.1-7.4$, same solid-to-solution ratio) are accessible as supplemental files, [Annex. III](#), [Fig. III.1](#).

[35] A. Barroug, E. Lernoux, J. Lemaitre, P.G. Rouxhet, Adsorption of Catalase on Hydroxyapatite, *J. Colloid Interface Sci.* 208 (1998) 147–152. doi:10.1006/JCIS.1998.5759.

Fig.6 represents the variation of BSA adsorption by the solids as a function of the concentration remaining in the solution after reaching equilibrium. The shape of the obtained isotherms is of Langmuir type. The quantity adsorbed increased quickly and reached plateaus at relatively low protein concentrations, which is indicative of a high affinity between the adsorbent and the adsorbate.

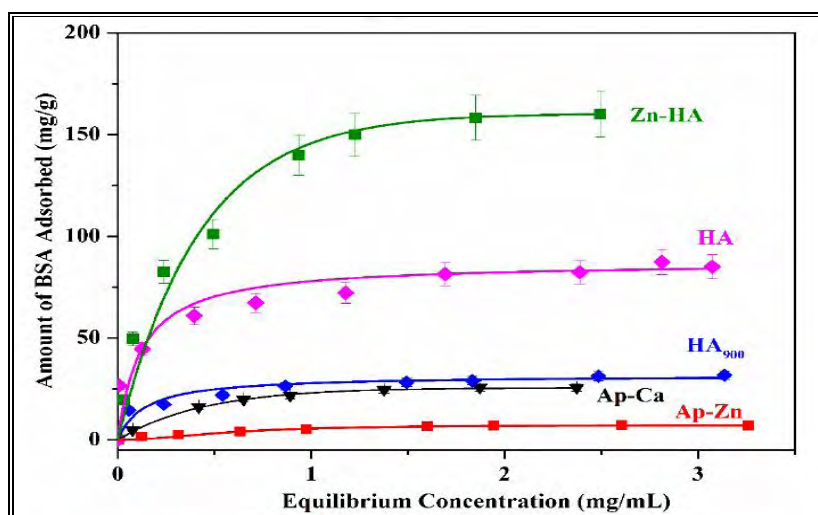


Fig.6: Adsorption isotherms of BSA (0-3.5mg/mL) onto the prepared apatites in 1mM potassium nitrate at room temperature ($T = 25^{\circ}C$) and pH in the range 7.1 -7.4: evolution of the amount of BSA adsorbed as a function of its equilibrium concentration.

The amount adsorbed was normalized by the mass unit of the solids to allow a comparison of the different materials. The adsorption parameters (N and K) were determined [21,26] by the commonly used linearized form of the Langmuir equation $[C_e/Q = C_e/N + 1/KN]$, where Q (mg/g) is the adsorbed amount, C_e (mg/L) is the equilibrium concentration, N (mg/g) is the maximum sorption capacity of the solid, and K (mL/mg) is the binding coefficient. The conformity of the adsorption data to the Langmuir isotherm was tested by plotting C_e/Q as a function of C_e , which gives a linear tendency with correlation coefficients of about 99%. The linearization (of the Langmuir equation) obtained for the investigated samples in the domain of concentration explored are shown in supplemental files, Annex. III, Fig. III.2.

The adsorption parameters determined by linear regression are reported in Table.3. The maximum amount adsorbed (N) was normalized to the unit of mass and to the surface area of the solids, to point out the factors of particular importance in their behaviour upon contact with the biological medium. The evolution of the affinity constant was not considered in the discussion due to the lack of enough experimental points at low coverage and to the irreversible aspect of the process at the apatite interface as reported elsewhere [26,35].

Table.3: Adsorption parameters of the prepared apatites: affinity constant (K) and maximum amount adsorbed (N) normalized to the unit of mass and the surface area of the solids.

Adsorbent	Langmuir Parameters				R ²
	N ± ΔN (mg/g)	K ± ΔK (ml/mg)	N ± ΔN (mg/m ²)	K ± ΔK (ml/mg)	
Ap-Zn	8.86 ± 0.62	1.47 ± 0.10	14.29 ± 1.00	1.47 ± 0.10	0.98
Ap-Ca	30.03 ± 2.10	2.87 ± 0.20	43.48 ± 3.04	2.87 ± 0.20	0.99
HA ₉₀₀	47.39 ± 3.32	6.59 ± 0.46	4.10 ± 0.29	5.25 ± 0.37	0.99
HA	87.72 ± 6.14	8.77 ± 0.61	1.11 ± 0.08	8.49 ± 0.59	0.99
Zn-HA	172.41 ± 12.07	4.83 ± 0.34	1.48 ± 0.10	3.82 ± 0.27	0.99

The results demonstrate that the synthesis conditions affect significantly the physicochemical characteristics of the prepared solids, which consequently impact their surface reactivity. As can be seen, the samples precipitated in aqueous solutions at relatively low temperature exhibited higher binding capacities per unit of mass, compared to the solids calcined at high temperature. The thermal treatment of HA crystals prepared at 80°C reduced the adsorption capacity of its calcined powder (HA₉₀₀). The maximum coverage sequence noticed for the Hydroxyapatites (Zn-HA > HA > HA₉₀₀) is following the evolution of their XRD patterns and microstructure. Thus, the most active apatite surface (Zn-HA) exhibited the lowest crystallinity index, the smallest crystal dimensions, and the highest surface specific area.

When the uptake data are normalized by the specific surface area, the plot of the maximum amount adsorbed as a function of the BET-specific surface area of the solids showed a different trend (Fig.7). Hence, the precipitated apatites (HA and Zn-HA) with large surface values showed less sorption efficiency, while their capacity was slightly improved as the temperature of treatment increased (HA₉₀₀). This effect is particularly noticeable for the samples prepared by solid-state reaction (Ap-Ca followed by Ap-Zn) and having values of SSA less than 1 m²/g that exhibited the largest monolayer coverage. These findings suggest, in addition to SSA as an important parameter, the existence of specific interactions and additional factors that contribute to the phenomena occurring at the apatite surface upon contact with the surrounding medium. Complementary work should be undertaken with simple and active adsorbates for a better understanding of the surface properties and the interfacial phenomena of lacunar apatite having empty tunnels and low specific surface area.

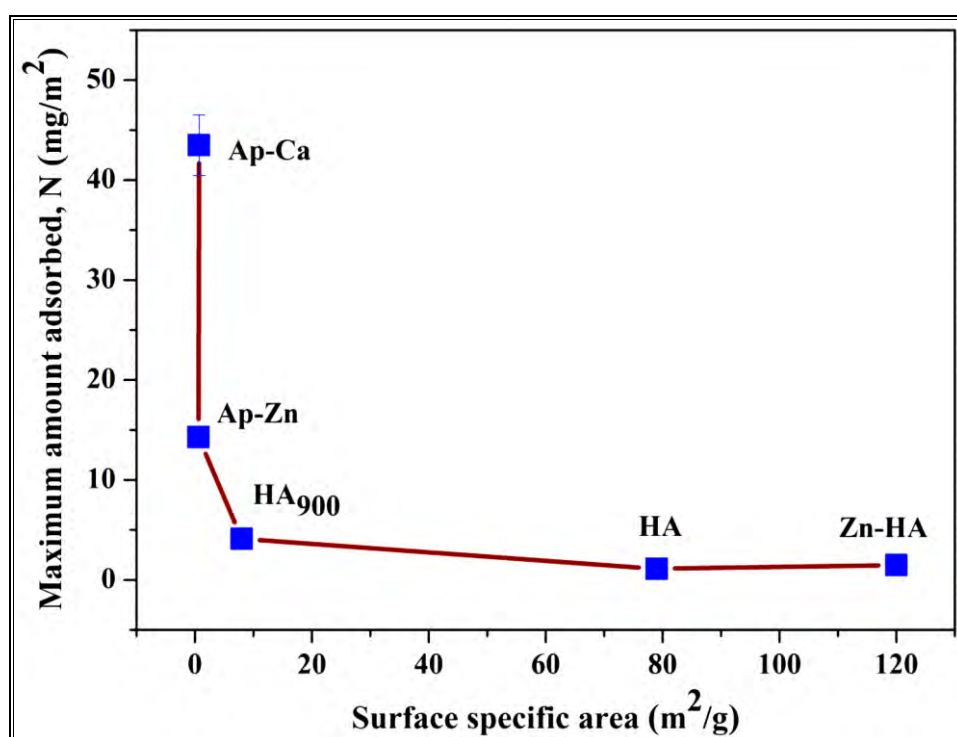


Fig.7: Maximum amount adsorbed (N) of BSA as a function of solids specific surface area.

It is proven in this work that various parameters i.e., crystallinity index, surface defects, size dimensions, and specific surface area play a key role in the interactions process. The adsorption of biomolecules at the apatite surface is of key importance in the field of biomaterials and the control of the specific properties of the apatite mineral (solubility, reactivity, resorption ...) may contribute to improving its biological function as a component of calcified tissues. Furthermore, the information gained in this study regarding the driving forces at the mineral surface with regards to its chemical and biological environments can also be beneficial for the development of effective sorbents for potential use in wastewater purification.

IV. Conclusion

In this work we reported on the synthesis, physicochemical characterization, and surface properties of various lacunar- and Hydroxy- phosphorus apatites. The XRD studies showed that all examined compounds crystallize in the hexagonal system with ***P6₃/m*** (No 176) as a space group. Using Rietveld refinements, we have shown that while the Y sites are empty in the lacunar apatites, in the case of hydroxyapatites those sites are fully occupied by the anions OH⁻. We have shown that the majority of Pb²⁺ cations are located in the (6h) sites of the lacunar apatite.

The interaction of the prepared compounds with a model protein (BSA) revealed a fast kinetic process for the precipitated samples, compared to the crystals obtained by solid chemical reaction. However, all the obtained isotherms were Langmuirian in shape. The difference in the adsorption parameters of the materials was discussed considering the surface characteristics of the specimens. It can be concluded that the degree of crystallinity, surface defects, and crystals size, as well as surface areas, do, to some extent, contribute to the surface properties of apatite materials.

Chapter. IV: Structural Study of Fluoroapatite and Demineralization Effects of Phosphoric Acid.

Abstract;

For its large use, phosphoric acid occupies the second position in the world production of acids after sulfuric acid. It can be made by two processes: dry or wet. The second is the most used. The obtained acid contains different metallic impurities such as Cd^{2+} , Mg^{2+} , Pb^{2+} , Cu^{2+} , Cr^{3+} , As^{3+} , ..., etc. The presence of these impurities leads to severe purification operations.

We focus our study on cadmium elimination from phosphoric acid using the new methods for processing and purification cadmiferous liquids: The principle of decadmiation is to precipitate the cadmium metal soluble in phosphoric acid 29-30%, the precipitate out and form sludge. The supernatant/residue can be removed by decantation when the precipitate is heavy and coarse. For this work, the precipitate collected by filtration or/and centrifugation. The reagent used is MSN and other Specimens/Materials ([Abstract Fig. IV Style](#)).



Abstract Fig. IV Style: KOURIBGA ; Sidi-Chennane - $\text{Ca}_{10-z}\text{M}_z(\text{XO}_4)_6\text{F}_2$. SAFI; Maroc Phosphore- PAC 29/54% decanted and non-decanted. Laboratoires; S3M-Apatites Lacunaire- $\text{APb}_{4-y}\text{M}_y(\text{PO}_4)_3$ and Central OIS/L/Q- the ICP analysis room.

Industrial problematic

For the example of the shaped part presented in this chapter; Phosphoric acid is essentially obtained from phosphate rock. Generally, it can be produced in two main ways. The first is known as the wet process (WPA: Wet process Phosphoric Acid) and consists of the attack of the phosphate rock by a strong acid, most often sulphuric acid. The second is based on a thermal process, in which the phosphate rock is reduced to elements that are then oxidized, and hydrated to obtain phosphoric acid.

However, the wet process is the most frequently used, even though it has some disadvantages. Indeed, the phosphoric acid obtained inevitably contains the majority of the impurities previously present in the phosphate ore originally mined. Contaminants are mainly heavy metal cations such as cadmium, arsenic, lead, chromium, zinc, tin, iron, copper, barium, strontium, and molybdenum,..., etc. and organic matter and other oxides (Al_2O_3 , CaO , Fe_2O_3 ,... etc.) depending on the nature of the rock used. The massive soil fertilization with phosphate fertilizers containing these toxic metals, that are dissemination in soils and aquatic environments, leads to an accumulation of these metals in the soil, contributes to the contamination of flora and fauna, and affects the living being through the food chain, thus posing a resulting risk to human health. Furthermore, the contamination of heavy metals in food, in particular cadmium and arsenic, results from the use of phosphoric acid in the production of fertilizers, which continues to be a concern about public health. The economic impact of the heavy metals issue is considerable and the sector needs a more efficient and economical technology than currently exists. Also, recent regulatory measures have been taken to further limit the level of cadmium in phosphate fertilizers.

The many methods have been proposed to reduce the heavy metal content of phosphoric acid, as discussed below:

The International patent applications **WO2017/023153** and **WO80/02418** describe processes for reducing heavy metals from phosphoric acid. They consist of the use of alkaline sulphides which, in the presence of phosphoric acid, release hydrogen sulphide in situ. The generated sulphide combines with the metals present in the acid to give the corresponding metal sulphides. The precipitation is made possible by the partial neutralization of phosphoric acid using alkaline solutions such as sodium or potassium hydroxide, ammonia or calcium hydroxide. The addition of the partial neutralization step is justified by the fact that outside of copper sulphide, which can precipitate negative **pH** values, most sulphides of the target metals remain soluble and therefore impossible to remove. This neutralization reduces the pH to a value higher than 1; **pH** value necessary to promote the precipitation of sulphides and consequently, extract them by simple filtration and/or decantation. These processes present the disadvantage of the effect of partial neutralization of phosphoric acid, which lowers its commercial value and reduces its spectrum of use.

The European patent **EP008611A1** describes a process for the purification of heavy metals and especially of molybdenum from a phosphoric acid obtained by a wet process. This process introduces a prior purification of phosphoric acid by extraction using an organic solvent and is specifically aimed at reducing molybdenum. This present process has the disadvantage of being expensive, because of the use of organic solvent for phosphoric acid purification.

We also quote patent **WO91/00244**, which describes a process for reducing heavy metals from the generally concentrated phosphoric acid, as well as the fine sludge that accumulates in it. The latter process uses phosphoric acid having a content expressed as a proportion of 'P₂O₅' by weight of between 50 and 60% and a solids content of less than 5%, which is subjected to a control of the calcium sulfate saturation of the phosphoric acid to form by precipitation a compound of formula (SO₄)_{1-x}(PO₄)_x(H)_yCa_{1-z}M, (x) and (y) being the stoichiometric coefficients according to the proposed innovation, (z) indicates the chemical

substitution of calcium by other metal cations, and (M) represents one or more metal cations contained in the starting phosphoric acid. The process of demineralization depends on the saturation of the raw phosphate formula used or on their that substitution. This process, even though the adsorption of metals is not selective, requires precise control of the Physico-chemical parameters of the treatment and leads to a phosphoric acid enriched in sulphate ions, which requires an additional desulphurisation operation.

Another example is **MA27222 A1**. The process can be applied during the manufacturing process or after the manufacture of a solution for the elimination of arsenic; it can be applied to phosphoric acid, with a concentration of ' P_2O_5 ' which can vary from 3 to 72%. Depending on the process, the arsenic precipitation reaction takes place at a temperature greater than or equal to the ambient temperature, depending on the invention, the arsenic-laden sludge from the precipitation can be separated from the acid by conventional solid-liquid separation methods, such as decantation, centrifugation or filtration. The reducing agents used are sodium bisulfite and formaldehyde on phosphoric acid 26% in ' P_2O_5 '; sodium bisulfite of iron and aluminium on phosphoric acid 54.5% in ' P_2O_5 '; sodium bisulfite, hydrazine, and iron on phosphoric acid 42% in ' P_2O_5 '.

The processes presented below, and others disclosed in the literature, while they utilize different reagents and approaches and may have advantages and applicability in the production of purified phosphoric acid, their high capital costs, high treatment costs, and low efficiency compromises their overall industrial-scale general adoption.

I. Introduction.

Morocco is a country that has an important global position in the production and processing industries of phosphates of all kinds, it is the leading exporter of phosphate, phosphoric acids, and fertilizers worldwide, as well as in the research and development of new phosphate materials on an industrial or academic scale.

Phosphate ores have a huge reserve in the Moroccan subsoil and are of great importance in various areas of daily life. OCP plays an important economic and social role in the six regions of MOROCCO, where its four mining centres and two industrial centres are located: BENGUERIR, KHOURIBGA, LAAYOUNE, YOUSSEUFIA, as well as JORF LASFAR and SAFI for the production of phosphoric acids. It creates wealth and jobs, provides training, and obtains supplies or subcontracts from a dense network of local companies that it sometimes helps to create.

The Sherifian Phosphate Office Group (OCP), a world leader on the phosphate market and its by-products, as well as our Chaouïa-Ouardigha region and more precisely the city of KHOURIBGA, capital of phosphate in the world, recognized worldwide by its quality of phosphate “K09” and its enormous reserve, which justifies the need for scientific and technical research in the field of phosphate materials, rather phosphoric acid. [Fig.1](#), below shows the engineer who leads the extraction work in the phosphate mines of the Sidi-Chennane sector, Sherifian Phosphate Office Group, OCP, KHOURIBGA, MOROCCO.



Fig.1: The discovery mining of the Sidi Chennane phosphate deposit, KHOURIBGA.

Although it is difficult to make a complete review of the multiple applications of solid phosphates, two main categories can be mentioned:

- ☞ The first category comes from traditional productions of low added value but of high tonnage: phosphoric acids, fertilizers, detergents in constant decline in production and phosphates used in the agrifood industry,..., etc.
- ☞ The second category comes from high value-added products, corresponding to smaller tonnages and at more or less advanced stages of development and in a wide variety of fields of activity: optics (luminophores, lasers, frequency doublers), electrochemistry with the recent and remarkable breakthrough of LiFePO_4 phosphate, catalysis (zeolites), biomaterials in the pharmaceutical industry, materials for storing radioactive or heavy elements, flame retardants and many others.

Phosphoric acid is a chemical compound of great industrial importance because it is used in many applications such as the manufacture of phosphate fertilizers, metal surface treatments, organic synthesis, detergent manufacture, uses in the food industry, ..., etc.

In this chapter, we are interested in the purification of wet-process phosphoric acid, as well as the structural study on phosphate. These liquid and solid materials contain many metallic cations that are considered impurities. Among these impurities, some are recoverable such as (U, rare earth,..., etc.) and must be recovered, and others that are penalizing for the subsequent use of the acid such as (Cd, As, Cu, Zn, ..., etc.) and must be eliminated.

The purpose is to develop scientific research on phosphocalcic apatites of the KHOURIBGA region and phosphoric acid obtained from the SAFI Industry, to prepare new porous material, capable of effectively eliminating inorganic. To contribute to the valorization of phosphates, which represent a source of natural and economic wealth of great importance for MOROCCO on the one hand, and to seek to prepare porous materials and reducing agents capable of effectively eliminating inorganic pollutants (heavy metals, fluoride ions, etc.)

present in phosphoric acid on the other hand. To this end, the research and development of solid materials in our laboratory to synthesize and develop solid apatitic matrices and reagents called MSN, capable of trapping these pollutants, are necessary and constitute our main concern before the beginning of our research work during my internship entitled "Initiation for the Contribution to the Study of the Purification of Phosphoric Acids 29% and 54%", conducted in the Central Laboratory OIS/L/Q of Maroc Chemistry, SAFI. Particular attention was paid to the deficient apatites because the heavy metals existing in the phosphate deposit from which the product to be extracted is phosphoric acid (ACP 29% and 54%), which are included in the composition of these mineral materials.

II. Generality on Manufacturing and Pre-treatment of PAC.

II.1. Introduction.

Maroc Phosphore, created in 1981, is the most recent division of the SAFI Chemistry Cluster attached to the central laboratory (OIS/L/Q), was for us the framework in which we undertook our research during the internship. It produces phosphoric acid from BENGUERIR phosphate (Morocco Phosphorus II) and Gantour phosphates, the YOUSOUFIA region (Morocco Phosphorus I). As an example, Morocco Phosphorus II, this complex consists of the following three units: production services, material services, and design and technical improvement services. We are interested as follows the production service described below, see [Fig.2](#):

- **The Laundry:** It consists of four treatment lines for BENGUERIR phosphate, its nominal production, and 360 Tonnes/hours. The purpose of the washing is to enrich the phosphate in P_2O_5 to satisfy the requirements of the phosphoric acid manufacturing process.

- **Sulphuric workshop:** It consists of three nominal production units of 1700 Tonnes/days. The production of sulphuric acid is necessary for the production of phosphoric acid.
- **Phosphoric workshop:** The phosphoric workshop of the MP II division was designed for the production of an acid containing 54% P_2O_5 according to the NISSAN process. This workshop consists of three grinding lines, three reaction lines, and four concentration lines, each line is provided with phosphate from the laundromat and sulphuric acid from the sulphuric workshop. Its production is 1500 T P_2O_5 /days.
- **Energy and fluid workshop:** Consists of a thermoelectric power plant, a freshwater treatment unit, and a seawater pumping station. This workshop feeds continuously the complex with all the usefulness it needs.

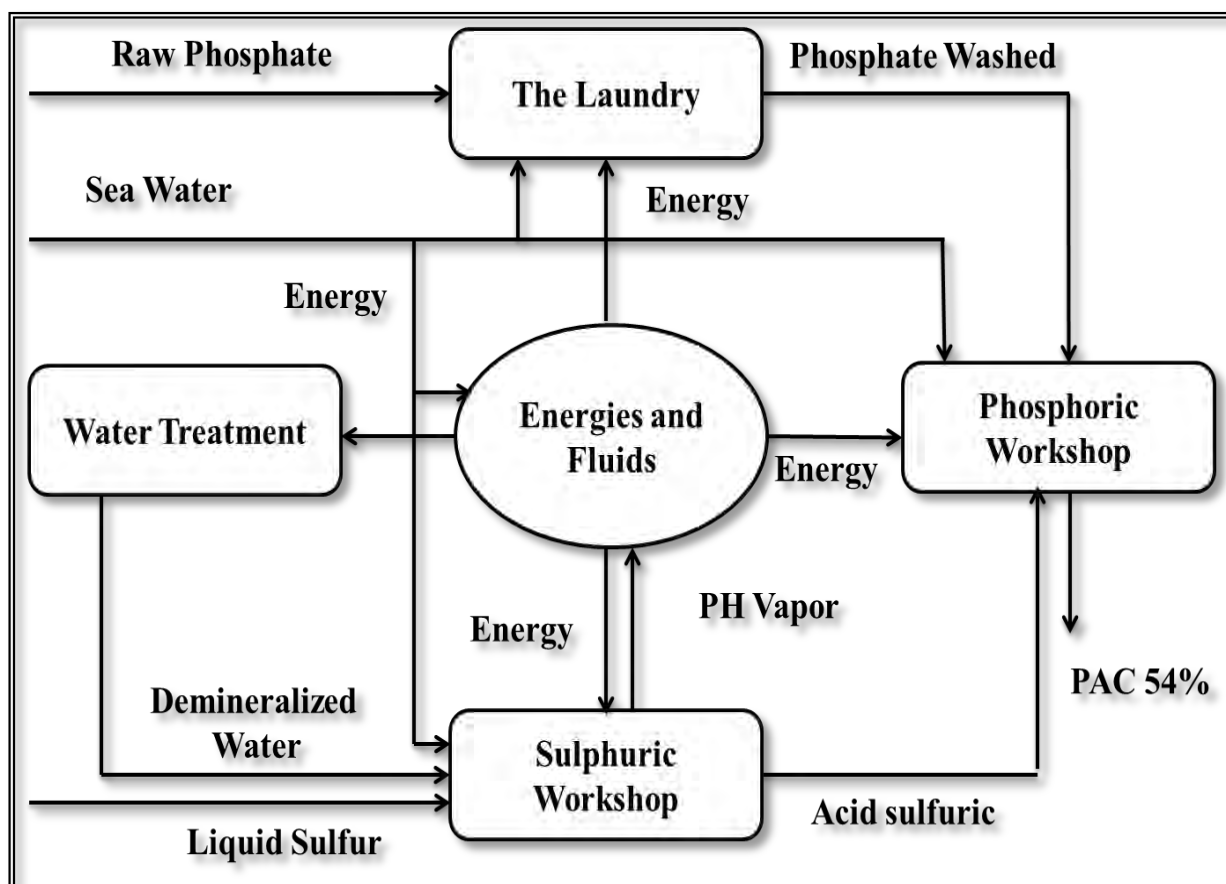


Fig.2: Diagram of the functioning of the production service of Maroc Phosphore II.

II.2. Phosphoric Acid Manufacturing Processes.

In Morocco Phosphorus and Morocco Chemical of SAFI, the process used is by a wet process using sulphuric acid as the attack acid. The most suitable process, given its interesting yield, is the di-hydrate process, which comes in two forms:

- ☞ The NISSAN process.
- ☞ The RHONE POULENC process is presented in [Annex. IV](#) on [Fig. IV.1](#) (which differs in stay time and installation).

These two processes produce quality phosphoric acid with multiple and interesting uses. The manufacture of 54% P_2O_5 phosphoric acid in the phosphoric workshop of the Morocco Phosphorus Division (IDS/PP) is carried out according to the NISSAN process. The production steps are divided into four sections, as shown in [Fig.3](#): grinding, reaction, filtration, concentration, clarification, and storage.

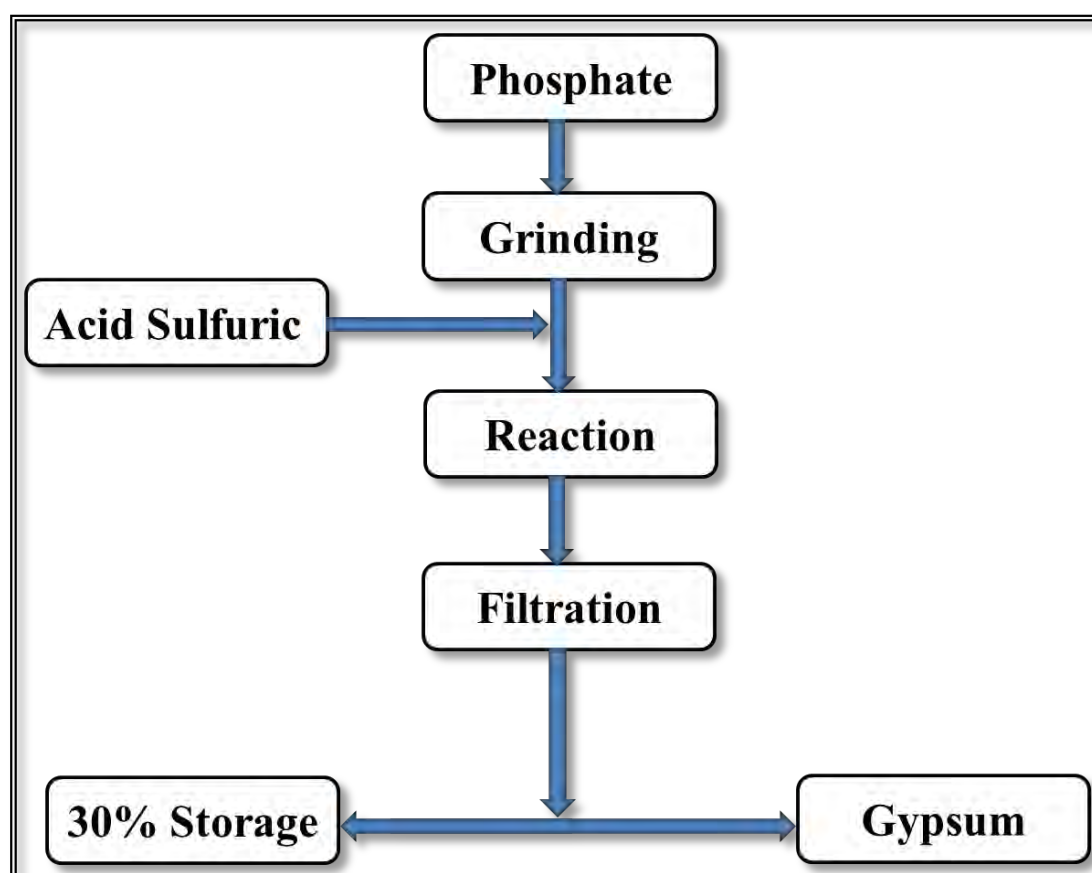


Fig.3: Diagram of the phosphoric acid production chain.

a) The grinding section.

The phosphate stored in the storage hall is conveyed to the mill which is designed to grind it into small grains; this operation consists of reducing the granulometry of the phosphate to increase the attack surface to improve the reaction yield. Indeed, the phosphate obtained from the Laundromat is moistened with water before feeding the bar grinder. This grinder is cylindrical and covered with shielding plates. The grinding unit consists of three identical lines, each with a capacity of 81.25t/h of washed phosphate. The grinding operation has the following advantages:

- Reduce the grain size of the washed phosphate and increase their surface area, to facilitate the attack of the ore by sulphuric acid during the reaction phase.
- Reduce losses that are generated during ore attack. These losses are all the greater when the P_2O_5 content is high (fine grain), the sulphuric excess is low and the temperature is low. Losses may be due to:
 - Unattacked phosphate, which results mainly from the coating of the grains (coarse grains) of phosphate by calcium sulphides which precipitate at the surface and so inhibit the progress of the reaction.
 - A syncrystallized phosphate due to the trapping of P_2O_5 in the crystalline network of precipitated sulphides.

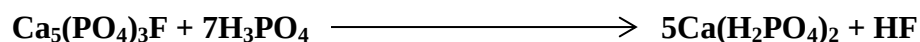
The phosphate pulp produced is stored in an agitated tank with a capacity of 320m³ in which an agitator keeps the solid particles in suspension. A pump represses the debit of the main pulp to the reaction section of the phosphoric workshop.

b) Reaction, Crystallization and Filtration Section.

At MP II, the production of phosphoric acid is based on the NISSAN process, which is distinguished by the crystallization of calcium sulphate hemihydrate (semihydrate) into dihydrate. The process is carried of three steps: digestion, crystallization and filtration.

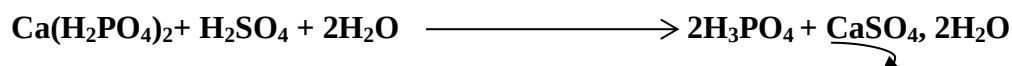
➤ **The reaction:** is done in two steps:

- The Solubilization of phosphate fluorapatite grains realized out in a premixed where the raw phosphate pulps are attacked by weak phosphoric acid (back PAC) to give monocalcium phosphate according to the reaction:



The transformation of phosphate ore into soluble monocalcium phosphate improves the conditions of attack by H_2SO_4 .

- Attack of monocalcium phosphate by H_2SO_4 : carried out at two digesters in series, depending on the reaction:

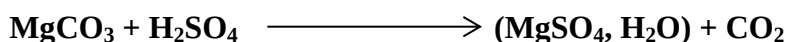
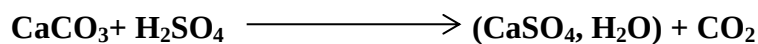


In the first digester, 33% of the sulphuric acid is added. The remaining 67% is introduced at the second digester. Temperatures in the digesters are maintained at $80 \pm 5^\circ\text{C}$ in the first and $93 \pm 3^\circ\text{C}$ in the second by injecting fresh air jets into the spray mixture. Gases leaving the tanks are passed through washers before being evacuated into the atmosphere. At the outlet of the second digester, the spray mixture consists of:

- Phosphoric acid contaminated, with a concentration between 26 and 30% in P_2O_5 .
- Free sulphate ions.
- An amount of unreacted phosphate.
- Semi-hydrated calcium sulphate crystals.

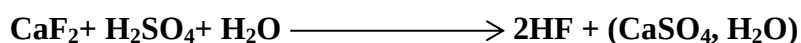
Other qualified secondary reactions should also be mentioned. Indeed, the impurities contained in the phosphate will generate secondary reactions, which can influence the main reactions. Among these impurities, we can mention:

- Carbonates of calcium and magnesium that reacted with sulphuric acid to give calcium sulphate and magnesium sulphate, monohydrates according to the following reaction:

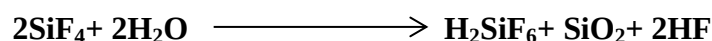
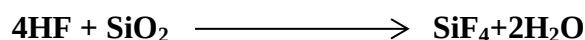


The production of $\text{CO}_2(\text{g})$ promotes the formation of foams in the presence of organic matter.

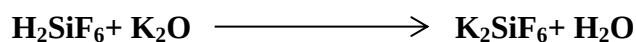
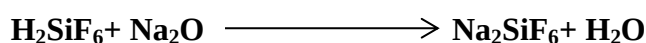
- Calcium fluoride reacts with sulphuric acid according to the following reaction:



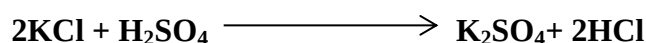
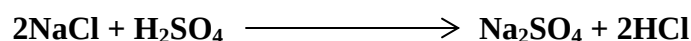
- Silica in the presence of hydrofluoric acid (HF) generates fluosilicic acid (H_2SiF_6), both of which are highly corrosive and toxic:



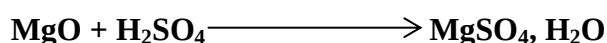
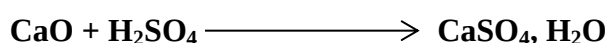
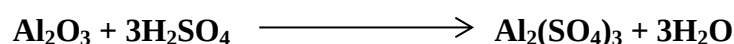
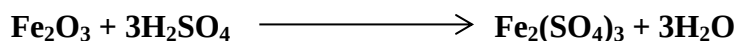
- The metal oxides contained in phosphate in the presence of fluosilicic acid produce fluosilicates:



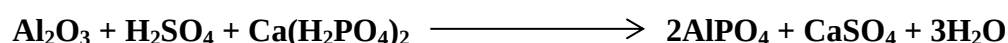
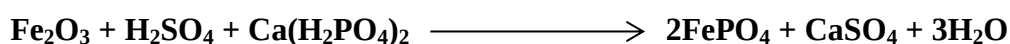
- Sodium and potassium chlorides are at the root of high corrosion, as they generate hydrochloric acid according to the following reactions:



- The basic reaction is also accompanied by several secondary reactions between sulphuric acid and oxides such as:



- Reactions with iron and aluminium oxides do not stop at the formation of sulphate but can give rise to iron and aluminium phosphates which may give rise to metastable supersaturated solutions from which the hydrates slowly precipitate, the precipitation of these phosphates which will then be separated with gypsum dihydrate continues a considerable loss of P_2O_5 . these reactions are as follows:



- **Crystallization - Recrystallization:** This is the transformation of calcium sulphate hemihydrate into dihydrate; this transformation is carried out by the controlled cooling of the liquid sludge. Crystallization depends on temperature, it is noted that the solubility of the hemihydrate increases when the temperature decreases, while the solubility of the dihydrate decreases. The porridge in this crystallization phase is characterized by its temperature and H_2SO_4 content. It is also necessary to indicate here the essential advantages of crystallization:

- The very fine hemihydrate crystals are difficult to filter. By gradual cooling, they can already be transformed into dihydrate in the part reserved for the attack.
 - The hemihydrate crystals eventually contain P_2O_5 . This P_2O_5 is thus released by recrystallization. The P_2O_5 yield of the process is therefore significantly improved.
- **Filtration:** The slurry from the fourth crystallizer is pumped to a tank where it will be mixed with a flocculant (to improve filtration) before being pumped to the rotary filter operating under vacuum. At this level, weak acid, strong acid and gypsum are recovered separately. After the separation of the 1st filtrate (strong acid) the filter

cake is washed four times in counter-current. The gypsum produced is discharged into the sea.

The Attack - Filtration section has three NISSAN lines with a nominal capacity of 500T of P_2O_5 /day/line in the form titrating of acid 29 to 30% P_2O_5 . Fig.4 describes the diagram of the Reaction-Filtration unit within the Morocco Phosphorus II division (MP II).

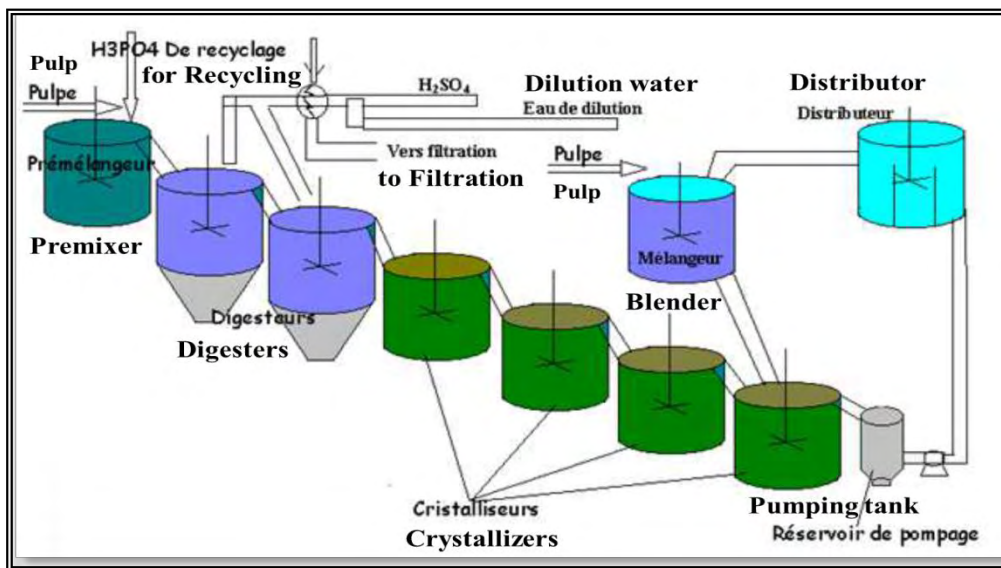


Fig.4: Schematic of the Reaction-Filtration unit, Morocco Phosphorus II (MP II).

To conclude this important section, the optimum operating conditions for dihydrate precipitation are 26-32% in P_2O_5 and 70-85°C. The sludge temperature is controlled by the use of a flash cooler. This also degasses the sludge making it easier to pump. The temperature can be controlled, for example, by using a circulated air cooler.

c) Concentration Section.

The concentration of phosphoric acid consists of the evaporation of the water excess in the acid leaving the Reaction - Filtration. Its concentration will increase from 26-30% to 52.5 - 53.5% in P_2O_5 . The entire phosphoric acid concentration unit consists of five identical lines, each with a capacity of 375t of P_2O_5 per day, and a fifth of 250t of P_2O_5 .

Phosphoric acid, whose concentration is about 29 to 30% at P_2O_5 , is conveyed from in the settling tanks to the Concentration unit and mixed at the outlet of the exchanger with the

concentrated acid (about 53.5% at P_2O_5) in circulation. In the exchanger, the phosphoric acid is heated to 76°C and 4.5 bar.

Phosphoric acid, whose concentration is 54%, boils at a temperature of 77°C. The boiling of the acid causes the evaporation of water and the disengagement of some of the constituent elements (chlorine and fluorine).

d) Clarification and Storage:

At the exit of the phosphoric acid concentration unit, it is conveyed back to hot tanks where it stays for a certain number of hours, to reduce the rate of solid. The extracted sludge is turned back into the storage tank and the acid takes two different paths depending on its quality. The first path to export marketing, the other path to purification.

Indeed, many claims have been registered to customers about the non-compliance of phosphoric acid with contractual requirements, which particularly concern the increase in chemical elements (in particular the amount of free sulfides). In this context, the following section describes how to produce phosphoric acid that meets the compliance thresholds.

II.3. Pre-treatment of the PAC.

Given the increased demand for the technical qualities of phosphoric acid, for various uses, including in particular the food and detergent industries, it is necessary to meet the new demands for phosphoric acid quality. The main purpose of the pre-treatment workshop, MP IV to JORF LASFAR, is to reduce the content of free amount of free sulfides, arsenic, and solids in the 54% unclear P_2O_5 acid, called pre-treated acid. This acid is intended entirely used by the EMAPHOS unit to produce purified acid. The acid at the outlet of the MP IV unit must have the following characteristics, [Table.1](#):

Table.1: Phosphoric acid of customer specifications.

P_2O_5	SO_4^{2-}	As^{3+}	Solid
>53.9%	< 0.3%	<0.5ppm	<0.2%

The manufacturing process used is the PRAYON process, which consists of treating acid in three steps:

- Desulphation ($-\text{SO}_4^{2-}$), followed by desaturation to reduce the content of free sulfate in the acid.
- The desarrriage ($-\text{As}^{3+}$) followed by settling to reduce arsenic content.
- Washing of gases (fluorinated gases and H_2S gases) before their release into the atmosphere.

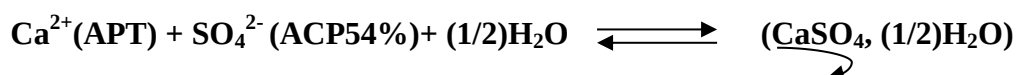
To this end, the pre-treatment workshop includes the following main equipment:

- ☞ An agitated and heated desulphation tank.
- ☞ A desaturation equipped with an agitator.
- ☞ A desarrriage reactor.
- ☞ A decanter equipped with an agitator.
- ☞ A storage tank called a liquid column.
- ☞ The washing section.

The current capacity of this workshop is 520 Tons per day of pretreated acid.

a) Desulphation and Desaturation.

Acid desulphurization consists of reducing its level of free sulfate SO_4^{2-} , by adding CaO-rich compound, in this purification process, the compound used is ground phosphate. The desulphation reaction is carried out in a desulphation tank between the free acid sulfate 54%, and phosphate CaO according to the following reaction:



The 54% acid enters with an SO_4^{2-} content higher than 2%, and after desulphation, this titer is reduced to about 0.2%. Well, ground phosphate (APT) is used to increase the attack surface, to have a better reaction yield, so the pulp is heated between 95 and 100°C to crystallize a calcium sulfate hemihydrate, having good decantation properties.

The addition of silica to the mixture, the purpose of which is to promote the crystallization of the calcium sulfate produced and to reduce the fluorine content of phosphoric acid.

The phosphoric acid leaving the desulphation tank is loaded with solids; this is why the desaturation is used to increase the residence time of the reaction and to cool the acid, to promote the crystallization of impurities. This acid will be sent to the desariage stage.

The parameters influencing desulphation are:

- The fineness of the phosphate used.
- The CaO content of phosphate.
- Temperature;
- The residence time in the reactor.
- Desulphation control is achieved by adjusting the $\text{CaO}/\text{SO}_4^{2-}$ molar ratio between 0.9 and 1.1.

Calculation of the amount of phosphate to be added: The amount of phosphate to be added is calculated based on the acid, of the sulfate, and of CaO content of the added phosphate such that the molar ratio $\text{CaO}/\text{SO}_4^{2-}$ is 1.

★ The amount of SO_4^{2-} available in the acid 54% of P_2O_5 :

$$\mathbf{P_1} \times [\% \text{SO}_4 (\text{Acid Soluble}) - \% \text{CaO} (\text{Acid Soluble})] \times 96/56 / 100 = \mathbf{P_2} (\text{SO}_4)$$

Where $\mathbf{P_1}$ = is the mass flow of the acid in (T/h)

★ The CaO necessary to implement is: $\mathbf{P_2} (\text{SO}_4^{2-}) 56/96 = \mathbf{P_3} (\text{CaO})$

So the phosphate to be used is:

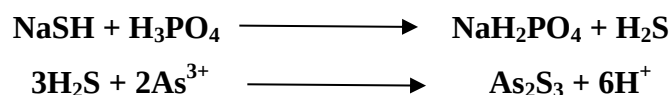
$$\mathbf{P_3} (\text{CaO}) * 100 / [(\% \text{CaO total in phosphate} - \% \text{SO}_4 \text{ in phosphate}) * 56/96] = \mathbf{P_4}$$

Where $\mathbf{P_4}$ = phosphate mass flow rate injected into the desulphation reactor in T/h.

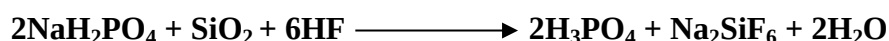
b) Desarsination and Decanting.

Phosphoric acid is a raw material for some food products, pharmaceuticals, and detergents, for this reason, it is required to treat phosphoric acid, before using it in these fields. The desarriage of acid consists in reducing its arsenic content ($\text{As}^{3+} < 0.5\text{ppm}$) by adding NaSH to 30%, in a tubular reactor at a temperature between (70°C and 90°C) under pressure to improve the exchange between the liquid and gaseous phase (H_2S) because the solubility of the latter in acid is low.

The desarriage reaction is very violent and rapid, it occurs with the emission of $\text{H}_2\text{S}(\text{g})$ according to the following reactions:



It is to be expected that free fluorine (HF) will be transformed into fluosilicates in the presence of reactive silica, already present in phosphoric acid according to the following reaction:



The amount of NaSH used is about 1.5kg NaSH/TP₂O₅. The residence time in the reactor is 2 minutes. Desulphated and desarriage acid contain a certain amount of arsenious precipitates that are difficult to settle, as well as the solids formed during desulphurization, and the desaturation of the acid is carried to the settling tank where it undergoes solid-liquid separation by adding commercial flocculants, suitable for about 0.024kg flocculant /TP₂O₅ to provide overturned pretreated acid (overflow evacuation at the top of a tank), and an acid loaded with sludge about 25% by weight. This sludge is currently being recycled to the attack filtration lines, pending the refurbishment of the clarification line.

The addition of the appropriate flocculant allows:

- Aggregation of particles increase the sedimentation rate, which will result in a decrease in the surface area of the decanter.
- Reduce the turbidity of the liquid.
- Increase the solid concentration of the sediment.

The parameters influencing the desariage are:

- Pressure in the desariage reactor.
- The density and injection rate of the NaSH solution.
- The residence time in the reactor.

The parameters influencing decantation are:

- The size of the crystals.
- The settling speed.
- The density and injection rate of the flocculant solution.

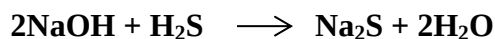
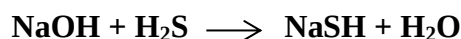
Gas washing: Among the various means used at the pre-treatment unit to protect the environment, we can mention the action on the gases liberated during the desariage of the acid. This is a practical action on the effluent to remove these most harmful constituents from it before it is released into the atmosphere.

At the exit of the disarseniation reactor, phosphoric acid contains gaseous H_2S . The acid is degassed in a buffer tank. These gases are sucked into a washing tower where they are washed with a diluted soda solution, with raw water. This soda reacts with H_2S to form NaSH, which is recovered for the preparation of the NaSH solution. The H_2S content leaving the washing tower must be less than 10ppm. The reactions involved are:



This soda reacts with H_2S to form NaSH or Na_2S depending on the pH of the solution and is recovered for the preparation of the NaSH solution in the reactor. The soda solution rotates in closed circulation in the scrubbers thanks to the pump through nozzles to increase

the exchange surface. The pump supplies the scrubber with sodium hydroxide. The neutralization reactions are:



The pH of the solution, is an indicator of the type of product formed, the gases leaving the unit are extracted by the fan. An H_2O detector is placed at the fan outlet to ensure the quality of the wash and immediately notify the operator of an anomaly in the wash circuit.

II.4. Pretreated acid and general review.

Table.2 shows the required profile of the pretreated acid according to the shareholder program contract and EMAPHOS request.

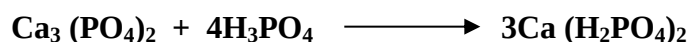
Table.2: Presents the required profile of the pretreated acid according to the shareholder program contract and requests EMAPHOS.

Element	Program Contract	Requests EMAPHOS
P_2O_5 %	≥ 53.9	≥ 55
Solid rate %	≤ 0.2	≤ 0.2
SO_4^{2-} %	≤ 0.2	≤ 0.2
RM	$\text{CaO} \leq 0.2 \rightarrow \text{RM} = 1.7$	0.9 à 1.1
TOC ppm	≤ 200	≤ 200
As ppm	≤ 1	≤ 0.5
F %	≤ 0.32	≤ 0.32
Al_2O_3 %	≤ 0.40	≤ 0.40
MgO %	≤ 0.85	≤ 0.70
Fe_2O_3 %	≤ 0.45	≤ 0.45
K_2O %	≤ 0.12	≤ 0.12
Na_2O %	≤ 0.25	≤ 0.25
Cr ppm	Not specified	≤ 400
V ppm	Not specified	≤ 500
Titration %	Not specified	≤ 7
Delivery (T) in $\text{P}_2\text{O}_5/\text{day}$	450 (Unit Nominal)	480 (Unit Nominal)

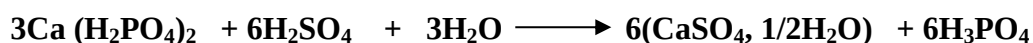
a. The reactions at stake:

The desulphation reaction is carried out in two steps:

- **Step 1:** the attack of phosphoric acid 54% by phosphate to form soluble monocalcium phosphate.

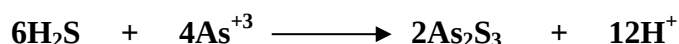
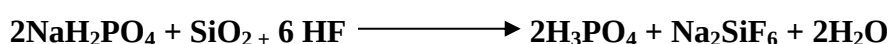
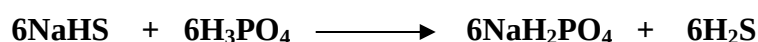


- **Step 2:** The reaction between monocalcium phosphate and sulphuric acid to form phosphoric acid and gypsum.

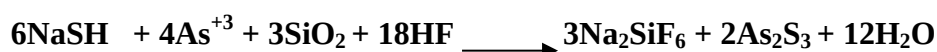


The CaSO_4 formed will be crystallized into hemihydrate, depending on the operating conditions of Temperature, P_2O_5 concentration, and sulfate content.

- **The disarseniation reaction;**



- **The main reaction is:**



According to the main reaction, 6 moles of NaHS react with 4 moles of As^{+3} ; therefore the amount of sodium hydrosulphide to be mixed with acid per ppm of arsenic in acid is 1.18 grams of anhydrous NaHS per ppm per ton of acid.

c. Block schematic of the pre-treatment workshop:

The block of a schematic of the pre-treatment workshop is shown in [Fig.5](#), below:

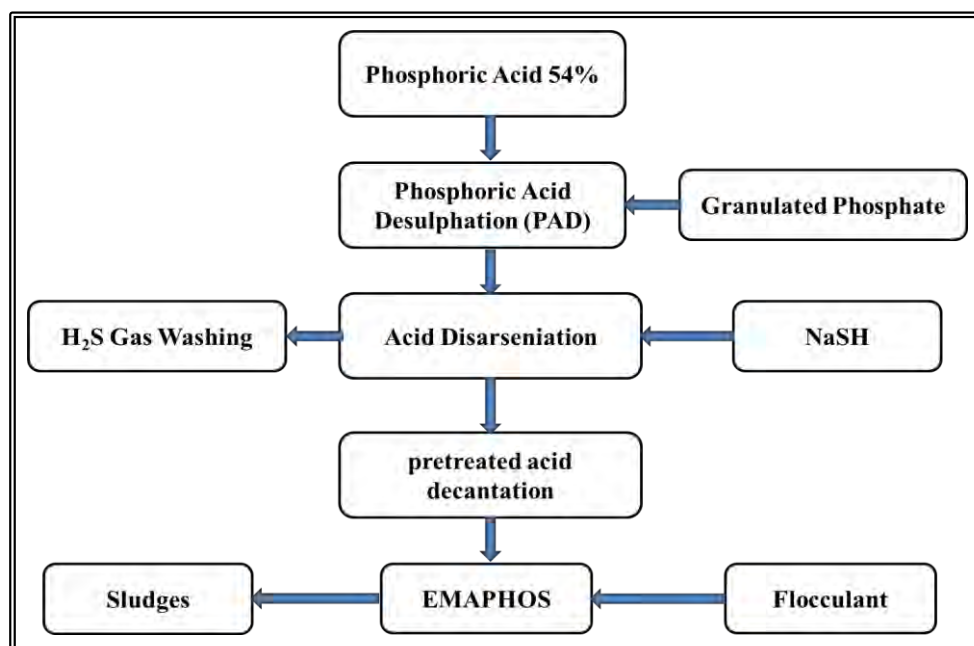


Fig.5: The block diagram of the pre-treatment workshop.

d. Desulphatisation and desaturation of phosphoric acid (see in Fig.6):

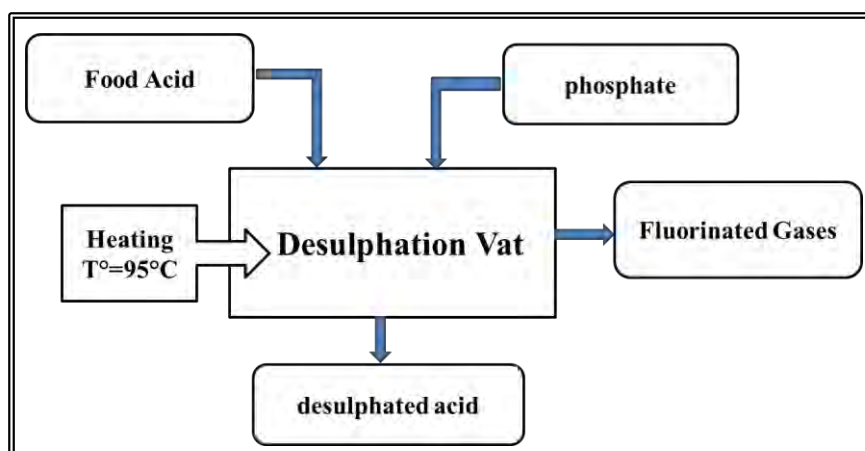
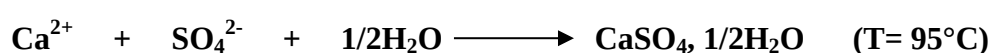


Fig.6: The desulphatisation and desaturation scheme of phosphoric acid.

e) Phosphate profile

The phosphate profile designed for desulphation: is of type “K09” whose characteristics are shown below:

- Granulometry: 0.5% > 3.15 μm; Ground phosphate 1/1.5% > 250/260 μm
- Chemical composition: %P₂O₅ = 30-31%; %SO₄²⁻ = 1.5 - 2 %; %CaO = 50-51.5 %
- Settings:

- The temperature in the desulphation tank: 95°C.
- %SO₄²⁻ of food acid 54% in P₂O₅, exit steps: 2 to 2.6%.
- The molar ratio of desulphated acid: 0.95 to 1.1.

f) The desarseniation unit: is presented in [Annex. IV](#) on [Fig. IV.2](#).

III. Experimental Studies on KHOURIBGA Phosphate Apatite.

According to the previous survey, we found it interesting to study the material key to the industrial revolution, the interest is focused on the phosphate of my city of origin, we chose the original apatite of KHOURIBGA, but before the history, so it will be useful in our report to point out the necessary tools for enriching phosphate ore, by some insight on treatments: drying, calcination and also flotation.

III.1. Presentation.

a) History.

The first traces of phosphate were discovered in MOROCCO in 1912 in the Ouled-Abdoun Zone of KHOURIBGA. Pure phosphate is a whitish powder, the product of the decomposition of bones fish, and others that settle to the bottom of the sea. This decomposition, followed for millions of years, long before man existed, some current continents were covered by the seas in part or totally, I would like to recall the story of the prophet Nuh (alayhi salam). As the sea receded, it left huge fish cemeteries whose bones, by decomposing over the centuries, formed apatitic phosphate. Its deposit was in 4 superposed layers of different richness at a depth of 6 to 12 meters, the most important of which varies from 2 to 6 meters thick. Phosphate consists of several elements including Calcium, Phosphorus, Fluorine, Chlorine, and Organic Matter, as well as some oxides and metallic trace elements. Most chemical elements are considered among the most important elements in life. Among the many mining resources of the Moroccan subsoil, the 1st place goes to phosphate both by the extent of the deposits and by the importance of the tonnages extracted.

Phosphate reserves are estimated at 57.8 million tonnes and 75% of world reserves. Phosphate mining began in the Ouled-Abdoun regions (KHOURIBGA province) in 1921, the first prospecting was carried out in 1908 until 1921.

KHOURIBGA; the richest deposit in the world, Fig.7. The Ouled-Abdoun deposit is presented externally as a plateau at an average altitude of 800 meters, cut off from erosion valleys, with an average coverage of about 40 meters. In the east, towards Oued-Zem, the covering is variable and is low on average. The deposit, of the sedimentary type, consists of a set of continuous phosphate layers, with almost no slope, of variable power, separated by more or less sterile intercalations. For the time being, only layers n°1 and n°2 are exploited (third is thus from the surface, layer 0 being generally insufficient for profitable exploitation under the present conditions), n°1 containing 75% $\text{Ca}_3(\text{PO}_4)_2$ Tricalcium phosphate. It is the richest of all phosphate layers in the world.

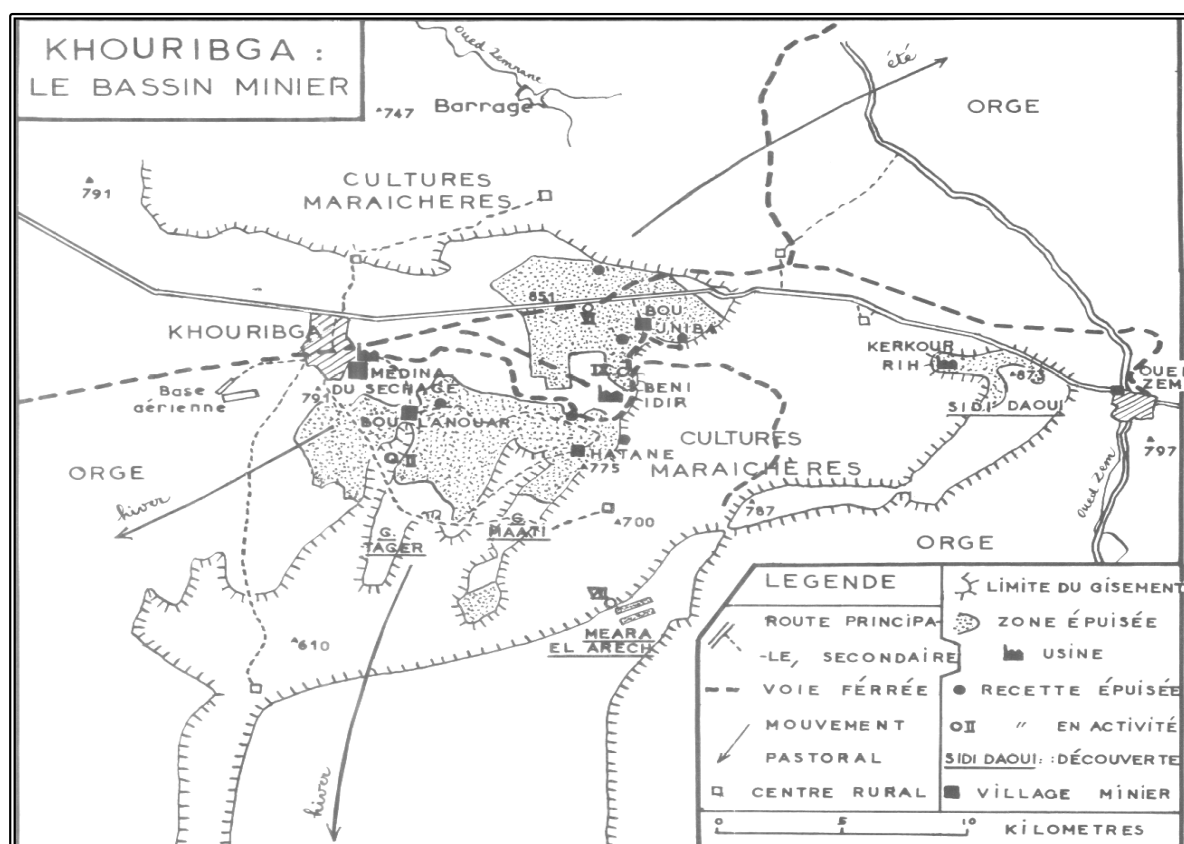


Fig.7: Moroccan mining town is KHOURIBGA.

Phosphate is the result of the decomposition of organic and inorganic matter, and generally the decomposition of skeletons of fish and another origin, which have been abandoned by oceans and seas for millions of years and following subterranean disturbances, the layers have been found at depths ranging from 5 to 49 m in general. It is mainly used in the manufacture of fertilizers for soil enrichment. Phosphate ore is generally composed of four parts: raw phosphate, waste rock, clay, and water. Hence, the need to enrich the poor phosphate qualities from the extraction site.

b) Drying and Calcination.

Pure phosphate consists of phosphate grains called "ooliths", bone debris known as Apatite $\text{Ca}_3(\text{PO}_4)_2$, we can distinguish: fluoroapatite: $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2 = 3\text{Ca}_3(\text{PO}_4)_2\text{CaF}_2$, chloroapatite: $\text{Ca}_{10}(\text{PO}_4)\text{Cl}_2 = 3\text{Ca}_3(\text{P})_2\text{CaF}_2$ and rarely hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)(\text{OH})_2 = 3\text{Ca}_3(\text{PO}_4)_2\text{Ca}(\text{OH})_2$.

The qualities of the phosphates extracted at the OCP level are defined by the percentage of anhydride: **GPL** (good phosphate of lime or bone phosphate based on calcium). [Table.3](#) shows the different qualities selected according to the percentage.

Table.3: The different phosphates according to the percentage of GPL.

Source qualities	% GPL
Super High content	GPL > 75%
Very high content	$73 < \text{GPL} \leq 75$
High normal content	$71.5 < \text{GPL} \leq 73$
High Medium content	$69.5 < \text{GPL} \leq 71.5$
Medium content	$68 < \text{GPL} \leq 69.5$
Low content	$61 < \text{GPL} \leq 68$
Very low content	$58 < \text{GPL} \leq 61$

The raw ore, as it leaves the mine, is in the form of fine, greenish, or yellowish sand, fairly compact and containing 12 to 15% water (Fig.1). It whitens when dried and calcined at high temperatures. Its low content of iron and aluminium oxides makes it particularly appreciated by manufacturers of TSP superphosphates (fertilizers).

The mining centre of KHOURIBGA, Fig.7, (4 mining sites: Sidi Daoui, Merah El Ahrach, Sidi Chennane, and Beni Amir), is equipped for a daily production of 20000 tonnes of merchant phosphate corresponding to the extraction of 25000 tonnes of raw phosphate, four-fifths of which comes from underground operations, including three extraction sites (or recipes), and one fifth from a more recent open pit operation.

In 1951 and 1952, it was the first start of discovery mining in Sidi-Daoui and the beginning of the development of drying and calcination facilities. The discovery is equipped for an average daily production of 2500 tons of merchant phosphate.

The stones phosphate is then screened to remove the waste rock it contains on high-capacity vibrating screens (22000tone/day). It then contains about 15% moisture, a percentage that must be reduced to below 2%. This operation was carried out in 17 rotary furnaces heated by mazout or by fuel oil, where the phosphate is brewed with a stream of hot air.

The ore is then screened again at a 6 mm square mesh, then placed in silos (capacity: 250000 tonnes) before being transported to the port of CASABLANCA by self-draining 54 and 65 tone hopper cars for export. Part of the extracted tonnage is calcined by heating at 700°C/900°C/950°C of the screened wet phosphate, to order to decompose the lime carbonate and organic matter, the product obtained is better suited for certain subsequent treatments (chemical industry, fertilizer preparation,...., etc.)(1).

[1] Journal le monde diplomatique, juin 1962. Pages 18 et 19.

The unit of the Béni-Idir and near the Sidi Daoui plant started up in 1965 to process the phosphate supplied by the extraction units. For the Béni-Idir plant, the input is wet phosphate, the treatment consists of drying the phosphate, after this operation the phosphate is ready to be transported.

The Béni-Idir drying and calcination plant started with four ovens, and as part of an extension of the plant, four other kilns were commissioned in 1970, which allowed reaching an annual production capacity of 9.3 MT (Megaton). This capacity has increased to 10.7 MT following the contribution of the Béni-Idir of reorganization project.

Phosphate screened at the 15*50 mm² mesh feeds the wetland park, which has four stocks with a total capacity of 500,000 tonnes. Fig.8 shows the drying and calcination plant at Béni-Idir, as well as the control technician in the control room, who is my father "**may Almighty God bless his soul**".

Béni-Idir includes the following units, as shown in Fig.9 below:

- A wetland park with a total capacity of 400,000 tonnes; for the storage of product screened at 15 x 50mm² mesh size (Fig.10).
- A calcination unit built to enrich the phosphate by raising its temperature to 700°C/900°C/950°C to reduce the CO₂ rate (from 7% to 1%) according to the customer's request, with the elimination of certain elements such as water and organic matter.
- Dry enrichment plant to improve the GPL content to 67% by going through the following steps: Drying; Screening at 3mm; Grinding to 1mm to break up mixed entanglement (phosphate gang); Elimination of 360-micron rejects. A dry phosphate stock.
- A loading station for the trains that transport the dried phosphate to the port of Casablanca.
- A drying unit consisting of 8 ovens with a capacity of around 360 tonnes each.

- A screening workshop.
- Petroleum coke grinding facility.
- A boiler room containing two water tube boilers producing the water vapour necessary to ensure the conditioning of fuel oil.
- A fuel oil unloading facility.



Fig.8: The drying and calcination plant as well as the control room, in Béni-Idir.

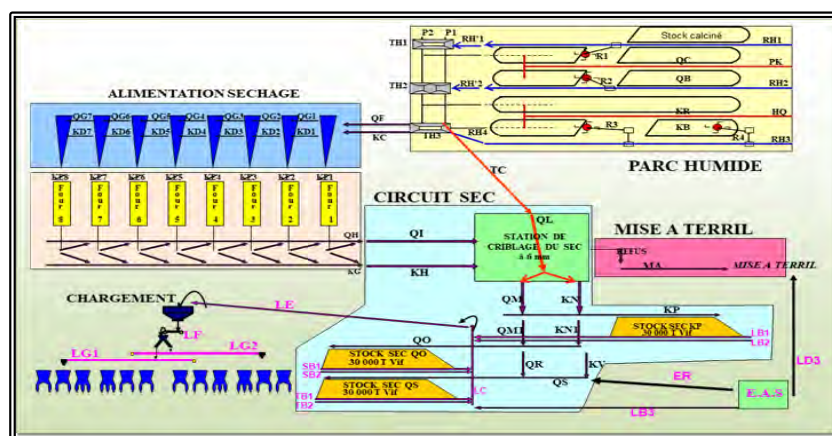


Fig.9: Synoptic schematic of the drying and calcination plant at Béni-Idir.

Sidi Chennane is the new mine (Exploitation in Discovery) that started operating in October 1994. In the first phase, extract 6 million tonnes/year. Production reached 10 to 12 million tonnes in 2000. On that date, the operation of Sidi Daoui was completely stopped. Sidi Chennane, therefore, spans the provinces of K HOURIBGA, and BENI-MELLAL. The deposit that will be exploited covers an area of 3000ha. The land was transferred to OCP by the State for an increase valued at 40% of the price, the part located in the province of K HOURIBGA being collective land. In this phosphate zone, the resources are located in a 30km triangle, formed by K HOURIBGA; Oued-Zem, and Fqih-Ben Salah. However, the opening of the Sidi Chennane mine marks the displacement of mining activities in the province of BENI-MELLAL, which covers 95% of the deposits in this area. The known reserves of this mine are estimated at 900 million tonnes. The estimated operating life is 25 years. All recoverable Sidi Daoui equipment is transferred to the new Sidi Chennane mine. Mr. El Houssaïn Youzalen, director of mining operations at K HOURIBGA, believes that the takeover of the Sidi Daoui equipment and the "best" use of existing infrastructure has saved \$200 million. The project's internal profitability is 20%. Work began in 1991. The mining equipment is a turnkey project. It is carried out by the Spanish company 'ENI', which has used some 20 local and foreign subcontractors. [2]

[2] Journal l'économiste, Edition N°:99 Le 14/10/1993

In Sidi Chennane, a destoning hopper with integrated screening is used to receive the all coming loaded into trucks or monstrous machines 170ton. The phosphate is separated from the sterile by a first screening at $90 \times 90 \text{mm}^2$. The sterile material is broken up for storage. The phosphate is then screening to a mesh of $15 \times 50 \text{mm}^2$ (Fig.10) and refusals are crushing. The resulting product is stored in two parallel areas with a capacity of 174000m^3 each. Three machines manage these storage areas. Two storage units with a capacity of 2000t/h distribute the product in both areas. Then a central wheel loader of 2800t/h feeds the conveyor by band from these two areas.

The designers of this hopper have planned a diversion of all comers. Indeed, the third layer, with low content, will be exploited for the first time.

Also, the Béni-Idir factory's treatment is being reorganized, the aim being to make better use of the facilities for the management of the multiple qualities, the number of which has increased from 8 to 20 furnaces. This reorganized consists of coupling, lengthening and moving several conveyors with flow rates ranging from 150 to $3,000 \text{ T/h}$. In Fig.10 we see the $15 \times 50 \text{mm}^2$ mesh screening screen.



Fig.10: $15 \times 50 \text{mm}^2$ meshed screener of Béni-Idir.

c) Flotation.

In recent years, the OCP group has vigorously embarked on the recovery of the economic value of the phosphate layers GPL poor, which has prompted the managers to implement new technologies for the valorization of these increasingly GPL poor layers.

With this in mind, the OCP group created the Merah El Ahrach washing unit in the M'fassis commune in 2010, which is located 25 km southeast of the town of K HOURIBGA, on either side of the RN11 national road, heading towards Fkih Ben-Salah. The function of which is to enrich the phosphate and prepare it for transport via slurry pipeline. This unit is the largest poor phosphate washing plant, with 6 washing lines with a total capacity of 350T/h (3MT/year), 2 grinding workshops with a unit capacity of 240t/h, 3 flotation workshops with a unit capacity of 300 t/h, a tank farm with a capacity of 800000 tonnes and 3 decanters with a diameter of 135m. This giant investment aims to adapt the Merah El Ahrach laundry to the treatment of layer 3, to satisfy the demand of the national and international market, in terms of quantity and quality. the ores low and very low, contents (LC and VLC) are physically treated by wet processing of laundry at Merah El Ahrach. [Fig.11](#) shows the General Plan of the Laundromat.

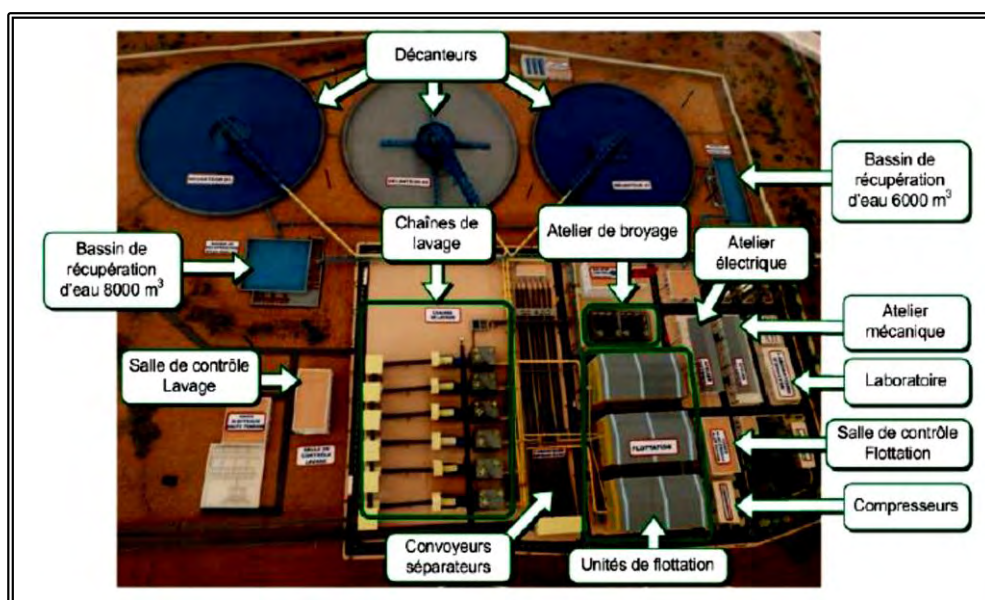


Fig.11: General plan of the Merah El Ahrach Laundromat.

It began its activities in 2010, and on March 21, 2012, is part of the implementation of the OCP group's industrial project and its ambitious strategy reconciling the expansion of industrial activities, preservation of water resources, and respect for the environment, placed at the heart of the Moroccan group's concerns. The ore to be processed in the project facilities is a soft, sedimentary phosphate with sterile proportions of up to 40%. The latter is made up of limestone and flint blocks. These waste rock will be disposed of for stone removal and screening operations.

Commissioning of the new laundromat as part of the OCP industrial development program; record production of medium content phosphate at 2.4 million tonnes, which made it possible, for the first time, to ship a richer phosphate to Jorf Lasfar throughout 2010, bringing the KHOURIBGA South back into operation.

Enrichment consists of ridding the ore of its poorest grain size fractions, i.e. grains larger than 125 μm and smaller than 40 μm . This valorization is carried out using specific treatments to increase its GPL content and prepare it for transfer by Pipeline to Jorf Lasfar.

According to GAUSS' granulochemical analyses, the phosphate from the laundromat is generally made up of three slices:

- The coarse particle slice "greater than 2.5mm very low in GPL": It is a mixture of limestone cement agglomerate and large silica grains often free, the content of this slice is less than 50% in GPL.
- The fine-particle slice "lower than 40 μm low in GLP": Relatively rich in CO_2 and SiO_2 , contains practically only clays. The content of this tranche is less than 68% GPL.

The intermediate slice is rich in GLP, with a content of less than 70% GLP. At the exit of the various extraction zones, the phosphate ore is conveyed to the Merah El Ahrach laundromat where it will undergo specific treatments to increase its content of GPL, the sequence of phases of phosphate treatment at the laundry is shown in [Fig.12](#) below. The objective of each laundromat production line as shown in [Fig.13](#):

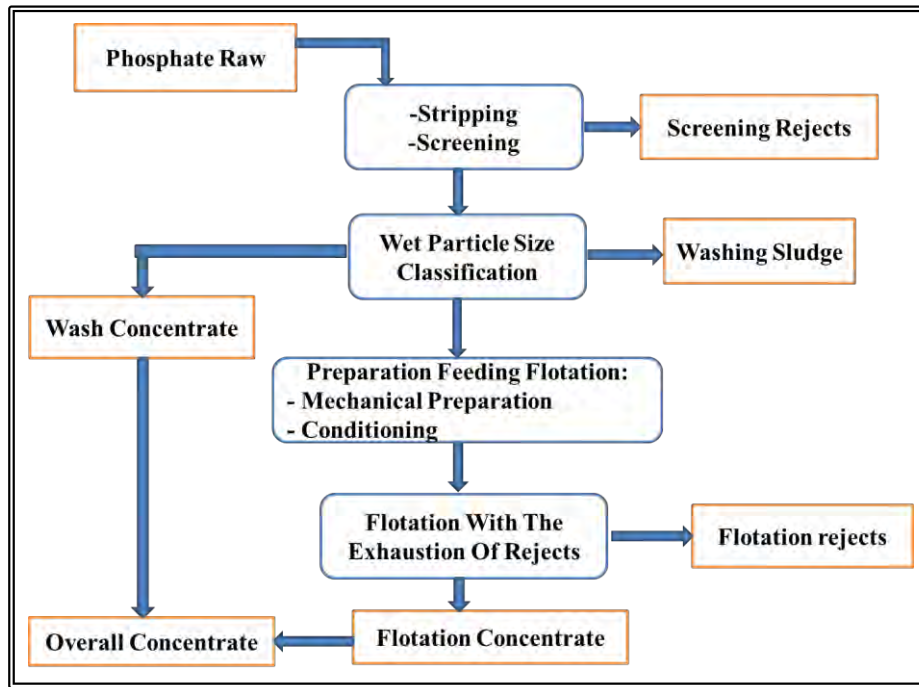


Fig.12: The treatment phases at the laundromat.

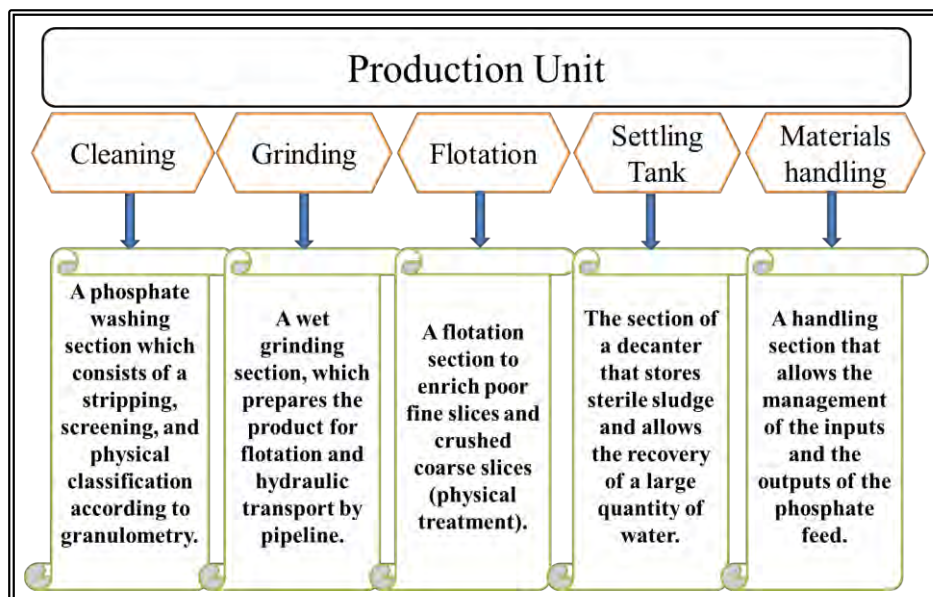


Fig.13: Production chains.

We are interested in the new technique "flotation", because the enrichment of phosphate ore (tranche 40 - 125 μ m), is a physicochemical treatment by a wet process which is based on the surface properties of the grains to be separated. It consists in to depress the mineral "apatite" ore and floating the undesirable elements constituting the gangue by adding the reagents, to increase the GPL content of the ore.

Generally, the flotation principle is based on the hydrophobic and hydrophilic properties of solid surfaces. These properties can be natural or stimulated, using a suitable reagent that is added to the water bathing the solid particles. When air is introduced as small bubbles into such a medium, selective transport of hydrophobic particles occurs. Particles with hydrophobic surfaces attach to air bubbles when they collide with them.

However, flotation consists of the flotation of carbonates that are collected by adding the ester and silicates that are collected by adding the amine. While phosphate is depressed by the addition of phosphoric acid with a concentration of 54% in P_2O_5 ; this is the reverse flotation. In the end, this flotation product will be evacuated towards adaptation. The principle of Flotation in Fig.14.

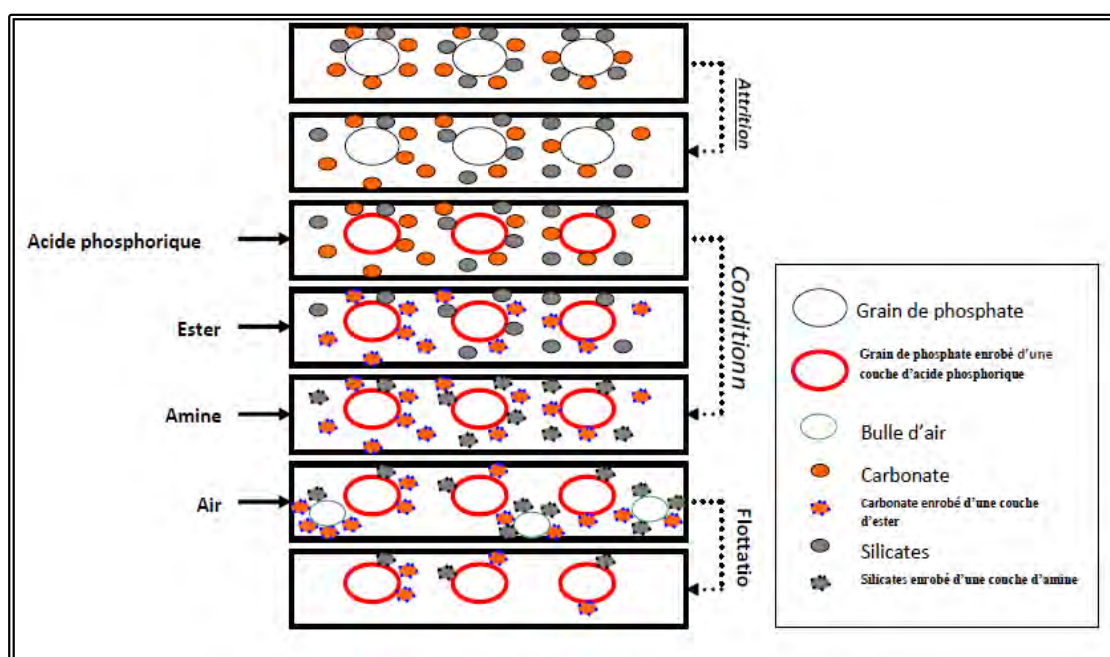


Fig.14: Principle of Flotation.

Flotation conditioning according to the laundry process is indicated in Table.4. Namely, the two reagents Ester and Amine are diluted ten times for each.

Table.4: Flotation conditions according to the laundromat process.

Reagents	Mass in g/Tonne Apatite low content (BT)	Mass in g /Tonne Apatite very low content (TBT)
ACP 54%	300	600
Ester	200	400
Amine	60	120

d) Conclusion.

Drying is an irreversible thermal process, designed to reduce the moisture content of some products (such as raw phosphate) but gives little considerable enrichment. Unlike calcination, drying does not significantly alter the physicochemical properties of the minerals that could play a role in their further processing. In particular, the thermal treatment of phosphates requires huge amounts of energy to remove unwanted materials, which, together with fuels, are the two main sources of environmental pollution. This is associated with energy loss problems. Flotation modifies the consumption and production modes as well as the transport of phosphates richer in P_2O_5 . The advantage of flotation is that it consumes less water than washing. Also, the fines and fillers inside the apatite paste are conserved to a maximum. For this reason, flotation technologies are becoming more strategic, energy-efficient, and effective.

III.2. Structural and Optical Study of Fluorapatite of the KHOURIBGA.

a) DRX of the Very Low Content Fluoroapatite (TBT-C and TBT-F).

The Very Low Content Fluoroapatite sample called TBT in P_2O_5 , processed in our laboratory, in two different ways. The apatite named TBT-C (Phosphate Calciné de Très Basse Teneur); washed ground and calcined up to 900°C , and the apatite TBT-F (Phosphate Flotté de Très Basse Teneur) dried at 105°C ; before it undergoes a flotation treatment according to the conditions listed in [Table.4](#). DRX analyses performed by the laboratory D2PHASER (see [Chapter. I](#)), showing the apatitic phase of the two samples; [Fig.15](#). The

diffractograms are similar to each other show the hexagonal system phase, except for two peaks that appear in the TBT-C phase; indicated by the stars, do not exist in the TBT-F phase.

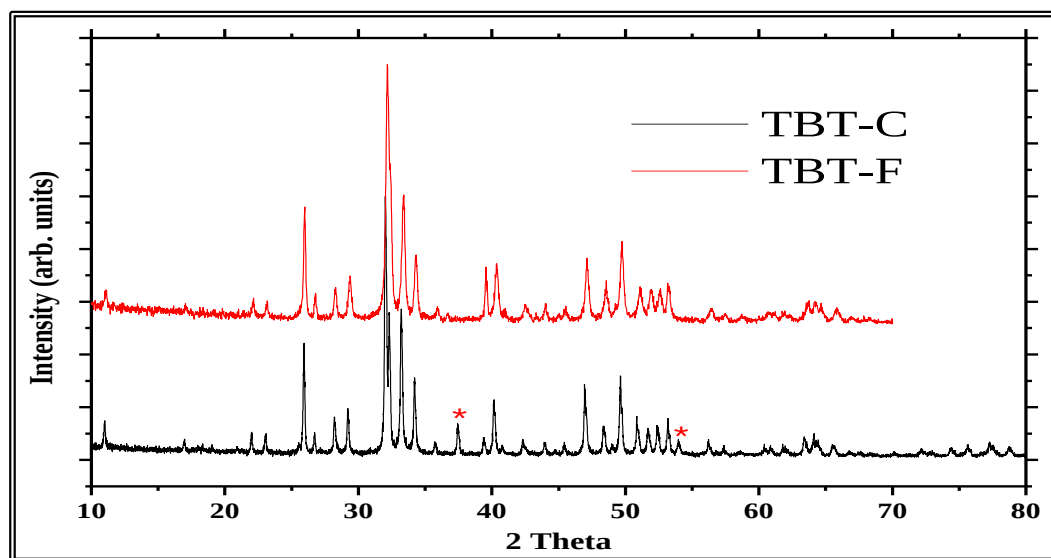


Fig.15: DRX of crude fluorapatite; TBT-C and TBT-F.

However, indexing by HighScore software [3] is useful, aiming for completeness and accuracy. The indexing of the Fluoroapatite TBT-C phase shows that it is similar to several references, the most justifiable (synthesized Fluoroapatite)[4] is cell underlined in Fig.16. It appeared that several peaks are not indexed, thus showing the presence of impurities, which are of the minor - Phases. However, the detection of these phases by HighScore [3] software is difficult, and it requires a lot of time, we will come back to these elements in more detail later. We notice that the flotation method is more efficient than calcination, justified by the peaks that appear in the TBT-C phase, and the crystallinity of the material.

[3] T. Degen, M. Sadki, E. Bron, U. König, G. Nénert; Powder Diffraction 29 (2014) S13-S18

[4] Heijligers, H., Depart. Phys. Chem. Techn. Univ. Eindhoven, Eindhoven, The Netherlands., Private Communication Verbeeck, R. et al., Ber. Bunsenges. Phys. Chem., 84, 159, (1980)

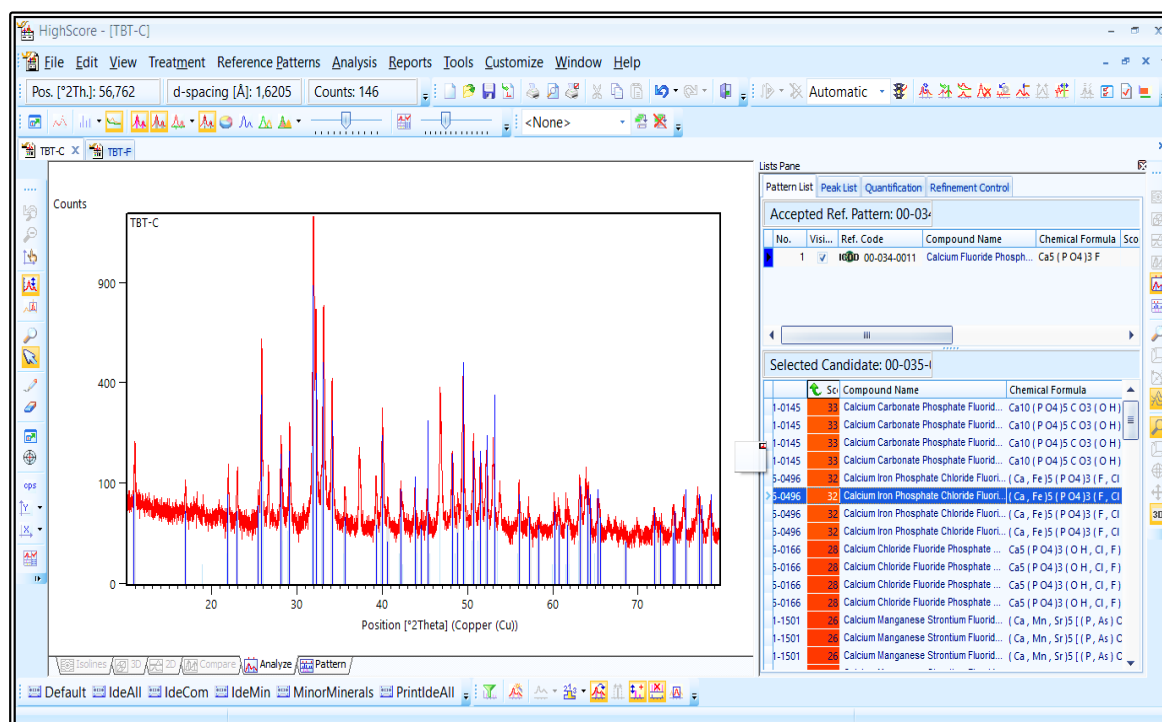


Fig.16: Indexation of TBT-C fluorapatite by HighScore.

b) Refinement.

Geochemical studies have demonstrated the high capacity of an apatitic mineral to retain a large amount of water, organic matter, and a variety of trace elements such as heavy metals and rare earth elements. Given the importance of apatitic phosphates both nationally and internationally, a comparison with other natural apatite is warranted. Indeed, we are based on the chemical and structural characterization of HAHOTOE rock phosphate from TOGO [5]. The objective of the ref study is to determine the chemical composition and crystal structure of TOGO sedimentary phosphorite for purification and commercial exploitation. The raw studied ore is a mixture of phosphate and grey clayey rock. The treatment of the ore made by the elimination of clays in the raw material, in which about 30g of rock were ground and introduced into 1L of demineralized water. The sludge was enclosed for 1 hour and centrifuged at 3000 rpm for 30 minutes. The filtrate containing clays was separated from the phosphate-rich solid residue, this operation was repeated 10 times.

[5] Gado Tchangbeddji, Gnande Djeteli, Koffi Ani Kili, Jean Michel Savariault and Jean Louis Lacout, Bull. Chem. Soc. Ethiop. 2003, 17(2), 139-146.

The solid residue was dried at 100°C for 24 hours and calcined at 800°C for 4 hours. The final compound is a washed product whose chemical composition is the raw ore and a solid obtained after washing, centrifugation, filtration, and calcination.

One gram of the raw compound has been calcined at 600°C for 12 hours, and 1g of the final compound (washed), are dissolved separately in 2ml concentrated HCl (36%). The resulting solutions are diluted and analyzed by atomic absorption spectrometry to determine the chemical compositions Ca, Cd, Mn, K, Cu, Mg, Si, and Fe. Phosphorus is measured colourimetrically with phosphomolybdate blue. The carbon percentage was determined using a CHNS analyzer (for more detail see [Annex. IV](#) in [Fig. IV.3](#)). The results presented in [Table.5](#), show that the treatment of crushed phosphate rock allows the separation of clays containing the majority of metal oxides of calcium phosphate. Nevertheless, the final material contains traces of clays, silica, and other metal oxides (MgO, Al₂O₃, Fe₂O₃,..., etc.). But the concentration of cadmium and manganese varies, as the concentrations of phosphates (P₂O₅) indicate that they are included in the phosphate compound, regarding their molecular structure. The presence of fluoride and carbon in the material after calcination at 800°C indicates that the calcium phosphate contained in the rock is carbonate fluorapatite, with a low substitution of calcium by cadmium and manganese. All the results discussed in ref [5].

Table.5: Chemical composition (in weight percentage) of raw and washed materials by atomic absorption spectrometry^[5].

Parameters	Raw material	Washed material
%CaO	35.80	55.6
%P ₂ O ₅	28.20	38.30
% SiO ₂	12.5	2.10
% Fe ₂ O ₃	7.2	0.03
%Al ₂ O ₃	5.6	0.01
% MgO	3.8	0.01
%K ₂ O	2.6	0.02
% Na ₂ O	2.8	0.01
%CO ₃ ²⁻	0.75	0.68
% F	0.15	0.40
Cd (ppm)	49	58
Mn (ppm)	74	86
Zn (ppm)	35	3.5
Cu (ppm)	45	2.7

The structure is refined using the FULLPROF system [6], shows the proposed molecular formula: $\text{Ca}_{9.925}\text{Cd}_{0.004}\text{Mn}_{0.013}[(\text{PO}_4)_{5.886}(\text{CO}_3)_{0.113}]\text{F}_2$ (FAP = 95.11% and quartz = 4.89%). Which crystallizes in the hexagonal system, space group $P6_3/m$. The cell parameters are: $a = 9.3547(5) \text{ \AA}$; $c = 6.8929(4) \text{ \AA}$.

We can conclude, as we indicate in this interesting study, that the final (washed) ore is a crystalline solid, obtained after washing, centrifugation, filtration, and calcination, of the mother material. The treatment is of considerable enrichment. Indeed, most impurities are eliminated except those residing in the apatitic skeleton, because this capacity is due to their particular crystal structure which allows isomorphic substitutions in “6h and 4f” crystallographic sites. A good agreement is obtained between the experiment and the theory, between the experimental radiographic diagram and the calculated radiographic diagram ($R_p = 0.149$; $R_{wp} = 0.173$; $R_F = 0.0558$; $R_B = 0.079$).

To returning in our apatites TBT-C and TBT-F, the atomic coordinates of carbonate fluoroapatite[5], only for ions ‘P, F, O and Ca’, are used as starting parameters, for structural refinements by the Rietveld method that is performed using the FULLPROF program[6].

Fig.17 shows the comparison between the experimental radiographic diagrams and the calculated radiographic diagrams of natural fluorapatite TBT-C and TBT-F. The results of the Rietveld refinements concerning structural and non-structural parameters and interatomic distances and O-P-O angles are given in Table.6. The resulting data for mesh parameters, atomic coordinates, isotropic temperature factors, and occupation at sites 6h and 4f of the different cations are listed in Table.7. The graphical exploitation of the crystal structure is shown in Fig.18, the results showing the junction for these two sites M (6h) and M (4f) (occupied by both Ca^{2+} cations) with the polyhedron $(\text{PO}_4)^{3-}$, which delimits the centre of the hexagon by fluoride ions, extending along the plane (001).

[6] J. Rodriguez–Carvajal, ‘An introduction to the program fullprof 2000’, Saclay, July (2001).

Ca(I) shows the 6h site of the hexagonal, illustrating the arrangement of metal and oxygen around the sites (6h), connected to the $5(\text{PO}_4)^{3-}$ tetrahedrons. Ca(II) sees prism 4f surrounded by $6(\text{PO}_4)^{3-}$ tetrahedron.

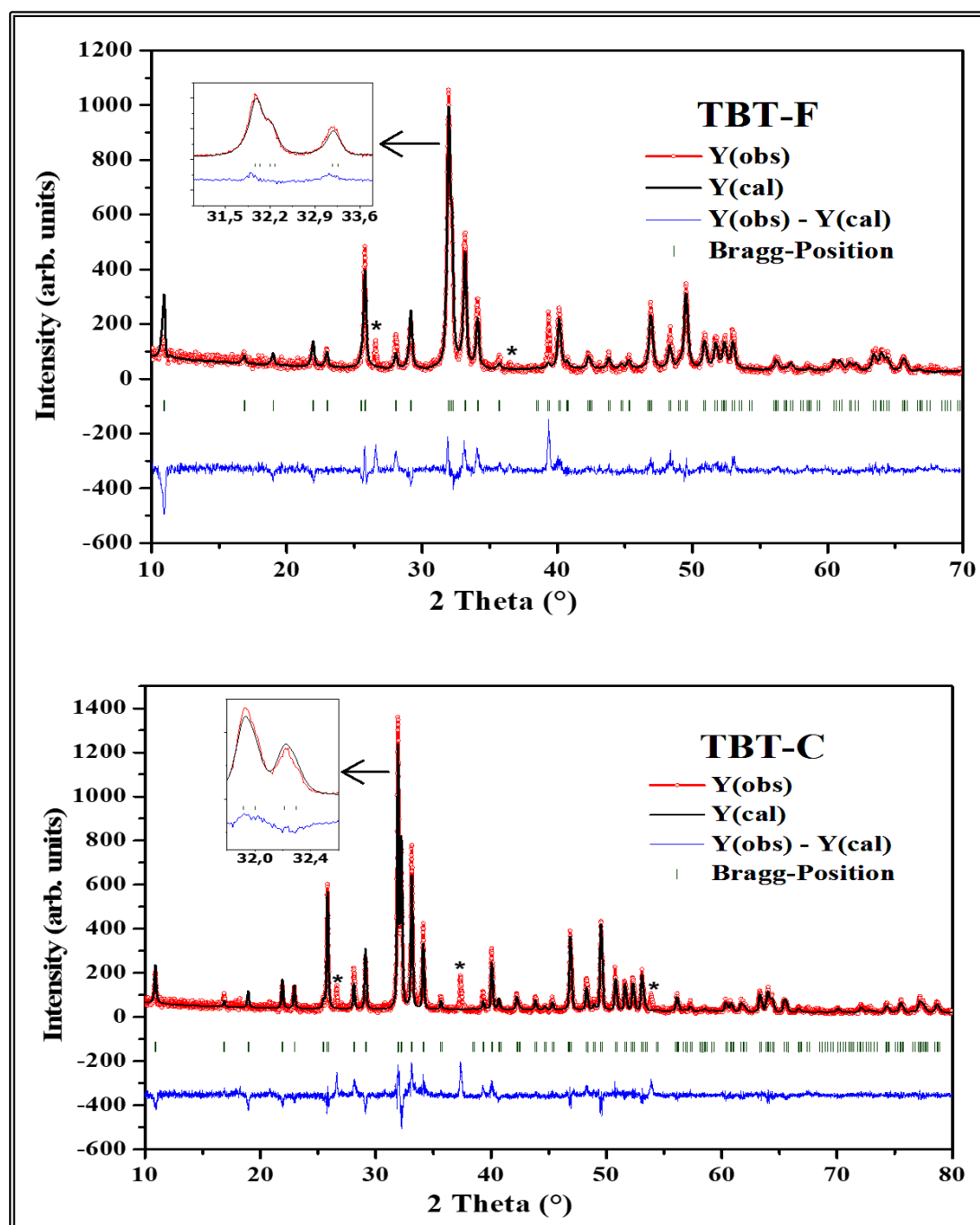


Fig.17: Rietveld plot for TBT-F and TBT-C. The upper symbols illustrate the observed data $Y(\text{obs})$, and the calculated pattern (solid line) for $Y(\text{cal})$. The vertical markers show calculated positions of Bragg reflections in Bragg-Position and the lower curve is the difference diagram schematize in the $[Y(\text{obs}) - Y(\text{cal})]$.

Table.6: Results for Rietveld refinement method for X-ray powders data and selected interatomic distances in (Å), and 'O-P-O' angles in (°) of $\text{Ca}_5(\text{PO}_4)_3\text{F}$ for TBT-C and TBT-F.

structural and non-structural parameters				interatomic distances and angles		
Apatite		TBT-C	TBT-F	Atom	TBT-C	TBT-F
Step width (2 θ)		0.010142°	0.020283°	Ca(I)-O1	2.680(5)	2.635(4)
Zero-point(deg.2 θ)		0.077(2)	0.193(10)	2*Ca(I)-O2	2.325(3)	2.474(5)
Pseudo-Voigt function $\text{PV}=\eta\text{L}+(1-\eta)\text{G}$	η	0.9768(274)	0.9768(367)	2*Ca(I)-O2	2.451(4)	2.357(3)
				Ca(I)-O3	2.306(4)	2.342(6)
Caglioti parameters	U	0.2570(245)	0.2150(114)	<M(6h)-O>	2.4405	2.452
	V	-0.1407(170)	-0.0791(826)			
	W	0.0393(29)	0.0512(146)			
No. Of reflections		256/2	202/2	3*Ca(II)-O1	2.379(5)	2.370(4)
No. Of refined parameters		32		3*Ca(II)-O2	2.898(7)	2.902(4)
Z		2		3*Ca(II)-O3	2.524(6)	2.431(5)
Atom Number		7		<M(4h)-O>	2.6003	2.5677
User-weighted Chi2		2.87	3.31			
%R _F		10.2	10.3	P-O1	1.565(10)	1.541(8)
%R _B		16.8	14.5	2*P-O2	1.564(4)	1.599(5)
%R _p		15.7	14.7	P-O3	1.573(8)	1.552(5)
%R _{wp}		20.3	21.0	<P-O>	1.567	1.564
%cR _p		32.5	31.4			
%cR _{wp}		33.9	36.3	3*Ca(I)-F	2.287(3)	2.315(4)

Table.7: Refined structural parameters in (Å) of $\text{Ca}_5(\text{PO}_4)_3\text{F}$ for TBT-C and TBT-F.

Space group: $P 6_3/m$						
Atom	Wyckoff	x/a	y/b	z/c	B (Å ²)	Occupancy
TBT-C						
a = 9.3658(5)		c = 6.8968(4)		V (Å ³) = 523.92(5)		
F	2a	0.0000	0.0000	0.25000	0.61(61)	2
Ca(I)	6h	0.2390(7)	-0.0101(9)	0.25000	2.36(16)	6
Ca(II)	4f	0.3333	0.6667	0.0018(15)	2.09(22)	4
P	6h	0.3955(11)	0.3651(11)	0.2500	2.10(23)	6
O(1)	6h	0.3275(24)	0.4875(18)	0.2500	6.49(3)	6
O(2)	12i	0.3281(12)	0.2470(16)	0.07116	6.49(3)	12
O(3)	6h	0.5885(26)	0.4777(20)	0.2500	6.49(3)	6
TBT-F						
a = 9.3492(2)		c = 6.9089(14)		V (Å ³) = 522.99(19)		
F	2a	0.0000	0.0000	0.2500	1.64(99)	2
Ca(I)	6h	0.2392(9)	-0.016(1)	0.2500	1.05(28)	6
Ca(II)	4f	0.3333	0.6667	0.0012(2)	2.09(53)	4
P	6h	0.4068(18)	0.3787(19)	0.2500	2.10(58)	6
O(1)	6h	0.3286(35)	0.4899(31)	0.2500	6.06(5)	6
O(2)	12i	0.3281(13)	0.2474(20)	0.0780(21)	6.06(5)	12
O(3)	6h	0.5985(38)	0.4715(29)	0.2500	6.06(5)	6

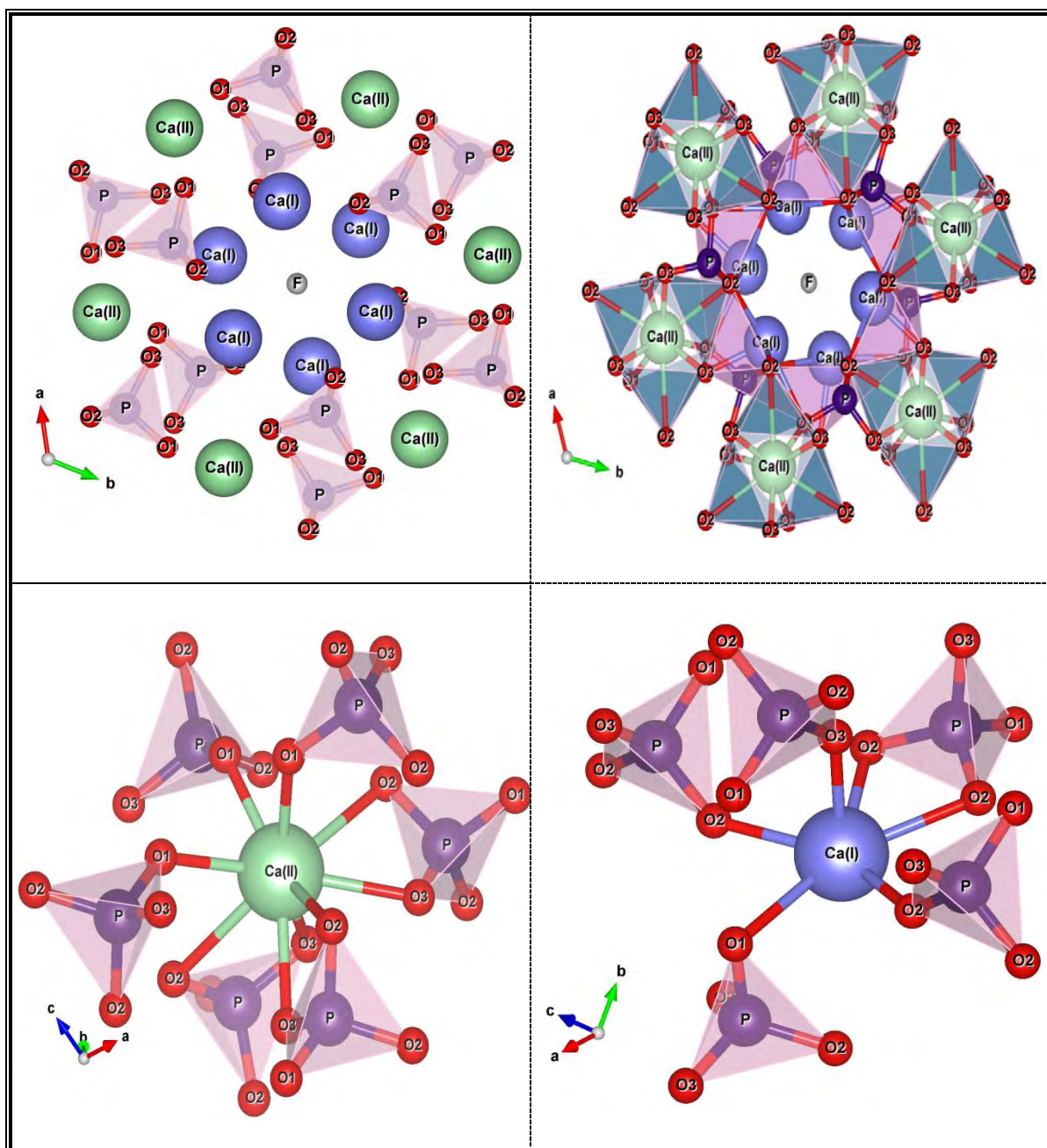


Fig.18: Projection of cell along (001) for natural fluorapatite. Ca (I) and Ca(II) cations are presented on the faces of PO_4^{3-} tetrahedron.

Despite the analysis on TBT-F (twenty minutes) carried out during the semi-duration period compared to TBT-C (forty minutes), the DRX shows that the purpose of flotation is to enrich the ore with a more favourable structure than that obtained after washing and calcining (TBT-C).

The mesh parameters, interatomic distances are reasonable, similar, and in agreement with those found in ref [5] and other references. Where the distances Ca(I)-O6 in the site (6h) vary from 2.302Å to 2.680Å. For F-Ca(I)3 from 2.287Å to 2.315Å. The distances Ca(II)-O9 in the mixed site (4f) vary from 2.370Å to 2.902Å. P-O has an average of 1.5 Å.

c) Impurities in Fluorapatite; TBT-C and TBT-F.

The deposits of Moroccan phosphates, more precisely of Khouribga mining sites, contain as much quality of Tricalcium phosphate which varies according to the content of P_2O_5 (the phosphorus which is a noble element in phosphates). Classifies them according to the extraction rock, as follows: K01: 28.6%, K02: 30.21 to 30.66%, K09: 31.12%, K10: 32.04 to 32.49%, K12: 32.49%, K20: 32.95%, K40: 33.41%, K41: 33.87%.

However, the "K09" quality is the most widely used, known in the world, studied, and most representative. For the determination of the impurities encountered in the Fluorapatite structure TBT-C and TBT-F, it is essential to start by studying the nature and proportion of the impurities present in the ore, based on three different references.

We can quote: The final project, entitled "Physicochemical characterization of the granulometry slices of a phosphate "K09", carried out by Mr. MASTOUR Yassine [7], carried out in the central laboratory of JORF LASFAR- OCP. The aim is to improve the phosphate qualities "K09", for this purpose the physicochemical analysis of the granulometry slices by sieving, whose field of application is between 80 µm and 500 µm, carried out on phosphates is part of a more detailed analysis for each slice. Indeed, particle size affects chemical performance.

Because the smaller the particle size, the larger the interfacial surface between the phosphate grains and the reaction medium. This influences the speed of material transfer. On the other hand, very small particles (with a diameter of <60µm) will lead to a rapid speed an attack rate, and excessive release of ions, which will lead to local oversaturations and an increase in syncrystallised P_2O_5 losses. Large particles (of diameter>500µm) will not have

enough time to be completely attacked. They will tend to be covered with a protective layer of gypsum, thus limiting attack, and then the percentage of unattacked increases, it is, therefore, necessary to accept a compromise, but in general, it is necessary to define a homogeneous granulometry range containing neither too many fine nor too many coarse particles.

According to the results obtained on a sample of phosphate "K09" taken from the KHOURIBGA trains, by interpreting it from the subject ref [7], the slices higher a 500 μ m and lower 125 μ m have relatively low P₂O₅ grades compared to the other slices. However, the phosphate yield in P₂O₅ necessarily attaches to the diameters of the phosphate granules which must be around/or >160 μ m, offering a large surface area for attack by sulphuric acid, and therefore having the good yield in P₂O₅.

Our objective is to have the idea of the chemical compositions to refine the structures; TBT-C and TBT-F. For this purpose, the results of the analysis of the chemical elements on the phosphate sample "K09" with a granule diameter greater than >160 μ m [7]. The analyses for; P₂O₅ and CaO as well as minor elements (traces) by plasma spectrometer (ICP) by the perchloric attack, analysis of CO₂ carbon dioxide by volumetry (by Bernard Calcimeter), analysis of total silica [SiO₂(T)] by gravimetry by using aluminium nitrate, determination of the reactive silica content [SiO₂(R)] by atomic absorption spectrophotometer (SAA), and finally the analysis of fluorine by the specific electrode (by the Inometry apparatus), are represented in the [Table.8](#), with the sample control, as phosphate used in the phosphoric acid manufacturing process in the Morocco Phosphorus III unit, cite to justify and compare the study carried out on ref [7].

[7] Yassine MASTOUR, projet de fin d'études, Avril-Juin/2011, « Caractérisation physico-chimique des tranches granulométriques d'un phosphate K09 », Licence Sciences et Techniques (LST)- Université Sidi Mohamed Ben Abdellah, Fès.

In the same context, we can mention the end of study project entitled "*Amelioration of the chemical efficiency of a phosphoric acid production unit by minimizing syncrystallised losses (MP IV)*", carried out by Mr. ICHIBA Abderrahmane and Mr. BENHLIMA Youssef [8], carried out at the Maroc Phosphore IV plant, JORF LASFAR-OCP. In their work, to verify the correspondence of the current pulp to the requirements of PRAYON [9], they carried out chemical element analyses on the phosphate of the pulling at the thickening level over three months (January-February-March/2019). The results of the analysis of the chemical elements represented in [Table.8](#).

We also mention the analyses of PRAYON [9], during the study of the adaptation of the line for the reception of the pulp in 2012 (before the scheduled start of the Slurry pipeline project on the KHOURIBGA-JORF LASFAR axis), the designer of process PRAYON, carried out a chemical analysis of the phosphate rock used "K09" of KHOURIBGA origin to give a typical profile of the chemical composition and tolerance limits of each element.

Attached is [Table.8](#), which groups the results of the "K09" type profile of all references, cited.

[8] ICHIBA Abderrahmane et Mr. BENHLIMA Youssef, Mémoire de Projet de Fin d'Etudes, Janvier-juin/2019, « Amélioration du rendement chimique d'une unité de production d'acide phosphorique en minimisant les pertes en syncristallisé (MP IV) », Ecole Mohammadia D'ingénieurs, Université Mohammed-V de Rabat.

[9] Manuel opératoire Prayon 2012, philosophie de contrôle.

Table.8: Results of the "K09" type profile, of all references cited.

Chemical Element in % and in ppm	Phosphate dried at 105°C [7]		Phosphate of the Pulp [8]	Phosphate dried to 105°C [9]
	Granulated >160µm	Control		
P ₂ O ₅	32,27	31.55	30.92	31.12
CaO	50,88	50.89	50.93	51.58
F	3.49	3.11	3.76	3.82
CO ₂	5.77	6.72	7.31	6.5
SiO ₂ (Total)	1.59	1.87	2.94	2.5
SiO ₂ (Reactive)	1.50	1.35	1.20	1.20
SO ₃	2.08	2.15	1.94	1.9
Na ₂ O	0.83	0.81	0.90	0.85
MgO	0.28	0.37	0.72	0.45
Al ₂ O ₃	0.47	0.45	0.43	0.4
Fe ₂ O ₃	0.22	0.22	0.22	0.27
K ₂ O	0.07	0.07	0.06	0.07
Cd (ppm)	16	13	----	----

According to the results presented in Table.14, these analyses focus on:

- The major elements: %P₂O₅, %CaO, %CO₂, %F, %CO₂, %SiO₂ and %SO₃.
- Oxide elements: %Na₂O, %Al₂O₃, %MgO, %Fe₂O₃, %K₂O and 'Cd' in ppm.

It should be noted that the difference between the same major composition in ref [7, 8, and 9] is less than 1.5%, as well as for the same minor element less than 0.2%. Of course, these and other elements are all involved in the reactions involved in the manufacture of phosphoric acid. The higher the ratio [CaO content / P₂O₅ content], the higher the specific consumption of sulphuric acid for phosphate dissolution. As an indication, the ratio ref [9] equals 1.6575 greater than ref [8] than 1.6472, followed by ref [7] whose ratios 1.613 (control) and 1.5767 (Granulate>160µm). So the quality of phosphate ref [9] and ref [8] are good qualities for phosphoric acid production.

The theoretical model is a simplified image of reality, considering that phosphate ref [9] having the same proportions of chemical elements as present in our TBT-C apatite, and phosphate ref [8] having the same proportions of chemical elements as present in our TBT-F apatite. The refinements of the Rietveld structural simulation performed using the order of the elements in percentages (%) is conserved in all ref [7, 8 and 9], except for the two elements MgO and Al₂O₃, we targeted all the chemical elements except 'Al₂O₃, K₂O, and Fe₂O₃. The departure refinements according to Table.7, including P, F, O, Ca ions, are used as starting parameters. Carbon and Sulphur are Phosphorus substitutions on the 6h site, thus Magnesium substitutes calcium in the two crystallographic sites 6h [M(I)] and 4f [M(II)], sodium according to the results of the refining of the lacunar apatites resides in the sites 4f [M(II)] from where it substitutes Calcium in this site.

The results of Rietveld refinements concerning structural and non-structural parameters are given in Table.9, as well as the interatomic distances in (Å) and the O-X-O angles in (°) in Table.10. The resulting data for atomic coordinates, isotropic temperature factors and occupancy at sites '6h and 4f' of the different cations are listed in Table.11.

Depending on the nature of the chemical elements present in the ore, by refinement, we have shown the minor phase coexistence of the CaSiO₃ [10], perovskite of simple structure, indicated by the stars in Fig.19, their parameters structural and non-structural, are indicated in Table.9.

[10] Persson, Kristin, title = "Materials Data on CaSiO₃ (SG:14) by Materials Project", abstract Note = "Computed materials data using density functional theory calculations. These calculations determine the electronic structure of bulk materials by solving approximations to the Schrodinger equation. For more information, see <https://materialsproject.org/docs/calculations>", doi = "10.17188/1276483", place = "United States", year = "2014", month = "7", note = "An optional note".

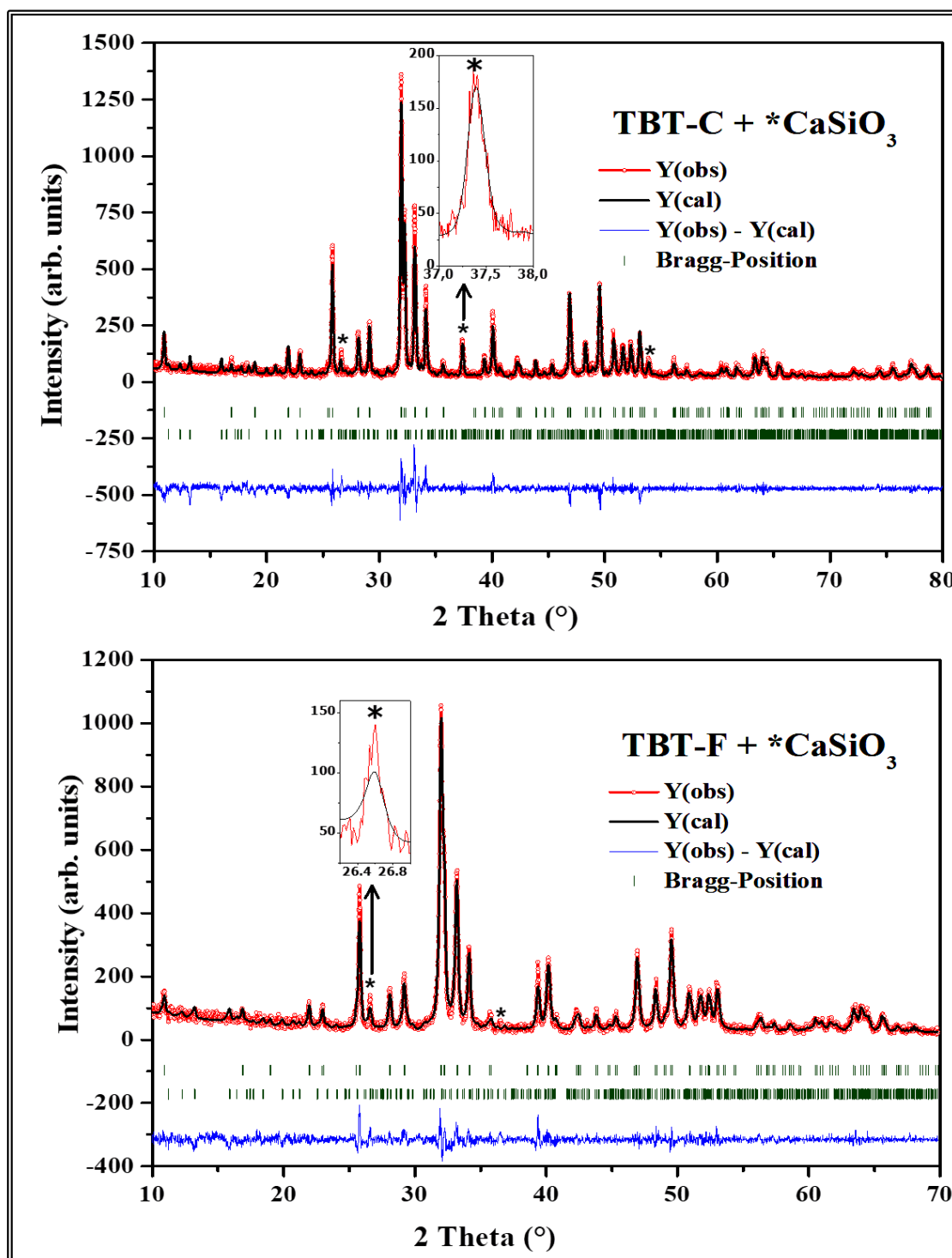


Fig.19: Rietveld plot for TBT-F + CaSiO₃ and TBT-C + CaSiO₃. The upper symbols illustrate the observed data $Y(obs)$, and the calculated pattern (solid line) for $Y(cal)$. The vertical markers show calculated positions of Bragg reflections in Bragg-Position and the lower curve is the difference diagram schematize in the $[Y(obs) - Y(cal)]$.

Table.9: Results for Rietveld refinement for TBT-C, TBT-F, and CaSiO₃.

		TBT-C	CaSiO ₃	TBT-F	CaSiO ₃
Step width (2θ)		0.010142		0.020283	
Zero-point (deg.2θ)		0.056(2)		0.176(3)	
Pseudo-Voigt function PV=ηL + (1 -η) G	η	0.9768(27)		0.9768(37)	
Caglioti parameters	U	0.2059(24)		0.2150(24)	-0.0658(14)
	V	-0.1407(17)		-0.0791(41)	
	W	0.0482(167)		0.0512(150)	0.0900(167)
No. Of reflections		258/2	1003/2	202/2	727/2
No. Of refined parameters		34	4	34	4
Z		2	12	2	12
Space group		P 6 ₃ /m	P 2 ₁ /c	P 6 ₃ /m	P 2 ₁ /c
a (Å)		9.3609(76)	7.2101(14)	9.3474(55)	7.2448(26)
b (Å)		9.3609(76)	7.4202(15)	9.3474(55)	7.4066(24)
c (Å)		6.8925(61)	15.7194(32)	6.9063(34)	15.8244(61)
Beta		90.00	94.99(9)	90.00	95.37(1)
V (Å ³)		523.1(8)	837.8(3)	522.6(5)	845.4(5)
Atom Number		12	15	12	15
User-weighted Chi2		2.09		1.54	
%RF		2.77	0.722	1.62	1.57
		6.73	1.64	2.85	1.69
		13.9		10.9	
		18.4		14.5	
		22.1		21.1	
		26.8		24.1	

Table.10: Refined structural parameters for TBT-C and TBT-F.

Atom	Wyckoff	x/a	y/b	z/c	B (Å ²)	Occupancy
TBT-C= [Ca _{5.98} (1)Mg _{0.02} (1)][Ca _{3.772} (2)Mg _{0.002} (2)Na _{0.226}](PO ₄) _{5.5} (SO ₄) _{0.009} (CO ₃) _{0.491}]F ₂						
F	2a	0	0	0.25	0.698	2
M(I)=Ca(1)/Mg(1)	6h	0.2386(5)	-0.0092(7)	0.25	1.20(11)	5.98(5)/0.02(5)
M(II)=Ca(2)/Mg(2)/Na	4f	0.3333	0.6667	0.0053(9)	0.326(13)	3.772(5)/0.002(5)/0.226(5)
X=P/S/C	6h	0.3938(8)	0.3623(9)	0.25	3.00(19)	5.500(5)/0.009(5)/0.491(5)
O(1)	6h	0.3286(14)	0.4830(11)	0.25	3.11(17)	6
O(2)	12i	0.3348(8)	0.2560(8)	0.0608(8)	3.11(17)	12
O(3)	6h	0.5885(13)	0.4638(13)	0.25	3.11(17)	6
TBT-F= [Ca _{5.981} (1)Mg _{0.019} (1)][Ca _{3.744} (2)Mg _{0.014} (2)Na _{0.242}](PO ₄) _{5.541} (SO ₄) _{0.004} (CO ₃) _{0.455}]F ₂						
F	2a	0	0	0.25	1.64(2)	2
M(I)=Ca(1)/Mg(1)	6h	0.2256(3)	-0.0218(4)	0.25	1.05(7)	5.981(15)/0.019(15)
M(II)=Ca(2)/Mg(2)/Na	4f	0.3333	0.6667	0.0023(5)	2.09(5)	3.744(15)/0.014(15)/0.242(15)
X=P/S/C	6h	0.4079(5)	0.3677(7)	0.25	4.53(13)	5.541(15)/0.004(15)/0.455(15)
O(1)	6h	0.3306(9)	0.4799(7)	0.25	5.89(14)	6
O(2)	12i	0.3244(6)	0.2434(6)	0.0776(6)	5.89(14)	12
O(3)	6h	0.5985(13)	0.4715(10)	0.25	5.89(14)	6

Table.11: Interatomic distances in (Å) and O-X-O angles in (°) for TBT-C and TBT-F.

Atom	TBT-C	TBT-F	Atom	TBT-C	TBT-F
M(I)-O1	2.6844(12)	2.6041(8)	X-O1	1.5298(17)	1.5424(11)
2*M(I)-O2	2.5377(9)	2.4749(6)	2*X-O2	1.5640(7)	1.5717(5)
2*M(I)-O2	2.2683(6)	2.3549(4)	X-O3	1.5789(12)	1.5452(11)
M(I)-O3	2.4164(12)	2.4517(4)	<X-O>	1.5576	1.5531
<M(6h)-O>	2.4767	2.4714	3*M(I)-F	2.2778(6)	2.2181(6)
3*M(II)-O1	2.3930(10)	2.4350(6)	2*O1-X-O2	109.0(10)	106.0(6)
3*M(II)-O2	2.85161(8)	2.9251(4)	O1-X-O3	108.8(15)	111.0(10)
3*M(II)-O3	2.45280(9)	2.4357(8)	O2-X-O2	113.0(6)	98.5(4)
			2*O2-X-O3	108.5(7)	117.0(7)
<M(4f)-O>	2.5658	2.5986	<O-X-O>	109.5	108.125

The results indicate that a good correlation is obtained between the experiment and the theory, between the experimental radiographic diffractograms and the calculated radiographic diffractograms (%Rp= 6.73/1.64 for TBT-C/CaSiO₃ and %Rp=2.85/1.69 for TBT-F/CaSiO₃). The apatites of KHOURIBGA, sulfated carbonated fluorapatite, are identified as Ca_{10-z}M_z(XO₄)₆Y₂, Natural calcium phosphate of hexagonal structure with space group *P6₃/m*, containing carbon and sulfur (X : P, C, S), 'Y' is usually a monovalent anion (Y:F, Cl and rarely OH), M being several cations, di- and trivalent and other, are the impurities encountered in the structure. Among these impurities, some are vaporizable such as (M: U, rare earth...) and must be recovered, and others that are penalizing for the subsequent use of the acid such as (M: Cd, As, Cu, Zn,..., etc.) and must be eliminated. These chemical elements are defined as complex substitutions in the apatitic skeleton. This suggests that the number of impurities present in KHOURIBGA "K09" ore is quite low, this confirmed by the Rietveld method using the FULLPROF program [6].

Fig.20 shows the structure of fluorophosphate substituted, it can be described as consisting of tetrahedral groups $[XO_4]^{3-}$ and two non-equivalent sites 6h and 4f with a cation marked M(I) and M(II), respectively. The majority of 'Ca²⁺(1)' cations reside in the 6h sites, the remainder is occupied by a variety of trace elements such as heavy metals, and rare earth elements, M(I) which delimit the hexagonal centred by fluoride ions along a reticular plane (001). These hexagons of sextupled coordination cavities, with a much larger section, are surrounded by M (I) cations. These cations are inserted into six folding sites that form the walls of the hexagons; each polyhedron is connected to 4 $[XO_4]^{3-}$ tetrahedrons by corners and to one $[XO_4]^{3-}$ by edges. These M(1) sites are linked to M(2) sites, which corresponds to the mixed site 4f occupied by the majority of 'Ca²⁺(2)' cations and a variety of trace elements such as heavy metals, and rare earth elements, as well as monovalent mixed cations 'Na⁺/K⁺'. These cations are coordinated with nine oxygen anions belonging to six distinct tetrahedrons; each polyhedron is connected to 3 $[XO_4]^{3-}$ tetrahedrons by corners and three others by edges (Tables.10 and 11).

Fig.21 shows the second phase structure, simple perovskite CaSiO₃, alone and with the majority phase sulfated fluorapatite carbonate (FAPCS), atomic coordinates, isotropic temperature factors, and crystallographic site occupancy of the different ions are listed in ref [10]. Attached are approximate calculations for the percentages of the two phases present in the ore.

$$\%TBT + \%CaSiO_3 = 100\% \text{ and } [(I_{TBT} - I_{CaSiO_3}) / I_{TBT}] \times 100 = \%TBT$$

$$\text{For : } TBT-C = [(1357.92249 - 166.33501) / 1357.92249] \times 100 = 87.75\% \text{ and } CaSiO_3 = 12.25\%.$$

$$\text{For : } TBT-F = [(1051.92908 - 140.53702) / 1051.92908] \times 100 = 86.74\% \text{ and } CaSiO_3 = 13.36\%.$$

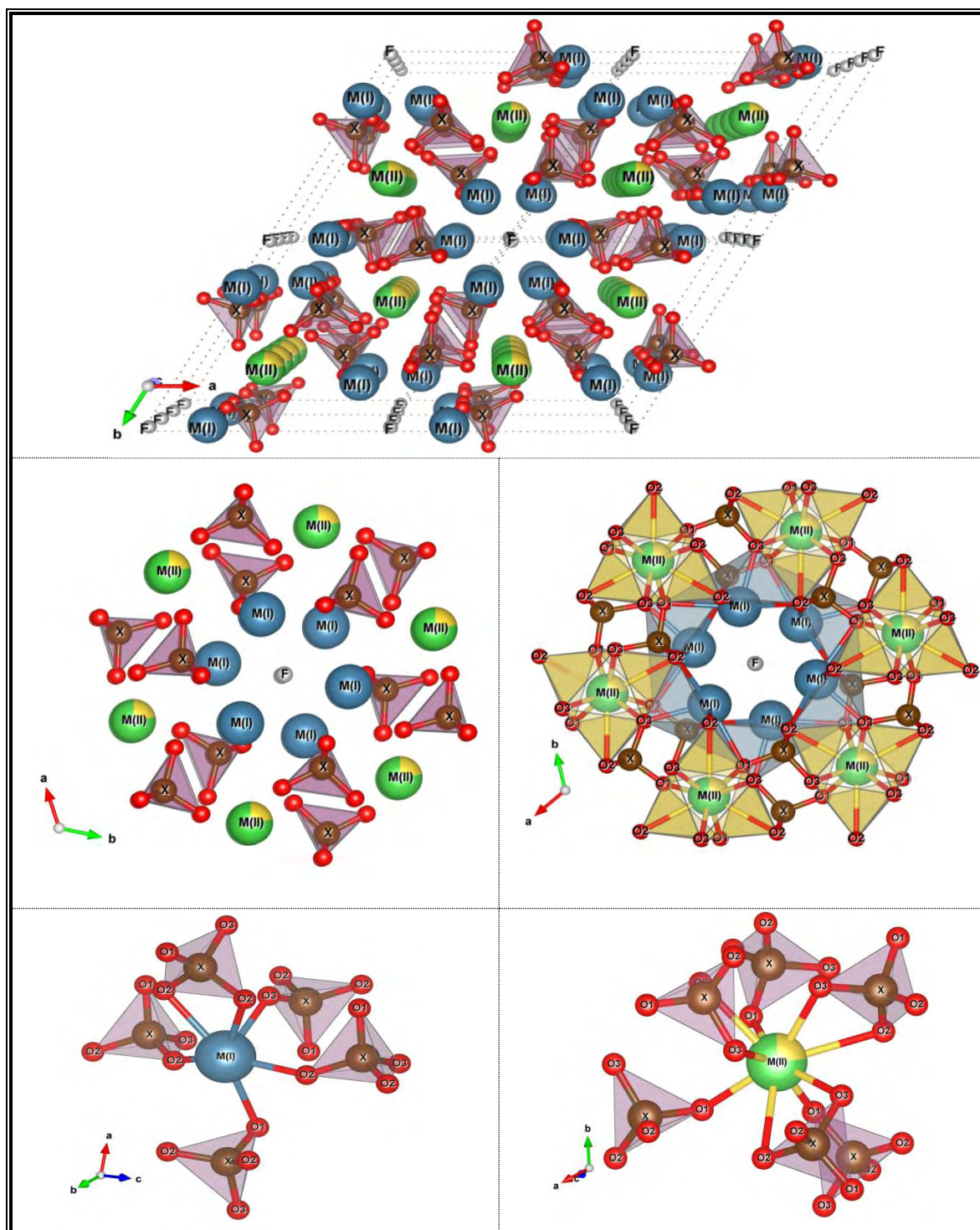


Fig.20: Polyhedral view in the *ab*-plane of the crystal structure of $\text{Ca}_{10-z}\text{M}_z(\text{XO}_4)_6\text{F}_2$ showing the Hexagonal $\text{P6}_3/\text{m}$. M(1) shows the site M(6h) illustrating the cations and oxygen arrangement around (6h) sites connected to the $5(\text{PO}_4)^{3-}$ tetrahedra. M(2) views the M(4f) prism surrounded by the $6(\text{PO}_4)^{3-}$ tetrahedra.

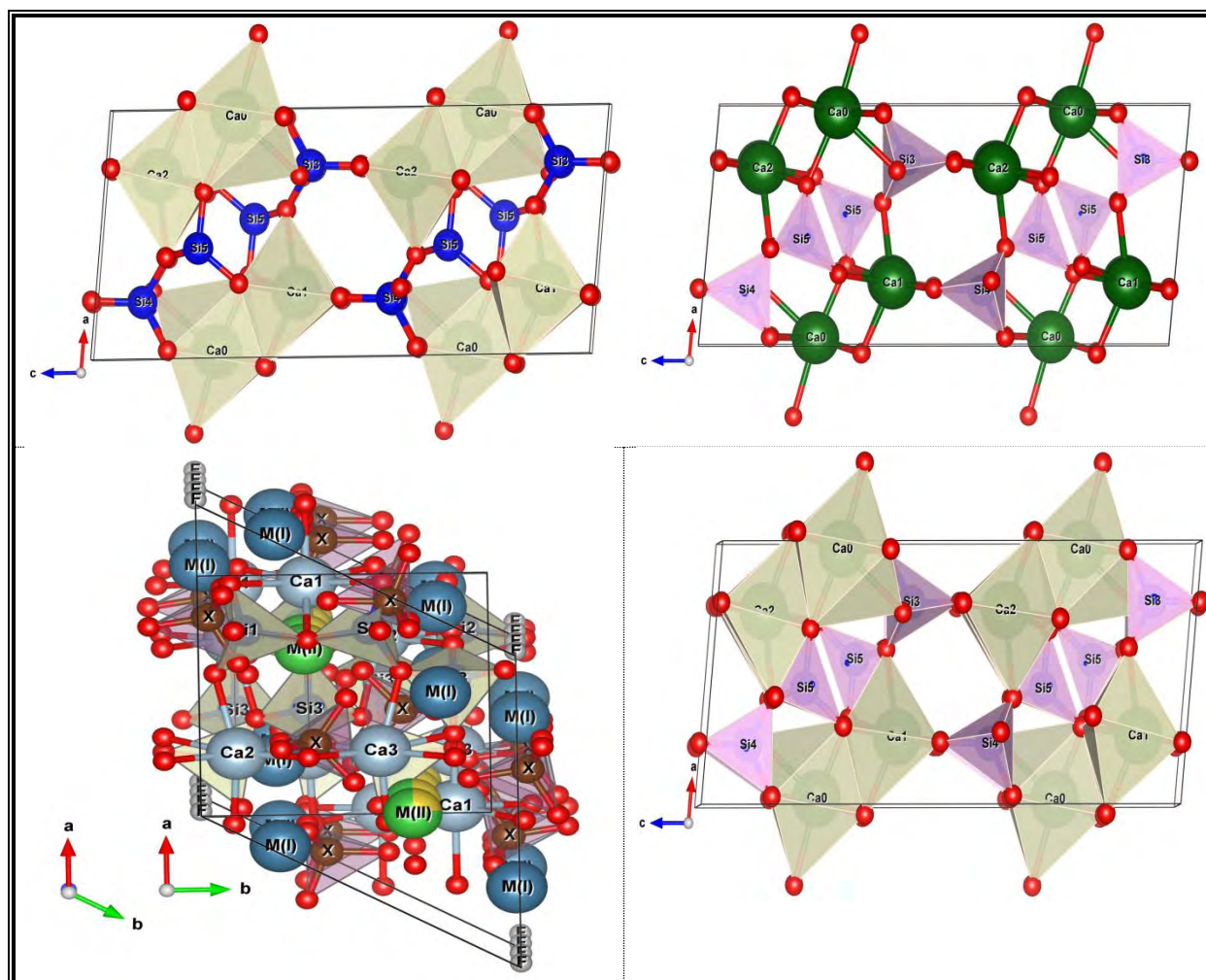


Fig.21: structure of the second phase CaSiO_3 and the majority phase fluorophosphate substituted (TBT).

Fluorophosphates TBT-C and TBT-F, of structure polycrystalline and differs from pure synthetic apatites due to complex substitutions in the apatitic skeleton. These substitutions of Ca^{2+} and P^{5+} cations in the two crystallographic sites 6h and 4f are considered undesirable elements even at very low concentrations (S, C, Mg, Fe,..., etc). The X-ray diffraction characterization of both TBT-C and TBT-F reveals the crystalline fluorapatite (FAP) phase containing the impurity CaSiO_3 , after refinements of Rietveld's.

However, the mesh parameters, interatomic distances are reasonable, similar, and in agreement with those found in refs [4, 5] and other references. Where the distances $\text{Ca(I)}-\text{O}_6$ in the site (6h) vary from 2.268Å to 2.684Å, for $\text{F}-\text{Ca(I)}_3$ from 2.218Å to 2.278Å. The

distances Ca(II)-O₉ in the mixed site (4f) vary from 2.393Å to 2.926Å. P-O₄ has an average of 1.5Å. The O-X-O angles range from 98.5° to 113°.

d) Optoelectronic property of TBT-F.

The TBT-F samples were calcined at different temperatures (600°C, 800°C, 1000°C, and 1200°C). The Optical analysis for each calcined TBT-F, performed in the MSN department, by PerkinElmer LAMBDA™ 1050 UV/Vis/NIR, in the range from 250 to 800nm. The methods of analysis and calculation are discussed in detail in Chapter. I. Fig.22 shows the reflectance data converted to absorbance F(R) using the Kubelka-Mank function [11] that will be used in the calculations of the optical bands.

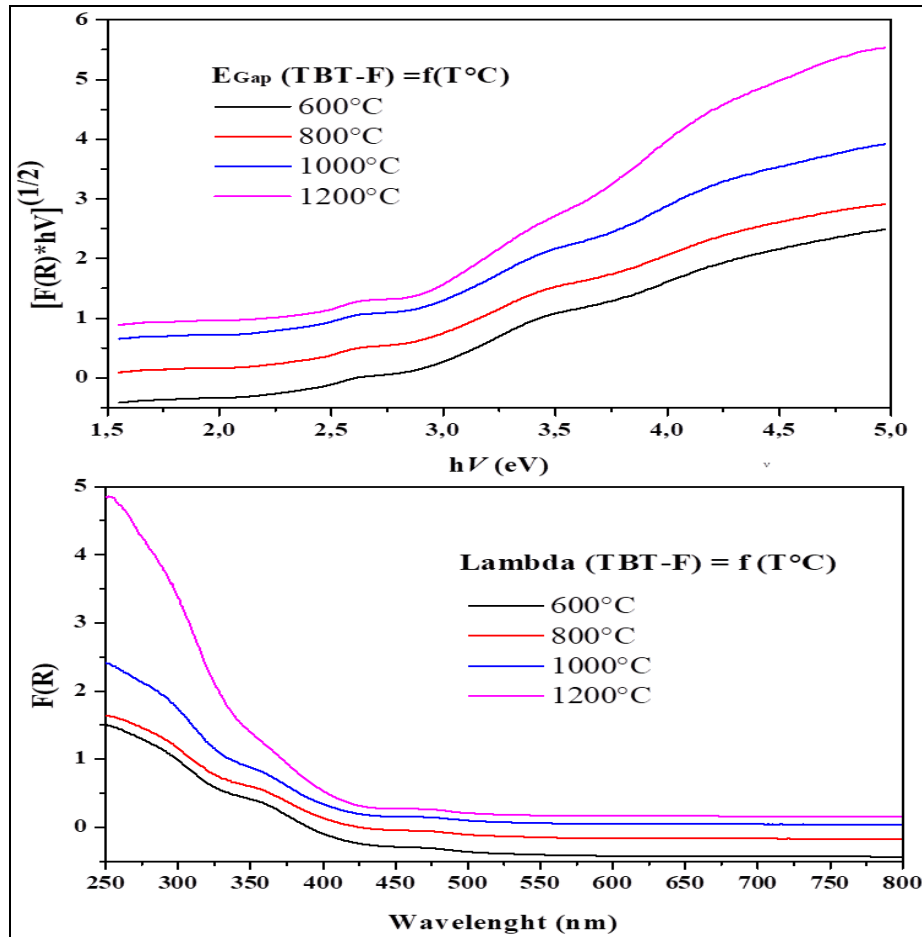


Fig.22: $[F(R) \cdot h\nu]^{1/2}$ and $F(R)$ for TBT-F apatites, depending on the energy of the incident photons ($h\nu$) and optical absorption respectively.

[11] Kubelka P and Munk F Übersetzung 1931 J. Z. J. Tech. Phys. 12 593.

The results presented in Fig.23, obtained by the Tauc plots method [12], calculate the Bandgaps (E_{Gap}), and the determination of Lambdas Max by LabSpec Software. Indeed, we can extend the line $[F(R)*h\nu]^{1/2} = 0$ to intercept the axis ($h\nu$) (Intercept/Slope), to estimate the values of the permitted indirect deviation energy ($n=2$) of the TBT-F as a function of temperature. The deconvolution of wavelengths was automatically estimated by the LabSpec software V.5.

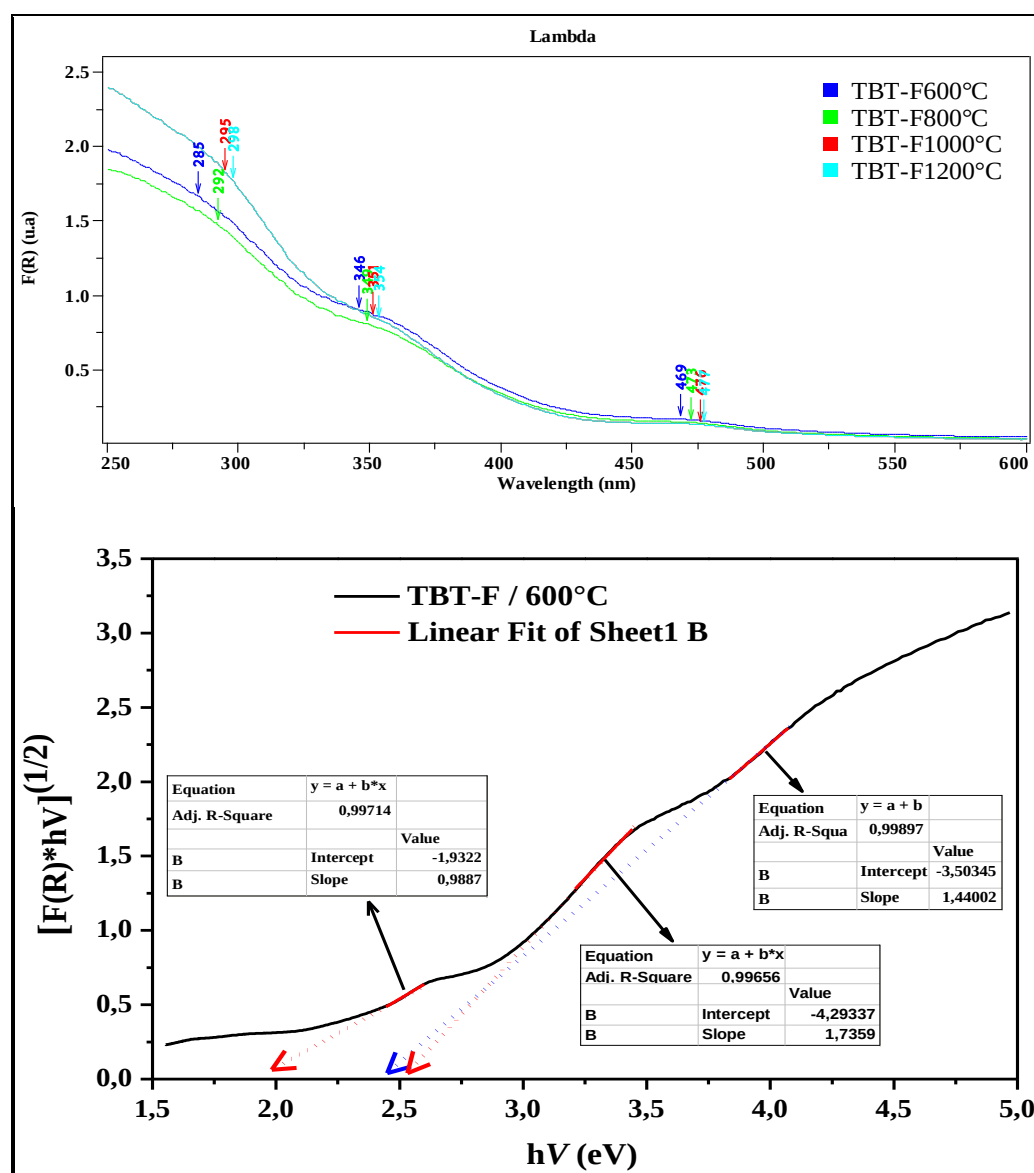


Fig.23: Results of TBT-F, Lamdas Max shows the optical absorption as a function of wavelength at different temperatures, and the Bandgaps obtained by the Tauc plots method illustrates at 600°C.

[12] J. Tauc 1968 *J. Mater. Res. Bull.* 3 37.

From the optoelectronic analyses, it can be seen that the traces obtained having kept to the same forms, shows that the temperature does not affect the chemical composition of TBT-F. The variation is subdivided into three different regions from 250 to 323nm, from 325 to 425nm, and from 425 to 500nm. The energy gap results and Lambdas Max are presented in Table.12. Fig.24 shows linear variations of Gaps (ev) and Lambdas energies as a function of temperatures, of which these Bandgaps and Lambdas of the different TBT-F increase slightly.

Table.12: Bandgaps and Lambda Max of the different regions of TBT-F, according to temperatures.

Température (°C)	600	800	1000	1200
Lambda Max (nm)	285	292	295	298
	346	349	351	354
	469	473	476	477
E _{Gap} (ev)	1.9542	2.0474	2.0571	2.0851
	2.4733	2.5068	2.5665	2.6509
	2.4329	2.4344	2.6880	2.8448

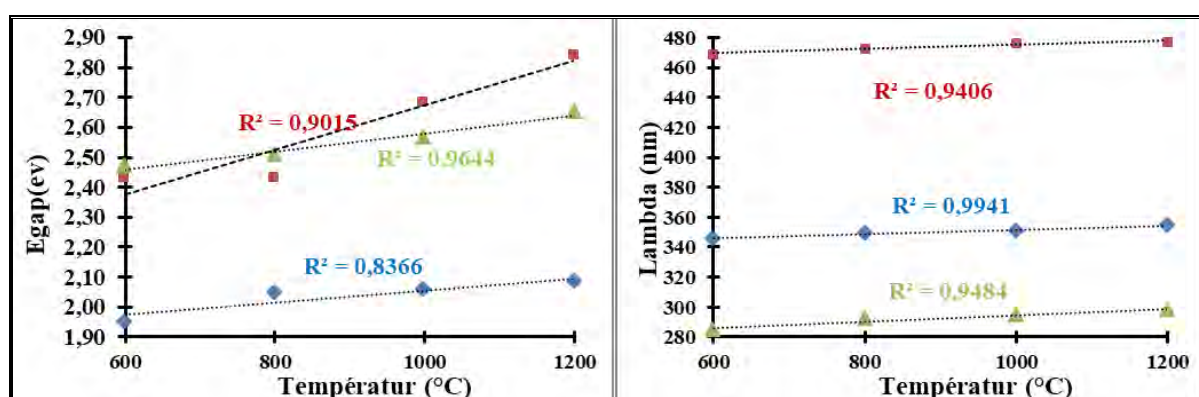


Fig.24: Variations of Bandgaps (eV) and Lambdas Max energies according to temperatures.

Generally, the light at a wavelength of about 400 nm or less consists of low-energy photons. The shortest radiation wavelengths in the ultraviolet spectrum, particularly those between 100 and 500 nanometers. TBT-F apatite is composed of an optical material with light transmission characteristics in distant ultraviolet regions. This argument provides transitions between the electron energy levels of the apatite molecule. The X-ray diffraction results, using radiation from Cu_{Kα} concerning emissions associated with electronic transitions (Electron-Electron Interactions) proved the existence of several substitutions in the TBT-F

skeleton, which are behind the difference between the values of the Gap energy obtained and the one reported in ref [13] entitled "*Electronic and crystallographic structure of apatites*" for more detail see the Introduction to the chapters, paragraph 5" Theoretical modelling". However, our value of the energy gap is lower than that obtained theoretically (5.9 eV [13]).

From Fig.26, it is suggested that the temperature-dependent increase is related to the stability of crystal and electronic structures and the effect of the degree of distortion of the P-O₄, M(I)-O₆, M(II)-O₉, Si-O₄, and Ca-O₆, bonds. The optoelectronic properties of TBT-F apatite confirmed that the mobility of the field-effect increases with increasing temperature, indicating that the substituents were effectively acting as carrier suppressors by increasing the number of oxygen donors in the apatitic system. It has been reported that a high concentration of carriers can lead to the high mobility of apatite oxides due to complex substitutions as well as the presence of impurity. Generally, X=P⁵⁺ is pentavalent and provides five electrons of valence; these can act either as a potential donor or as an acceptor, called an amphoteric dopant. About the 'O' bond, oxygen radicals react preferentially with P° radicals, because the chemical stabilization most favourable to the crystalline state gives P-O. Thus, oxygen radicals react mainly with sites M (I)-O₆ and M (II)-O₉, where there is a variety of trace elements such as heavy metals, and rare earth elements. Because the region with low energy loss reflects the valence and conduction band structures of solids. This indicates that the concentration of the electron carrier is increased by the existence of these substitutions, which leads to an increase of 'E_g'. These types of materials can be electrically semiconductor [14] and visibly transparent, with a unique combination of properties.

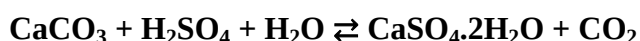
[13] L. Calderin and M. J. Stott, physical review B 67, 134106 (2003).

[14] Leon A. Avakyan, Ekaterina V. Paramonova, José Coutinho, Sven Öberg, Vladimir S. Bystrov, and Lusegen A. Bugaev, Journal of Applied Physics 148, 154706 (2018).

e) Conclusion.

The sedimentary phosphates in KHOURIBGA, of the chemical formula $\text{Ca}_{10-z}\text{M}_z(\text{XO}_4)_6\text{F}_2$, contain phosphorus, carbonates, sulfides, and often more calcium, sodium, magnesium, aluminium, iron, and potassium,..., etc., and also a second minor phase CaSiO_3 . Sedimentary phosphates are being porous, offer a larger area for chemical reactions. The nature and quality of phosphate are considered as an essential parameter that greatly influences the filtration process, so it is essential to study the nature and proportion of impurities in the key material of the industrial revolution. The majority of sedimentary ores contain organic matter that can generate foam during acid production. So we wonder what a good phosphate is, and if these impurities are considered as a bonus or a penalty. We present below the effect of the main impurities on the quality of the acid produced.

- Alumina has a positive impact on crystallization and therefore improves gypsum filtration. Not only is crystal growth promoted by alumina in all directions, but it is also considered an accelerator of crystal growth to have a good length/width ratio.
- Carbonates improve reactivity by making a faster decomposition of phosphate grains, also, they increase the consumption of H_2SO_4 (CO_2 formation), the organic matter present sulfate foams are produced according to the following reaction:



- The presence of free fluorine in the acid will affect the shape of the crystals and will be of the needle type, which has the particularity of very poor filtration. It is worth noting that the SiO_2/F ratio makes it possible to avoid the HF form, which is considered to be a source of corrosion and air pollution problems, by playing on the content of the granulometry of slice which must be satisfactory and decisive in the crystallization process.
- Silica has a positive effect on corrosion if it is reactive, by binding with fluorine to form H_2SiF_6 , which is less corrosive than HF. On the other hand, the silica is

insoluble present in great quantity and causes an increase in the erosion of equipment (agitators in the attack tank, spray cocktail pumps).

- Magnesium has an unfavourable effect on viscosity, on the other hand, it has a favourable effect on corrosion when it binds with fluorine.
- Iron forms insoluble compounds containing FePO_4 during concentration.
- Sulfates go hand in hand with the performance of the installation and affect the efficiency of the attack-filtration section. The shape and size of crystals are affected by sulfates in the presence of high quantities, not to forget their influence on the losses of syncrystallised or unattacked P_2O_5 .
- Organic matter can slow down filtration and washing by forming a thin film of organic matter on the surface of the cake when filtering.
- Na_2O and K_2O prevent the crystallization of gypsum.

The ***P6₃/m*** crystal structure, which can contain a wide range of oxidation state and stoichiometric elements, is an important component of solid-state chemistry. As a result, natural Fluoroapatite can contain a wide variety of anions and metal cations, while maintaining their unique molecular structure. In the previous section, it is clear that the molecular structure of the phosphate rock is the main source of dissolved or suspended impurities of phosphoric acid from the wet process. Various factors contributing to the contamination of phosphoric acid can occur, and or where secondary sources are described as follows: sulphuric acid, reagents used in flotation, washing water,..., etc.

TBT-F natural apatite is composed of an optical material with light transmission characteristics in distant ultraviolet regions. The electrical properties of TBT-F confirmed that the mobility of the field-effect increases with increasing temperature, indicating that the substituents effectively act as a carrier suppressor by increasing the number of oxygen donors in the apatitic system. These materials are visibly transparent, can be conductor or semiconductor electrically, characterized by an indirect bandgap. These selected apatites of

the natural structure are very similar to the other apatites, whose oxygen radicals react mainly with sites M (I) and M (II). Given the 'O' bond, oxygen radicals react preferentially with radicals P° , since the most favourable stabilization for the formation of chemical bonds in the crystalline state gives $P-O_n$.

IV. Experimental Studies on Phosphoric Acid (PAC).

IV.1. Phosphoric Acid (PAC) Manufacturing.

As part of the collaboration between our RMI and S3M laboratories with the MSN department, we carried out the phosphoric acid manufacturing laboratory test bench [15], during our visit to the Department of Research and Development "R&D", JORF LASFAR, OCP, with the support of the head of clusters development at OCP/UM6P, Dr. Mohamed Amalhay.

The test presented in this section is a discontinuous phosphoric acid manufacturing test that approaches the characteristics of phosphate behaviour during the manufacture of this acid, but its discontinuous nature does not allow a good simulation to be given to industry. In this test, two phases can be distinguished: the preparation of the tank foot and the tests to measure the performance of phosphate during the manufacture of phosphoric acid.

The phosphoric acid manufacturing laboratory test bench consists of a thermostatic water bath, a 2L beaker, and a 250 rpm central speed stirrer, as shown in Fig.25, below

[15] Centre d'Etudes et de Recherches des Phosphates Minéraux (CERPHOS) Groupe OCP.

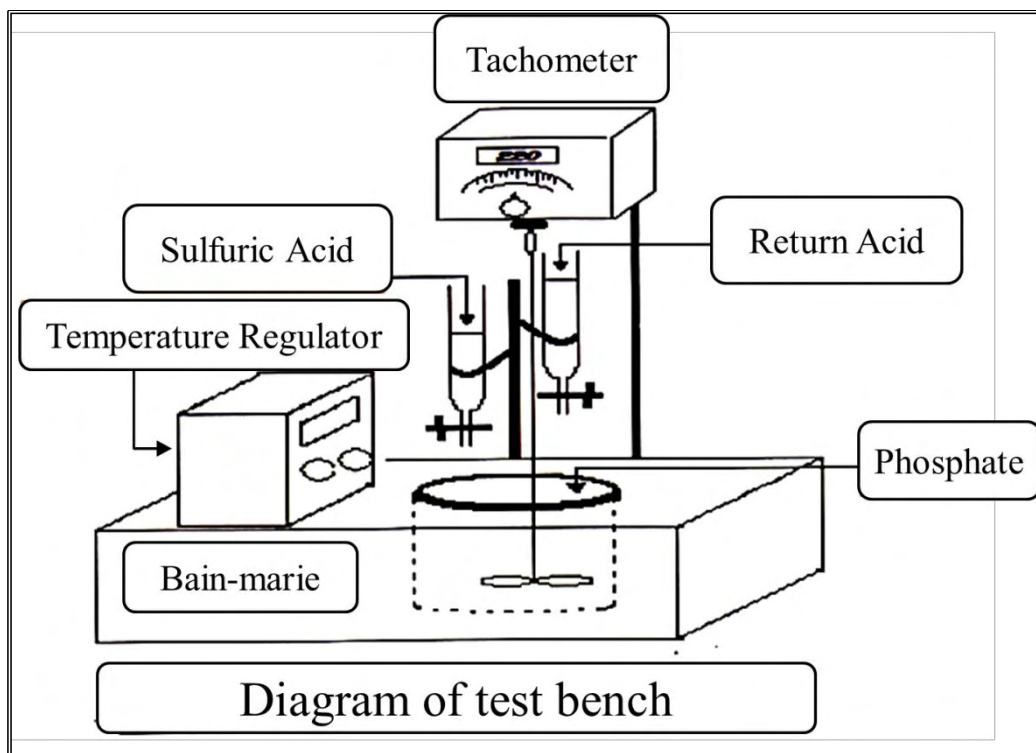


Fig.25: Laboratory test bench for the manufacture of phosphoric acid ^[15].

a) Preparation of the tank foot.

Starting from tap water melange with sulphuric acid to a concentration of 25g/l, into which phosphate and phosphoric acid and sulphuric acid 65% to be introduced, a series of successive attacks are used to prepare a phosphoric acid at the concentration fixed by the desired concentration for the acid produced, and a porridge, which is used as a tank base for the tests themselves.

➤ **Preparation of 65% sulphuric acid.**

From a given mass (M) of 98% sulphuric acid, an acid of 65% mass 'm' is prepared by dilution with a quantity 'q' of water calculated by the following relationship: $M \cdot 0.98 = m \cdot 0.65$, therefore the mass H_2SO_4 at 65% is $m = (M \cdot 0.98) / 0.65$ and the amount of water necessary for dilution is: $q = m - M$.

A quantity of 98% sulphuric acid is taken, then the quantity of water required to dilute this acid to 65% is calculated, the calculated quantity of water is introduced into an

Erlenmeyer and placed in a cold bath, then the 98% sulphuric acid is added drop by drop. To ensure that the acid obtained is the desired one, we measure its density.

➤ **Procedure for the preparation of the tank foot.**

The preparation of the tank foot involves two stages: attack and filtration;

- **Attack:** the beaker is put in the thermostated water bath at a temperature of 88°C (to have a temperature of 80°C inside the beaker), it is heated for about 20min; in the case of a phosphate type "K09", a charge of 400g of phosphate and 500g of sulphuric acid is supplied at 65% divided into 6 feeds. Each feed is spread over 10 minutes, and 10 minutes wait between the end of one feed and the beginning of the next until the 400g of phosphate is consumed, and at the end, the porridge is allowed to mature for 1 hour to ensure good crystallization and then good filtration; the porridge remains in the reactor between the attack and filtration for 2h30min.
- **Filtration:** 800g of the porridge liquid is filtered on a 200mm diameter Büchner under an average depression of 400mmHg, created by a liquids rings pump. Often, the vacuum drop below 400mmHg due to air penetration through the pores of a filter cake. A quantity of filtrate is collected which is brought to 1200cm³ by washing the cake with a sufficient quantity of washing water heated to 60°C; this filtrate is separated and used as the foot of the tank from the next attack operation. A second washing of the cake is done with tap water to recover the second filtrate which will be used as the first washing acid for the next test.
- **Repetition of operations:** The filtrate obtained which will be used as the base of the vat is adjusted to 25g/l of H₂SO₄, and an attack operation identical to the first one is repeated; the adjustment of H₂SO₄ can be done by calculation after dosage, either by adding a larger quantity to that of the previous test if the H₂SO₄ concentration is less than 25g/l, or by adding a smaller quantity if the concentration is greater than 25g/l.

However, the adjustment quantity should not exceed 10% compared to the previous quantity. Because any abrupt variation can disturb the concentration of sulphides in the acid, which requires further tests to be carried out to restore the permanent regime. The filtration is carried out as before but part of the filtrate from the second washing of the previous operation is used as the first washing until the first filtrate is completed at 1200cm³. The second washing is always done with a sufficient quantity of tap water.

b) Testing constituting the test.

Testing can be started when a sufficient amount of the porridge and recycling acid is obtained at the title set by the desired concentration in the production acid. In the first tests, we try to adjust the sulfate parameters and rates of solid to 25g/l and 35% respectively and wait until the steady-state is reached. Afterwards, a few samples are sent for chemical analysis, which will allow the performance of the phosphate studied to be measured based on the results of the analyses. Below is a description of the two-part procedure:

- **Attack:** We heat 800g of porridge in a water bath until it maintains the temperature of 78°C±2°C under the agitation of 250 rpm/minute; 200g of phosphate is introduced at the same time, with the corresponding quantity of sulphuric acid to 95% of the phosphate lime and a quantity of recycling acid fixed respectively by the solid rate and the production acid title. These alimentations are divided into 5 loads of 40g of phosphate, we aliment the attack for 15 min then we wait 15 min to start the other alimentation to ensure a good attack.
- **Filtration:** 800g of porridge is measured and filtered on a Buchner under a depression of 400mm of mercury, by timing the appearance of the dry surface. The filtrate obtained is the strong acid; then the cake is washed for the first time by 300ml of a weak acid of 1050 density maintained at a temperature of 60°C, and we timing the appearance time of the dry surface. The filtrate obtained is the average acid. Then a second washing with 300ml of water at 60°C is carried out, and the

time of appearance of the dry surface is measured. The filtrate thus obtained is the weak acid, and at the end, the cake is wrung out for 30 seconds. From the acid of the first wash and the production acid (or 2nd wash), the recycling acid of the next test is reconstituted as it is adjusted to the desired sulphuric level; after filtration, the thickness of the cake is measured and weighed wet, then 100 grams are taken and subjected to a temperature of 60°C, and after 48 hours it is weighed dry to deduce its humidity (either 10g of gypsum is weighed during 4 hours of drying or the infrared desiccator is used to measure humidity). For acids we take a determined volume then weighs strong, medium and weak acid, then we measure their density ($d=m/v$).

c) Interpretation of the results.

The gypsum factor is a parameter for determining the amount of gypsum produced by the introduced phosphate P_2O_5 . It is presented by the following relationship:

$$P = \text{dry gypsum produced} / T (P_2O_5) \text{ phosphate}$$

' P_2O_5 ' losses are expressed as the percentage of ' P_2O_5 ' trapped in the gypsum produced; they are represented in three forms:

- The lost of ' P_2O_5 ' Unattacked: these are losses due to the attack of the outer layer of phosphates by sulphuric acid which will cause the formation of gypsum outside the grains, and the inside remains in the form of phosphate, this phenomenon is called: enrobing.
- ' P_2O_5 ' syncrystallised: these are losses due to the formation of bicalcique phosphate.
- Water-soluble ' P_2O_5 ': this is the impregnation ' P_2O_5 ' on the gypsum cake.

- **Calculation of filterability:** Filterability 'F' is a very important parameter to characterize the performance of phosphate at the filtration level, the relationship is defined by the ratio: $F=0.61*GPS/(P*\text{root}(t))$.

with **GPS**: the weight of dry gypsum produced and **P**: gypsum factor.

- **Calculation of 'P₂O₅' content:** 'P₂O₅' analyses cannot be performed on all acids produced. To do this, a few acid samples are sent to the analytical laboratory to measure the percentage of 'P₂O₅', and then a curve is drawn to give a correlation between the density and the 'P₂O₅' content (see Annex. IV in Fig. IV.4). If we take "K09" as an example, their results are shown in Table.13. The graphical presentation of the 'P₂O₅' analyzed as a function of the measured density is shown below in Fig.26.

Table.13: The P₂O₅ analysis and the density d(Kg/m³) measured.

	P ₂ O ₅	d (Kg/m ³)
Test 1	27.3	1332
Test 2	28.03	1340
Test 3	29.9	1358

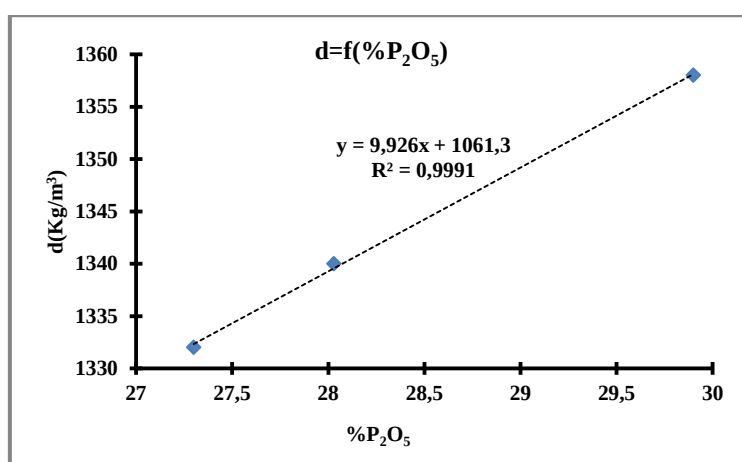


Fig.26: Graphical presentation of the $d=f(\%P_2O_5)$.

We notice according to the graph that the density rate as a function of 'P₂O₅' is a right slope of 9.926. So for each given density, we can deduce the corresponding 'P₂O₅' content.

- **Specific phosphate consumption:** This parameter is used to calculate the amount of phosphate required to produce the desired amount of P_2O_5 . It is expressed in (tone of phosphate/tone of P_2O_5 produced), and can be calculated by the following relationship: $Q_1/(Q_2-Q_3)$.

With Q_1 : the amount of phosphate feeds. And Q_2 : the amount of P_2O_5 containing in the fed phosphate. For Q_3 : the amount of P_2O_5 lost in the gypsum.

- **Specific consumption of sulphuric acid:** It is used to calculate the quantity of sulphuric acid needed to produce a quantity of P_2O_5 in produced acid; it is calculated by the following relationship “ Q_1/Q_2-Q_3 ”.

With Q_1 : the quantity of sulphuric acid of title 100%, fed. And Q_2 : the quantity of P_2O_5 contained in the phosphate fed. And Q_3 : the quantity of P_2O_5 lost in the gypsum.

- **Chemical yield:** Chemical yield is a criterion for predicting P_2O_5 losses in gypsum and therefore inquire about information on the performance of phosphate at the attack level. It is expressed as the mass of P_2O_5 produced by the mass of ‘ P_2O_5 ’ of the phosphate consumed. It can be calculated by the following relationship:

$$[(Q_1-Q_2)/Q_1]*100$$

with Q_1 : the amount of ‘ P_2O_5 ’ contained in the phosphate and Q_2 : the amount of ‘ P_2O_5 ’ contained in the gypsum produced.

- **Sulphate balance sheet:** $Q_1+Q_2+Q_3+Q_4=Q_5+Q_6$
- With Q_1 : the quantity of ‘ H_2SO_4 ’ introduced into the reactor.
 - Q_2 : the amount of ‘ H_2SO_4 ’ contained in the recycling acid.
 - Q_3 : the amount of ‘ H_2SO_4 ’ contained in the phosphate.
 - Q_4 : The amount of residual ‘ H_2SO_4 ’ in the recycled porridge.
 - Q_5 : The amount of ‘ H_2SO_4 ’ residual in the new porridge.
 - Q_6 : The amount of ‘ H_2SO_4 ’ consumed (transformed into gypsum).

‘ Q_2 ’ can be calculated by the dosage of the recycling acid by ‘ $BaCl_2$ ’ (see [Annex. IV](#), [Fig. IV.5](#)), and the concentration of sulphate in the acid multiplied by its volume: ‘ $Q_2=C*V$ ’.

With the help of phosphate analysis, it is easy to determine the amount ‘ Q_3 ’ of SO_4 contained in the phosphate, and we have $Q_4=C_{SO_4}*V_{acid}$.

With $V_{acid}=M_{acid}/d_{acid}=M_b*(1-TS_{n-1})/d_{acid}$. So $Q_4= C_{(SO_4) n-1}*M_b*(1-TS_{n-1})$.

With ‘ M_b ’ a mass of the porridge = 800g. But the solid rate (TS) can only be known after 48 hours, so ‘ Q_4 ’ cannot be calculated before starting the next test.

For ‘ Q_5 ’ it can be calculated in the same way as ‘ Q_4 ’, but ‘ TS_{n-1} ’ is replaced by ‘ TS_n ’ and ‘ $C_{(SO_4)n-1}$ ’ by ‘ $C_{(SO_4)n}$ ’, therefore ‘ $Q_5=C_{(SO_4)n}*M_b*(1-TS_n)$ ’.

We deduce for ‘ Q_6 ’ we can calculate it stoichiometrically by the relationship we have $n(H_2SO_4)=n(gypsum)$, therefore ‘ $Q_6/Mm(H_2SO_4)=m(gypsum)/Mm(gypsum)$ ’.

Hence: ‘ $Q_6=m(gypsum)*Mm(H_2SO_4)/Mm(gypsum)$ ’, ‘ m ’ is the mass and ‘ Mm ’ the molecular mass.

And so, using this balance, we can calculate the quantity of sulphuric acid consumed in the reaction. This allows us to deduce the quantity with which we will feed the next test.

As an example, we will take the sulphate balance study for a given phosphate "K09". The results are summarized in [Table.14](#) below:

Table.14: The sulphate balance study for a given phosphate "K09".

SO_4^{3-}	TS Solid Rate	$d(Kg/m^3)$	TB(g) Fallen From Burette	SULPHURIC ENTRIES (g)						OUTPUTS OF SULPHURIC (g)	
				H_2SO_4 65%	$Q_1=H_2SO_4$ 100%	$Q_2=H_2SO_4$ (RA)	$Q_3=SO_3$ (PP)	$Q_4=H_2SO_4$ res(i-1)	H_2SO_4 Total	$Q_5=H_2SO_4$ res(i)	$Q_6= H_2SO_4$ Gypsum
16	37	1355	1627	270	175.5	8.63	3.33	3.01	190.5	11.86	178.61
19	36	1338	1671	265	172.25	8.63	3.33	5.83	190	15.19	174.86
16	35	1343	1665	267	173.55	8.63	3.33	7.27	192.8	12.89	179.89
15	36	1342	1704	270	175.5	8.63	3.33	6.2	193.7	11.78	181.87
21	36	1327	1700	274	178.1	9.6	3.33	5.53	196.6	17.22	179.34
25	36	1325	1657	274	178.1	10.3	3.33	8.1	199.8	20.01	179.82

Note: This Sulphate balance sheet study stays because of several constraints, such as; The vaporization of water during the tests, and the entrainment of sulphate ions with steam. The impossibility of calculating the solid rate so after 48 hours of the test.

Our visit is based on the valuation and comparability of our purified acid sample called PAC/MSN on the manufacturing efficiency of phosphoric acid, which we use as the return acid in the tests. In general, the results remain secure at the OCP, the volume recovered is large compared to the volume of tests, and its colour is lighter than that obtained by the laboratory test bench for the manufacture of phosphoric acid OCP [15]. Thus the gypsum residue is of large volume and a slightly lighter colour than that obtained by the OCP. For more details, we indicate in the following section some results obtained by our MSN materials applied to the acid as it is.

For more information on what has been said above, and what follows in the next part, we can quote in particular, The analyses of the various tests at the Central Laboratory of Maroc Chemistry, for the period from 01 January 2012 to 15 February 2012 [16], concerning the contents of essential elements in the acid produced and the raw phosphate G10 (YOUSOUFIA Phosphate) currently used by Maroc Phosphore I. The different results are given in Table.15.

[16] Jihad DARYF, Rachid SEMLALI EL IDRISSE, mémoire de projet de fin d'études, « *Optimisation de la désulfatation-décantation de l'acide phosphorique des lignes Nissan à Maroc Phosphore I* », 2012, Ecole Nationale des Sciences Appliquées de Safi Département : Génie Industriel- Université Cadi Ayyad.

Table.15: Representative composition of raw phosphate G10 and its acids 30% and 54% P_2O_5 .

Element	Raw phosphate G10	Acid 30% P_2O_5	Clarified Acid 30% P_2O_5	Acid 54% P_2O_5
CaO%	48	-	-	-
H ₂ O%	4	-	-	-
CO ₂ %	5.80	-	-	-
SiO ₂ %	7.57	-	-	-
H ₂ SO ₄ %	-	2.48	2.20	3.09
MgO%	0.62	0.74	-	1.51
Cd(ppm)	8.40	-	-	-
M.org%	2.06	-	-	-

The phosphoric acid produced contains a wide variety of impurities that require Physico-chemical treatments to eliminate the most harmful ones. To know these impurities, we first present the composition of different qualities of raw phosphate treated at the level of Morocco Phosphorus I [15], Table.16.

Table.16: Analysis of impurities of the different qualities of YOUSSEFIA Raw Phosphate.

Element	Y ₁ Design	Y ₁ Exploitation	Y ₂	Y ₂₃	Y ₂₁	Y _{1C}
CaO%	51.77	51.02	53.89	52.63	51.97	50.40
SO ₃ %	1.47	1.58	2.38	2.55	1.82	1.59
CO ₂ %	5.88	5.89	3.69	3.89	4.74	5.11
F ⁻ %	4.15	3.92	4.02	3.92	4.17	3.46
SiO ₂ %	2.94	3.81	1.14	3.64	3.82	5.34
MgO%	0.3	0.56	0.49	0.74	0.65	0.63
Al ₂ O ₃ %	0.49	0.45	0.29	0.32	0.4	0.48
Na ₂ O%	0.77	--	--	--	0.94	1.04
K ₂ O%	0.08	--	--	--	0.07	0.06
Cl(ppm)	250	240	235	240	300	--
M.org%	0.01	2.08	0.25	0.36	--	0.15
Humidity%	1.1	2.47	1.14	0.24	0.43	1.5
Cd(ppm)	--	--	--	--	--	12.58
As(ppm)	--	--	--	--	--	6.37

Since the start of the NISSAN workshop, the main qualities of phosphates used are Y₁, Y₂, Y₂₃, Y₂₁ and Y_{1C} [16].

IV.2. Demineralization of Phosphoric Acids 29% and 54%.

a) Presentation.

In this study, we were interested in the study of phosphoric acid purification by lacunar apatites, MSN and TBT-C. For this purpose, we have prepared several mixed phospho-Lead samples of the chemical formula $APb_{4-y}My(PO_4)_3$ [A: Na, K, Li. M: Ca, Cd, Cu, Zn, Ni, Sr, Fe], with Potassium, Lithium, Sodium, Calcium, Cadmium, Copper, Zinc, Nickel, Strontium, and Iron, as well as MSN reactants. After the synthesis of the samples, the next step the identifications of them by DRX, thus confirming the presence or not of the desired phases and characterizing the purity of the compounds. Phospho-Lead apatites, MSN, and TBT-C are tested on the phosphoric acid matrix are not purified.

All tests with the lacunar apatites, carried out on the phosphoric acid matrix 29% and 54% in P_2O_5 , not decanted and decanted by filtration, are not purified, called pretreated acids, 'Raw', in the original rock phosphate of YOUSOUFIA. ACP samples extracted from Morocco Phosphorus II and III. The tests carried out at the Central Laboratory OIS/L/Q of Maroc Chemistry, SAFI, for 25 days from 05/07 to 31/07, 2017, and the analyses carried out on each of the samples, by ICPE-9000 [(of Shimadzu Europa GmbH) for more details see [Chapter. I](#)]. In the tests, to simplify the chemical formula we eliminated the tetrahedron PO_4^{3-} in the apatites formula, so we used the PAC notation 29% and 54%.

b) ICP analyses on the PAC54% undecanted and decanted (filtered).

According to all the analyses, for example, those presented in [Table.17](#), these analyses include:

- **Elements in per cent % (dag/Kg):** SO_3 , MgO , CaO , Al_2O_3 , Fe_2O_3 , Na_2O , and K_2O .
- **Trace elements in ppm (mg/Kg):** Zn, Cr, U, V, V, Ti, Sr, Y, Ni, Zr, Cu, Mn, Cd, La, As, Th, Ba, Li, Er,..., etc.

Table.17: Comparison between PAC undecanted and decanted.

Element	PAC54% (RAW)	PAC 54% (Filtered)	difference between PAC54% (RAW) and PAC 54% (Filtered)	Adsorption Yield in %
% (dag/Kg)				
Al ₂ O ₃	0.62	0.59	0.03	4.84
CaO	0.87	0.01	0.86	99.31
Fe ₂ O ₃	0.33	0.34	-0.01	-3.03
K ₂ O	0.145	0.15	0	-2.07
MgO	1.7	1.69	0.01	0.59
Na ₂ O	0.28	0.07	0.21	75.36
SO ₃	3.58	2.38	1.2	33.52
ppm(mg/Kg)				
Cd	20.3	18.6	1.7	8.37
As	8.73	8.19	0.54	6.19
Cr	205	228	-23	-11.22
Cu	35	39	-4	-11.43
Mn	32	36	-4	-12.5
Ni	39	32	7	17.95
Sr	64	1.13	62.87	98.23
Ti	71	74	-3	-4.23
U	191	203	-12	-6.28
V	149	164	-15	-10.07
Zn	317	345	-28	-8.83
Ag	0.44	0.43	0.01	2.27
Ba	4.85	0.51	4.34	89.48
Be	1.34	1.48	-0.14	-10.45
Co	0.77	0.89	-0.12	-15.58
Er	3.51	2.33	1.18	33.62
Eu	0.62	0.1	0.52	84.03
La	11.1	0.02	11.08	99.82
Li	4.65	3.8	0.85	18.28
Mo	2.81	3.18	-0.37	-13.17
Pb	0.71	0.23	0.48	67.61
Sb	2.91	3.32	-0.41	-14.09
Sn	0.005	0.23	-0.23	-4580
Th	5.16	5.02	0.14	2.71
Y	61	39	22	36.07
Zr	35	32	3	8.57

The Comparison of the results of the two PAC, undecanted and filtered (filtered), showed that the 'CaO' element in solid form has disappeared, and so of the 'Na₂O' element remains at a low content. 'SO₃' is eliminated by 1/3 compared to the undecanted ACP solution. The settling process removes suspended solids from the rest of the gypsum (CaSO₄) and their derivatives (Ca_{1-x}Na_{2x}Al_{2x/3}SO₄), and consequently, a difference between the contents of the minor elements in ppm has appeared a small increase and decrease in the concentrations of the cations. Except for 'Sr, Ba, Eu, and La' cations, which are removed by a high content, such that the removal yield is greater than 80%, these cations can be said to remain suspended in the undecanted PAC or they are trapped in the residual gypsum. The Sn

cation exists in low content 0.005ppm; the use of mineralization acids for ICP calibration, containing this element increases its content to 0.23ppm.

c) The lacunars apatites tests on the PAC 54% undecanted and decanted (filtered).

The apatite tests performed at room temperature on the decanted PAC (Table.18) and the undecanted PAC (Table.19). On 100ml of acid 100mg of apatite is added under magnetic agitation with an equal speed $V=400\text{tr/min}$, at the end of the experiment, the reaction mixtures are filtered on the filter papers. The recovered solutions are analyzed by the ICP-9000 device, see results Table.18 and Table.19.

Table.18: apatites tests on undecanted PAC54%.

Apatites Testing					Adsorption Yield in %		
Element	PAC54%(RAW)	NaPb _{3.25} Fe _{0.5}	NaPb ₃ Ni	KPb ₃ Zn	NaPb _{3.25} Fe _{0.5}	NaPb ₃ Ni	KPb ₃ Zn
% (dag/Kg)							
Al ₂ O ₃	0.62	0.47	0.5	0.47	24.19	19.35	24.19
CaO	0.87	0.007	0.006	0.004	99.2	99.31	99.54
Fe ₂ O ₃	0.33	0.32	0.33	0.32	3.03	0	3.03
K ₂ O	0.145	0.125	0.129	0.128	13.79	11.03	11.72
MgO	1.7	1.51	1.57	1.54	11.18	7.65	9.41
Na ₂ O	0.28	0.042	0.046	0.038	85	83.57	86.43
SO ₃	3.58	2.22	2.26	2.24	37.99	36.87	37.43
ppm(mg/Kg)							
Cd	20.3	17.6	18.6	17.6	13.3	8.37	13.3
As	8.73	8.48	8.63	7.46	2.86	1.15	14.55
Cr	205	213	216	218	-3.9	-5.37	-6.34
Cu	35	38	37	40	-8.57	-5.71	-14.29
Mn	32	33	34	34	-3.13	-6.25	-6.25
Ni	39	30	58	30	23.08	-48.72	23.08
Sr	64	0.53	0.5	0.55	99.17	99.22	99.14
Ti	71	69	70	71	2.82	1.41	0
U	191	187	192	189	2.09	-0.52	1.05
V	149	153	156	156	-2.68	-4.7	-4.7
Zn	317	323	323	411	-1.89	-1.89	-29.65
Ag	0.44	0.36	0.38	0.36	18.18	13.64	18.18
Ba	4.85	0.44	0.13	0.15	90.93	97.32	96.91
Be	1.34	1.38	1.4	1.39	-2.99	-4.48	-3.73
Co	0.77	0.82	0.88	0.84	-6.49	-14.29	-9.09
Er	3.51	2.11	2.17	2.18	39.89	38.18	37.89
Eu	0.62	0.086	0.087	0.092	86.13	85.97	85.16
La	11.1	0	0	0	100	100	100
Li	4.65	3.35	3.51	3.27	27.96	24.52	29.68
Mo	2.81	2.86	2.93	2.94	-1.78	-4.27	-4.63
Pb	0.71	0.69	1.18	1.21	2.82	-66.2	-70.42
Sb	2.91	3.03	3.15	3.09	-4.12	-8.25	-6.19
Sn	0.005	0.078	0.09	0.118	-1460	-1700	-2260
Th	5.16	4.49	4.74	4.4	12.98	8.14	14.73
Y	61	36	37	36	40.98	39.34	40.98
Zr	35	30	31	31	14.29	11.43	11.43

Table.19: apatites tests on ACP54% decanted.

Apatites Testing								Adsorption Yield in %					
Element	PAC(Decanted)	NaPb _{3.5} Ni _{0.5}	NaPb ₂ CaCd	NaPb ₃ Cu	LiPb ₄	NaPb ₂ CaSr	NaPb ₄	NaPb _{3.5} Ni _{0.5}	NaPb ₂ CaCd	NaPb ₃ Cu	LiPb ₄	NaPb ₂ CaSr	NaPb ₄
%(dag/Kg)													
Al ₂ O ₃	0.59	0.49	0.49	0.48	0.48	0.49	0.48	16.95	16.95	18.64	18.64	16.95	18.64
CaO	0.006	0.009	0.009	0.006	0.008	0.009	0.008	-50.00	-50.00	0.00	-33.33	-50.00	-33.33
Fe ₂ O ₃	0.34	0.32	0.31	0.31	0.32	0.31	0.31	5.88	8.82	8.82	5.88	8.82	8.82
K ₂ O	0.148	0.122	0.118	0.118	0.123	0.123	0.123	17.57	20.27	20.27	16.89	16.89	16.89
MgO	1.69	1.55	1.53	1.52	1.53	1.54	1.50	8.28	9.47	10.06	9.47	8.88	11.24
Na ₂ O	0.069	0.050	0.049	0.048	0.049	0.052	0.045	27.54	28.99	30.43	28.99	24.64	34.78
SO ₃	2.38	2.25	2.21	2.17	2.17	2.15	2.21	5.46	7.14	8.82	8.82	9.66	7.14
ppm (mg/Kg)													
Cd	18.6	17.7	93.4	17.2	17.2	16.1	17.4	4.84	-402.15	7.53	7.53	13.44	6.45
As	8.19	7.72	7.74	7.08	7.77	7.33	7.69	5.74	5.49	13.55	5.13	10.50	6.11
Cr	228	209	209	212	210	213	211	8.33	8.33	7.02	7.89	6.58	7.46
Cu	39	35	36	51	37	38	36	10.26	7.69	-30.77	5.13	2.56	7.69
Mn	36	33	33	33	33	33	33	8.33	8.33	8.33	8.33	8.33	8.33
Ni	32	35	29	30	29	30	29	-9.38	9.38	6.25	9.38	6.25	9.38
Sr	1.13	0.59	0.52	0.56	0.63	2.59	0.57	47.79	53.98	50.44	44.25	-129.20	49.56
Ti	74	68	68	69	68	70	69	8.11	8.11	6.76	8.11	5.41	6.76
U	203	187	184	189	186	189	189	7.88	9.36	6.90	8.37	6.90	6.90
V	164	150	150	152	150	153	151	8.54	8.54	7.32	8.54	6.71	7.93
Zn	345	310	314	320	319	323	318	10.14	8.99	7.25	7.54	6.38	7.83
Ag	0.43	0.35	0.31	0.33	0.36	0.36	0.31	18.60	27.91	23.26	16.28	16.28	27.91
Ba	0.51	0.21	0.22	0.22	0.24	0.26	0.25	58.82	56.86	56.86	52.94	49.02	50.98
Be	1.48	1.34	1.36	1.38	1.36	1.36	1.36	9.46	8.11	6.76	8.11	8.11	8.11
Co	0.89	0.81	0.76	0.85	0.81	0.83	0.82	8.99	14.61	4.49	8.99	6.74	7.87
Er	2.33	2.08	2.10	2.14	2.14	2.16	2.15	10.73	9.87	8.15	8.15	7.30	7.73
Eu	0.099	0.094	0.087	0.096	0.092	0.095	0.099	5.05	12.12	3.03	7.07	4.04	0.00
La	0.02	0.00	0.00	0.00	0.00	0.00	0.00	100.00	100.00	100.00	100.00	100.00	100.00
Li	3.80	3.36	3.35	3.22	7.38	3.34	3.19	11.58	11.84	15.26	-94.21	12.11	16.05
Mo	3.18	2.86	2.79	2.97	2.93	2.91	2.94	10.06	12.26	6.60	7.86	8.49	7.55
Pb	0.23	2.87	4.66	3.21	3.00	6.82	3.53	-1147.83	-1926.09	-1295.65	-1204.35	-2865.22	-1434.78
Sb	3.32	2.94	3.04	3.16	3.07	3.28	3.02	11.45	8.43	4.82	7.53	1.20	9.04
Sn	0.234	0.165	0.000	0.133	0.191	0.064	0.131	29.49	100.00	43.16	18.38	72.65	44.02
Th	5.02	4.48	4.53	4.83	4.79	4.88	4.72	10.76	9.76	3.78	4.58	2.79	5.98
Y	39	36	36	36	36	37	36	7.69	7.69	7.69	7.69	5.13	7.69
Zr	32	30	30	30	30	31	30	6.25	6.25	6.25	6.25	3.13	6.25

According to the results of the three lacunars materials presented in Table.18, show that the major elements in % are all adsorbed by different yields such as ‘CaO and Na₂O’ elements

almost separable from the solution, followed by the other elements with an adsorption efficiency below 40%. The difference in adsorption yields for the same element between the three materials is small. It should be noted that the NaPb_3Ni material does not adsorb hematite (Fe_2O_3). The 16 cations among 26 minor elements in ppm have been adsorbed, including ‘Sr; Ba; Eu, and La’, have completely disappeared from the solution, the rest of the cations with yields of less than 40% are; ‘Cd, As, Ni, Ti, U, Ag, Er, Er, Eu, Li, Th, Y, and Zr. The non-adsorbed cations with negative yields are due to the use of mineralization acids used to do ICP calibrator, are; Cr, Cu, Mn, V, Zn, Be, Co, Mo, Sb, and Sn. We notice that there is a release of ‘Pb’ by the two materials NaPb_3Ni and KPb_3Zn . Thus NaPb_3Ni releases ‘Ni’ and KPb_3Zn releases ‘Zn’.

The undecanted PAC solution contains a rate of solid that is gypsum and other suspended solid elements. To make a correct analysis, i.e. a logical interpretation, we tested the decanted (filtered) PAC. According to the results in [Table.19](#), all major elements are adsorbed by yields of less than 35%, except the ‘CaO’ element separated by filtration. The lacunars materials adsorb all impurities in medium and low concentrations. The Lanthanum (La) is gone, only the NaPb_2CaCd adsorbs the Tin (Sn) cation completely, but it releases the ‘Cd’ cation. The materials from which their cations released into the PAC, NaPb_3Cu releases ‘Cu’, $\text{NaPb}_3\text{Ni}_{0.5}$ releases ‘Ni’, a release of ‘Sr’ by the adsorbent NaPb_2CaSr , LiPb_4 releases ‘Li’. All materials release ‘Pb’ by different percentages in the PAC solution.

d) Comparison between 54% PAC and 29% PAC decanted (filtered).

From the results presented in [Table.20](#) below, it is clear that the concentration has the effect of increasing the impurity content. Except for the elements CaO; Na_2O and SO_3 , as well as the cations ‘Sr; Ba; Ba; Eu; La and Sn’, which exist in suspension in the PAC29%, because the vaporization followed by acid filtration, has the effect of decreasing their concentrations.

Table.20: Comparison of PAC54% and PAC29% decanted.

Element	PAC54%	PAC29%	difference between PAC54% and PAC30%
% (dag/Kg)			
Al ₂ O ₃	0.59	0.17	0.42
CaO	0.006	0.22	-0.22
Fe ₂ O ₃	0.34	0.13	0.21
K ₂ O	0.148	0.04	0.11
MgO	1.69	0.84	0.85
Na ₂ O	0.069	0.1	-0.03
SO ₃	2.38	2.58	-0.2
ppm (mg/Kg)			
Cd	18.6	13	5.6
As	8.19	6.71	1.48
Cr	228	146	82
Cu	39	18	21
Mn	36	14	22
Ni	32	16	16
Sr	1.13	34.6	-33.47
Ti	74	35	39
U	203	89	114
V	164	89.3	74.7
Zn	345	220	125
Ag	0.43	0.18	0.25
Ba	0.51	1.02	-0.51
Be	1.48	0.7	0.78
Co	0.89	0.34	0.55
Er	2.33	1.14	1.19
Eu	0.099	0.21	-0.11
La	0.02	2.93	-2.91
Li	3.8	1.35	2.45
Mo	3.18	0.93	2.25
Pb	0.23	0.22	0.01
Sb	3.32	3.16	0.16
Sn	0.234	0.35	-0.12
Th	5.02	1.2	3.82
Y	39	17	22
Zr	32	9	23

e) The lacunars apatites tests on PAC29% settled at room temperature and T=65°C.

The tests performed at room temperature on the PAC29% decanted are summarized in [Table.21](#). On 100ml of acid, 50mg of lacunar apatite is added under magnetic agitation with an equal speed V=400rpm. At the end of the experiment, the reaction mixtures are filtered on filter paper. The recovered solutions are analyzed by the ICP device (see [Table.21](#) results).

The tests performed at 65°C with the same lacunar materials and the same operating procedure previously used at room temperature. The recovered solutions are analyzed by the ICP device, see the results in [Table.22](#).

Table.21: apatites tests on PAC29% decanted at room temperature.

Apatites Testing										Adsorption Yield in %							
Elements	PCA(Filtered)	NaPb _{1.25} Fe _{0.5}	NaPb ₃ Ni	NaPb ₃ Cu	NaPb ₂ SrCa	NaPb ₄	NaPb ₂ Zn	NaPb ₃ Sr	NaPb ₃ Ca	NaPb _{1.25} Fe _{0.5}	NaPb ₃ Ni	NaPb ₃ Cu	NaPb ₂ SrCa	NaPb ₄	NaPb ₂ Zn	NaPb ₃ Sr	NaPb ₃ Ca
%(dag/Kg)																	
Al ₂ O ₃	0.17	0.17	0.17	0.17	0.17	0.16	0.16	0.16	0.17	0.00	0.00	0.00	0.00	5.88	5.88	5.88	0.00
CaO	0.221	0.110	0.110	0.104	0.102	0.109	0.124	0.118	0.115	50.23	50.23	52.94	53.85	50.68	43.89	46.61	47.96
Fe ₂ O ₃	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K ₂ O	0.037	0.040	0.041	0.041	0.040	0.048	0.039	0.040	0.040	-8.11	-8.11	-10.81	-8.11	-29.73	-5.41	-8.11	-8.11
MgO	0.84	0.84	0.83	0.84	0.85	0.84	0.84	0.82	0.85	0.00	0.00	0.00	-1.19	0.00	0.00	2.38	-1.19
Na ₂ O	0.097	0.109	0.111	0.109	0.109	0.105	0.109	0.108	0.106	-12.37	-12.37	-12.37	-12.37	-8.25	-12.37	-11.34	-9.28
SO ₃	2.58	2.44	2.44	2.45	2.42	2.38	2.39	2.39	2.42	5.43	5.43	5.04	6.20	7.75	7.36	7.36	6.20
ppm (mg/Kg)																	
Cd	13.0	12.0	13.0	12.0	12.0	13.0	12.0	11.0	13.0	7.69	7.69	7.69	7.69	0.00	7.69	15.38	0.00
As	6.71	7.12	6.56	6.89	6.29	6.95	6.26	6.24	6.80	-6.11	-6.11	-2.68	6.26	-3.58	6.71	7.00	-1.34
Cr	146	144	148	147	146	146	146	147	149	1.37	1.37	-0.68	0.00	0.00	0.00	-0.68	-2.05
Cu	18	21	19	71	21	19	18	19	19	-16.67	-16.67	-294.44	-16.67	-5.56	0.00	-5.56	-5.56
Mn	14	14	14	14	14	14	14	14	14	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ni	16	15	58	16	15	16	16	16	16	6.25	-262.5	0.00	6.25	0.00	0.00	0.00	0.00
Sr	34.60	3.61	3.47	3.38	7.57	4.28	3.03	12.00	3.31	89.57	89.57	90.23	78.12	87.63	91.24	65.32	90.43
Ti	35	34	35	35	35	34	35	35	35	2.86	2.86	0.00	0.00	2.86	0.00	0.00	0.00
U	89	87	89	90	88	88	88	89	90	2.25	2.25	-1.12	1.12	1.12	1.12	0.00	-1.12
V	89.3	88	90.2	89.2	89.2	88.6	89	89.3	90.5	1.46	1.46	0.11	0.11	0.78	0.34	0.00	-1.34
Zn	220	216	225	219	217	217	301	220	223	1.82	1.82	0.45	1.36	1.36	-36.82	0.00	-1.36
Ag	0.18	0.14	0.18	0.15	0.13	0.14	0.15	0.20	0.18	22.22	22.22	16.67	27.78	22.22	16.67	-11.11	0.00
Ba	1.02	0.15	0.15	0.11	0.13	0.14	0.16	0.16	0.14	85.29	85.29	89.22	87.25	86.27	84.31	84.31	86.27
Be	0.70	0.69	0.73	0.71	0.69	0.70	0.71	0.69	0.71	1.43	1.43	-1.43	1.43	0.00	-1.43	1.43	-1.43
Co	0.34	0.33	0.38	0.35	0.36	0.35	0.35	0.35	0.36	2.94	2.94	-2.94	-5.88	-2.94	-2.94	-2.94	-5.88
Er	1.14	1.12	1.15	1.15	1.11	1.14	1.16	1.12	1.13	1.75	1.75	-0.88	2.63	0.00	-1.75	1.75	0.88
Eu	0.21	0.2	0.21	0.2	0.2	0.2	0.21	0.2	0.21	4.76	4.76	4.76	4.76	4.76	0.00	4.76	0.00
La	2.93	1.49	1.50	1.42	0.76	1.57	1.32	1.47	1.39	49.15	49.15	51.54	74.06	46.42	54.95	49.83	52.56
Li	1.35	1.36	1.29	1.38	1.39	1.34	1.31	1.33	1.33	-0.74	-0.74	-2.22	-2.96	0.74	2.96	1.48	1.48
Mo	0.93	0.92	0.99	0.95	0.92	0.93	0.93	0.92	0.93	1.08	1.08	-2.15	1.08	0.00	0.00	1.08	0.00
Pb	0.22	5.76	6.64	4.55	2.80	5.88	8.23	4.11	5.74	-2518.18	-2518.18	-1968.18	-1172.73	-2572.73	-3640.91	-1768.18	-2509.09
Sb	3.16	3.18	2.96	2.97	2.81	3.03	2.86	2.85	2.63	-0.63	-0.63	6.01	11.08	4.11	9.49	9.81	16.77
Sn	0.350	0.160	0.460	0.080	0.250	0.310	0.220	0.280	0.270	54.29	54.29	77.14	28.57	11.43	37.14	20.00	22.86
Th	1.20	1.26	1.11	1.31	1.15	1.23	1.20	1.24	1.05	-5.00	-5.00	-9.17	4.17	-2.50	0.00	-3.33	12.50
Y	17	16	17	17	16	17	17	17	17	5.88	5.88	0.00	5.88	0.00	0.00	0.00	0.00
Zr	9	6	7	7	6	6	6	9	12	33.33	33.33	22.22	33.33	33.33	33.33	0.00	-33.33

Table.22: apatites tests on PAC29% decanted at T=65°C.

Apatites Testing										Adsorption Yield in %							
Elements	PCA(Filtered)	NaPb _{1.25} Fe _{0.5}	NaPb ₃ Ni	NaPb ₃ Cu	NaPb ₂ SrCa	NaPb ₄	NaPb ₂ Zn	NaPb ₃ Sr	NaPb ₃ Ca	NaPb _{1.25} Fe _{0.5}	NaPb ₃ Ni	NaPb ₃ Cu	NaPb ₂ SrCa	NaPb ₄	NaPb ₂ Zn	NaPb ₃ Sr	NaPb ₃ Ca
% (dag/Kg)																	
Al ₂ O ₃	0.17	0.17	0.17	0.16	0.16	0.16	0.16	0.16	0.17	0.00	0.00	5.88	5.88	5.88	5.88	5.88	0.00
CaO	0.221	0.211	0.213	0.213	0.211	0.212	0.215	0.217	0.202	4.52	3.62	3.62	4.52	4.07	2.71	1.81	8.60
Fe ₂ O ₃	0.13	0.13	0.13	0.13	0.12	0.12	0.13	0.12	0.13	0.00	0.00	0.00	7.69	7.69	0.00	7.69	0.00
K ₂ O	0.037	0.042	0.037	0.040	0.036	0.047	0.038	0.036	0.041	-13.51	0.00	-8.11	2.70	-27.03	-2.70	2.70	-10.81
MgO	0.84	0.84	0.85	0.83	0.81	0.82	0.83	0.81	0.83	0.00	-1.19	1.19	3.57	2.38	1.19	3.57	1.19
Na ₂ O	0.097	0.122	0.123	0.124	0.121	0.116	0.121	0.122	0.129	-25.77	-26.80	-27.84	-24.74	-19.59	-24.74	-25.77	-32.99
SO ₃	2.58	2.55	2.56	2.50	2.46	2.50	2.53	2.49	2.50	1.16	0.78	3.10	4.65	3.10	1.94	3.49	3.10
ppm(mg/Kg)																	
Cd	13.0	12.0	12.0	12.0	12.0	12.0	12.0	12.0	12.0	7.69	7.69	7.69	7.69	7.69	7.69	7.69	7.69
As	6.71	6.14	6.33	6.19	6.55	5.74	6.10	6.40	6.62	8.49	5.66	7.75	2.38	14.46	9.09	4.62	1.34
Cr	146	145	147	147	144	145	144	142	147	0.68	-0.68	-0.68	1.37	0.68	1.37	2.74	-0.68
Cu	18	22	19	73	22	19	18	18	19	-22.22	-5.56	-305.56	-22.22	-5.56	0.00	0.00	-5.56
Mn	14	14	14	14	14	14	14	14	14	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ni	16	16	58	16	16	15	15	15	16	0.00	-262.50	0.00	0.00	6.25	6.25	6.25	0.00
Sr	34.60	2.94	2.39	3.08	9.23	2.54	2.49	8.34	2.49	91.50	93.09	91.10	73.32	92.66	92.80	75.90	92.80
Ti	35	35	35	35	35	34	34	34	35	0.00	0.00	0.00	0.00	2.86	2.86	2.86	0.00
U	89	90	90	91	89	88	87	87	89	-1.12	-1.12	-2.25	0.00	1.12	2.25	2.25	0.00
V	89.3	88.9	90.5	90.1	88.5	88.3	88.1	87.1	89.5	0.45	-1.34	-0.90	0.90	1.12	1.34	2.46	-0.22
Zn	220	221	224	225	222	220	302	214	224	-0.45	-1.82	-2.27	-0.91	0.00	-37.27	2.73	-1.82
Ag	0.18	0.16	0.20	0.19	0.14	0.14	0.15	0.17	0.20	11.11	-11.11	-5.56	22.22	22.22	16.67	5.56	-11.11
Ba	1.02	0.12	0.17	0.18	0.19	0.17	0.11	0.12	0.16	88.24	83.33	82.35	81.37	83.33	89.22	88.24	84.31
Be	0.70	0.70	0.71	0.71	0.70	0.69	0.69	0.68	0.72	0.00	-1.43	-1.43	0.00	1.43	1.43	2.86	-2.86
Co	0.34	0.35	0.39	0.34	0.35	0.32	0.33	0.33	0.32	-2.94	-14.71	0.00	-2.94	5.88	2.94	2.94	5.88
Er	1.14	1.13	1.17	1.16	1.13	1.21	1.13	1.12	1.18	0.88	-2.63	-1.75	0.88	-6.14	0.88	1.75	-3.51
Eu	0.21	0.21	0.22	0.22	0.21	0.2	0.21	0.21	0.22	0.00	-4.76	-4.76	0.00	4.76	0.00	0.00	-4.76
La	2.93	1.21	1.10	1.19	0.74	1.14	1.05	0.70	0.99	58.70	62.46	59.39	74.74	61.09	64.16	76.11	66.21
Li	1.35	1.39	1.34	1.34	1.37	1.34	1.29	1.32	1.28	-2.96	0.74	0.74	-1.48	0.74	4.44	2.22	5.19
Mo	0.93	0.91	0.94	0.96	0.94	0.96	0.88	0.95	0.97	2.15	-1.08	-3.23	-1.08	-3.23	5.38	-2.15	-4.30
Pb	0.22	9.00	7.70	7.33	4.96	8.39	7.93	5.92	8.76	-3990.91	-3400.00	-3231.82	-2154.55	-3713.64	-3504.55	-2590.91	-3881.82
Sb	3.16	2.63	2.92	2.88	2.72	2.80	2.68	2.87	2.73	16.77	7.59	8.86	13.92	11.39	15.19	9.18	13.61
Sn	0.350	0.330	0.310	0.320	0.320	0.230	0.370	0.230	0.330	5.71	11.43	8.57	8.57	34.29	-5.71	34.29	5.71
Th	1.20	1.29	1.26	1.18	1.25	1.44	1.19	1.26	1.37	-7.50	-5.00	1.67	-4.17	-20.00	0.83	-5.00	-14.17
Y	17	17	17	17	17	17	17	16	17	0.00	0.00	0.00	0.00	0.00	0.00	5.88	0.00
Zr	9	7	10	8	6	6	6	9	9	22.22	-11.11	11.11	33.33	33.33	33.33	0.00	0.00

According to the results of [Table.21](#), concerning the apatite tests at room temperature, in dilute acid medium half of the ‘CaO’ content is removed, the very low adsorption of the element SO₃, the materials have no adsorption affinity on the other elements in %, these are ‘Al₂O₃, Fe₂O₃, K₂O, MgO, and Na₂O’. We notice that there is high adsorption of ‘Sr and Ba’ cations, average adsorption of ‘La’ and ‘Sn’ cations, the low adsorption of ‘Cd, Ag, Eu, Sb,

and Zr' cations. The non-adsorbed cations are 'As, Cr, Cu, Mn, Ni, Ti, U, V, Zn, Be, Co, Er, Li, Li, Mo, Th, and Y'. The solid NaPb₂Ni releases 'Ni', NaPb₂Cu releases 'Cu', and NaPb₃Zn releases 'Zn'. All materials release 'Pb' by different percentages in the PAC solution.

The results in [Table.22](#), show that magnetic agitation under the effect of temperature (T=65°C) increases the number of chemical elements in % not adsorbed. Strong adsorption of Sr and Ba cations, moyen adsorption of the La cation, the only advantage is that the arsenic adsorption yield increases but remains very low. Low adsorption of Cd, Sb, Ag, Sn, and Zr cations. The non-adsorbed cations are Cr, Cu, Mn, Ni, Ti, U, V, V, Zn, Be, Co, Er, Eu, Li, Mo, Th, and Y. The solid NaPb₂Ni releases Ni, NaPb₂Cu releases Cu, and NaPb₃Zn releases Zn.

All materials release Lead, but the Pb released by the apatite matrix at T=65°C increases concerning ambient temperature, by different percentages in the PAC solution.

f) Crystallographic structure of the lacunar adsorbents.

DRX analyses of lacunar adsorbents, performed by D2PHASER, showing the lacunar apatitic phase; [Fig.27](#). The diffractograms are similar to each other show the hexagonal system phase with the space group $P6_3/m$, only the LiPb₄ material shows additional peaks, thus showing the presence of impurities that appears in the apatitic phase. The structural study of materials, NaPb₂CaCd, NaPb₂CaSr, NaPb₄, and NaPb₃Sr is discussed in [Chapter. II](#), for the material KPb₃Zn the study is discussed in [Chapter. III](#). According to all the results, the best adsorbents of the most toxic 'Cd' and 'As' cations among the elements existing in the PAC; the solid solution KPb₃Zn used in the undecanted PAC54%, the solid solution NaPb₂CaSr used to purify the decanted PAC54%, the NaPb₃Sr tested on the PAC29%.

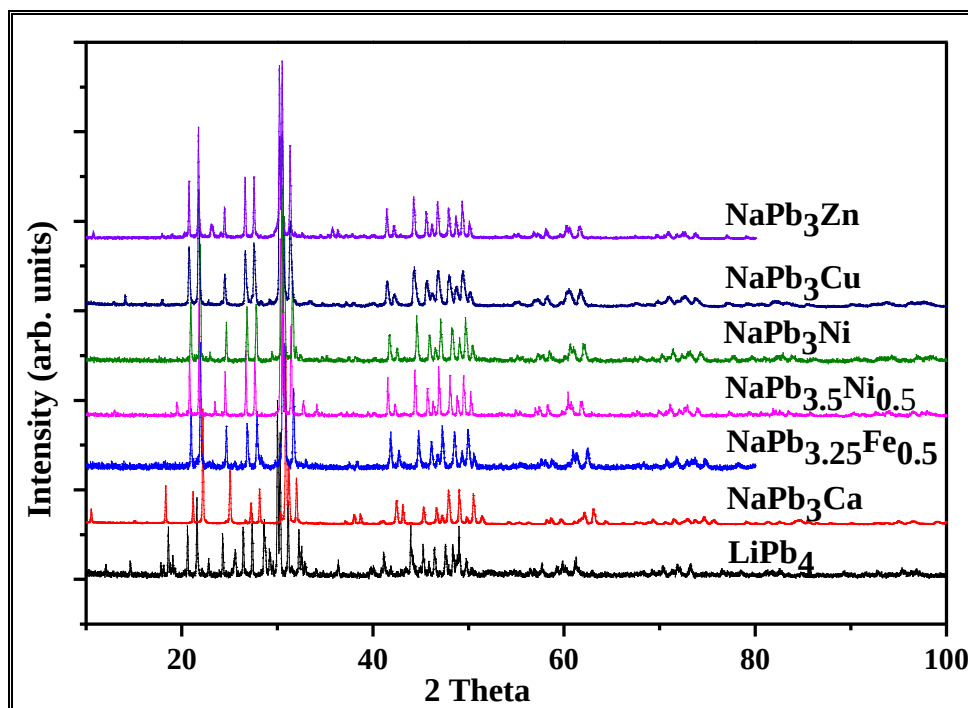


Fig.27: DRX diffractograms of the various lacunar adsorbents.

g) Heavy metal removal process by MSN on PAC.

The proposed innovation concerns the removal of metals, such as cadmium, arsenic, chromium, lead, zinc, tin, iron, copper, barium, strontium and molybdenum and organic matter from phosphoric acid, by the formation of MSN-metallic precipitates and/or organometallic complexes. The reagents used in the process are MSN, whose influence of high, medium, and low concentrations of reagents on the efficiency of the PAC demetallization process was investigated.

The purpose of the above-mentioned tests is to show that the treatment of the invention makes it possible to adapt the concentrations of MSN, depending on the content of heavy metals, such as Cd^{2+} , Ba^{2+} , Pb^{2+} , Cr^{3+} , and Cu^{2+} , present in phosphoric acid.

- **Example 1:** To show the synergy of heavy metal removal obtained by MSN reagents, a treatment of phosphoric acid solution prepared from pure commercial acid (58.6% P_2O_5) and then loaded with heavy metals was carried out. Two phosphoric acid solutions, with a concentration of 33 and 45% P_2O_5 respectively

called PAC33% and PAC45% were prepared. These two solutions were loaded with heavy metals generally present in the phosphoric acid obtained by the wet process.

The two phosphoric acid solutions loaded with heavy metals underwent different demetallization treatments in the presence of one of the MSN reagents. A 2-gram solution of MSN per litre of demineralized water was prepared from the commercial product. Direct addition of 5ml of the already prepared MSN solution to the phosphoric acid solution loaded with heavy metals and stirring of the mixture for 10 minutes. After a rest period of 4 hours, the liquid phase, called solution.1 for PAC33% and solution.2 for PAC45%, was filtered and recovered. The two types of solutions 1 and 2, were analyzed by ICP. The results of the analysis are presented in Table.23 below.

Table.23: Results of ICP analyses on solutions 1 and 2.

		Cadmium	Chrome	Lead	Iron	Copper	Barium
PAC 33% in P₂O₅	Content in ppm	27.3	31.5	25.2	37.4	27.6	25.1
solution.1	Content in ppm	2.3	1.5	1.2	5.7	6.7	12
	Disposal Percentage	91.6%	95.2%	95.2%	84.8%	75.7%	52.2%
PAC 45% in P₂O₅	Content in ppm	28.5	30.3	27.1	40.3	26.8	26.6
solution.2	Content in ppm	5.6	3.2	1.5	15.6	15.4	23
	Disposal Percentage	80.4%	89.4%	94.5%	61.3%	42.5%	13.5%

The results obtained clearly show the improvement made to the demetallization treatment on dilute acid solution.1.

- **Example 2:** Phosphoric acid treatment tests were performed. This is phosphoric acid obtained from the Morocco Phosphorus III unit at JORF LASFAR, with a concentration of 29% P₂O₅; noted PAC29% is not purified, called pretreated acid. The purpose of these tests is to determine the minimum concentration of cadmium. Indeed, an excess of MSN inevitably leads to a partial neutralization of the acid to be treated. To do this, 5ml of MSN solution with a concentration (x) grams per litre (x varies from 0.2 to 60 g/l) to 50ml of PAC29% phosphoric acid was added directly. After stirring followed by a resting period until the solution was settled

(about 1 hour), the liquid phase was filtered and recovered, which was analyzed by ICP. The results of the analyses are presented in [Table.24](#) below.

Table.24: Results of ICP analyses on MSN-PAC29%.

Concentration of MSN	MSN	Cd in ppm	Disposal efficiency in %
	ACP29%	17.34	-----
60g/l	MSH	2.75	84.14
	MSK	2.07	88.06
	MSNa	0.98	94.35
40g/l	MSH	1.109	93.60
	MSK	1.17	93.25
	MSNa	1.43	91.75
20g/l	MSH	0.97	94.41
	MSK	1.12	93.54
	MSNa	1.67	90.37
2g/l	MSNa	2.464	85.79
0.2g/l	MSNa	2.81	83.79

The use of an MSN solution at 0.2g grams per litre results in the elimination of almost 84% of Cadmium. For more details of the schematic describing the decadmiation process by MSN see [Annex. IV](#) on [Fig. IV.6](#).

h) Removal of Cadmium by TBT-C on PAC 29%.

One can in particular use as an adsorbent of heavy metals, the natural apatite of formula $Me_5(XO_4)_3(Y)$, with M^{2+} being a divalent cation (M: Ca^{2+} , Sr^{2+} , Pb^{2+} , ...), XO_4^{3-} usually, a trivalent anion group (XO_4^{3-} : PO_4^{3-} , VO_4^{3-} , AsO_4^{3-} ,) and 'Y' a monovalent anion (Y^- : F^- , OH^- , Cl^- ,.....), well calcined as well ground, or the same apatite used for the production of phosphoric acids by a wet process. Indeed, on one litre of PAC29% in P_2O_5 , a sample of Morocco Phosphorus III, we added under the effect of agitation (300 rpm) and temperature ($T=100^\circ C$), 31.21g of TBT-C, natural calcium phosphate of KHOURIBGA origin, calcined up to $900^\circ C$ and well ground. Vaporization with a yield equal to 1/3 or 33.34% of the initial volume increases the PAC concentration by 29%. After a resting period during the necessary cooling time, the liquid phase was filtered and recovered. The ICP analysis, shows the elimination yield equal to 98.90%, noted that the Cd content in the PAC29% equal to 17.34ppm and the recovered solution equal to 0.19ppm.

i) Conclusion.

It is difficult to compare and interpret the adsorption yields of the same apatite used in the tests on PAC, 54%, and 29%. Indeed, the masses used are different and so are the concentrations of the reaction media. The materials, even in diluted environments, release the Pb cations. It can be seen that there is a cation exchange between the materials and the two PACs. According to the results of the tests, the elements present in the PAC are adsorbed by the matrix apatites lacunar by high, medium, and low yield, as well as elements non-adsorbed. This shows that the adsorption phenomenon is selective by the lacunar materials used.

- The lacunar materials adsorb all the elements that exist in the decanted PAC54%, unlike the case of the undecanted PAC54% which has a been solid content.
- In diluted PAC29% acid medium, the temperature has an unfavourable effect on the adsorption efficiency, because the number of non-adsorbed elements increases.

The demetallization of PAC by MSN overcomes the above-mentioned disadvantages in the industrial problem by proposing a simple, economical and efficient process for the reduction and/or elimination of heavy metals from phosphoric acid obtained by the wet process is not purified. Without going through either neutralization or a purification step. Also, it reduces or eliminates organic matter and facilitates the clarification of phosphoric acid.

Natural apatite is also effective for the removal of the metals in question, but its use is not suitable for industrial use.

Conclusion of the chapter

In recent decades, there has been a growing awareness of the importance of ecological balances threatened by industrial pollution. A new mindset presides; companies are seeking to satisfy customer requirements for impurities in their products. Among these companies, the Office Chérifien des Phosphates (OCP), a world leader in the phosphate and its derived products market, ensures to reduce the impurities contained in its products, mainly phosphoric acid.

In this perspective, Maroc Phosphore (MP) is interested in the purification of wet-produced phosphoric acid. This medium contains several impurities, in particular free sulfides, heavy metals, etc. To eliminate these elements, the NISSAN phosphoric workshop adopts a process described by grinding, reaction, filtration, concentration, clarification, and storage. The PRAYON manufacturing process, which consists of treating the acid in three steps: Desulphation ($-\text{SO}_4^{2-}$); followed by desaturation to reduce the level of free sulfate in the acid; desarsination ($-\text{As}^{3+}$) followed by decantation to reduce the level of arsenic; gas washing (fluorinated gases).

The work we have done in this chapter has allowed us to identify our problem in the demetallization of phosphoric acid, as it is, not clarified, called pretreated acid. Thus the purpose of this chapter is to find the root causes responsible for the existence of heavy, toxic metals, to purify them in the acid, and to take corrective actions for this anomaly.

The description of the OCP group and its activities allowed us to have a general idea of the role of the different phosphoric acid production units within the MP1, MP2, MPIII, MPIV divisions and to give the reader a clear vision of the manufacturing process so that he can better follow our work.

To make a study with success, we carried out all possible tests and simulations in the laboratories, including the aim of eliminating undesirable impurities present in the ore, as well

as in the acid, however, these elements reside in the skeleton of the apatitic structure, difficult to eliminate.

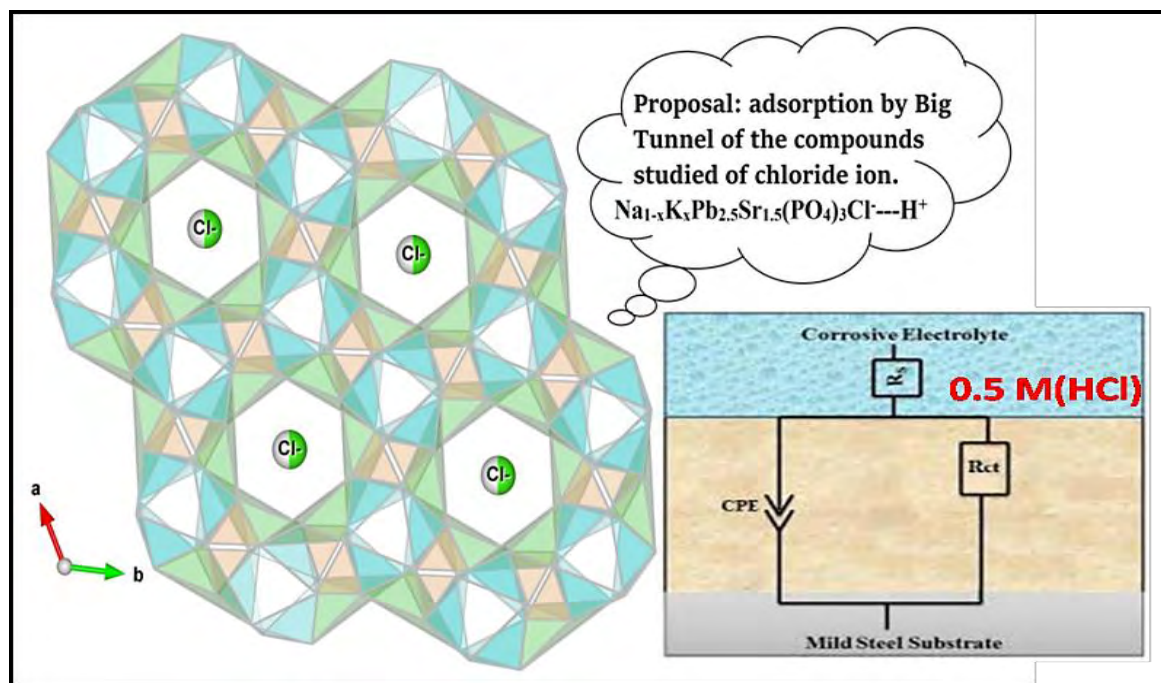
The objective of our subject is the reduction of free sulfates ($\%SO_4$), heavy metals, present in phosphoric acid and which are impurities like many others present in this acid, that is why this chapter will contain a presentation of different impurities including major elements and minor elements, existing in phosphate rock and phosphoric acid, as well as the different operations necessary to reduce or even remove these impurities.

Chapter. V:

New Lacunar Apatites $\text{APb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$ ($\text{A} = \text{Na}, \text{K}$) as Corrosion Inhibitors For Carbon Steel in Hydrochloric Acid Solution: Experimental, Structural, Vibrational, Optical, and Electrochemical Studies.

Abstract;

New corrosion inhibitors labelled lacunar apatites $\text{APb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$ ($\text{A} = \text{Na}, \text{K}$) in the system of $(\text{Na/K})_2\text{O} - \text{SrO} - \text{PbO} - \text{P}_2\text{O}_5$ were successfully synthesized using a solid-state chemical reaction. These apatites were tested as corrosion inhibitors for carbon steel in hydrochloric acid solution at various concentrations. Because, of the importance of these types of materials for use in corrosion inhibitor applications, it seems to us of interest to perform the Structural, Vibrational, and Optical Studies, by using X-ray Diffraction and Raman, Infrared, and UV-Vis spectroscopy techniques for the compositions of lacunar strontium-lead phosphate apatites of sodium or potassium. The results of physical and chemical properties can be analyzed for the engineering aspects of materials structure, surfaces, and interfaces ([Abstract Fig. IV Style](#)).



Abstract Fig. IV Style: The Phenomenon, Proposed by Lacunar Apatites $\text{APb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$ ($\text{A} = \text{Na}, \text{K}$) as Corrosion Inhibitors For Carbon Steel in Hydrochloric Acid Solution.

I. Introduction.

In most industries whose facilities are constituted by metallic structures, the phenomenon of corrosion is invariably present. This problem originates very important material and economic losses due to partial or total replacement of equipment and structures, and plant-repairing shutdowns. Material losses and corrosion consequences are priced so high that in some countries like the U.S. and England these factors have been estimated from 3 to 4% of the GDP.

Corrosion not only has economic implications but also social and these engage the safety and health of people either working in industries or living in nearby towns. The oil industry in Mexico is one of the most affected by corrosion because this phenomenon exerts its effects from the very moment of oil extraction, causing a constant struggle against it. The use of corrosion inhibitors (IC) constitutes one of the most economical ways to mitigate the corrosion rate, protect metal surfaces against corrosion, and preserve industrial facilities [1, 2].

Inorganic CIs are those in which the active substance is an inorganic compound. This is one of the simplest ways to improve the passivity of metal by adding electropositive metal salts to the medium. These metal ions must have a more positive redox potential more positive than the metal constituting the surface to be protected and also a more positive potential than that required for discharging a proton so that the electropositive metal to be reduced is deposited on the surface. The deposited metal promotes the cathodic depolarization by overvoltage reduction and formation of an adherent deposit. Among the metals used for this purpose are mercury (Hg), palladium (Pd), iridium (Ir), platinum (Pt), rhodium (Rh), and rhenium (Re).

[1] Sastri VS. Green Corrosion Inhibitors. Theory and Practice. John Wiley & Sons: Hoboken, NJ; 1998.

[2] Sastri VS. Corrosion Inhibitors Principles and Applications. John Wiley & Sons: New York; 1998.

Moreover, there are inorganic anions providing passivation protection to metal surfaces through their incorporation into the oxide layer; the most widely used of these are chromate (CrO_4^{2-}), nitrate (NO_3^-), molybdate (MoO_4^{2-}), phosphate ($H_2PO_4^-$), and silicates. Despite the wealth of information in the literature on the adsorption properties of well-crystallized apatites as corrosion inhibitors for carbon steel in hydrochloric acid solution. The possible fields of application of apatites are many and varied.

Organic inhibitors have been the most widely used in petroleum refining processes because of their ability to form a protective layer on the metal surface in media with high hydrocarbons content. At present, several organic inhibitors are belonging to different chemical families i.e. fatty amides [3,4], pyridines [5-7], imidazolines [8-11] and other 1,3-azoles [12-14], and polymers [15] have shown excellent performance as corrosion inhibitors [16].

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Despite many inorganic, organic, and polymeric compounds have been showing good performances as Corrosion Inhibitors for different metals and alloys, many of these compounds are toxic and do not fulfil completely the requirements imposed by the environmental protection standards. The new generation of environmental regulations requires the replacement of toxic chemicals with green chemicals. The final choice of the inhibitor for a particular application is restricted by several factors, including increased environmental awareness and the need to promote environmentally friendly processes, coupled with the specificity of action of most acid inhibitors, which often requires the combined action of compounds to achieve an effective corrosion inhibition. This is the reason why in the last year's big efforts have been made by researchers in this area to develop new environmentally-friendly corrosion inhibitors.

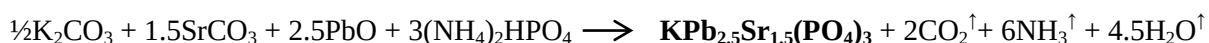
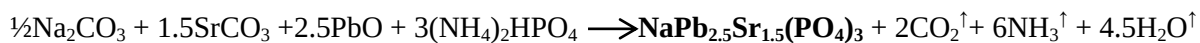
Recently we found a new voltammetric sensor based on $NaCaPb_3(PO_4)_3$ modified carbon paste electrode [17]. Strontium-Lead Phosphate, of Potassium or Sodium without Y anion vacancies $APb_{2.5}Sr_{1.5}(PO_4)_3$ ($A = Na, K$), caught our particular attention. Because of the importance of these new types of lacunar materials as a corrosion inhibitor for carbon steel in hydrochloric acid solution, they are generally considered because of their good effectiveness of inhibition and have been studied using Electrochemical and Impedance Spectroscopy (EIS) at various concentrations. In the present study field, we have used X-ray Diffraction and Raman, Infrared, and UV-Vis spectroscopies to explain the typical physical characteristics and properties of the polycrystalline solids. Apatites are very useful for various applications in sciences and engineering related to energy and device performance. The results of physical and chemical properties can be analyzed for the engineering aspects of materials structure, surfaces, and interfaces.

[17] S. Lahrich, B. Manoun, M.A. El Mhammedi, Sodium doping effect on physicochemical properties of $K_{1-x}Na_xCaPb_3(PO_4)_3$ ($0 \leq x \leq 1$) for the determination of mercury(II): Application in seawater samples, Mater. Res. Bull. 59 (2014) 349–357.

II. Experimental studies.

II.1. Preparation of the inhibitor compounds.

The lacunar apatite inhibitors were synthesized by high-temperature solid-state reaction for a detailed synthesis of the apatite materials see [Chapter. I](#) in reactions N°2 and 3.



The initial crystal structure of the samples NaPb_{2.5}Sr_{1.5}(PO₄)₃ and KPb_{2.5}Sr_{1.5}(PO₄)₃ was identified by X-ray diffraction (XRD). Raman and Infrared spectroscopic methods were employed to study the influence of the vibrational modes of phosphate groups. Ultraviolet/Visible/Near-Infrared spectroscopy was also used to investigate the optical properties.

II.2. Physico-chemical characterizations.

The diffraction data were recorded using the D2 PHASER diffractometer, with the Bragg–Brentano geometry, equipped with Cu (K alpha) radiation. The Raman spectrometer was calibrated by fluorescence lines of a neon lamp. The precisions of spectral measurements, as estimated from the wavelength calibration procedure and peak fitting results, the non-polarized Raman spectra were collected in the back-scattering geometry, in the range of 180–2280cm⁻¹, at a resolution of about 3cm⁻¹. The PerkinElmer Frontier™ of near-; mid- and far-Infrared (Fourier Transform spectrometer was used). An exceptional signal-to-noise ratio and photometric performance assure optimal spectra.

The optical absorption analysis was carried out by PerkinElmer LAMBDA™ 1050 UV/Vis/NIR spectrometer equipped with an integrating sphere to accurately get the optical absorption edge near UV. The cylindrical pellets obtained using a manual hydraulic press were sintered at 750 °C for 8 hours; the final pellets are with a thickness of more than 1 mm. The spectra were converted from reflectance to absorbance by using solving the Kubelka–

Munk function [18] and the optical band gap energy was estimated using the onset of the absorption edge by Tauc plots [19]. For more details of the key materials components, see [Chapter. I.](#)

II.3. Specimens and solution treatment.

Apatite rod specimens were mounted on Teflon. The space between the apatite electrode and Teflon was filled with epoxy resin. Before starting the experiments the electrode surface was abraded using emery paper up to 1200 grade then rinsed thoroughly with deionized water. The apatite is regarded as a working electrode; it has been set close to the centre of the cylindrical electrolysis cell under stationary conditions without stirring.

They used a circular cross-sectional area of the MS rod exhibited to the corrosive solution in the electrochemical measurements was 0.2cm^2 . A saturated KCl calomel electrode (i.e. SCE, 0.2444V vs.SHE) is the reference one, a platinum electrode is used as a counter electrode (CE) which was separated from the working electrode compartment by a fritted glass. To minimize the IR drop, the reference electrode was inserted into a Luggin capillary. The solution of an aggressive environment was prepared from analytical reagent-grade chemicals (HCl, Fluka, 99.5%) and bidistilled water so that to obtain 0.5M (HCl). The concentration 10^{-2}M , 10^{-3}M , 10^{-5}M , and 10^{-6}M of apatite were added as an inhibitor to the previously prepared aggressive solution.

[18] V. Džimbeg-malčić, Ž. Barbarić-mikočević, K. Itrić, Kubelka-Munk Theory in Describing Optical Properties of Paper (1), Tech. Gaz. 18 (2011) 117–124.

[19] J. Tauc, Optical properties and electronic structure of amorphous Ge and Si, Mater. Res. Bull. 3(1968)37–46.

II.4. Electrochemical experimental methods.

The electrochemical measurements were performed in a conventional three-electrode cell, using VersaSTAT.4 potentiostat and controlled by the Tacussel corrosion analysis software model (Volta master 4) at stationary condition (for more details see [Annex. V](#)).

Before each electrochemical test, the working disk electrode was faced towards the cell bottom, the stationary electrochemical test started by measuring the Open Circuit Potential E_{ocp} of the electrode versus time until the steady-state conditions set on the electrode surface. Then, the measured stable electrode potential was taken as the corrosion potential E_{corr} . It is noteworthy that it's impossible to obtain a stable potential because the **OCP** is an equilibrium one.

After measuring the E_{ocp} , the electrochemical measurements were carried out. Polarization curves were plotted from two independent measurements in a freshly prepared test solution for each run: the first one is the cathodic measurement which was undertaken from the open circuit potential towards about -1.5V, the second one was performed from the open circuit potential to about +1.5V at the potential scan rate of 10mV.s^{-1} . Those polarization curves were recorded for 1h for each part.

The linear region of polarization curves (lower than $\pm 20\text{mV}$) was used to determine polarization resistance (R_p); three replica experiments were repeated for each experimental condition. The inhibition efficiency values **IE (%)**, were calculated using the following equation:

$$IE\% = \left(\frac{I_{corr}^0 - I_{corr}}{I_{corr}^0} \right) \times 100$$

Where I_{corr} stands for corrosion current density value in the presence of apatite and I_{corr}^0 is the corrosion current density value for the bare copper electrode.

Impedance spectra were plotted in the 10mHz–1MHz frequency range with 10 points per decade and 10mV (peak to peak) amplitude of the excitation signal. The spectral data were obtained at immersion time for 1h [20] at the open circuit potential E_{ocp} . The impedance data were explained based on equivalent electrical circuits, **EEC**, by fitting the measured data using the ECLAB program. The modelling of the electrochemical process was performed by electrical circuit elements, such as resistors, capacitors, and **CPE**.

III. Discussions.

III.1. Structural study.

The Indexing of X-ray powder diffraction patterns for these compositions ($x=0$ and 1) was performed utilizing the computer DICVOL software[21] integrated into the Fullprof program [22]. The patterns are similar to those of $Na_{1-x}K_xPb_{4-y}Ca_y(PO_4)_3$ [23], [24], [25], the X-ray diffraction pattern for the compositions were assigned to a hexagonal apatite structure. As shown in Fig.1, the inset shows the shift to the low value of 2θ ($^\circ$). This is based on Bragg's equation: $n\lambda = 2d\sin(\theta)$, because potassium a larger atomic radius $K^+(1.55 \text{ \AA})$ when compared with sodium $Na^+(1.24 \text{ \AA})$ [26].

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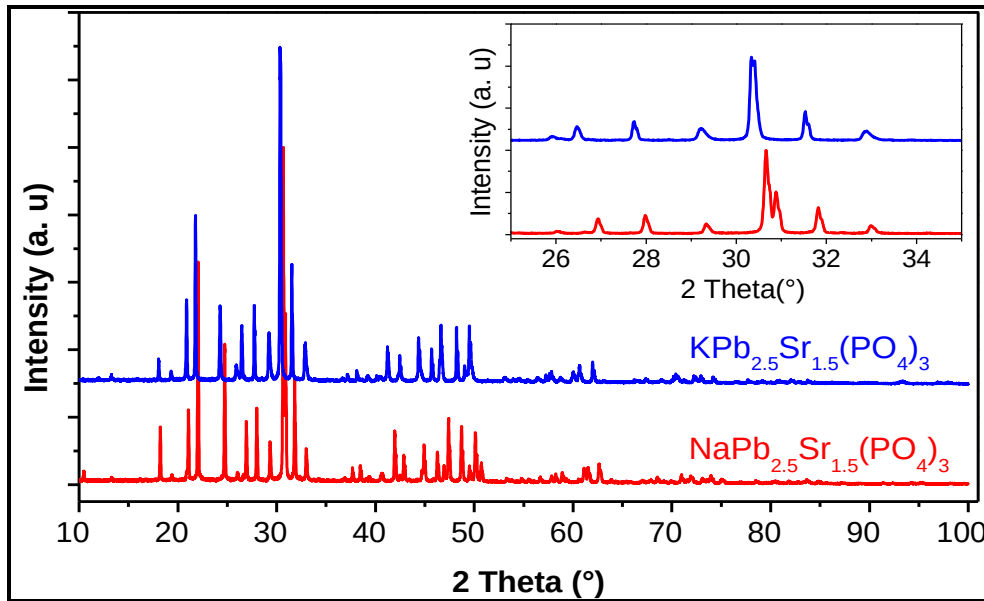


Fig.1: X-ray powder diffraction patterns of $APb_{2.5}Sr_{1.5}(PO_4)_3$ ($A = Na, K$) collected at room temperature.

The structure refinement was done by the Rietveld method using WINPLOTR software [27], as a starting model we used the atomic coordinates of $NaPb_3Ca(PO_4)_3$ [23] with space group $P6_3/m$ and 17 atomic parameters (including positions, occupancies, and isotropic thermal displacements), 6 background coefficients, 1 scale factor, 1 zero point, 6 cell parameters, 2 line asymmetry parameters, using a pseudo-Voigt function, 6 halfwidth parameters, these halfwidths of the diffraction peaks as a function of 2θ was evaluated by the Caglioti equation. Also, one preferred orientation parameter was refined in the direction of the diffraction vector perpendicular to (001). The final results are shown in Chapter. II, with estimated deviations in parentheses. The agreement between the theoretical and experimental diffractogram is given by the values of the Reliability factors **R_p**, **CR_p**, **R_{wp}**, and **CR_{wp}** defined by the following relations:

$$R_p = \sum |Y_{iobs} - Y_{icalc}| / \sum Y_{iobs} ; \quad CR_p = \sum |Y_{iobs} - Y_{icalc}| / \sum (Y_{iobs} - Y_{fci})$$

$$R_{wp} = \sqrt{\sum w_i [Y_{iobs} - Y_{icalc}]^2 / \sum w_i |Y_{iobs}|^2} ; \quad CR_{wp} = \sqrt{\sum w_i [Y_{iobs} - Y_{icalc}]^2 / \sum w_i |Y_{iobs} - Y_{fci}|^2}$$

[27] T. Roisnel, J. Rodríguez-Carvajal, WinPLOTR: A Windows Tool for Powder Diffraction Pattern Analysis, Mater. Sci. Forum. 378–381 (2001) 118–123.

The final plot of Rietveld refinement of $\text{NaPb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$ and $\text{KPb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$ are given in Fig.2 the refinement was run with the presence of the second phase as impurity type $\text{Pb}_3(\text{PO}_4)_2$ [28]. At this stage of the refinements, the structural model indicators converged to the very satisfactory values of the reliability factors as illustrated in Chapter. II. The resulting data for atomic coordinates, isotropic temperature factors, and occupation in the 6h and 4f sites, and the interatomic bond distances and angles are given in Chapter. II.

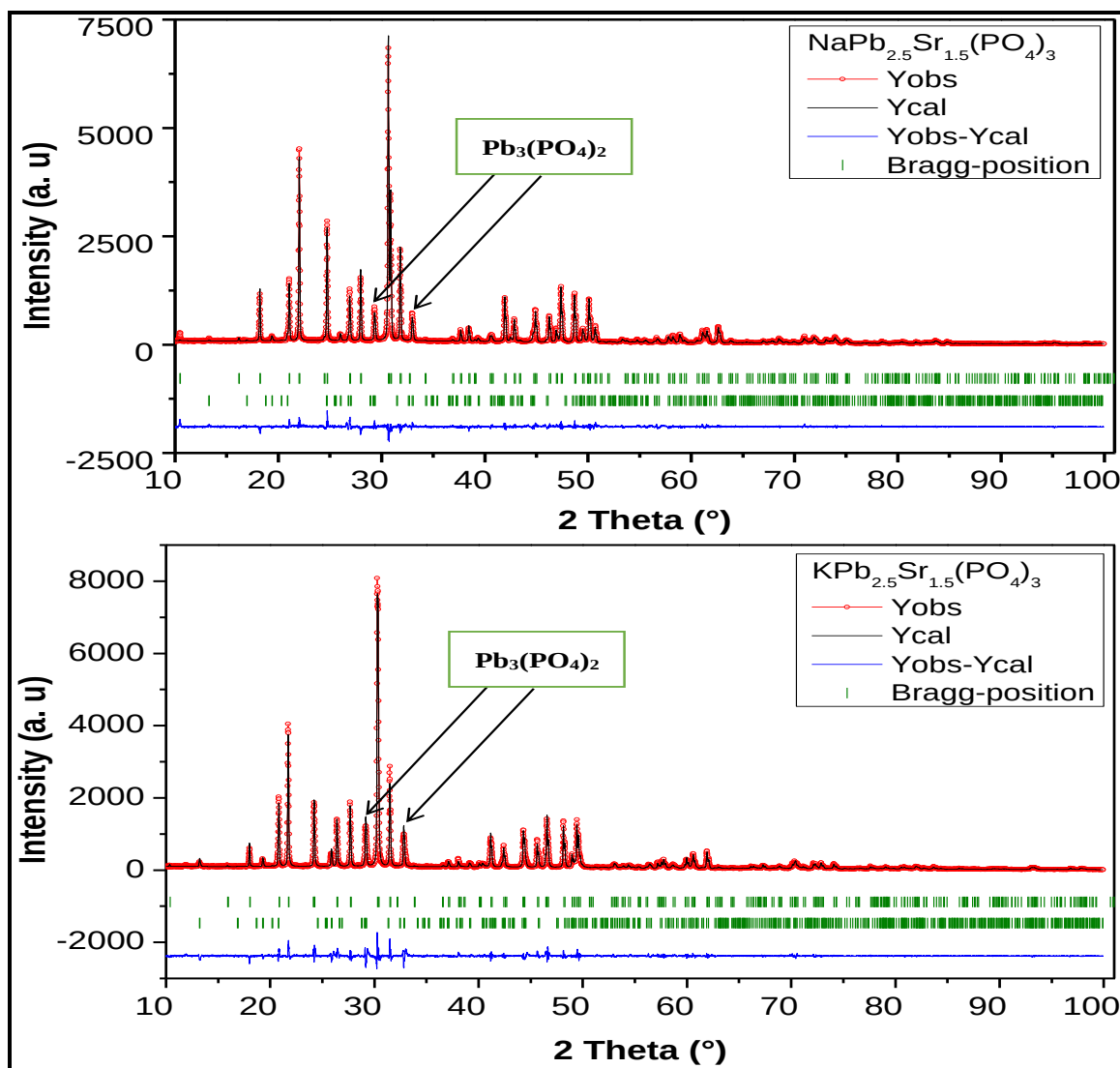


Fig.2: Final plot of Rietveld refinement of $\text{NaPb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$ and $\text{KPb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$, the refinement was done with $\text{Pb}_3(\text{PO}_4)_2$ such as the second phase.

[28] C. Joffrin, J.P. Benoit, L. Deschamps, M. Lambert, Étude par diffraction et diffusion de rayons X de la transition de phase ferroélastique du phosphate de plomb : $\text{Pb}_3(\text{PO}_4)_2$, J. Phys. 38 (1977) 205–213.

In the lead lacunar apatites, the stereo activity of Pb^{2+} cations is manifested only in the **6h** sites, the other lead cations; located in the mixed sites **4f**, outside such tunnels, do not seem to be stereoactif. The graphical exploitation of the results for the refinement has been displayed in Fig.3. The solid solutions of $APb_{2.5}Sr_{1.5}(PO_4)_3$ ($A = Na, K$) crystallizes in the hexagonal system, with space group $P6_3/m$ (N^0176), is characterized by $[PO_4]^{3-}$ tetrahedra and two non-equivalent sites **6h** and **4f** with cation labelled M(1) and M(2), respectively. Rietveld refinements showed that more than 80% of Pb^{2+} , and more than 58% of Sr^{2+} , are located in the (**6h**) sites. The sites (**4f**), half occupied by Pb^{2+} (2)/ Sr^{2+} (2) divalent cations, and half by Na^+ or K^+ alkali monovalent cations. The metal coordination with oxygens, showing that the structure is described as built up from $[PO_4]^{3-}$ tetrahedral groups and two sites (**6h**) and (**4f**) as illustrated in Fig.3. These tunnels M (1) of sixfold coordination cavities $M(1)-O_6 = [Pb^{2+}(1)/Sr^{2+}(1)]-O_6$; with a much larger section are surrounded by strontium-lead cations. These cations are inserted into six-fold sites that constitute the walls of the tunnels; each polyhedron is linked to 4 $[PO_4]^{3-}$ tetrahedra via corners and to one $[PO_4]^{3-}$ via edge. These big tunnels M(1) are connected by the small tunnel M(2) which corresponds to the mixed site **4f** half occupied by Pb^{2+} (2)/ Sr^{2+} (2) divalent cations, and half by Na^+ or K^+ alkali monovalent cations. These cations are coordinated to nine oxygen anions $M(2)-O_9 = [Pb^{2+}(2)/Sr^{2+}(2)/Na_{1-x}K_x]-O_9$ ($x=0$ or 1); belonging to six distinct tetrahedra; each polyhedron is linked to 3 $[PO_4]^{3-}$ tetrahedra via corners and to three others via edges.

The difference in ionic radius size between; $r(K^+) = 1.55\text{\AA} > r(Na^+) = 1.24\text{\AA}$ [26], influences the increase of parameters $c(\text{\AA})$ and $a(\text{\AA})$, and therefore the increase of cell volume of $KPb_{2.5}Sr_{1.5}(PO_4)_3$ compared to $NaPb_{2.5}Sr_{1.5}(PO_4)_3$, the hexagonal tunnels are larger with K^+ . The substitution of Na^+ by K^+ with a large radius causes an increase in 'P-O_n' distances of the $[PO_4]^{3-}$ tetrahedral. The interatomic distances and the angles are listed in Chapter. I. The 'P-O' distances are reasonable and were determined to be around $1.5250\text{\AA}$ and $1.5708\text{\AA}$ and the

‘O–P–O’ angles are between 104.06° and 116.16° . The ‘M(1)–O₆’ in the site (6h) distances vary from $2.0879\text{\AA}$ to $2.9281\text{\AA}$ for Pb^{+2} (1)/ Sr^{+2} (1)-O₆, for ‘M(2)-O₉’ distances in the mixed site (4f), and from $2.5513\text{\AA}$ to $2.8355\text{\AA}$ for (Pb^{+2} (2)/ Sr^{+2} (2)/ Na^+ or K^+)-O₉. All average distances are similar and agree well with those found in previously reported works [29],[25], [17].

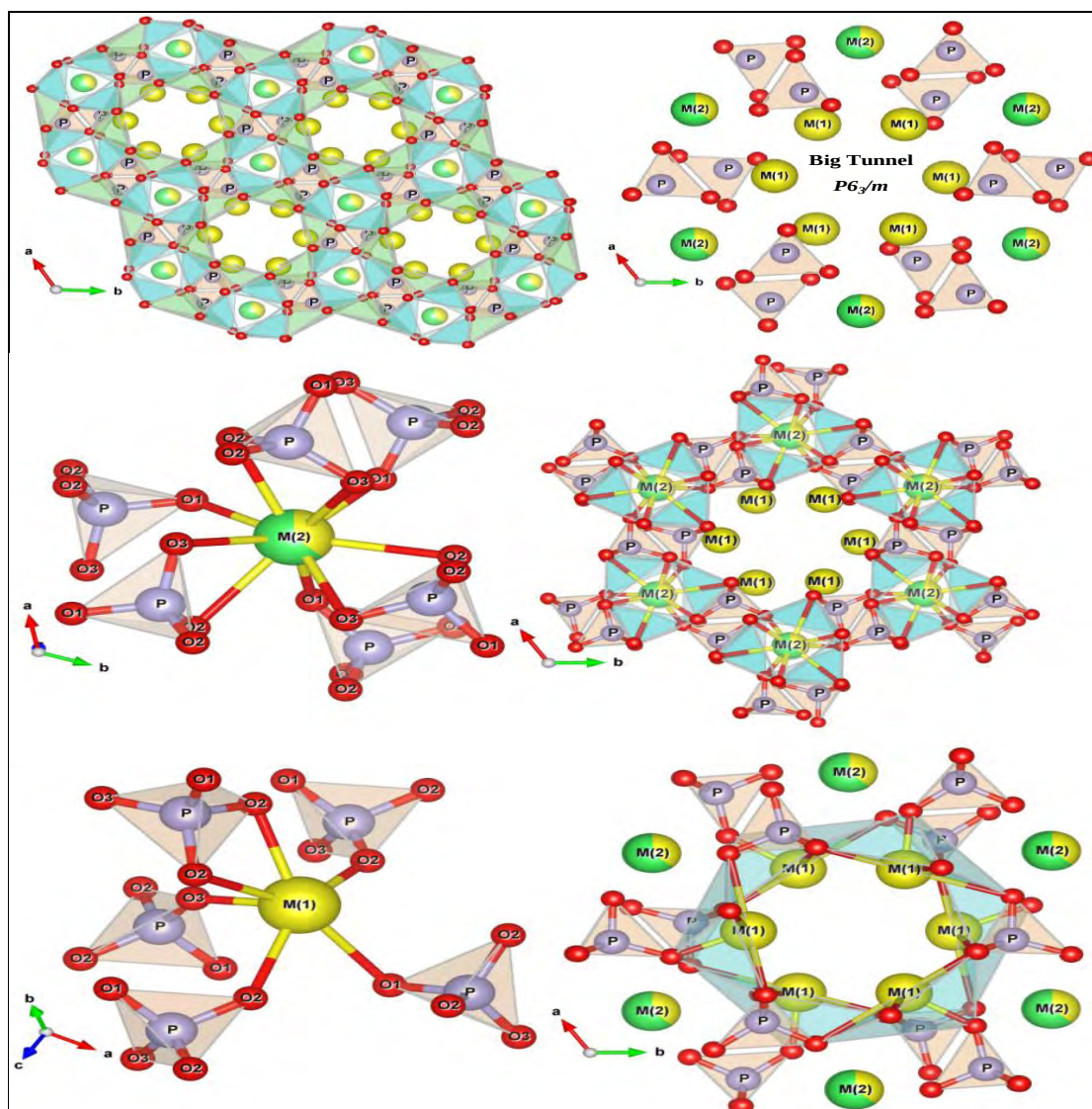


Fig.3: Structural view of $\text{NaPb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$ and $\text{KPb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$. The large tunnel of lacunar apatite illustrates the metal and oxygens arrangement around (6h) and (4f) sites connected to the $[\text{PO}_4]^{3-}$ tetrahedra.

[29] M. Azdouz, B. Manoun, M. Azrour, L. Bih, L. El Ammari, S. Benmokhtar, P. Lazor, Synthesis, Rietveld refinements and Raman spectroscopy studies of the solid solution $\text{Na}_{1-x}\text{K}_x\text{Pb}_4(\text{VO}_4)_3$ ($0 \leq x \leq 1$), J. Mol. Struct. 963 (2010) 258–266.

III.2. Vibrational study.

The group theory analysis of Raman- and Infrared-active modes for the characterization of the apatite crystals are widely studied in the lead-phosphorus, -vanadium, and -arsenic apatite structures, for more details see [25], [17]. Factor group analysis of the $\text{APb}_4(\text{XO}_4)_3$ shows the internal and external modes for the tetrahedral phosphates ions.

Referring to the X-ray diffraction, the structure remains similar for the compositions $\text{APb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$ ($A = \text{Na}, \text{K}$), this observation is well confirmed by the same number of bands active by infrared and Raman for two compounds.

Fig.4 represents the analysis results for Raman and Infrared active modes, for the compounds $\text{APb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$ ($A = \text{Na}, \text{K}$) recorded at ambient conditions. First of all, the hydroxyl asymmetric stretching is not observed in both Raman and Infrared spectra around $3000\text{-}4000\text{cm}^{-1}$. This confirms that apatite does not contain a hydroxyl group or water intercalated in apatite tunnels. The Raman and FTIR spectra have been analyzed, with the peak-fitting function in LabSpec software, the drawing is carried out by origin software [30]. A ‘Gauss/Lorentz’ function was chosen for peak profiles, and the Savitzky-Golay algorithm was used as a data smoothing method. The background intensity was subtracted before fitting, and the fitting process proceeded until minimum residuals were reached.

However, the observed Raman modes can be classified into three general families of lattice vibrations: (Na^+ or $\text{K}^+/\text{Pb}^{2+}(2)/\text{Sr}^{2+}(2)$)- O_9 ($\text{M}(2)\text{-O}_9$), $\text{Pb}^{2+}(1)/\text{Sr}^{2+}(1)\text{-O}_6$ ($\text{M}(1)\text{-O}_6$) external modes, these modes are observed at frequencies below 300cm^{-1} ; a pattern of bands was observed in the $300\text{-}700\text{cm}^{-1}$ region and is attributed to ‘ $\text{O}_n\text{-P-O}_n$ ’ bending vibrations [$\mathbf{V}_2$ (from 391 to 544cm^{-1}) and $\mathbf{V}_4$ (from 552 to 593cm^{-1})], and the series of high-frequency bands observed above 800cm^{-1} is assigned to ‘ P-O_n ’ stretching modes [$\mathbf{V}_3$ (from 1074 to 1097cm^{-1}) and $\mathbf{V}_1$ (from 926 to 998cm^{-1})]. The strong bands are observed at 954cm^{-1} for $\text{KPb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$ and at 963cm^{-1} for $\text{NaPb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$ in the Raman spectra, and are

observed as shoulder in the Infrared spectra, at 984cm^{-1} and 998cm^{-1} respectively for $\text{KPb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$ and $\text{NaPb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$.

The larger size and masse of the K^+ ion has an effect on the occupation in the two sites **6h** and **4f**, by the movement of divalent cations, which is evident in the Raman and Infrared spectra. From the spectra in Fig.4, once sodium is substituted by potassium, the stretching frequencies observed of the $\text{V}(\text{P}-\text{O}_n)$, shift towards lower frequencies, on the other hand, most of the frequencies of the $\text{V}(\text{O}_n-\text{P}-\text{O}_n)$ bending modes observed shift towards higher frequencies. Theoretically, these shifts could be explained either by the change in the molar mass or by the fact that K^+ ($r_i = 1.55\text{\AA}$) has a larger radius compared to that of Na^+ ($r_i = 1.24\text{\AA}$).

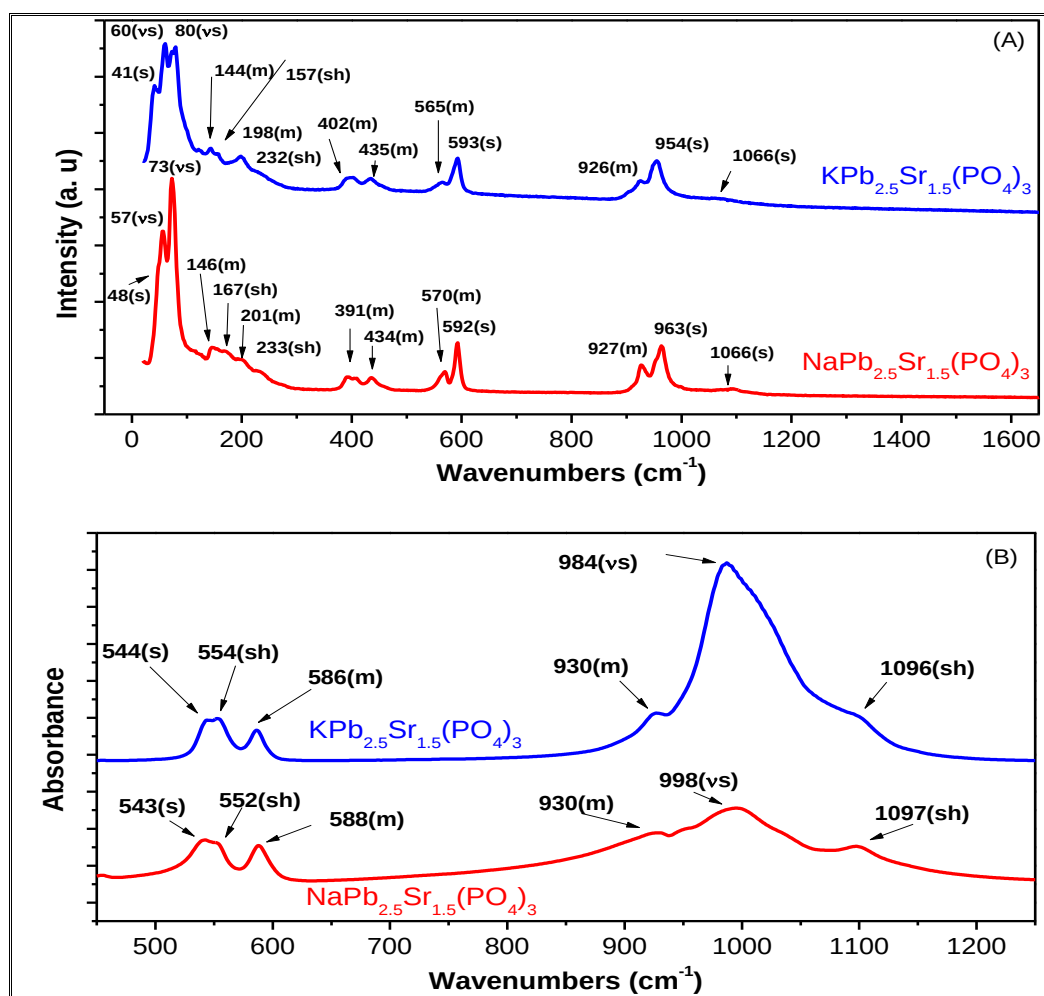


Fig.4: Raman and Infrared spectra of $\text{NaPb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$ and $\text{KPb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$ respectively in figure (A) and (B) and the assignment of the observed absorption bands.

III.3. Optical properties.

In this work, UV-vis spectroscopy was employed to obtain the absorption domain of these materials as well as calculating the optical bandgap. Fig.5(A) shows the evolution of the absorption coefficient as a function of the wavelength in the range (250-800 nm) at room temperature, an intense band (λ_{Max}) at 273(nm) and 269(nm)for $NaPb_{2.5}Sr_{1.5}(PO_4)_3$ and $KPb_{2.5}Sr_{1.5}(PO_4)_3$ respectively. The obtained reflectance data are converted to absorbance using the Kubelka-Mank function which is considered as a relevant method to obtain the bandgap. The Kubelka-Munk equation at any wavelength can be written as: $F(R) = (1 - R)^2 / 2R$

The type and nature of the valence band to band transitions were determined by analysis of the dependence $[F(R)*h\nu]$ as a function of $(h\nu)$. Using Tauc's relationship it is possible to determine the relationship between the absorption coefficient and the incident photon energy $(h\nu)$, in the high absorption region, as follows [19], [31]. $F(R)h\nu = A(h\nu - E_g)^{1/2}$

Where $F(R)$ is the linear absorption coefficient, $\nu = C/\lambda$ is the light frequency and A is a constant. The $[F(R)*h\nu]^2$ versus the photon energy $(h\nu)$ plots in Fig.5(B) at $[F(R)*h\nu]^2 = 0$ allows to estimate the optical band gap values which are found to be $E_g=4.28$ eV and $E_g=4.35$ eV for $NaPb_{2.5}Sr_{1.5}(PO_4)_3$ and $KPb_{2.5}Sr_{1.5}(PO_4)_3$ respectively.

[30] R.A. May, K.J. Stevenson, Software Review of Origin 8, J. Am. Chem. Soc. 131(2009) 872.

[31] G.P. Joshi, N.S. Saxena, R. Mangal, A. Mishra, T.P. Sharma, Bandgap determination of Ni-Zn ferrites, Bull. Mater. Sci. 26 (2003) 387–389.

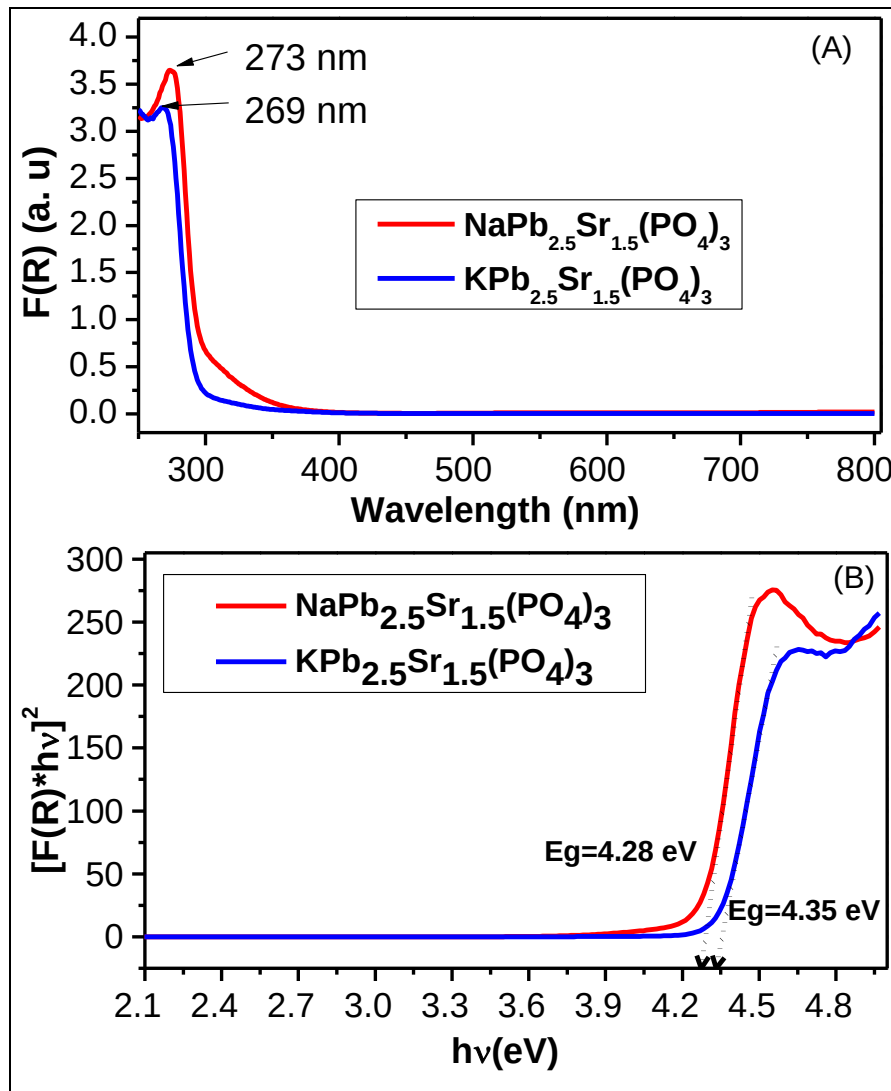


Fig.5: Figure (A) shows the optical absorption as a function of the wavelength, and figure (B) illustrates the Tauc plots for $\text{NaPb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$ and $\text{KPb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$.

III.4. Potentiodynamic polarization.

a) Effect of concentration.

Fig.6 represents the potentiodynamic polarization curves for MS in 0.5M (HCl) at temperature 298K, in the absence and the presence of a different concentration of $\text{APb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$ with $A = \text{K}$ and Na . The different electrochemical parameters including corrosion potential (E_{corr}), cathodic Tafel slopes (β_c), and corrosion current density (i_{corr}) were obtained by extrapolating the polarization curve. The inhibition efficiency ($\eta_{\text{Tafel}} \%$) can be calculated using the following equation. All these parameters are listed in Table.1. $\eta_{\text{Tafel}}(\%) = (1 - \frac{i_{\text{corr}t}}{i_{\text{corr}0}})$

Table.1: Electrochemical parameters and inhibition efficiency values of carbon steel in 0.5M HCl containing different concentrations of $\text{APb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$ ($A = \text{Na}, \text{K}$) at 298K.

Inhibitors	C (mol/L)	$-E_{\text{corr}}$ (mV/SCE)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	$-\beta_c$ ($\mu\text{A}/\text{cm}^2$)	β_a ($\mu\text{A}/\text{cm}^2$)	η (%)
0.5M HCl	--	436	494	114	65	--
$\text{NaPb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$	10^{-6}	459	278	136	123	44
	10^{-5}	424	206	105	128	58
	10^{-4}	443	167	100	46	66
	10^{-3}	496	121	117	60	76
	10^{-6}	444	153	111	98	69
$\text{KPb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$	10^{-5}	451	106	104	77	79
	10^{-4}	439	79	123	59	84
	10^{-3}	448	55	110	81	89

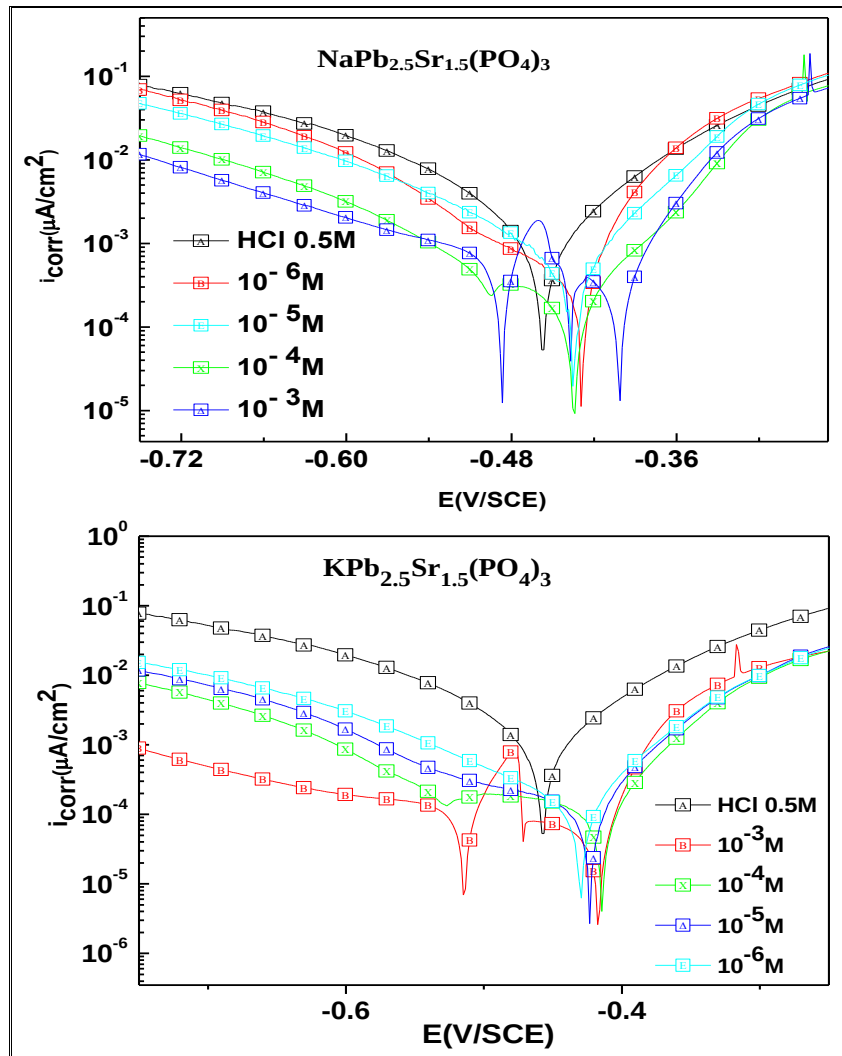


Fig.6: Potentiodynamic polarization curves for MS in 0.5M (HCl) containing different concentrations of $\text{NaPb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$ and $\text{KPb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$.

It is noted that the addition of $\text{KPb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$ and $\text{NaPb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$ pulls an important decrease of current densities for all concentrations with a slight shift in the corrosion potential (E_{corr}). The concentration effect of the apatite on these corrosion parameters is very significant (Table.1). In fact, the increase of the concentration of either $\text{KPb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$ or $\text{NaPb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$ increases the inhibition efficiency to reach 89 % and 76% at 10^{-3}M respectively. This can be explained by the adsorption of these mineral molecules on the mild steel (**MS**) surface. Moreover, one can deduce that the inhibitor effect of $\text{KPb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$ is more effective than that of $\text{NaPb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$. However, the influence of the concentration of these minerals did not significantly affect the cathodic Tafel slope values suggesting that the proton reduction mechanism is not affected by the addition of mineral compounds [32]. On the other hand, the main mechanism of inhibition involves a simple reaction that blocks the active sites without modifying the corrosion mechanism [33].

b) Effect of temperature.

The effect of temperature on the corrosion rate of **MS** gave us in general some information on the adsorption [33]. For this reason, we studied the change of the corrosion rate with the temperature in 0.5M (HCl) solution during 1h of immersion; both in the absence and presence of $\text{KPb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$ in the temperature range from 298 to 328K. The obtained results are shown in Fig.7 (A and B). The electrochemical parameters are given in Table.2.

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- [33] M.E. Belghiti, A. Nahlé, A. Ansari, Y. Karzazi, S. Tighadouini, Y. El Ouadi, A. Dafali, B. Hammouti, S. Radi, Inhibition effect of E and Z conformations of 2-pyridinealdazine on mild steel corrosion in phosphoric acid, Anti-Corrosion Methods Mater. 64 (2017) 23–35.

Table.2: Evolution of the electrochemical parameters of MS in 0.5M (HCl) according to temperature in the presence and the absence of $\text{KPb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$.

Medium	T(K)	$-\text{E}_{\text{corr}}$ (mV/SCE)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	$-\beta_c$ ($\mu\text{A}/\text{cm}^2$)	η (%)
HCl 0.5M	298	436	494	114	--
	308	464	837	178	--
	318	455	1202	266	--
	328	456	1659	247	--
$\text{KPb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$ 10^{-3}M	298	467	52	111	89
	308	451	218	103	74
	318	459	450	122	63
	328	460	730	117	56

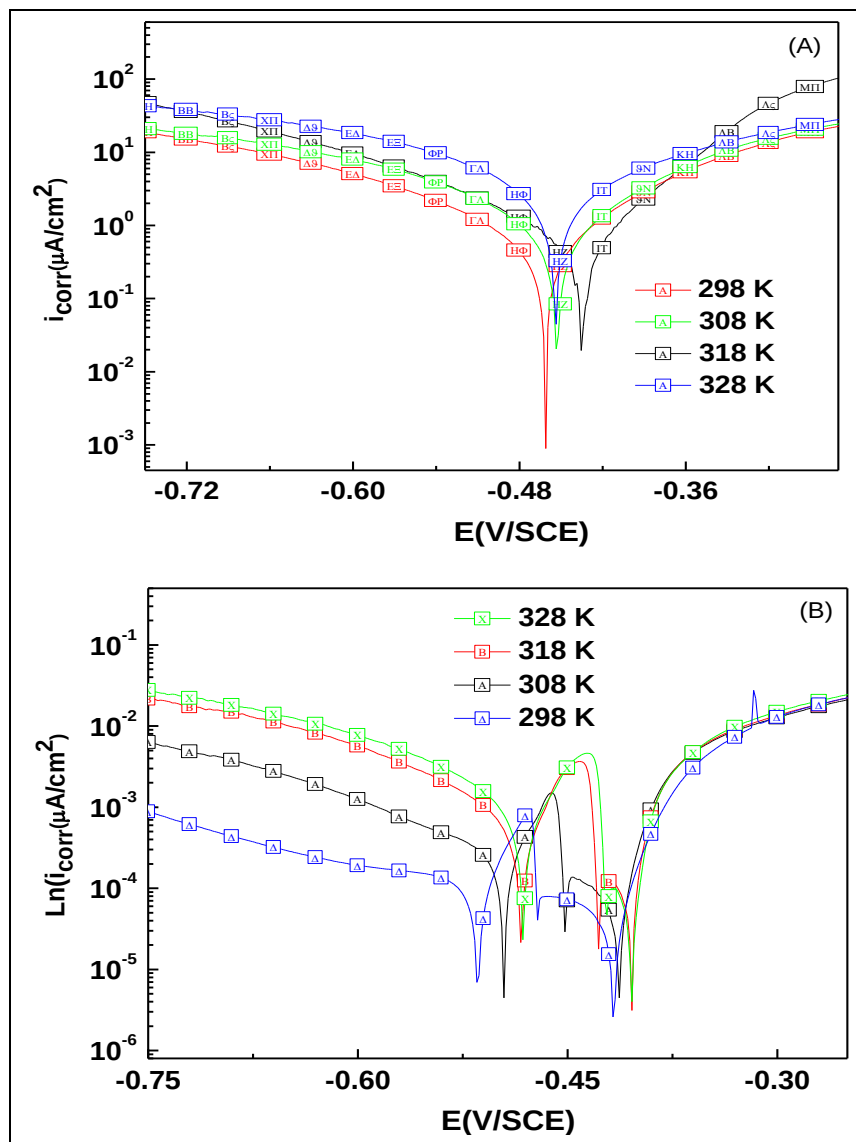


Fig.7: In (A) we show the polarization curves at different temperatures for MS in 0.5M(HCl) without inhibitor $\text{KPb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$ and in (B) shows the polarization curves at different temperatures for MS in 0.5M(HCl) in the presence of $\text{KPb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$ at 10^{-3}M .

The inspection of Table.2 reveals that the inhibitor efficiency decreases with the increase of the temperature. This decrease shows that the mineral does not exhibit well-marked adsorption on the MS surface. Besides, in the absence of $\text{KPb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$, it is found that the cathodic Tafel slopes stay almost constant indicating no change in the hydrogen reduction.

The activation parameters such as the energy of activation, the enthalpy, and entropy of activation were evaluated according to the Arrhenius law:

$$i_{\text{corr}} = A \exp\left(\frac{-E_a}{RT}\right) \quad \text{And} \quad i_{\text{corr}} = \frac{RT}{Nh} \exp\left(\frac{\Delta S_a}{R}\right) \exp\left(\frac{-\Delta H_a}{RT}\right)$$

Where i_{corr} is the corrosion current density, ' R ' is the ideal gas constant, ' T ' is the absolute temperature, ' h ' is the Planck constant and ' N ' is the Avogadro number.

The apparent activation energy was determined from the slopes of the $\ln(i_{\text{corr}})$ vs $(1/T)$ graph depicted in Fig.8(A). The straight lines are obtained with a slope $(-\Delta H_a/R)$ and intercept $(\ln(\frac{R}{Nh}) + \Delta S_a/R)$ from which these parameters can be calculated (Fig.8(B)).

Inspection of Fig.8 shows that the activation energy E_a value increases from $10.67 \text{ kJ mol}^{-1}$ to $21.07 \text{ kJ mol}^{-1}$ with $\text{KPb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$ addition. This can be explained by the fact that the molecules of $\text{KPb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$ create a barrier to charge and mass transfer and thereby justifying the physisorption phenomenon of inhibitor molecule on the mild steel surface. It is remarked that the enthalpy of activation value increases from $32.41 \text{ kJ mol}^{-1}$ to $45.95 \text{ kJ mol}^{-1}$. The positive values of ΔH_{ad} indicate that the mild steel corrosion process is endothermic [32,33]. The increase of the entropy (ΔS_a) values from $-62.15 \text{ J mol}^{-1} \text{ K}^{-1}$ to $-41.73 \text{ J mol}^{-1} \text{ K}^{-1}$ reveals an increase in disorder [32,33].

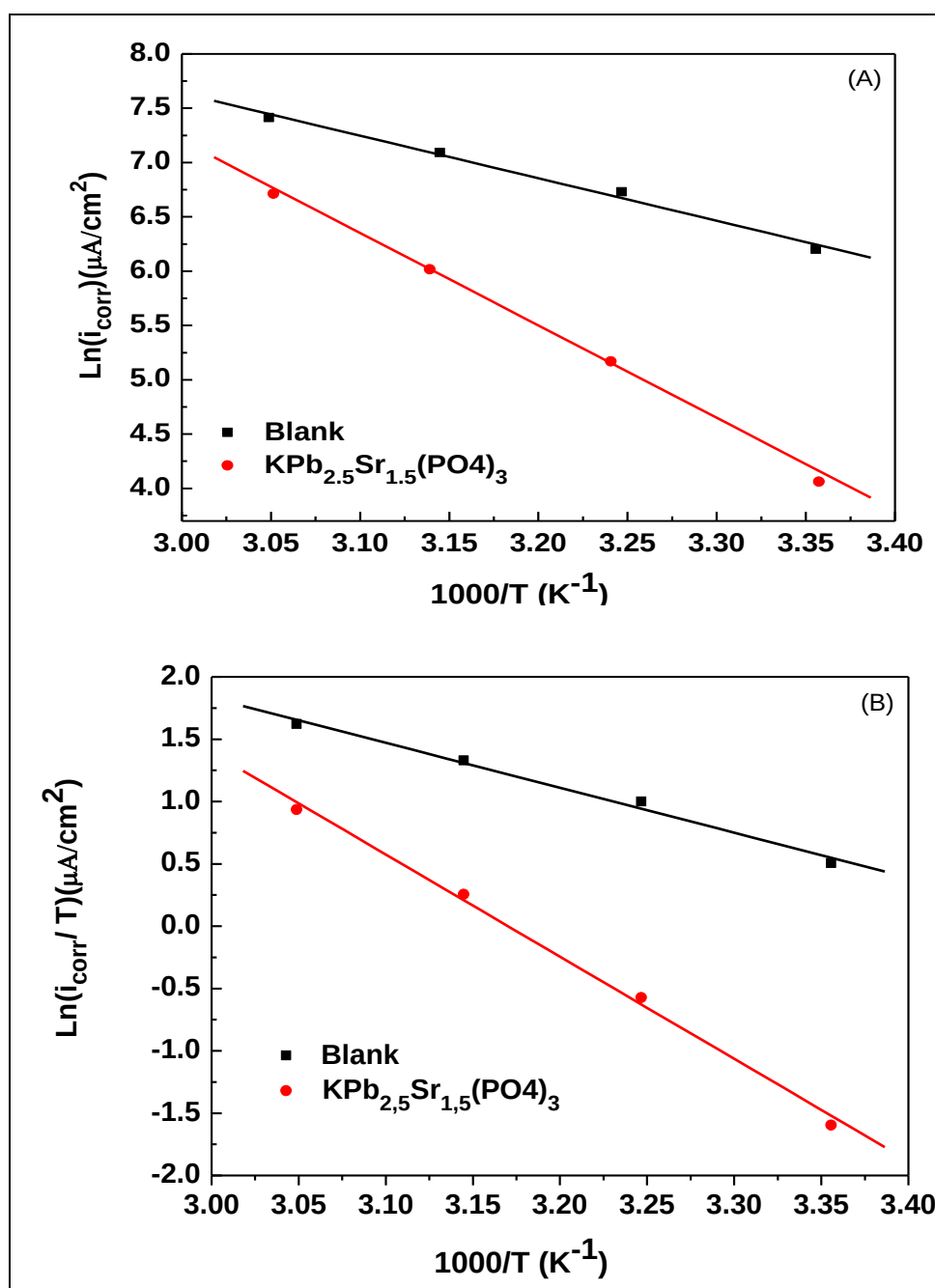


Fig.8: Figure (A) shows the Arrhenius plots for MS in 0.5M (HCl) in the absence and presence of 10^{-3}M of $\text{KPb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$ at different temperatures. And figure (B) Transition-state plots for MS in 0.5M (HCl) in the absence and presence of 10^{-3}M of $\text{KPb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$ at different temperatures.

III.5. Electrochemical impedance spectroscopy (EIS) measurements.

The electrical properties of the aqueous solutions with and without apatite inhibitors are measured. Fig.9 (a, b, c, d) represents the Nyquist plots obtained for different samples. Each plot has a distinctive semicircular graph. A semicircle diameter can be associated with the rate

of corrosion inhibition. The increase in resistance can be detected significantly with increasing concentrations of the corrosion inhibitor. Therefore, the corrosion rate decreases when the ratio of the mineral goes up.

The influence of the temperature on the corrosion rate is studied. Based on Fig.9c & 9d, one can note that the diameter of the semicircle becomes smaller as the temperature is increased from 303K to 333°C. The higher the temperature of the solution, the smaller is the diameter of the semicircle. This result means that the rate of corrosion inhibition is decreasing with the solution temperature increasing. The semicircles become less perfect and broad when the corrosion inhibitor concentration increases owing to roughness and other imperfections on the surface of the mild steel samples and the phenomenon known as the “dispersing effect”.

The metal/solution interface is represented by the following equivalent circuit, where the capacitance is replaced by the CPE (Fig.9). Where the resistor R_s reflects the solution and cable resistance, R_{tc} the load transfer resistor. CPE has the meaning of a double layer capacity distributed by frequency. The impedance of the CPE element is given by the following relation: $Z_{CPE} = Q^{-1}(j\omega)^{-n}$

Where ‘Q’ is a real constant independent of the frequency, ‘n’ is an exponent that depends on the frequency. For the values of $n = 1, 0, -1$, CPE is reduced to the classical elements of the electrical circuits: respectively capacity (C), resistance (R), and inductance (L). The value $n = 0.5$ corresponds to the impedance of Warburg (W). The other values of n describe approximately other types of frequency distribution behaviour of ‘C, R, L, or W’ with the distributed parameters. Capacitive semicircle dispersion is thus explained by heterogeneity due to surface roughness, impurities or dislocations, fractal structure, adsorption of the inhibitor, and the formation of a porous film. Using the Zview software version 2.2 and in coordination with the equivalent circuit shown above it was possible to

adjust the appropriate values to the impedance diagrams. Table.3 gives the values of the electrochemical impedance parameters relative to the medium invested.

The inhibition efficiency is calculated by charge transfer resistance as follows:

$$P\% = \frac{R_{ct} - R_t^0}{R_{ct}} \times 100$$

Where R_{ct} and R_{0t} are the charge transfer resistance values without and with inhibitor for mild steel in acidic media, respectively.

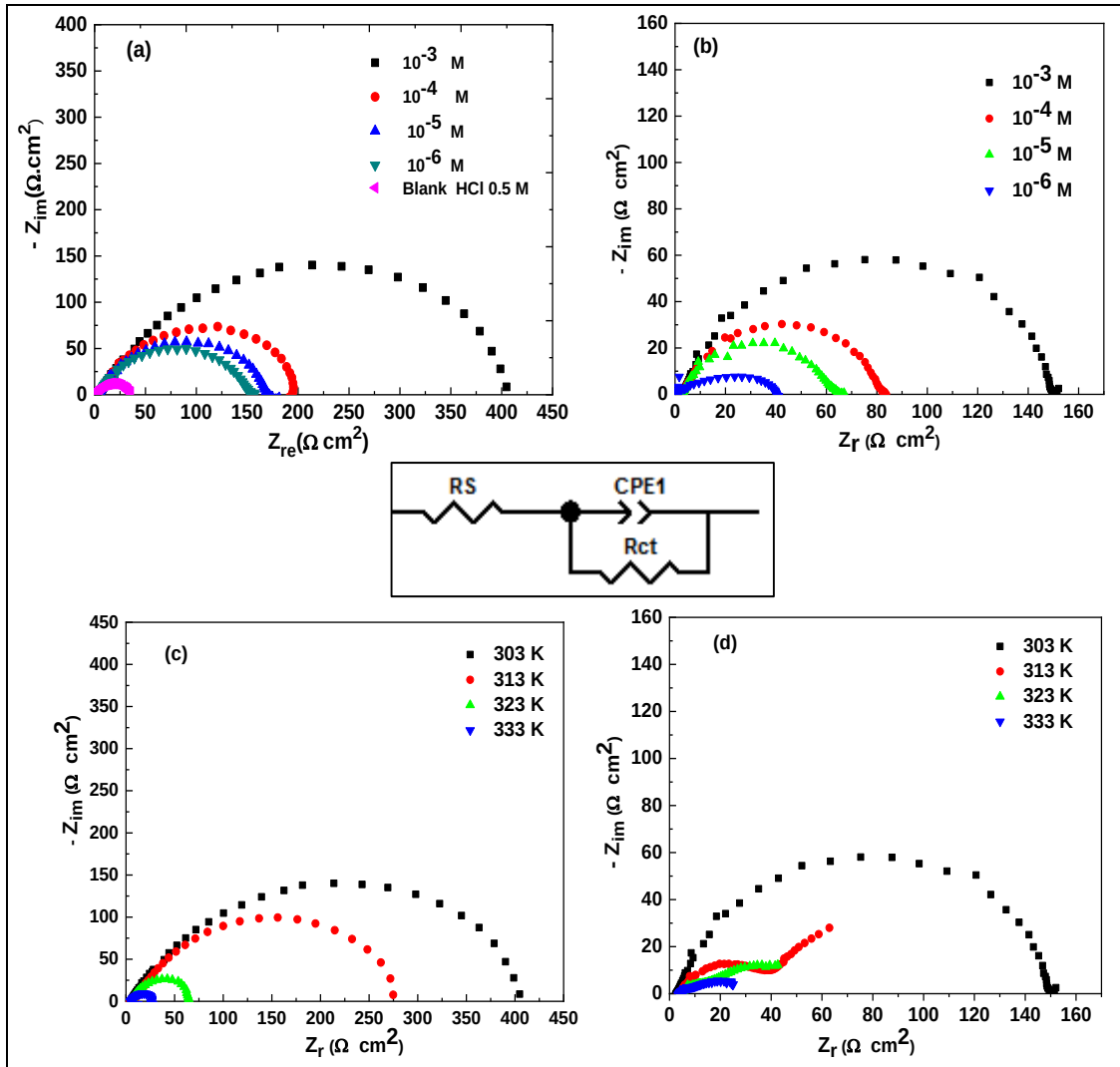


Fig.9: Nyquist plots of MS with different concentrations of $APb_{2.5}Sr_{1.5}(PO_4)_3$ ($K=a$ and $Na=b$) at 25°C, and different temperatures of ($K=c$ and $Na=d$) in 10^{-3} M at 25°C. And the equivalent circuit model of $\{APb_{2.5}Sr_{1.5}(PO_4)_3$ ($A = Na, K$)/0.5M HCl/mild steel} the system.

Table.3: Electrochemical parameters for mild steel in 0.5M (HCl) without and with different concentrations of $KPb_{2.5}Sr_{1.5}(PO_4)_3$.

Temperature	R_{ct}	Q	n	CPE-dl	P% =Inhibitor efficiency
298K	436.7	0.000285	0.72	90.02E-04	94.27
303K	338.8	0.00805	0.81	60.1E-04	92.62
313K	65.94	0.00145	0.82	41.5 E-04	62.08
323K	33.6	0.00521	0.66	5.51E-04	25.59

VI. Conclusion.

In this work new corrosion inhibitor compounds, namely $APb_{2.5}Sr_{1.5}(PO_4)_3$ ($A = Na, K$), have been successfully designed. We reported on their structural stability, vibrational, optical properties, and electrochemical studies. We have done a comprehensive investigation on the design and characterization of the apatite Strontium-Lead Phosphate, of Potassium and Sodium without anion vacancies. Lacunar apatites are obtained by a solid-state chemical reaction at high-temperature. Their inhibitive performance toward the corrosion for carbon steel in the hydrochloric acid solution for various concentrations has been studied using electrochemical impedance spectroscopy. The results of this work are listed below:

- The crystal structure of the samples ($A = Na, K$) was identified by X-ray diffraction (**XRD**). The Rietveld refinements showed a continuous solid solution adopting **$P6_3/m$** as a space group, with a low concentration of the second phase of $Pb_3(PO_4)_2$. The structure was described as built up from $[PO_4]^{3-}$ tetrahedra and M (I) of sixfold coordination cavities (**6h** positions), which delimit void hexagonal tunnels running along (0 0 1). The tunnels are connected by cations of mixed sites M (2), of ninefold coordination cavities (**4f** positions).
- Raman and Infrared spectroscopic techniques were used to see the behaviour of the general families of vibrations.

- The optical properties versus the photon energy ($h\nu$) were done using the data obtained from the optical absorption spectra. These materials are visibly transparent, they can be electrically semiconductor or insulating and they are characterized by an indirect bandgap.
- Raman and Infrared spectra show that once sodium is substituted by potassium, the stretching frequencies observed of the $\nu(P-O_n)$, the shift towards lower frequencies, on the other hand, most of the frequencies of the $\nu(O_n-P-O_n)$ bending modes observed shift towards higher frequencies. This indicates that the concentration of electron carriers is decreased by the existence of K^+ / Na^+ , increasing **Eg**. We have shown that the inhibition efficiency increased to 90% for the best inhibitor with an optimal concentration of $10^{-3}M$ at room temperature.

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General Conclusion

The development of new materials based on heavy metals and with specific, high-performance, and remarkable properties, without any adverse effects on the health of living beings and the environment, is increasingly the main objective of innovators and researchers from all disciplines and in all scientific and even industrial applications. These highly toxic heavy metals accumulate in the human body throughout life, causing neurological and renal damage of varying degrees of severity. From this point of view, apatitic compounds especially phosphates of hydroxylated, fluorinated, and new lacunar apatites, are of particular interest, can be materials with high retention capacities of heavy elements, they have considered as a solid containment matrix of metallic elements, studied for various scientific and industrial applications.

We conducted our study on two families of apatites. First of all, we had to synthesize these apatites by success. Different methods were used with a preference for the solid pathway. The characterization and purity of the prepared compounds were one of our main concerns. Their purities were verified mainly by X-ray diffraction, and by Infrared, Raman, and UV-visible absorption spectrometry.

Based on the results of molecular simulation, it was found that the occupation of monovalent and divalent cations even as pentavalent (case of phosphorus substituted by sulfur and carbon) at the 6h and 4f sites in Hexagonal structure, is done selectively, so that the material retains its structural stability, depending on mass and/or size, even also on the charge of the ions. The monovalent cations reside at the 4f site {M(2)}, and the divalent cations occupy the two crystallographic sites 6h and 4f with different percentages, except small cations which prefer the 6h site, such as cadmium in the $\text{Na}_{1-x}\text{K}_x\text{Pb}_2\text{CdCa}(\text{PO}_4)_3$ series and the case of ' Zn^{2+} ' which occupies the site in a rate greater than 94% in the material $\text{KPb}_3\text{Zn}(\text{PO}_4)_6$. When the number of divalent and/or monovalent cations equals or exceeds

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three, in the same site and/or in the two crystallographic sites, the simulation by structural refinement leads to several cases to be discussed, such as the case of the series $\text{Na}_{1-x}\text{K}_x\text{Pb}_2\text{CaSr}(\text{PO}_4)_3$. To validate the results we need another technique to be used, as an example of the Mössbauer technique.

The results of the vibrational spectroscopy were in good agreement with the X-ray measurements, note that we did not subtract the modes relative to sites '2a' (6_3 axes), which are vacant in the lead-phosphorus structures, the bands observed in the infrared and Raman spectra of these compounds do not differ significantly from those observed in Hydroxyapatite. The modes corresponding to tetrahedral vibrations (PO_4^{3-}) are interpreted using the C_{6h} factor group.

The Raman and Infrared modes, such that the spectra of all compositions are similar to each other and to the references, show some shifts in the wavenumbers depending on the nature of the substitutions and according to their stoichiometric coefficients, hence the frequencies observed on the vibration modes of the hexagonal structure change to lower frequencies, or to higher frequencies. However, the observed active modes can be classified in two for the infrared and three for the Raman. These general families of vibrations are; the external modes ($\text{M}(2)\text{-O}_9$ and $\text{M}(1)\text{-O}_6$), which are observed at frequencies lower than 300cm^{-1} , as well as the tetrahedral translation and rotation modes $[\text{PO}_4]^{3-}$ higher than 400cm^{-1} . A pattern of bands observed in the $400\text{-}800\text{cm}^{-1}$ region is attributed to 'O-P-O' bending vibrations [V_2 and V_4], and the series of high-frequency bands observed above 900cm^{-1} are attributed to P-O stretching vibrations [V_1 and V_3].

Lacunar apatite is composed of an optical material with light-transmitting characteristics in the far ultraviolet region. The optoelectronic properties of apatite have confirmed that the mobility of the field-effect decreases or increases with the nature and concentration of substitutions, clearly indicating that the '6h' and '4f' crystallographic sites

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effectively act as a carrier suppressor by reducing or increasing the number of oxygen donors in the apatite lattice.

Oxygen anions react mainly with the 6h and 4f sites $\{M(2)-O_9$ and $M(1)-O_6\}$, where there are monovalent and divalent cations. Because the region of low energy loss reflects the valence and conduction band structures of the solids, it indicates that the electron carrier concentration is decreased or increased depending on the nature of the substitutions, and their stoichiometric coefficients, resulting in the decrease or increase of the ' E_g '. These types of apatite materials can be electrically semiconducting and visibly transparent, with a very unique combination of properties.

The third chapter is devoted to the application of adsorption of Bovine Serum Albumin Protein (BSA) by synthetic apatites, Hydroxy- and new lacunar apatites $[\{Ca_5/Zn\}(PO_4)_6(OH)_2$ and $K_2Pb_{4/6}\{Ca_4/Zn_2\}(PO_4)_6]$. This study examines the impact of synthetic conditions on the physicochemical properties and surface reactivity of the prepared materials. The analysis of the interactions of the samples with the ASB protein, evaluated under the same experimental conditions, revealed a rapid kinetic process for the precipitated samples compared to crystals obtained by a chemical reaction in the solid-state. Thus, equilibrium conditions were reached in less than 20 min for the former while 6 hours of contact were required for the latter. However, all the isotherms obtained were in the Langmuirian form. The difference between the adsorption parameters of the materials, i.e. constant affinity and the amount adsorbed to saturation, is examined in terms of surface characteristics, chemical composition, crystal size, and specific surface area. It is concluded that the interaction of the protein with synthetic apatites is very sensitive to the microstructure of the crystals.

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The work we have done in Chapter Four has enabled us to identify our problem in the demetallization of phosphoric acid, as is, unclarified, for use in industry. The purification of 54% and 29% PAC phosphoric acids by the use of deficient materials shows that the impurities present in the PAC are adsorbed by the deficient apatite matrix in high, medium, and low yields, as well as the existence of elements non-adsorbed. This shows that the adsorption phenomenon is selective. It can be seen that there is a cation exchange between the adsorbent materials and the two PACs.

The last chapter presents the results of corrosion tests, of new lacunar inhibitors, $(\text{Na/K})\text{Pb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$. Their corrosion inhibition performance on carbon steel in solution in hydrochloric acid, at different concentrations and temperatures, were studied by electrochemical impedance spectroscopy. The results of this work show that the inhibition efficiency increases to 90% for the best inhibitor with an optimal concentration of 10^{-3}M at room temperature.

To complete this work, we expect to complete the study of the different solid solutions synthesized and to study their molecular and electronic properties by applying quantum computational methods, such as density functional theory (DFT). We also wish to identify and analyses the different materials by emission spectroscopic techniques such as fluorescence, luminescence, phosphorescence, Mössbauer studies,..., etc., and to look for new favourable applications in a way that poses no danger to living beings and the environment.

ANNEXS OF THE CHAPTRES

Annex. I: Synthesis, Experimental Techniques, and Methods of Analysis.

.....From page 316 To 325.....

Annex.II: Crystallographic & Vibrational Studies and Optoelectronic Properties of News Series of Lacunar Apatites Type



.....From page 326 To 330.....

Annex. III: Adsorption of Bovin Serum Albumin Protein by synthetic apatites and Structural Properties of Hydroxy- and New Lacunar Apatites



.....From page 331 To 332.....

Annex. IV: Structural Study of Fluoroapatite and Demineralization Effects of Phosphoric acid.

.....From page 333 To 339.....

Annex. V: New Lacunar Apatites $\text{APb}_{2.5}\text{Sr}_{1.5}(\text{PO}_4)_3$ (A = Na, K) as corrosion inhibitors for carbon steel in hydrochloric acid solution: Experimental, Structural, Vibrational, Optical, and Electrochemical studies.

.....From page 340 To 344.....

Infrared Absorption and Raman Scattering Spectroscopies.

Raman scattering spectroscopy and infrared absorption spectroscopy are two complementary methods of vibration analysis. They are based on the same physical origin: the vibration of the bonds between atoms of a molecule, which correspond to transitions allowed between different levels of vibrational energy. These techniques are based on the fact that an electromagnetic wave polarizes molecules as it passes through a medium. The latter, formed of positive and negative charges, give rise to a dipole moment induced by components ΔP_i ($i = 1, 2, \dots, n$). These are modulated by molecular vibrations. Each vibration is defined by its normal coordinates Q_j ($j = 1, 2, \dots, n$), where n is the total number of coordinates. This results in the equation: $P_i = f(Q_1, Q_2, \dots, Q_n)$.

In the Free State, XO_4^{n-} ions with tetrahedral symmetry have four fundamental vibration modes. These different modes are designated according to Herzberg notation [1] by V_1 , V_2 , V_3 , and V_4 , (Table. I.1).

- V_1 : is asymmetrical valence vibration mode of type 'A', active in Raman.
- V_2 : is a double degenerate deformation vibration mode of type 'E', active in Raman.
- V_3 and V_4 are two 'F₂' type triple degenerate vibration modes, one deformation vibration, mode and the other valence vibration mode, active in Raman, and infrared.

However, in real crystal structures, tetrahedra are generally deformed and distributed in crystallographic sites of low symmetry. In this case, all vibration modes can become active in Raman and Infrared, as in the case of SiO_4 tetrahedra, Table. I.1.

[1] G. Herzberg, Moléculaire spectra and molecular structure infrared and Raman spectra of polyatomique moléculaire, D. Van Nostrad compay, Princet on New Jersey, 167 (1956).

Table. I.1: Symmetry and main activity of SiO_4 tetrahedron with T_d symmetry and with C_{2v} symmetry in a D_{6h} structure [2].

Modes	Symmetry		Main activity	Wavenumbers cm^{-1} SiO_4
	Symbol T_d	Symmetry C_{2v} in D_{6h}		
Symmetric stretching	ν_1 or $\nu_s A_1$	$A_{1g} + E_{2g} + E_{1u}$	Raman	800–1050
Asymmetric stretching	ν_3 or F_2	$E_{2g} + E_{1u} + E_{1g}$	IR	900–1200
Symmetric bending	ν_{as}	$+ A_{2u} + A_{1g}$	Raman & IR	400–600
Asymmetric bending	ν_2 or $\delta_s E$	$A_{1g} + E_{2g} + E_{1u}$	IR	500–700
Rotational libration	ν_4 or $\delta_s F_2$	$E_{2g} + E_{1u} + E_{1g}$	Raman & IR	300
Translational libration	R'	$+ A_{2u} + A_{1g}$	Raman & IR	100–200
	T'			

When monochromatic light is directed at a molecule, it can be scattered or absorbed. Most of the scattered light will be scattered at the same frequency as the incident light. This phenomenon is called "Rayleigh scattering" or "elastic scattering" (Fig. I.1). The principle of Raman spectroscopy is relatively simple; it consists of sending monochromatic light onto the sample to be studied and analyzing the scattered light. The process involved is as follows: the incident photons are destroyed and their energy is used to create scattered photons and to create (Stokes process) or destroy (anti-Stokes process) vibrations in the studied samples (as an example the Raman scattering of $\text{KPb}_3\text{Sr}(\text{PO}_4)_3$ in Fig. I.1). Two types of rules govern this process: energy conservation and also symmetry which depend on the material studied.

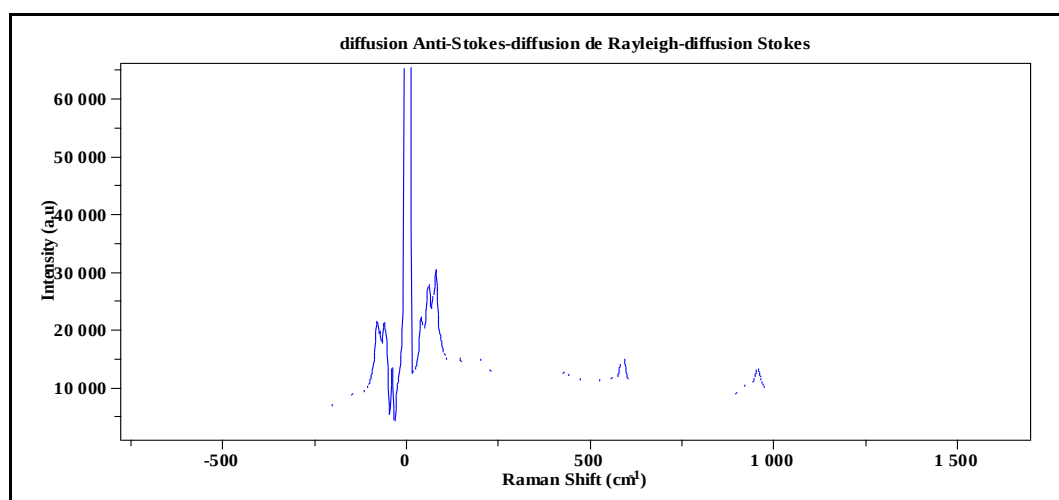


Fig. I.1: diffusion Raman of $\text{KPb}_3\text{Sr}(\text{PO}_4)_3$.

[2] J. Yarwood, Richard Douthwaite, Simon Duckett - 2009

When this monochromatic wave of frequency ' ν_0 ' arrives on the material, it gives rise to two types of scattered waves:

- An elastically scattered wave, i.e. at the same frequency ' ν_0 ' as the incident wave. This scattering called Rayleigh scattering is by far the most probable.
- Inelastically scattered waves which are :
 - The Stokes wave, frequency ' $\nu_0 + \nu_{vib}$ '. This shift results from the transfer of energy from the incident photon to the molecule.
 - The anti-Stokes wave, of frequency ' $\nu_0 - \nu_{vib}$ '. This shift results from the inverse energy transfer of the previous one.

These different processes are shown in Fig. I.2. The Raman shift (cm^{-1}), obtained by measuring the frequency shift concerning the excitation laser frequency, is plotted on the abscissa of a Raman spectrum.

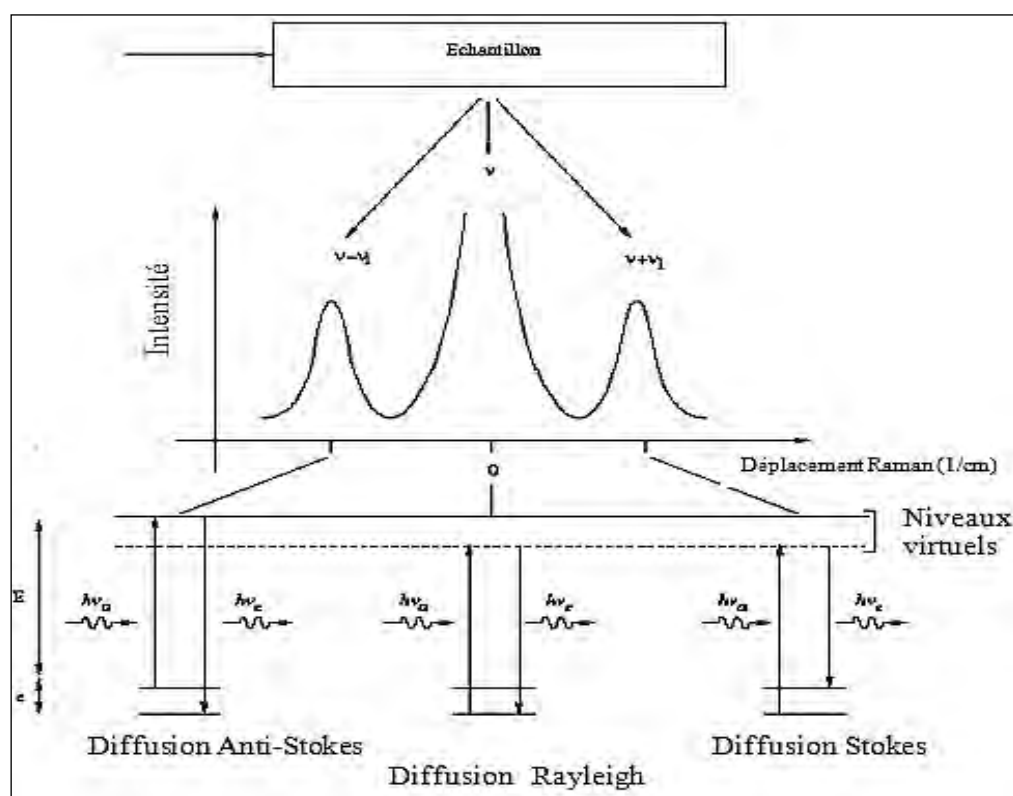


Fig. I.2 : Schéma de principe de la diffusion Raman [3].

[3] C. Kittel, Introduction to Solid State Physics, John Wiley, New York, (1967).

However, a small fraction of the light (~ 1 in 10^7 photons) will be scattered inelastically, at different frequencies than the incident photons. The energy difference between the incident and scattered light is proportional to the vibration energy of the scattering molecules. This process of energy exchange between the scattering molecules and the incident light is called the Raman effect. Raman spectroscopy thus makes it possible to study the vibrational transitions of atoms from the process of inelastic scattering of light.

The Raman spectrum is then made up of thin bands with frequencies between 10 and 3000cm^{-1} . The Raman intensity corresponds to a maximum centred around the zero position of the eigenmode of vibration.

The Raman and FTIR spectra have been normalized and analyzed with the peak adjustment function in LabSpec software V.5, and V.2. A Gauss/Lorentz function was chosen for the peak profiles, and the Savitzky-Golay algorithm was used as the data smoothing method. The background intensity was subtracted before adjustment, and the adjustment process continued until the minimum residuals were reached. As an example the Raman spectrum of $\text{K}_{0.5}\text{Na}_{0.5}\text{Pb}_3\text{Sr}(\text{PO}_4)_3$ in Fig. I.3.

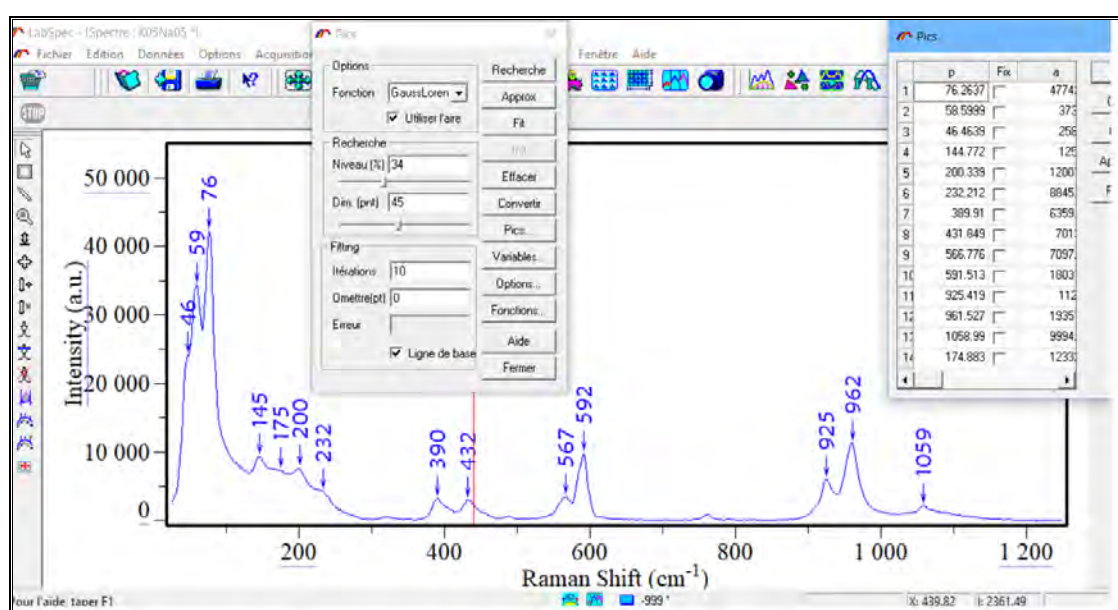


Fig. I.3: Raman spectra of $\text{K}_{0.5}\text{Na}_{0.5}\text{Pb}_3\text{Sr}(\text{PO}_4)_3$, after deconvolution by LabSpec software version .5, recorded at ambient conditions.

Fundamentals and Principles of Emission Spectrometry ICP.

ICP (inductively coupled plasma) emission spectrometry is a method used to perform emission spectrometry using inductively coupled plasma as the light source. To facilitate a deeper understanding of ICP analysis, this section describes the fundamentals of measurement performed with emission spectrometry.

Emission spectrometry is an analysis method in which a sample is electrically or thermally excited, causing it to emit light. The emitted light is divided into element-specific spectral lines with a spectrometer and the qualitative and quantitative analysis of the elements contained in the sample is performed by investigating the presence and intensity of these spectral lines. It is said that this method was first developed when Bunsen, who is credited with the development of the Bunsen burner, put different kinds of solvent into the burner and observed the colours of the flames.

An atom consists of an atomic nucleus and electrons that move around the nucleus with specific orbits. If energy is applied to the atom by some method, the atom absorbs the energy, and an orbital electron moves from the steady-state to an orbit with a higher energy level (E_2). Within a very short time (of the order of 10^{-7} to 10^{-8} s), however, this electron moves back to orbit with the lower energy level (E_1). At this time, the energy difference, ΔE , is radiated as light. If the frequency of the light is " ν ", the energy difference can be expressed as follows:

$\Delta E = E_2 - E_1 = h\nu$ with ' h ': Planck's constant, [Fig. I.4](#).

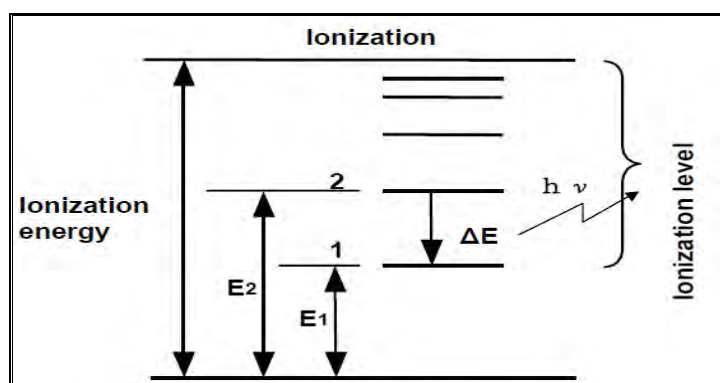


Fig. I.4: Fundamentals and Principles of Emission Spectrometry.

The frequency ' ν ', and the wavelength, λ , of the light satisfy the following relationship: ' $\lambda = c/\nu$ ' c: Speed of light (3×10^{10} cm/sec). The emitted light is directed into a spectrometer, where it is divided by a prism or a diffraction grating, and the element-specific atomic spectral lines are observed. The number of spectral lines normally observed in the ultraviolet, visible, and infrared regions varies from a few dozen (e.g., alkali metals) to a few thousand (e.g., rare-earth elements and uranium). The spectral lines can be divided into two types depending on the state of the light-emitting atom, neutral atomic lines (arc lines), and ion lines (sparklines). The part used to excite the sample and thereby generate these spectral lines is called the "light source". If a substance is caused to emit light and spectral lines corresponding to the atoms or ions of a certain element are discovered in the light, this confirms the presence of that element in the substance. This is the principle of qualitative spectrometry. If the amount of an element contained in a substance changes, then the intensity of the corresponding emission lines in the spectrum for that substance also changes. The line intensities for multiple standard samples (i.e., samples of known concentrations) of different concentrations are measured and the relationship between the intensities and concentrations is expressed in the form of a calibration curve. The line intensity of a sample with an unknown concentration is measured and the concentration is calculated from the calibration curve. This is the principle of quantitative spectrometry.

A calibration curve is created by obtaining the emission intensities of multiple standard samples with different concentrations by integrating over a fixed period, plotting the results on a graph with concentration represented by the horizontal axis and emission intensity represented by the vertical axis, and obtaining a relationship in terms of linear, quadratic, and higher-order expressions. This method is called the "intensity method". Another method is the "intensity ratio method" or "internal standard method". With this method, a spectral line (the internal standard line) for an element of which a fixed amount is contained in (added to) the standard sample and analytical sample are selected, and a calibration curve is created with the

vertical axis representing the ratio of the emission intensity of the target element to the emission intensity of the internal standard element. With this intensity ratio method, even in cases where the sample introduction is unstable due to differences in sample viscosity in the nebulizer, this can be corrected by obtaining the ratio, thereby improving precision and accuracy. Although better results can be obtained by selecting, as the internal standard element, an element that exhibits similar properties to the analytical element in terms of ionization energy, excitation energy, and distribution within the plasma, making an incorrect selection can lead to large errors. It is, therefore, necessary to perform thorough preparatory experiments, [Fig. I.5](#).



Fig. I.5: *Intensity Method (Time Integration Method) and Intensity Ratio Method (Internal Standard Method)* ^[1].

The spectrometers used for emission spectrometry must be able to separate very large numbers of atomic spectral lines and must therefore have greater resolution than the spectrometers used for atomic absorption spectrometry. A diffraction grating is used as the spectrometer's dispersive element. This is because relatively large diffraction gratings can be produced, making it possible to create bright spectrometers, and also because they enable the creation of spectrometers that attain a high resolving power, either by having a large number of grooves (e.g., sequential ICP spectrometers) or by using higher-order spectra (e.g., echelle

ICP spectrometers). A diffraction grating is created by ruling a large number of parallel, equally spaced grooves in the surface of glass onto which metal has been vapour-deposited.

When light strikes a diffraction grating from a certain direction, the light of a certain wavelength is intensified in a certain direction due to diffraction. The overall effect is that a spectrum is formed. If ' α ' is the angle the incident light makes with the perpendicular to the surface of the diffraction grating (incident angle), ' β ' is the angle the diffracted light makes with the perpendicular, ' d ' is the grating constant, and ' λ ' is the wavelength, then the following equation holds $n\lambda = d(\sin\alpha + \sin\beta)$ (Eq. I.1), with ' n ': Order of diffraction. Here, n is the order of diffraction, ' $n = 0$ ' corresponds to the direct image, and ' $n = 1, n = 2, n = 3, \dots$, etc', correspond to diffraction images of order '1, 2, 3, ..., etc'.

Echelle diffraction gratings use high orders, ranging from approximately 30 to 130. If we assume that the incident angle is constant, then Eq. I.1 gives the following: $d\beta / d\lambda = n / d(\cos\beta)$ (Eq. I.2). This is the angular dispersion. It varies in proportion to the order ' n ' and increases as the grating constant decreases. If light dispersed by angle $\Delta\beta$ forms an image consisting of two lines, and if the distance between these two lines in the focal plane is ΔL , $\Delta L / \Delta\lambda (dL / d\lambda)$ is called the "linear dispersion". $\frac{dL}{d\lambda} = \frac{f}{\sin\epsilon} \times \frac{d\beta}{d\lambda}$ (Eq. I.3).

Here, ' f ' is the focal length of the spectrometer, and ' ϵ ' is the angle of inclination between the focal plane and the optical axis. In practice, the reciprocal of this, the "reciprocal linear dispersion" is often used, and is expressed in units of nm/mm. The ability to separate two closely neighbouring wavelengths into two distinct lines is called the "resolution". If ' λ ' is the average wavelength of two separable spectral lines and ' $\Delta\lambda$ ' is the difference in wavelength, then the resolution, R , can be expressed as follows: $R = \lambda / \Delta\lambda$ (Eq. I.4). If N is the total number of grooves and n is the order, then the resolution, R , can also be expressed as follows: $R = \lambda / \Delta\lambda = nN$ (Eq. I.5). Therefore, the resolution increases as the total number of grooves, N , increases, or the diffraction order ' n ' increases.

The arrangement of a spectrometer's optical elements is called a "mounting". Fig. I.6 shows the mounting for an echelle spectrometer incorporating an echelle diffraction grating. The divergent light through the entrance slit is converted to parallel light by the collimator. It is then diffracted and divided by the diffraction grating and the prism, it undergoes aberration correction at the Schmidt mirror, and an image is formed by the telescope mirror at the exit slit. With the ICPE-9000, a two-dimensional semiconductor detector is used instead of an exit slit. The echelle spectrometer is designed to improve resolution by increasing the order of diffraction, as shown in (Eq. I.5), and to improve the angular dispersion by increasing the diffraction angle, ' β ' (i.e., reducing the value of ' $\cos\beta$ '), as shown in equation Eq. I.2. In general, the order is in the range 30 to 130 and the diffraction angle is in the range 60° to 70° . When light is divided with an echelle spectrometer, all light for which the product of the order and wavelength is the same will be radiated in the same direction and so an order-dispersive element is required to isolate light of the target wavelength. In light divided with an echelle spectrometer, if ' λ ' and ' λ' ' are wavelengths of two consecutive orders that appear at the same position in the spectrum, then the difference in the wavelength ' $\Delta\lambda$ ' is called the "free spectral range", and represents the wavelength range measured for each order. Applying ' $\alpha \cong \beta$ ' to Eq. I.1, gives the following: $n\lambda = (n+1)\lambda' = 2d \sin\beta$ (Eq. I.6) and $\Delta\lambda = \lambda - \lambda' = \lambda' / n$ (Eq. I.7)

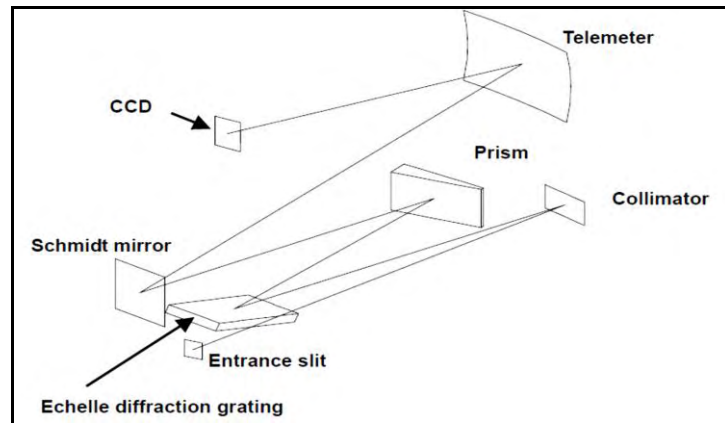


Fig. I.6: Spectrometer Incorporating Echelle Diffraction Grating ^[1].

In general, the range is from the 30th to the 130th order and from 1 to 10 nm. The prism divides the light so that it radiates in a direction perpendicular to the direction in which the light is dispersed by the diffracted grating. The light is separated according to order and all the wavelengths are dispersed onto a two-dimensional plane. Fig. I.7 shows the echelle pattern.

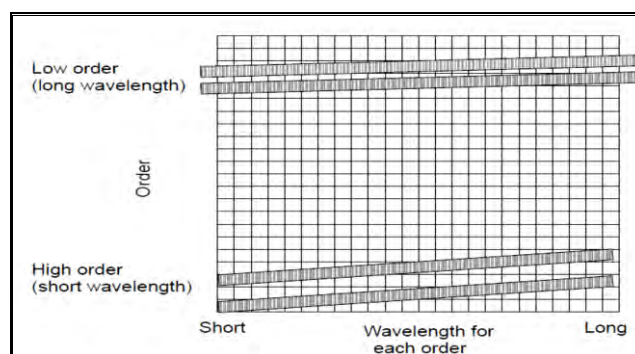


Fig. I.7: Echelle Pattern.

Light can be converted to electrical signals using a photomultiplier tube or a semiconductor detector. A photomultiplier tube uses the fact that electrons are generated when light strikes a photoelectric surface. It accelerates the electrons in a vacuum and amplifies the signal and detects them as current from an anode. A semiconductor detector uses the fact that electrons are generated in a solid-state element (Si) by incident photons. It accumulates electrons and performs detection by measuring the amount of electric charge. To measure two-dimensional spectra, the echelle spectrometer uses a semiconductor detector ‘CCD’. Approximately one million (1.024×1.024) independent elements (pixels) with vertical and horizontal dimensions of a few tens of microns are arranged within an area of one square inch. After accumulation time elapses, the amount of electric charge is read (i.e., measured) for each pixel. The spectral intensity of the target element is obtained as the amount of electric charge that accumulated in the pixel a certain number along and a certain number up.

[1]Shimadzu Multitype ICP Emission Spectrometer, ICPE-9000 Hardware INSTRUCTION MANUAL, Analytical & Measuring Instruments Division, Shimadzu Corporation KYOTO JAPAN.

Table. II.1: Several cases for refinement of $\text{NaPb}_2\text{CaSr}(\text{PO}_4)_3$.

	case-1	case-2	case-3	case-4(2)	case-5(3)
Space group	$P 6_3/m$				
a (Å)	9.6710(3)	9.6706(3)	9.6682(3)	9.6690(3)	9.6669(3)
c (Å)	7.1139(3)	7.1134(3)	7.1098(3)	7.1124(3)	7.1104(2)
V (Å ³)	576.21(4)	576.12(3)	575.55(3)	575.85(3)	575.44(3)
Density(g/cm ³)	6.774	6.533	2.820	6.515	6.560
M(I) = Pb(1)/Ca(1)/Sr(1)	2/0.838(3)/0.162(3)	1.943(3)/0.75/0.307(3)	1.889(5)/0.361(5)/0.75	1.951(7)/0.743(7)/0.307(7)	1.882(3)/0.361(3)/0.757(3)
M(II) = Pb(2)/Ca(2)/Sr(2)/Na	0/0.162(3)/0.838(3)/1	0.057(3)/0.25/0.693(3)/1	0.111(5)/0.639(5)/0.25/1	0.049(7)/0.257(7)/0.693(7)/1	0.118(4)/0.639(4)/0.243(4)/1
%*R _F	1.63	1.57	1.54	1.56	1.47
%*R _B	3.74	3.84	4.80	3.81	3.34
%*R _p	8.19	7.61	8.20	7.72	7.58
%*R _{wp}	11.0	10.4	11.3	10.5	10.4
%*cR _p	11.2	11.5	12.1	11.3	11.1
%*cR _{wp}	13.6	14.2	15.1	13.9	13.7

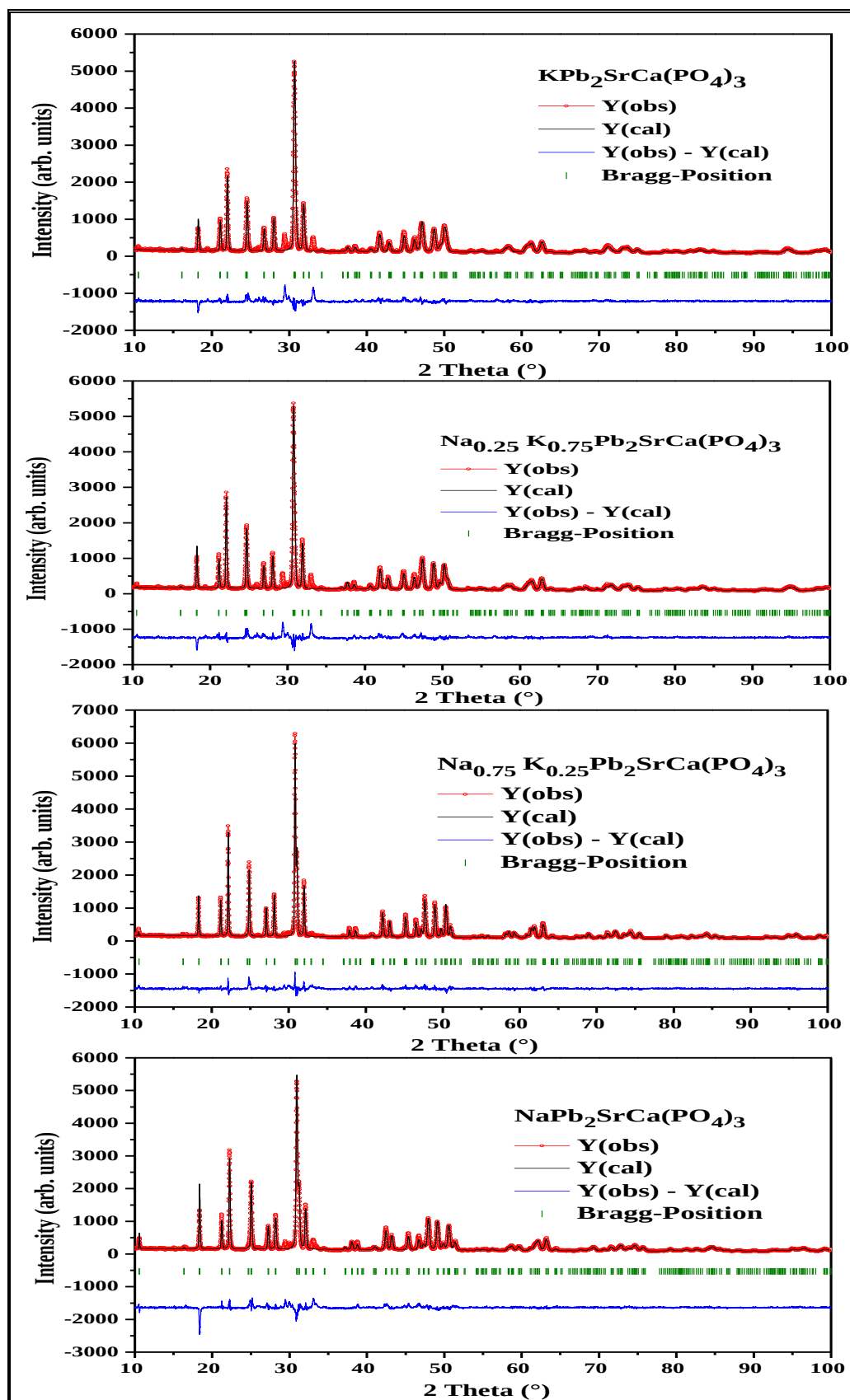


Fig. II.1: Rietveld first refinements plot of $\text{Na}_{1-x}\text{K}_x\text{Pb}_2\text{SrCa}(\text{PO}_4)_3$.

Table. II.2: Details of Rietveld's first refinement conditions plot of $\text{Na}_{1-x}\text{K}_x\text{Pb}_2\text{SrCa}(\text{PO}_4)_3$.

x		0	0.25	0.5	0.75	1
Zer- point (deg.20)		0.041 (5)	0.039 (2)	0.057(4)	-0.013(3)	-0.013 (5)
Pseudo-Voigt function $\text{PV}=\eta\text{L} + (1 - \eta) \text{G}$	η	0.366(11)	0.407(10)	0.416(10)	0.386(11)	0.393(10)
Caglioti parameters	U	0.2892(23)	0.1711(13)	0.4917(28)	0.5515(33)	0.718(5)
	V	-0.055(3)	-0.035(8)	-0.066(17)	-0.057(2)	-0.015(7)
	W	0.0022(2)	0.0186(13)	0.0192(25)	0.0163(29)	0.0053(38)
No. of reflections		500/2	478/2	505/2	518/2	540/2
No. of refined parameters		33				
Space group		$P 6_3/m$				
a (Å)		9.6694(5)	9.6856(3)	9.7004(5)	9.7188(4)	9.7437(6)
c (Å)		7.1144(4)	7.1558(2)	7.1763(4)	7.2135(4)	7.2617(5)
V (Å ³)		576.06(5)	581.35(3)	584.80(5)	590.07(5)	597.06(7)
Density(g/cm ³)		6.40	6.57	6.76	6.75	4.16
Z		2				
Atom Number		11	12			11
User-weighted Chi2		3.82	2.62	3.34	4.00	4.16
%*R _F		5.89	5.19	5.63	5.90	6.77
%*R _B		9.57	7.41	8.41	8.86	9.69
%*R _p		9.39	8.13	8.90	9.24	9.76
%*R _w p		22.4	10.9	12.3	13.6	14.0
%*cR _p		19.5	17.4	19.1	20.4	20.9
%*cR _w p		22.4	18.8	21.3	24.0	24.5

Table. II.3: Selected interatomic distances in (Å) and 'O-P-O' in (°) angles.

$\text{Na}_{1-x}\text{K}_x\text{Pb}_2\text{CaSr}(\text{PO}_4)_3$					
X	0	0.25	0.5	0.75	1
M(I)-O ₁	2.812(3)	2.816(4)	2.885(4)	2.890(4)	2.914(5)
2*M(I)-O ₂	2.444(6)	2.474(5)	2.458(12)	2.450(11)	2.450(15)
2*M(I)-O ₂	2.626(17)	2.624(14)	2.625(3)	2.675(3)	2.683(4)
M(I)-O ₃	2.342(2)	2.201(2)	2.275(2)	2.278(2)	2.205(3)
<M(I)-O>	2.556	2.529	2.561	2.573	2.563
3*M(II)-O ₁	2.462(15)	2.530(10)	2.498(10)	2.465(7)	2.566(10)
3*M(II)-O ₂	2.805(16)	2.837(12)	2.767(3)	2.873(2)	2.840(2)
3*M(II)-O ₃	2.531(15)	2.654(10)	2.653(10)	2.644(7)	2.684(10)
<M(II)-O>	2.599	2.674	2.639	2.661	2.697
P-O ₁	1.566(19)	1.506(14)	1.525(15)	1.569(5)	1.540(17)
2*P-O ₂	1.567(12)	1.544(9)	1.586(6)	1.543(6)	1.584(6)
P-O ₃	1.545(12)	1.542(9)	1.508(10)	1.551(6)	1.512(12)
<P-O>	1.559	1.531	1.540	1.554	1.545
2*O ₁ -P-O ₂	110.0(3)	109.6(11)	112.8(6)	107.7(6)	108.7(7)
O ₁ -P-O ₃	116.2(8)	108.9(6)	107.0(7)	109.9(7)	103.3(8)
O ₂ -P-O ₂	110.7(6)	109.6(5)	113.0(3)	116.9(1)	115.8(3)
2*O ₂ -P-O ₃	104.8(8)	109.5(7)	105.2(4)	107.6(5)	109.8(5)
<O-P-O>	110.43	109.4	109.5	110.53	109.4

Table. II.4: Details of Rietveld's first refinement conditions plot of $Na_{1-x}K_xPb_2SrCa(PO_4)_3$.

Atom	Wyckoff	Sym	x/a	y/b	z/c	B ($\text{\AA}^2$)	Occupancy	x
M(I) = Pb(1)/Ca(1)/Sr(1)	6h	M	0.2553(3)	0.2548(3)	0.25	1.45(5)	1.882(3)/0.361(3)/0.757(3)	0
			0.2556(3)	0.2564(3)		1.35(5)	1.865(5)/0.361(5)/0.774(5)	0,25
			0.2571(3)	0.2559(3)		1.47(6)	1.829(4)/0.334(4)/0.837(4)	0,5
			0.2589(3)	0.2560(3)		1.63(2)	1.844(4)/0.334(4)/0.822(4)	0,75
			0.2589(4)	0.2573(4)		1.07(9)	1.831(7)/0.513(7)/0.656(7)	1
M(II) = Pb(2)/Ca(2)/Sr(2)/Na/K	4f	3	0.6667	0.3333	0.5035(29)	0.35(2)	0.118(4)/0.639(4)/0.243(4)/1/0	0
					0.5011(20)	0.73(2)	0.135(2)/0.639(2)/0.226(2)/0.75/0.25	0,25
					0.5045(20)	0.15(1)	0.171(4)/0.666(4)/0.163(4)/0.5/0.5	0,5
					0.5114(14)	0.42(3)	0.156(5)/0.666(5)/0.178(5)/0.25/0.75	0,75
					0.4988(22)	0.80(5)	0.169(3)/0.487(3)/0.344(3)/0/1	1
P	6h	M	0.3769(17)	0.4054(14)	0.75	2.47(30)	3	0
			0.3759(12)	0.4050(11)		1.72(22)		0,25
			0.3722(13)	0.4017(12)		1.37(25)		0,5
			0.3709(4)	0.4035(8)		1.58(34)		0,75
			0.3715(14)	0.4039(15)		1.58(6)		1
O(1)	6h	M	0.4843(8)	0.3265(7)	0.75	8.62(46)	3	0
			0.4794(8)	0.3296(9)		7.04(8)		0,25
			0.4850(7)	0.3349(9)		5.55(37)		0,5
			0.4850(4)	0.3331(4)		7.43(5)		0,75
			0.4876(9)	0.3394(7)		6.14(7)		1
O(2)	12i	1	0.2707(18)	0.3555(15)	0.5689(8)	8.62(46)	6	0
			0.2698(15)	0.3526(12)	0.5736(9)	7.04(8)		0,25
			0.2686(8)	0.3596(7)	0.5657(8)	5.55(37)		0,5
			0.2752(7)	0.3523(8)	0.5676(6)	7.43(5)		0,75
			0.2759(3)	0.3666(17)	0.5617(7)	6.14(7)		1
O(3)	6h	M	0.4657(4)	0.5899(8)	0.75	8.62(46)	3	0
			0.4836(7)	0.5878(9)		7.04(8)		0,25
			0.4741(4)	0.5806(8)		5.55(37)		0,5
			0.4716(7)	0.5874(5)		7.43(5)		0,75
			0.4862(35)	0.5889(4)		6.14(7)		1

Table. II.5: The results calculations of $F(R)$ and $[F(R)*h\nu]^{1/2}$ depending on the wavelength (λ), ($h\nu$) and the diffuse reflectance (R), for example of sample $\text{NaPb}_2\text{SrCa}(\text{PO}_4)_3$ in the region of [250-290nm].

Lamda(nm)	%R	λ (meters)	R	F(R)	hV (J)	hV (eV)	$(F(R))*h\nu)^{1/2}$
290	29.38722	0.00000029	0.29387	0.84836	6.85448E-19	4.28405	1.90641
289	27.5442	0.000000289	0.27544	0.95299	6.8782E-19	4.29888	2.02405
288	26.21248	0.000000288	0.26212	1.03855	6.90208E-19	4.3138	2.11663
287	24.34295	0.000000287	0.24343	1.1757	6.92613E-19	4.32883	2.25597
286	22.71206	0.000000286	0.22712	1.31503	6.95035E-19	4.34397	2.39008
285	21.36761	0.000000285	0.21368	1.44683	6.97474E-19	4.35921	2.51138
284	19.67018	0.000000284	0.1967	1.64027	6.9993E-19	4.37456	2.6787
283	18.26503	0.000000283	0.18265	1.8288	7.02403E-19	4.39002	2.83345
282	16.43834	0.000000282	0.16438	2.12386	7.04894E-19	4.40559	3.0589
281	15.4788	0.000000281	0.15479	2.30762	7.07402E-19	4.42126	3.19415
280	14.55209	0.00000028	0.14552	2.50869	7.09929E-19	4.43705	3.33635
279	13.77282	0.000000279	0.13773	2.6992	7.12473E-19	4.45296	3.46691
278	12.79213	0.000000278	0.12792	2.97262	7.15036E-19	4.46897	3.6448
277	11.97247	0.000000277	0.11972	3.23611	7.17617E-19	4.48511	3.80976
276	11.32448	0.000000276	0.11324	3.47184	7.20217E-19	4.50136	3.95323
275	10.67973	0.000000275	0.1068	3.73516	7.22836E-19	4.51773	4.10785
274	10.37944	0.000000274	0.10379	3.86911	7.25474E-19	4.53422	4.18848
273	9.88456	0.000000273	0.09885	4.10782	7.28132E-19	4.55082	4.32365
272	9.5129	0.000000272	0.09513	4.30358	7.30809E-19	4.56756	4.43361
271	9.2791	0.000000271	0.09279	4.43485	7.33506E-19	4.58441	4.50901
270	9.13614	0.00000027	0.09136	4.51845	7.36222E-19	4.60139	4.55973
269	9.03502	0.000000269	0.09035	4.5792	7.38959E-19	4.61849	4.5988
268	8.83799	0.000000268	0.08838	4.70158	7.41716E-19	4.63573	4.66854
267	8.68279	0.000000267	0.08683	4.80193	7.44494E-19	4.65309	4.72692
266	8.49342	0.000000266	0.08493	4.92938	7.47293E-19	4.67058	4.79824
265	8.39306	0.000000265	0.08393	4.99927	7.50113E-19	4.68821	4.84124
264	8.36079	0.000000264	0.08361	5.0221	7.52955E-19	4.70597	4.86146
263	8.32192	0.000000263	0.08322	5.04984	7.55817E-19	4.72386	4.88413
262	8.19582	0.000000262	0.08196	5.14165	7.58702E-19	4.74189	4.93772
261	8.28178	0.000000261	0.08282	5.07876	7.61609E-19	4.76006	4.91683
260	8.00083	0.00000026	0.08001	5.28936	7.64538E-19	4.77837	5.02737
259	8.0216	0.000000259	0.08022	5.27328	7.6749E-19	4.79681	5.02941
258	7.97849	0.000000258	0.07978	5.30674	7.70465E-19	4.81541	5.05511
257	7.93459	0.000000257	0.07935	5.3412	7.73463E-19	4.83414	5.08135
256	8.02119	0.000000256	0.08021	5.27359	7.76484E-19	4.85303	5.05894
255	8.09335	0.000000255	0.08093	5.21838	7.79529E-19	4.87206	5.04225
254	7.82165	0.000000254	0.07822	5.43162	7.82598E-19	4.89124	5.15435
253	8.13693	0.000000253	0.08137	5.18551	7.85692E-19	4.91057	5.04617
252	8.07199	0.000000252	0.08072	5.23462	7.8881E-19	4.93006	5.08006
251	8.02368	0.000000251	0.08024	5.27167	7.91952E-19	4.9497	5.10815
250	8.02231	0.00000025	0.08022	5.27273	7.9512E-19	4.9695	5.11887

Table. III.1: Scherrer's Formula.

Crystallite size $D_p = (K \cdot \lambda) / (B \cdot \cos \theta)$	
D_p - Average crystallite size (nm)	
K - Scherrer constant. K varies from 0.68 to 2.08. K = 0.94 for spherical crystallites with cubic symmetry	
λ - X-ray wavelength. For XRD using Bruker D2 PHASER, Cu $K\alpha$.	
B - FWHM (Full Width at Half Maximum) of XRD peak.	
θ - XRD peak position, one half of 2θ	

input value			calculated value
(hkl)	Peak position 2θ (°)	FWHM B size (°)	D_p (nm)
HA-900			
(310)	39,820038	0,209353	42,18521
(002)	25,879095	0,157106	54,23138
HA			
(310)	39,692394	0,888871	9,93175
(002)	25,858093	0,230818	36,91097
HA-Zn			
(310)	39,668278	1,156323	7,634004
(002)	26,030031	0,308567	27,62013
AP-Ca			
(310)	38,79221	0,069673	126,3525
(002)	24,912022	0,072713	116,9514
AP-Zn			
(310)	----	----	----
(002)	26,477314	0,136283	62,59345

Table. III.2: Selected interatomic distances in (Å) and 'O-P-O' angles in (°).

	K₂Pb₄Ca₄(PO₄)₆	K₂Pb₆Zn₂(PO₄)₆		K₂Pb₄Ca₄(PO₄)₆	K₂Pb₆Zn₂(PO₄)₆
M(1)-O₁	2,793	2,877	P-O₁	1,515	1,54671
2*M(1)-O₂	2,554	2,652	2*P-O₂	1,553	1,55263
2*M(1)-O₂	2,583	2,614	P-O₃	1,511	1,505
M(1)-O₃	2,227	2,34	<P-O>	1,533	1,5392425
<M(1)-O>	2,549	2,6248	O₂-P-O₂	99,4	110,526
3*M(2)-O₁	2,526	2,525	2*O₁-P-O₂	113,1	111,806
3*M(2)-O₂	2,834	2,7762	O₁-P-O₃	112,8	112
3*M(2)-O₃	2,678	2,74	2*O₂-P-O₃	108,8	105,2
<M(2)-O>	2,6793	2,6804	<O-P-O>	108,5	105,1

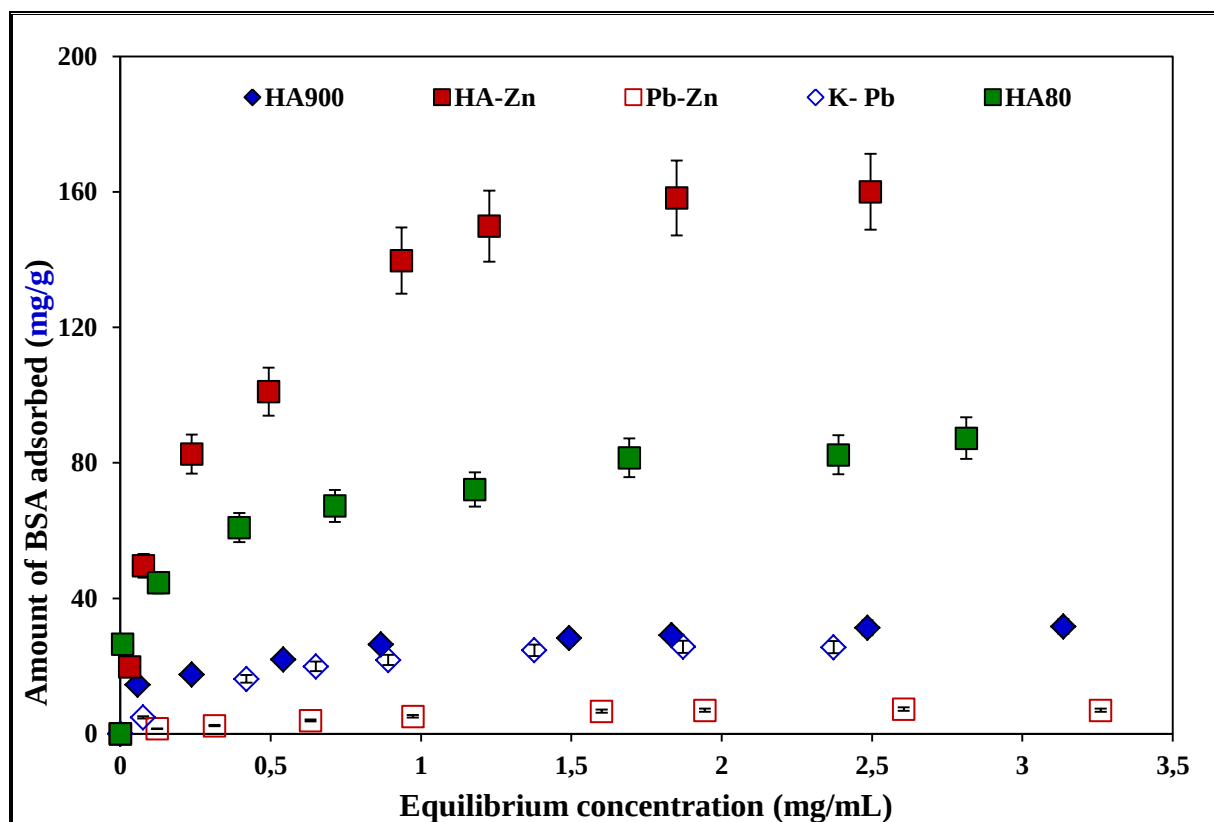


Fig. III.1: Table II provides the adsorption data used to determine the amount loaded by the apatite samples which is plotted in the adsorption isotherms.

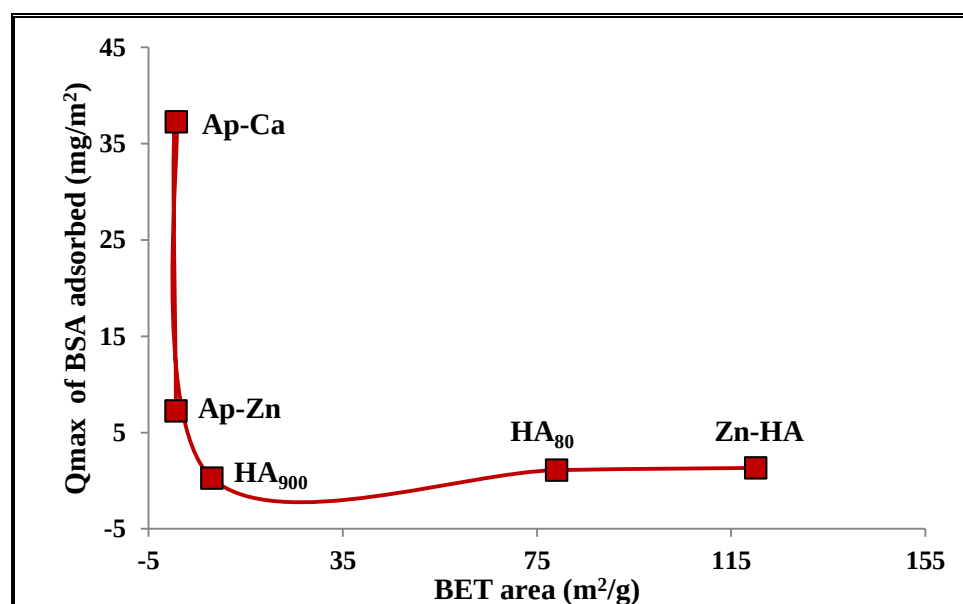


Fig. III.2: The figure shows linear regressions of representative Langmuir adsorption isotherms of BSA by apatite samples.

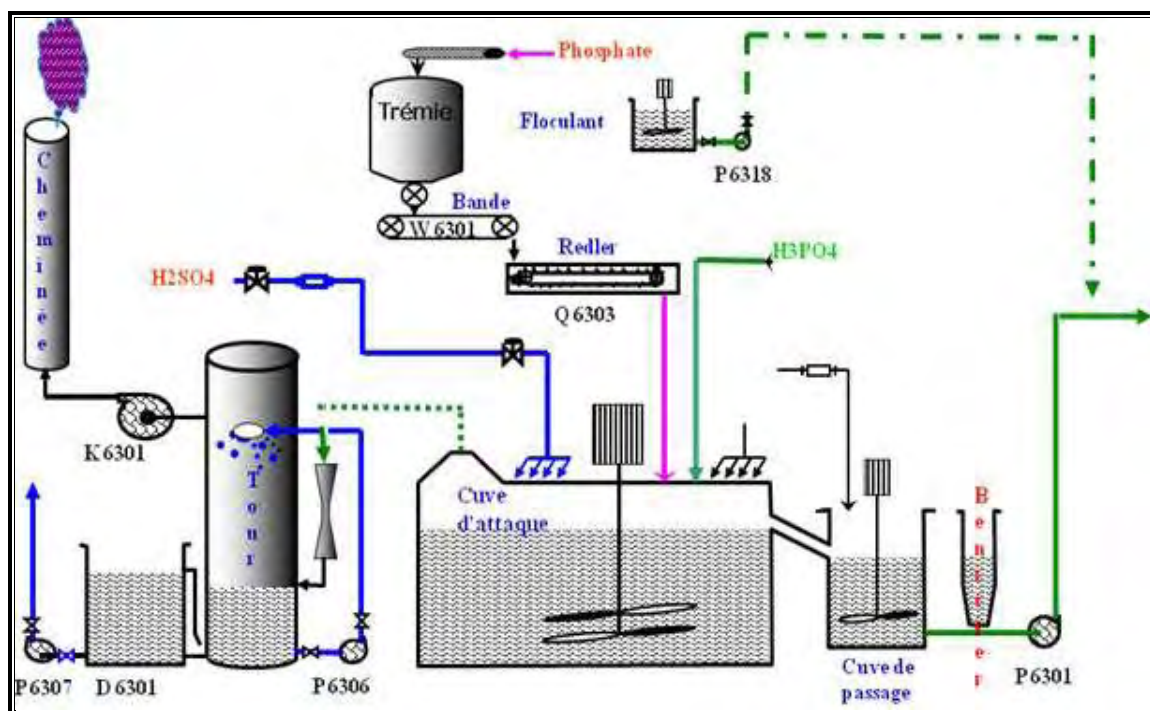


Fig. IV.1: Diagram of the reaction unit of the RHONE-POULENC process.

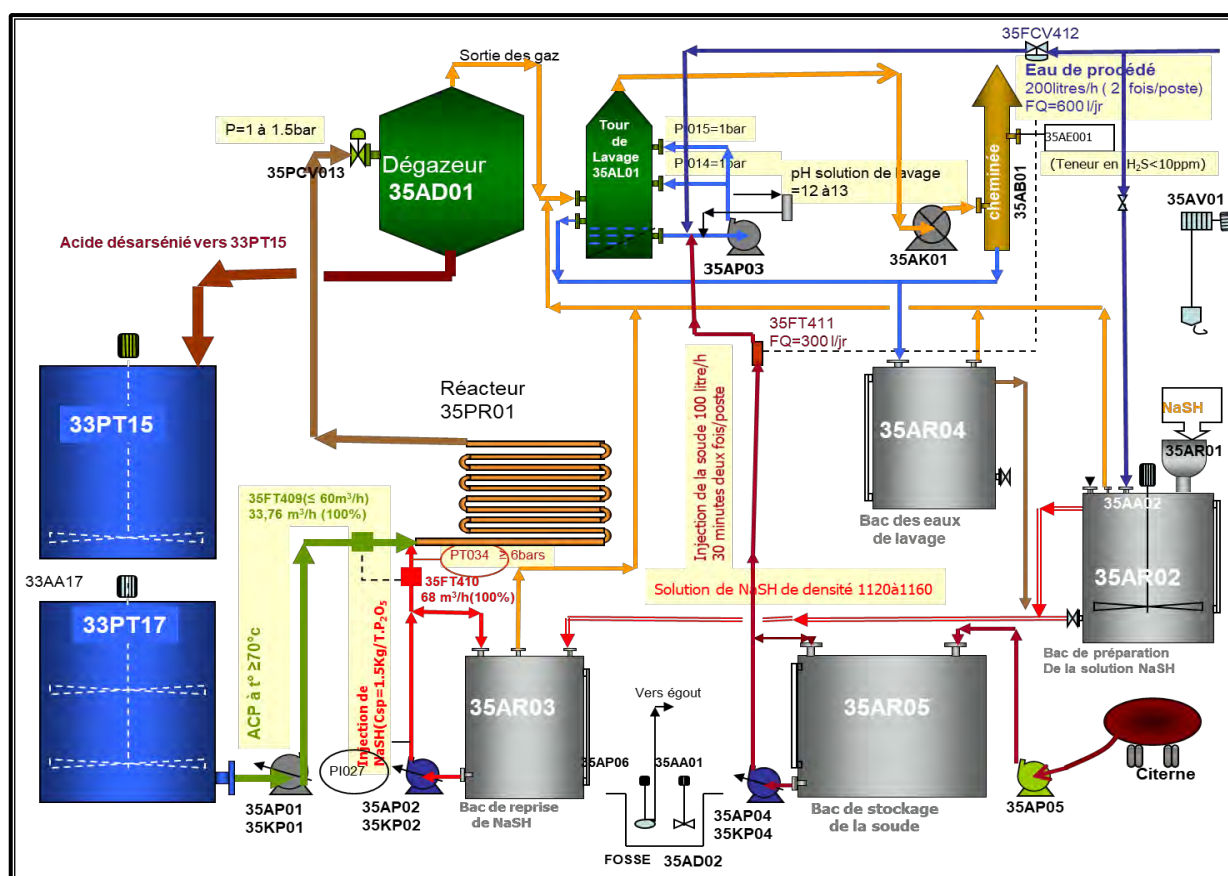


Fig. IV.2: The desarseniation unit in the MP IV.

Estimation of CHN/CHNS/O in percentage level to high concentration level.

The CHNS(O) Analyzer find utility in determining the percentages of Carbon, Hydrogen, Nitrogen, Sulphur and Oxygen of organic compounds, based on the principle of the "Dumas method" which involves the complete and instantaneous oxidation of the sample by "flash combustion". The combustion products are separated by a chromatographic column and detected by the thermal conductivity detector (T.C.D.), which gives an output signal proportional to the concentration of the individual components of the mixture.



Fig. IV.3: Key components of CHNS are autosampler, combustion reactors, chromatographic column, and T.C.D. detector.

Control of the Free Sulphate Content.

The control of the content of free sulfates (SO_4^{2-}) in the acid or the sludge is done in the researches and developments (R&D) laboratory according to the following procedure:

- 1) We calculate the density of the sample with a densimeter (Fig. IV.4).
- 2) We titrate 2cm^3 of the sample by barium chloride ($\text{BaCl}_2 - 0.2\text{N}$).

The colour indicator used is sulfonazo III and we use acetone as a catalyst.

Once the change is reached, we proceed to the reading of the burette drop (Fig. IV.5).

The reaction of the titration is written :



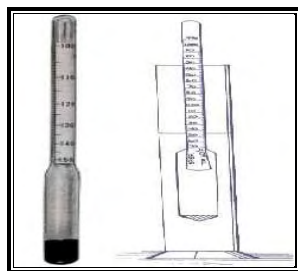


Fig. IV.4: Densimeter.

By calculating the density of the sample and the volume necessary for the change of the indicator (TB= burette fall), we determine the sulfate rate by the following relation:

$$\%H_2SO_4 = 1 + \frac{T.B \cdot 0.98}{Densité}.$$

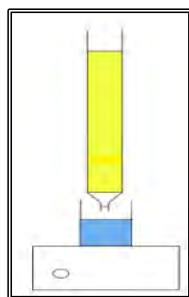


Fig. IV.5: Determination of the sample by BaCl₂.

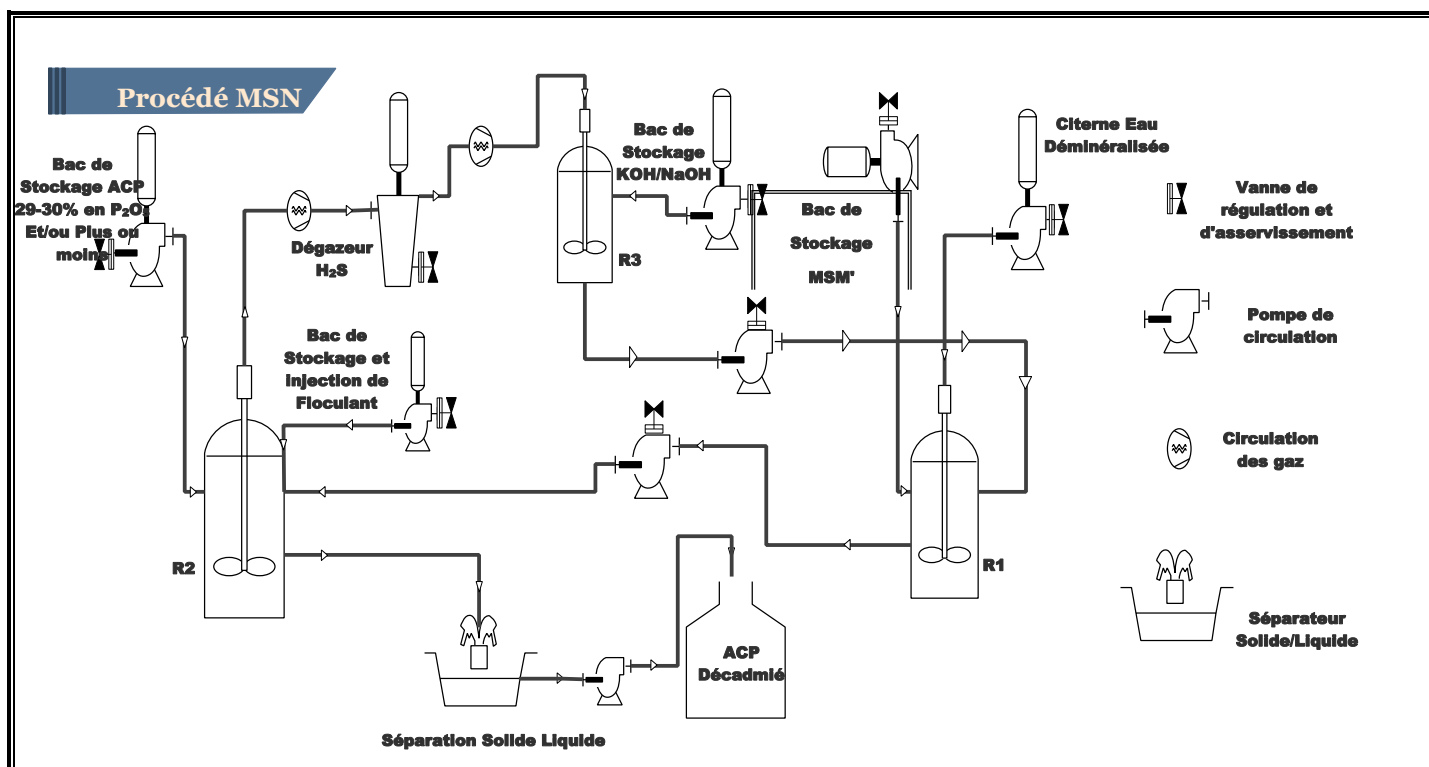


Fig. IV.6: Diagram describing the MSN decadmiation process.

Appearance and Configuration of ICPE-9000 [1]

The ICPE-9000 in Fig. IV.7 consists of the spectrometer case, the plasma stand, the RF power supply, the controller, and the vacuum system. Inside the spectrometer case, the echelle spectrometer is contained in a temperature-controlled bath. The controller incorporates the gas controller and the control power supply.

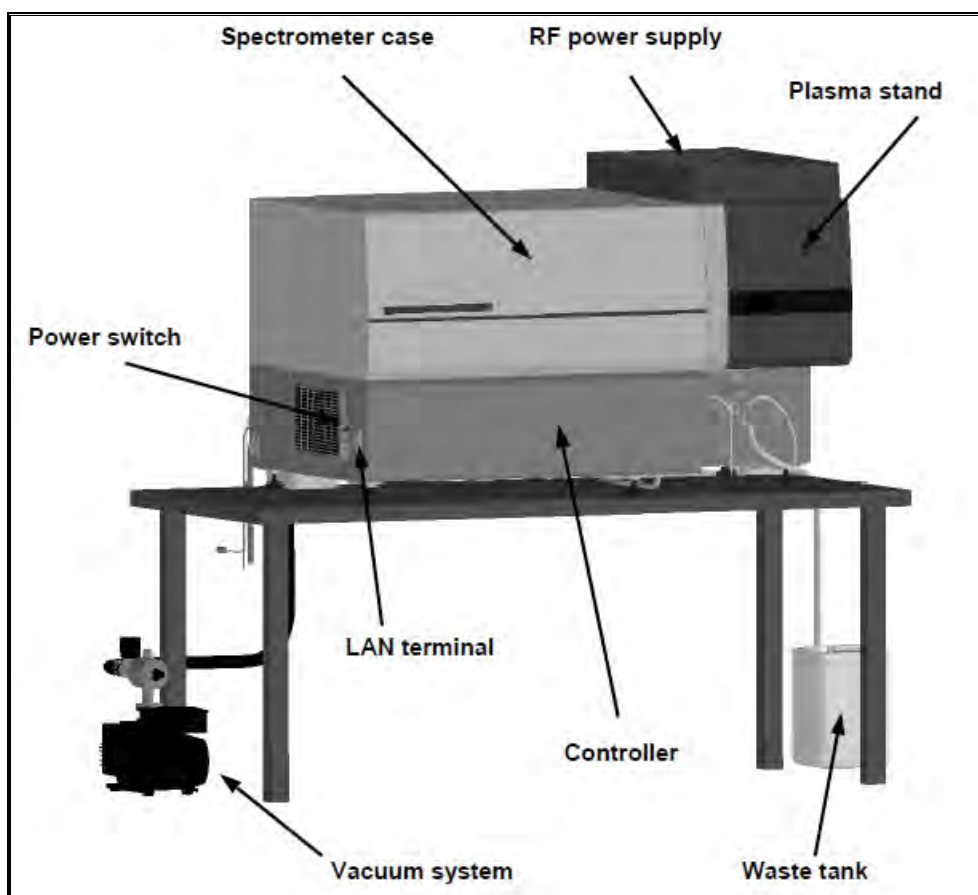


Fig. IV.7: Appearance of ICPE-9000.

A) Definition and Principles of Plasma.

In the field of physics, an American physical chemist Langmuir in the 1920s gave the name "plasma" to a region where electric charges of ions and electrons are balanced. This was the first time the word plasma appeared in this field. In short, the plasma means ionized gases such as gases ionized in the central emission area of a vacuum discharge tube, the gas between arc discharge electrodes, ionosphere,..., etc.

"Fig. IV.8" shows the plasma generation process. A magnetic field, 'H', is formed by an 'RF' current, 'I', flowing through an inductive coil, and an electric field of a strength proportional to the rate of change of the 'RF' magnetic field is generated. The electric field accelerates electrons and ions, and as a result of collisions between high-speed electrons and argon atoms, the argon atoms are ionized. The rate at which electrons are generated exceeds the rate at which they are destroyed, and plasma is formed. The plasma is maintained in a state where the generation and destruction (i.e., due to rebonding, dispersion, or gas flow) of ions and electrons balances. The current density in a cross-section of the conductor in which the RF current flows becomes as large as the current density at the surface. This phenomenon is called the "skin effect". The higher the frequency or the conductivity of the plasma, the more heat is concentrated in the periphery. With the introduction of the carrier gas, the temperature at the centre of the tube decreases even more and a doughnut-shaped ring of plasma is formed.

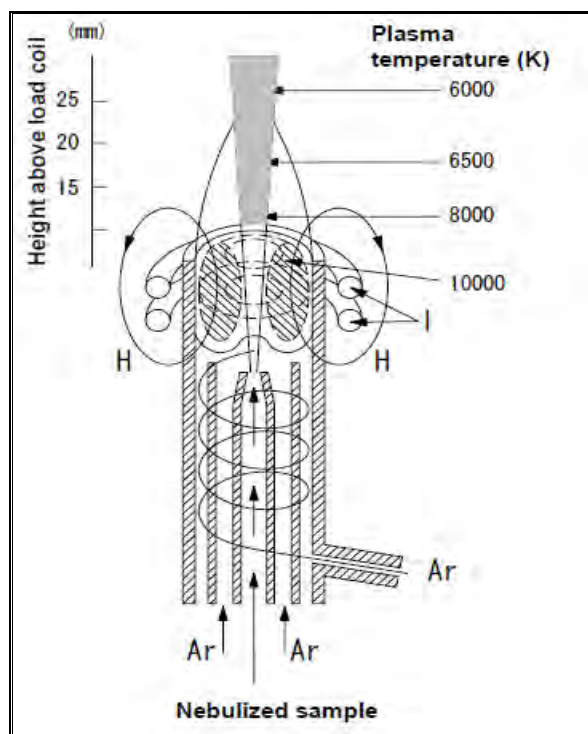


Fig. IV.8: Plasma of ICPE-9000.

B) Principle of RF Power Supply.

The energy used to generate 'ICP' is applied to the plasma in the form of 'RF' electric power. This 'RF' electric power is generated by an 'RF' power supply, which is configured as shown in Fig. IV.9.

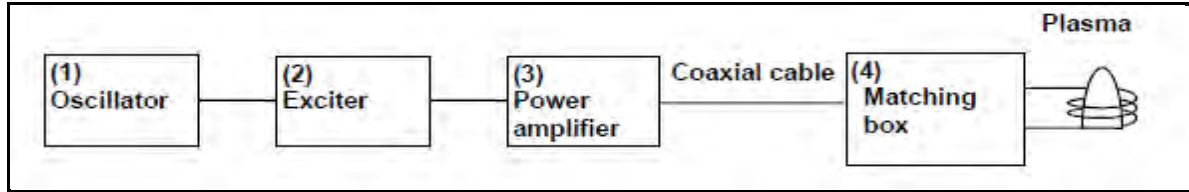


Fig. IV.9: Configuration of RF Power Supply.

(1) Oscillator: This unit sets the frequency of the RF output. Fluctuations in the frequency affect the analysis precision and so many ICP power supplies use a crystal oscillator because of the high level of frequency stability.

(2) Exciter: This unit amplifies the radio frequency generated by the oscillator to the magnitude enough to excite the PA (power amplifier (3)).

(3) Power Amplifier: This unit amplifies the power from the exciter to the output of kW order enough to ignite and maintain the ICP.

(4) Matching Box: The power amplified by the PA is allowed to the plasma through a coaxial cable with the characteristic impedance Z_0 . However, because the impedance of the plasma and the characteristic impedance of the cable is different, a matching circuit is required. The box incorporating the matching circuit is called the "matching box".

When the RF power reaches the load (impedance Z_r) via the cable (characteristic impedance Z_0), the reflection expressed by the following equation occurs $P_r = P_f \left(\frac{Z_0 - Z_r}{Z_0 + Z_r} \right)^2$

P_r : Reflected power and P_f : Incident power

As shown by this equation, the reflected power ' P_r ' is zero only when the impedance of the load, ' Z_r ' is equal to the characteristic impedance of the cable ' Z_0 '.

C) Detector.

Semiconductor detectors come in CCD (charge-coupled device) and CID (charge injection device) types. Repeated reading is possible with a CID but all the pixels are read in one operation with a CCD. The ICPE-9000 uses a CCD. The sensitivity of a photomultiplier tube is adjusted by changing the applied voltage. With a semiconductor detector, however, the sensitivity adjustment is not possible for individual pixels. Also, there is a limit to the amount of charge that can accumulate in a pixel. If a pixel is irradiated with light of an intensity that exceeds this amount, an overflow occurs. In this case, the accumulation time is decreased to prevent an overflow and the number of repetitions is increased. On the other hand, if the light intensity is relatively low, the accumulation time is increased and the number of repetitions is decreased.

Operating Principle of VersaSTAT.4.

The VersaSTAT.4 (Fig. V.1), combined with the Versa Studio software package, includes a simple, flexible, and extremely powerful system for performing a wide range of electrochemical techniques. The VersaSTAT.4 is a potentiostat/galvanostat with an optional Frequency Response Analyzer (FRA) contained in a single unit. It is controlled from any suitably equipped PC via a USB (Universal Serial Bus) interface using the Versa Studio electrochemistry software package (Fig. V.2).



Fig. V.1: VersaSTAT.4, in Laboratory of Materials Nanotechnology and Environment, Faculty of Science, University Mohamed-V, Agdal-Rabat

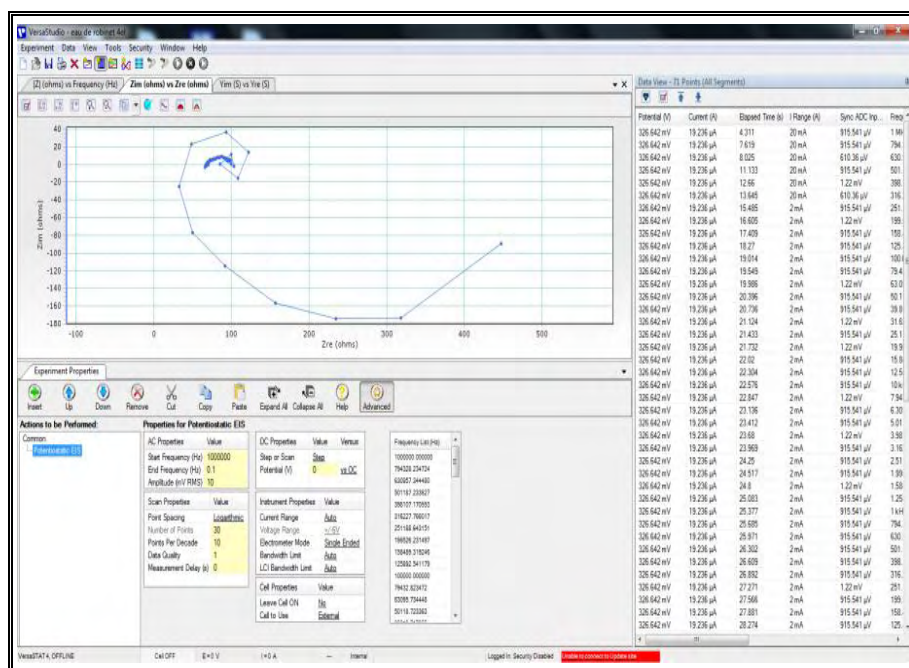


Fig. V.2: Interface de Versa Studio.

The host computer provides memory, data processing, input/output, and interface functionality. The VersaSTAT.4 electronically controls the measurement under the direction of the software and the parameter values entered from the host computer. The computer must be equipped with a USB port and the operating system must support the USB interface.

A) Potentiometric mode:

In this mode, the VersaSTAT.4 controls the potential of the work detection electrode about the reference electrode (Fig. V.3). The counter electrode is driven to the required potential (according to the ± 12 V conformity of the control amplifier) to establish the desired working potential. The range over which the potential of the working electrode can be monitored is ± 10 V.

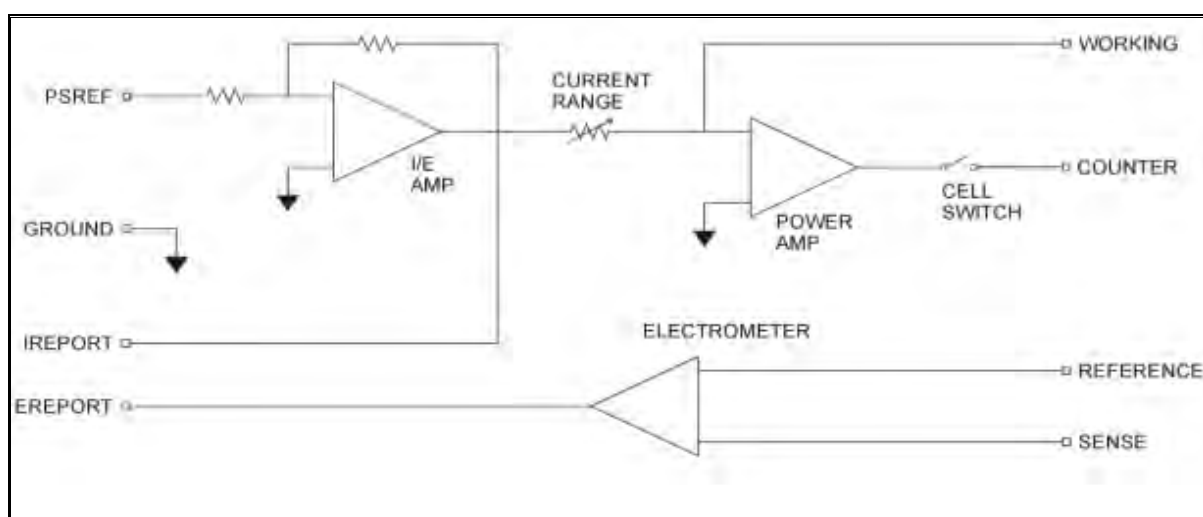


Fig. V.3: Block diagram of the potentiometer mode.

B) Galvanometric mode:

In galvanometric mode, the VersaSTAT.4 controls the current between the meter and the working electrodes at the specified fraction of the selected current range (up to the maximum of the current range, Fig. V.4). The counter electrode is driven to the required potential (by the ± 12 V conformity of the control amplifier) to establish the desired cell current. The reference electrode is not used in the control loop but is generally used to

measure the potential at a point on the electrochemical cell about the connection point of the working direction.

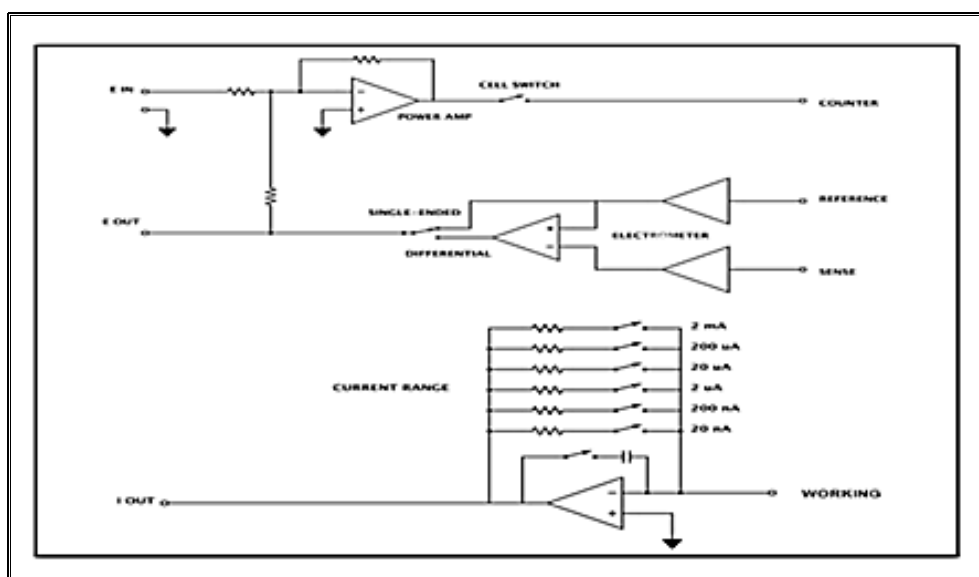


Fig. V.4: Block diagram of the galvanometer mode.

The opposite end of the cell cable (Fig. V.5) is colour-coded at the end, as follows:
Green - working electrode (WE). This wire connects to the electrode of interest at which the desired reactions will occur. The current (I) is measured through the WE.

- Red - Meter electrode wire (CE). This wire connects to the electrode in front of the WE and controls the output power of the VersaSTAT.4.
- Electrode wire Gray - Sensitive (SE). This usually connects to the working electrode (the combination is often referred to as the working direction) and is a component of the differential amplifier that measures/control the voltage between itself and the reference electrode.
- White - Reference electrode wire (RE). This connects to the reference electrode, a component of the differential amplifier that measures/control the voltage between itself and the sensing electrode.
- Black - Ground wire. The use of the ground wire depends on the application, but it is generally not used in most experiments. It can be used to provide a ground point to a Faraday shield for the experimental cell and is used in some open circuit experiments to form a Zero Resistance Ammeter (ZRA).

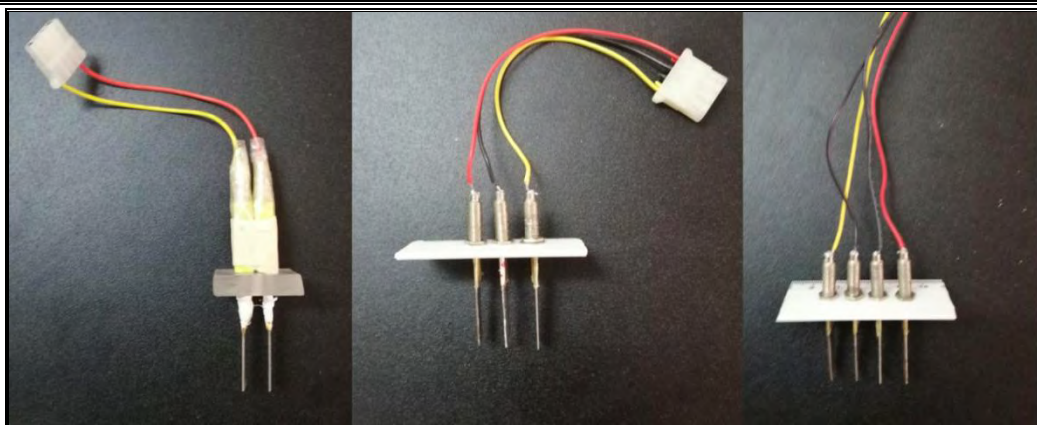


Fig. V.5: Electrochemical cells with 2, 3, and 4 electrodes.

The following descriptions and figures explain how to connect a 2-, 3-, or 4-terminal electrochemical cell to the terminals of the 4-cell VersaSTAT cable.

Batteries, capacitors, resistors, fuel cells, and some sensors are usually connected using a two-terminal connection (Figs. V.5&6). Also, the external dummy cell for VersaSTAT.4 is connected in this way. The cable connectors are designed to allow easy interconnection of the work/sensor and reference/meter cables.

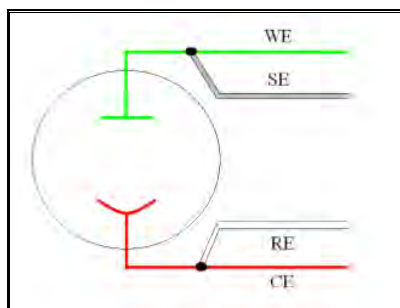


Fig. V.6: two-electrode configuration.

General aqueous electrochemistry, corrosion experiments, and most EIS experiments are connected using a three-terminal connection (Figs. V.5&7). The voltage in the working direction is monitored against a stable reference electrode placed near the working electrode.

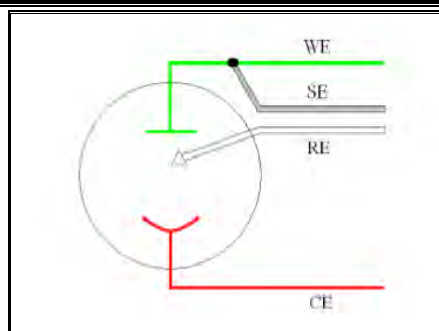


Fig. V.7: Three-electrode configuration.

Some applications require a connection to four terminals (Figs. V.5&8). In this case, the sensing electrode serves as a second reference electrode, useful for monitoring the potential between the reference and the sensing (for example, to monitor the potential across a membrane in an 'H'-cell configuration).

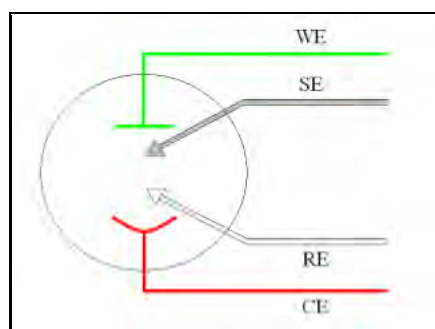


Fig. V.8: Four-electrode configuration.

The polarity of the potential on the counter-electrode will be opposite to the "applied potential". This is necessary to establish the correct polarity relationship between the working electrode and the reference electrode.

DICTIONARY

English - French -Arabic

DICTIONARY : English - French -Arabic

English	French	Arabic
Lacunar apatite	Apatite Lacunaire	الأباتيت المجوفة
Natural fluorapatite	Fluorapatite naturelle	الفلورأباتيت الطبيعي
Hydroxyapatite	Hydroxyapatite	هيدروكسي الأباتيت
Containment matrix of Metallic elements	Matrice de confinement des éléments métalliques	مصفوفة حصر العناصر المعدنية
Solid-State	Etat solide	الحالة الصلبة
Wet and dry routes	Voies sèche et humide	مسارات جافة ورطبة
Flotation of phosphate rock	Flottation de phosphate brut	تعويم الفوسفات الخام
Synthesis	Synthèse	تأليف: تركيب
Structural and vibrational characterizations	Caractérisations structurales et vibrationnelles	الخصائص الهيكلية والاهتزازية
Molecular structure	Structure moléculaire	تركيب الجزيئي
Optoelectronic properties	Propriétés optoélectroniques	الخصائص الكهروضوئية
X-ray diffraction	Diffraction des rayons X	حيود الأشعة السينية
Spectroscopie Raman analysis	Analyse par spectroscopie Raman	التحليل الطيفي رمان
Infrared spectrometer	Spectromètre infrarouge	مطياف الأشعة تحت الحمراء
Ultraviolet and visible spectroscopy	Spectroscopie ultraviolet et visible	مطيافية الأشعة فوق البنفسجية والمرئية
Crystalline structures	Structures cristallines	الهياكل البلورية
Substitutions	Substitutions	بدائل
The engineering aspects of materials structure, surfaces, and interfaces	Les aspects techniques de la structure, des surfaces et des interfaces des matériaux	الجوانب الهندسية لهيكل المواد والأسطح والواجهات
Calcined powder	Poudre calcinée	مسحوق مكلس
Bovine Serum Albumin	Albumine de Sérum Bovin	بروتين الزلال المصل البقري
Absorption processes	Processus d'absorption	عملية إدمصاص
Fast-kinetic process for the precipitated samples	Processus cinétique rapide pour les échantillons précipités	عملية الحركية السريعة للعينات المترسبة
Isotherms of Langmuirian shape	isothermes de forme langmuirien	متساوي الحرارة من شكل لانغموريان
Surface reactivity	Réactivité de surface	تفاعل السطح
Crystals size and specific surface area	Taille des cristaux et surface spécifique	حجم البلورات ومساحة السطح المحددة
Demineralization effects of phosphoric Acid	Effets de déminéralisation de l'acide phosphorique	آثار إزالة المعادن من حامض الفوسفوريك
Metallic impurities	Impuretés métalliques	الشوائب المعدنية
Purification cadmiferous liquids	Purification des liquides cadmifères	تنقية السوائل الكادمية
Decantation/ Filtration / Centrifugation	Décantation / Filtration / Centrifugation	ترسيب / ترشيح / طرد مركزي
Corrosion of carbon steel in hydrochloric solution	Corrosion de l'acier au carbone en solution chlorhydrique	تآكل الكربون الصلب في محلول هيدروكلوريك
Corrosion inhibitors	Inhibiteurs de corrosion	موانع للتآكل (مثبطات التآكل)
Hexagonal lattice and pattern of the crystal in space group $P6_3/m$	Réseau hexagonale et motif cristallin de groupe d'espace $P6_3/m$	شبكة الاتصال سداسية ونمط الكريستال لمجموعة الفضاء $P6_3/m$
Crystallographic sciences of materials	Sciences cristallographique des matériaux	علوم المواد البلورية
Hexagonal reticular distance	distance réticulaire hexagonal	مسافة بلورية سداسية