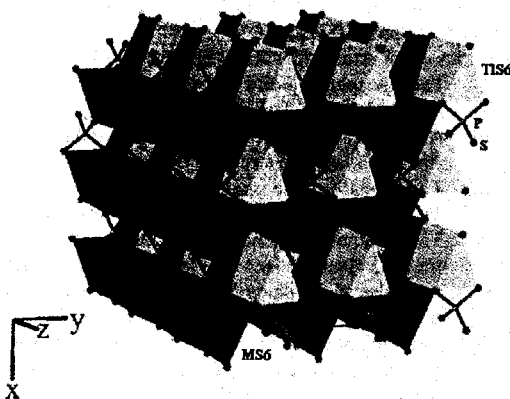


MS11 P01

Synthesis and crystal structure of the new thallium ortho-thiophosphates TIMPS₄ (M = Pb, Sr). M. El Azhari^I, I. Belkhal^I, Y. Wu^{II}, C. Näther^{II}, W. Bensch^{II} and W. Depmeier^{III} ^I *Laboratoire Matière Condensée et nanostructures, Faculté des Sciences et Techniques, Département des Sciences Chimiques, Université Cadi Ayyad, Marrakech Morocco.* ^{II} *Institut für Anorganische Chemie, Christian-Albrechts-Universität zu Kiel Germany.* ^{III} *Institut für Geowissenschaften / Kristallographie, Christian-Albrechts-Universität zu Kiel Germany.* E-Mail : elazhari@fstg-marrakech.ac.ma

Keywords : Layered compounds, Crystal structure, Inorganic synthesis.

The new thallium(I) ortho- thiophosphates TIMPS₄ (M = Sr, Pb) were prepared applying a stoichiometric mixture of P₂S₅, MS, S, and Tl₂S at high temperatures. The compound crystallizes in the orthorhombic space group Pnma and is isostructural with TlEuPS₄ [1]. It exhibits a layered structure. Each layer is composed of [(MS₆(TlS₆))_n]ⁿ⁻ zigzag chains, which consist of irregular trigonal prisms alternately centred by Tl and M atoms. The layers are stacked perpendicular to the crystallographic a axis and are held together by PS₄ tetrahedra [2]. The bond valence analysis method (BVM) is used to determine where is pointing the Pb 6s² lone pair.



Extended structure of TIMPS₄ projected along [001].

[1] : Carrillo-Cabrera, W.; Peters, K.; Schnering, H. G.; Menzel, F.; Brockner, W., *Z. anorg. Allg. Chem.* 621 (1995) 557-561.

[2] : I. Belkhal, M. El Azhari, W. Bensch and W. Depmeier; *Acta Cryst.* (2006). E62, i210-i212.

MS11 P02

Ion Exchange Properties of Aluminium Triphosphate Thomas P Marsh, Colin Slater, Adrian J. Wright, *School of Chemistry, University of Birmingham, Edgbaston, Birmingham, B15 2TT, United Kingdom.* E-mail: tpm214@bham.ac.uk

Keywords: Aluminium triphosphate, ion exchange, powder X-ray diffraction

The layered structures of zirconium phosphates (α -Zr(HPO₄)₂·H₂O and γ -Zr(PO₄)(H₂PO₄)₂·2H₂O) have received considerable amounts of interest due to their ion exchange properties [1-3]. Such ion exchange properties have potential application in ionic conductivity, e.g. Li⁺ conduction for battery applications where light materials

with high lithium content and mobility are desirable. Also there is considerable interest in materials that can absorb radioactive ions (e.g. Cs⁺, Sr²⁺) in the remediation of nuclear waste.

Our recent determination of the structure of aluminium triphosphate (AlH₂P₃O₁₀·2H₂O) [4] has shown that it possesses similar structural features to the zirconium phosphates but little research has yet been undertaken into its ion exchange properties.

Here we present our synthetic and structural studies on the ion exchange properties of AlH₂P₃O₁₀·2H₂O, focusing on Li, Na and Cs exchanges. These materials were studied by X-ray diffraction, TGA, flame photometry and ICP analysis. Structural characterisation has been undertaken by the analysis of powder x-ray diffraction data using the Rietveld method and the GSAS suite of programs [5].

[1] Clearfield A.; Troup J., *The Journal of Physical Chemistry*, 1970, 74, 314.

[2] Alberti G.; Constantino U.; Allulli S.; Massucci M.A., *J. Inorg. Nuc. Chem.*, 1975, 37, 1779

[3] Alberti G., *Accounts of Chemical Research*, 1978, 11, 163

[4] Rishi S.K.; Kariuki B.M.; Checker N.J.; Godber J.; Wright A.J., *Chem. Comm.*, 2006, 747

[5] Von Dreele R.B.; Larson A.C., *General Structure Analysis System*, Los Alamos National Laboratory: Los Alamos, NM, 1994

MS11 P03

New structural data on synthetic alluaudite-type phosphates M. Rondeux, F. Hatert and A.-M. Fransolet, *Laboratory of Mineralogy B.18, University of Liège, B-4000 Liège, Belgium.* E-mail: M.Rondeux@ulg.ac.be

Keywords: Alluaudite, phosphates, divalent cation

Alluaudites are Na-, Mn-, Fe-bearing phosphate minerals, which are known to occur as accessory minerals in granitic pegmatites. The crystal structure of natural alluaudite has been determined by Moore [1] in the C2/c space group; he derived the general structural formula, X(2)X(1)M(1)M(2)₂(PO₄)₃, with Z = 4. Recently, Hatert *et al.* [2] proposed a new structural formula for alluaudite, which takes into account the presence of new crystallographic sites in the channels of the structure: [A(2)A(2)']₂[A(1)A(1)A(1)A(1)']₂M(1)M(2)₂(PO₄)₃.

In natural alluaudites, divalent cations are localized in the A(1) (Mn, Ca), M(1) (Mn, Fe²⁺), and M(2) (Fe²⁺, Mn, Mg) crystallographic sites [3]. The exotic cations Cd and Co²⁺ have been inserted experimentally in the alluaudite-type compounds Na₂Cd₂M²⁺(PO₄)₃ (M²⁺ = Fe³⁺, Ga, Cr) [4] and M'Co²⁺₃(PO₄)(HPO₄)₂ (M' = Ag, Na) [5, 6].

Since alluaudite is a key mineral in the genetic evolution affecting the Fe-Mn-bearing phosphates minerals, it is of interest to investigate the crystal chemistry of the divalent cation in the alluaudite structure. With this purpose in mind, we decided to study the Na₂(Mn_{1-x}M²⁺_x)Fe²⁺Fe³⁺(PO₄)₃ (M²⁺ = Ca, Cd, Ni, Zn, Mg) solid solutions of alluaudite-type compounds.

The phosphates were synthesized hydrothermally between 400 and 600°C at 1 kbar, using horizontally arranged Tuttle-type cold-seal bombs. The powder X-ray diffraction patterns indicate that the Cd and Mg-bearing samples are constituted by pure alluaudite for x = 0 to 1, whereas the Ca-, Ni- and Zn-bearing compounds contain small amounts of impurities.

The Rietveld refinements of the powder X-ray diffraction patterns show that Cd occurs in the A(1), M(1) and M(2) sites of Na₂CdFe²⁺Fe³⁺(PO₄)₃, whereas Ca is localized in

the $M(1)$ site of $\text{Na}_2(\text{Mn}_{0.75}\text{Ca}_{0.25})\text{Fe}^{2+}\text{Fe}^{3+}(\text{PO}_4)_3$ and Mg in the $M(1)$ and $M(2)$ sites of $\text{Na}_2(\text{Mn}_{0.25}\text{Mg}_{0.75})\text{Fe}^{2+}\text{Fe}^{3+}(\text{PO}_4)_3$. The partially disordered distribution of Cd and Na between the $A(1)$ and $M(1)$ sites results from the similar ionic radii of Cd^{2+} (0.95 Å) and Na^+ (1.02 Å) [7]. The Rietveld refinements of the $\text{Na}_2(\text{Mn}_{1-x}\text{Mg}_x)\text{Fe}^{2+}\text{Fe}^{3+}(\text{PO}_4)_3$ alluaudite-type compounds are still in progress.

- [1] Moore P.B., *Am. Mineral*, 1971, 56, 1955.
 [2] Hatert F.; Keller P.; Lissner F.; Antenucci D.; Franolet A.-M., *Eur. J. Mineral*, 2000, 12, 847.
 [3] More P.B. & Ito J., *Min. Mag.*, 1979, 43, 227,
 [4] Antenucci D., *Unpublished Ph. D. Thesis, University of Liège*, 1992, 259 p.
 [5] Liu K.H. & Shih P.F., *Inorg. Chem*, 1994, 33, 3028,
 [6] Guesmi A. & Driss A., *Acta Cryst*, 2002, C58, i16. [7] Shannon R.D., *Acta Cryst*, 1976, A32, 751.

MS11 P04

Full structural study of the zeolitic zincophosphate $[\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3]_{0.4}[\text{H}_{0.2}\text{ZnPO}_4]$ Laura Rocas^a, Santiago García-Granda^a, Sergei Khainakov^b, Olena Khainakova^b, José R. García^b, ^a*Departamento de Química Física y Analítica and* ^b*Departamento de Química Orgánica e Inorgánica, Universidad de Oviedo, Spain.*
 E-mail: lrf@fq.uniovi.es

Keywords: zincophosphates, hydrothermal synthesis, organic template

The large number of open-framework metal phosphates which have been recently synthesized and studied is a consequence of their potential applications in the areas of catalysis, sorption and separation processes. The zinc phosphates constitute one of the largest families of open-framework materials that have been studied during the past few years. This is mainly due to their similarity with the zeolites: the total charge of the divalent zinc phosphates is the same as the aluminosilicate zeolites. In fact, several zinc phosphates possess zeolitic structures. Hydrothermal methods have been extensively used in the synthesis of this kind of compounds, employing organic amines as templates which act as structure-directing or space-filling agents. In many cases, the location and definite identification of those extra-framework organic species is problematical; their high degree of disorder makes impossible to study the role of N-H...O bonds in establishing or stabilizing the structure. We report here the hydrothermal synthesis and full structural determination of an organically templated zincophosphate $[\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3]_{0.4}[\text{H}_{0.2}\text{ZnPO}_4]$. The structure of this compound, which has the same tetrahedral connectivity than that in the zeolite edingtonite family, was reported by Harrison *et al.* six years ago. Nevertheless, the position of the organic template could then not be determined. In this work a complete study of the framework-template interactions is analyzed.

- [1] W.T.A. Harrison. *Acta Cryst.* (2001). E57, m248.

MS11 P05

Investigation of the micro/nanostructure and the structure defect of sedimentary phosphates by electron microscopy Fatima Zahra Boujral^{a,b}, Bouchra Sghir^b, Said Ossama^b, Rajaâ Cherkaoui El Moursli^b, ^a*Department of Physics, Faculty of Sciences and Technologies, Beni Mellal, Morocco.* ^b*Laboratory of Nuclear Physic, Faculty of Sciences, Rabat, Morocco.*

E-mail: boujral@yahoo.fr

Keywords: Phosphates, Microstructure, structure defect

The Moroccan sedimentary phosphates are essentially constituted by apatite, mineral which finds application in all domains; like medicine, nuclear wastes, biology and geology. These phosphates contain some ppm of uranium undergoes spontaneous fission since its geological formation. This spontaneous fission causes the (irradiation) defects in the structure, by recoil of the fission products.

This work focuses on the exam of the micro/nanostructure, the local structure and the irradiated defect in the structure of several grains of phosphate by electron microscopy observations. Several STEM imaging and X cartographies are obtained, the Scanning Electron Microscope (SEM) shows the internal morphology of the grains and its qualitative analysis, where as, the Transmission Electron Microscope (TEM) gives the quantitative analysis and the structure of the material studied here. This electronic microscopy offers the possibility to observe the sample during its analysis; it was possible to put in evidence the heterogeneities in the grains and to characterize all the precipitate zones seeming to be homogeneous.

On the other hand, the SEM was also served to study the irradiation defects especially the fission tracks and to exam the effect of heat treatment at various temperature between 100 and 900°C, on the structure and the micro/nanostructure of apatite.

The results of this study are summarized as follows:

- 1- The phosphate grains show various concentric zones: clear and dark one
- 2- All the grains studied here are the composition and the crystalline structure of apatite
- 3- The crystallite size is about
- 4- The grains present a micro and nanoporosity.
- 5- The irradiation damage, especially the fission track, is clearly observed by SEM, but confusion can take place since the fission track and the nanoporosity are the same form and size.
- 6- The optical microscope is used for identification of the fission tracks and the counting of their density
- 7- The heat treatment of apatite grains at various temperature (between 100 and 900°C) for about 2 hours leads to an improvement of the apatite crystalline structure and to the disappearance of irradiation damage (fission tracks), especially at 600°C.
- 8- The X ray diffraction analyses confirm some of these results, especially these concerning the structure and the crystallite sizes.

- [1] F.Z. Boujral, R. Cherkaoui El Moursli, A; Chouak, B.L.S.F.M.C, Vol. 13, n° 3, p. 62, 2001.

- [2] F.Z. Boujral, J. Carpena, R. Cherkaoui El Moursli, *Radiation Physics and Chemistry*, Vol. 61, p. 645-647, 2001.

- [3] F.Z. Boujral, Thèse de Doctorat d'Etat es-sciences Physique, Faculté des Sciences de Rabat/Maroc, 07 novembre 2001