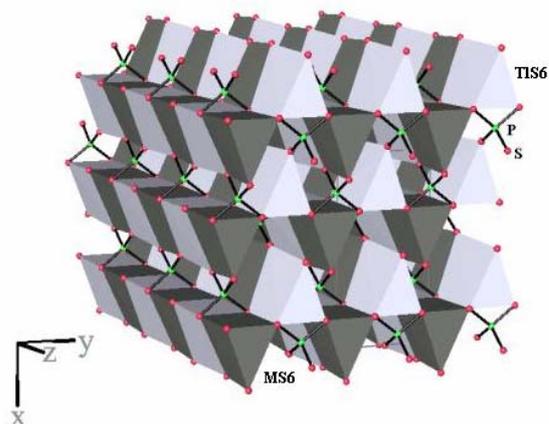


**MS11 P01**

**Synthesis and crystal structure of the new thallium ortho-thiophosphates TIMPS<sub>4</sub> (M = Pb, Sr).** M. El Azhari<sup>I</sup>, I. Belkhal<sup>I</sup>, Y. Wu<sup>II</sup>, C. Näther<sup>II</sup>, W. Bensch<sup>II</sup> and W. Depmeier<sup>III</sup> <sup>I</sup> *Laboratoire Matière Condensée et nanostructures, Faculté des Sciences et Techniques, Département des Sciences Chimiques, Université Cadi Ayyad, Marrakech Morocco.* <sup>II</sup> *Institut für Anorganische Chemie, Christian-Albrechts-Universität zu Kiel Germany.* <sup>III</sup> *Institut für Geowissenschaften / Kristallographie, Christian-Albrechts-Universität zu Kiel Germany.* E-Mail : [elazhari@fstg-marrakech.ac.ma](mailto:elazhari@fstg-marrakech.ac.ma)

**Keywords :** Layered compounds, Crystal structure, Inorganic synthesis.

The new thallium(I) ortho- thiophosphates TIMPS<sub>4</sub> (M = Sr, Pb) were prepared applying a stoichiometric mixture of P<sub>2</sub>S<sub>5</sub>, MS, S, and Tl<sub>2</sub>S at high temperatures. The compound crystallizes in the orthorhombic space group Pnma and is isostructural with TlEuPS<sub>4</sub> [1]. It exhibits a layered structure. Each layer is composed of [(MS<sub>6</sub>(TlS<sub>6</sub>)<sub>n</sub>)]<sup>n+</sup> 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 PS<sub>4</sub> tetrahedra [2]. The bond valence analysis method (BVM) is used to determine where is pointing the Pb 6s<sup>2</sup> lone pair.



Extended structure of TIMPS<sub>4</sub> projected along [001].

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**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](mailto:tpm214@bham.ac.uk)

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

The layered structures of zirconium phosphates ( $\alpha$ -Zr(HPO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O and  $\gamma$ -Zr(PO<sub>4</sub>)(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O) 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<sup>+</sup> 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<sup>+</sup>, Sr<sup>2+</sup>) in the remediation of nuclear waste.

Our recent determination of the structure of aluminium triphosphate (AlH<sub>2</sub>P<sub>3</sub>O<sub>10</sub>·2H<sub>2</sub>O) [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 AlH<sub>2</sub>P<sub>3</sub>O<sub>10</sub>·2H<sub>2</sub>O, 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].

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**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](mailto: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)<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>, 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)']<sub>2</sub>[A(1)A(1)'A(1)''<sub>2</sub>]M(1)M(2)<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>.

In natural alluaudites, divalent cations are localized in the A(1) (Mn, Ca), M(1) (Mn, Fe<sup>2+</sup>), and M(2) (Fe<sup>2+</sup>, Mn, Mg) crystallographic sites [3]. The exotic cations Cd and Co<sup>2+</sup> have been inserted experimentally in the alluaudite-type compounds Na<sub>2</sub>CdM<sup>2+</sup>(PO<sub>4</sub>)<sub>3</sub> (M<sup>2+</sup> = Fe<sup>3+</sup>, Ga, Cr) [4] and M<sup>r</sup>Co<sup>2+</sup><sub>3</sub>(PO<sub>4</sub>)(HPO<sub>4</sub>)<sub>2</sub> (M<sup>r</sup> = 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 Na<sub>2</sub>(Mn<sub>1-x</sub>M<sup>2+</sup><sub>x</sub>)Fe<sup>2+</sup>Fe<sup>3+</sup>(PO<sub>4</sub>)<sub>3</sub> (M<sup>2+</sup> = 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 Na<sub>2</sub>CdFe<sup>2+</sup>Fe<sup>3+</sup>(PO<sub>4</sub>)<sub>3</sub>, whereas Ca is localized in