

six sandwiches per unit cell stacked in rhombohedral symmetry [1]. Intercalated Cu atoms and additional M atoms are incorporated on octahedral and tetrahedral sites in the Van der Waals gaps between  $MS_2$  layers. Here we present the evolution of the complex superstructures of selected intercalated compounds at different temperatures between 14K and 400K using single-crystal X-ray diffraction data. The interest in these compounds is the phase transitions related to ordering of the intercalated atoms and charge-density wave transitions at different temperatures.

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**Keywords:** X-ray\_diffraction, dichalcogenides, superstructure

## MS67.P04

*Acta Cryst.* (2011) **A67**, C648

### Thermal studies of ammonium-cobalt-nickel phosphates, $NH_4[Co_xNi_{1-x}PO_4] \cdot H_2O$

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Ammonium-metal(II) phosphates of general formula  $NH_4M^{II}PO_4 \cdot H_2O$  were first described in 1864 by Debray [1]. These compounds have been used as pigments for protective paint finishes on metal and as fire retardants in paints and plastics, and they can be also applied as catalyst, fertilizers and magnetic devices.

The first crystal structure for a member of this family,  $NH_4CoPO_4 \cdot H_2O$ , was determined in 1968 by Tranqui et al. [2] using powder X-ray diffraction. In 1995, using neutron powder diffraction techniques, Carling *et al.* [3] determined the crystal structures of  $ND_4M^{II}PO_4 \cdot D_2O$  ( $M^{II} = Mn, Fe, Co, Ni$ ) compounds. In 1999, Yakubovich *et al.* [4] have contributed with the first structure, for  $NH_4CoPO_4 \cdot H_2O$ , obtained by single-crystal (X-ray diffraction) data. Apparently, all these layered compounds crystallize in the orthorhombic space group  $Pmn2_1$ .

In a previous work, we introduced a new family of ammonium-cobalt-nickel phosphates,  $NH_4[Co_{1-x}Ni_xPO_4] \cdot H_2O$  ( $x = 0.00, 0.34, 0.60, 0.71, 1.00$ ) [5]. In this series, although all crystals are orthorhombic, the space group changes as a function of the composition. In this communication, we report thermal studies for all synthesized compounds within this family. These thermal studies were focused in the structural changes, showing different thermal behavior as a function of the composition.

Acknowledgments: This work was supported by Spanish MICINN (Projects MAT2006-01997, MAT2010-15095 and 'Factoría de Cristalización' Consolider Ingenio 2010) and FEDER.

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**Keywords:** phosphate, cobalt, nickel

## MS67.P05

*Acta Cryst.* (2011) **A67**, C648

### Solvent-dependent 2D-coordination networks of CuI and bridging triazolopyrimidines

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Copper(I) iodide has been used as the inorganic component in the building of novel coordination polymers with diverse structural motifs. These motifs could be further connected by *N*-heterocyclic linkers to form more complex  $[Cu_nI_n]$ -based frameworks. Preparation of such compounds has been reported to be affected by many factors such as CuI-to-ligand ratio, flexibility and rigidity of the ligands, solvents and temperature [1,2].

In this communication, we describe the syntheses and the crystal structures of two new 2D-polymers, both obtained from the reaction between CuI and the multidentate ligand 1,2,4-triazolo[1,5-a]pyrimidine (tp):  $[Cu_2(\mu\text{-tp})(CH_3CN)(\mu\text{-I})(\mu_3\text{-I})_n]$  (**1**) and  $[Cu_2(\mu\text{-tp})(\mu_3\text{-I})_2]_n$  (**2**). Structural differences between both compounds seem to be due to a solvent influence, being acetonitrile for **1** and water for **2**.

In compound **1**, the triazolopyrimidine derivative acts as bridging ligand via N1 and N3 between chair-like  $[Cu_4I_4]$  units, resulting Cu...Cu distances from 3.04 to 6.02 Å. Acetonitrile molecules are also coordinated to metal centres. Strong stacking forces involving triazole and pyrimidine rings of tp ligands contribute to the stabilization of the structure. In compound **2**, tp moieties are placed at both sides of a  $[Cu_nI_n]$  half-folded layer, displaying also a bridging mode but, in this case, via its atoms N3 and N4 (see Figure 1). In both structures, Cu(I) ions show slightly distorted tetrahedral coordination geometries.

These are the first examples of Cu(I) compounds based on the nucleobase-analog ligand tp.

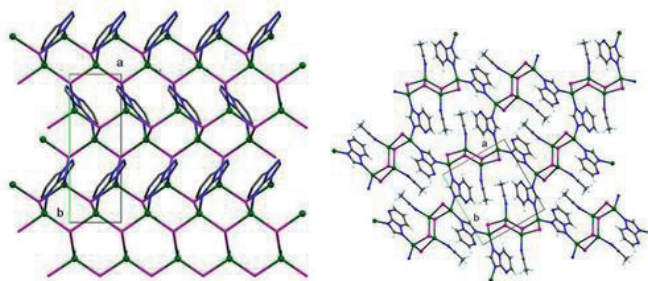


Figure 1. View of the 2D-networks of  $[Cu_2(\mu\text{tp})(CH_3)(\mu\text{I})(\mu_3\text{-I})_n]$  (**1**) (on the left) and  $[Cu_2(\mu\text{tp})(\mu_3\text{I})_2]_n$  (**2**) (on the right).

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**Keywords:** triazolopyrimidine, iodide, copper(I)

## MS67.P06

*Acta Cryst.* (2011) **A67**, C648-C649

### Novel perovskite-like compound with crystallographic shear structure in the Pb-Ba-Fe-Sn-O system

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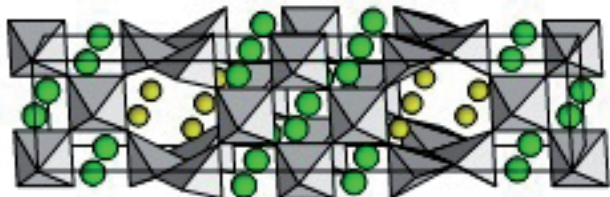
Perovskite structure is able to accommodate a wide range of cations of different chemical nature and oxidation state and is flexible for various structure transformations and changes in stoichiometry. Combining the perovskite structure with different topologically suitable structure blocks would create perovskite-based homologues series.

The novel  $A_nB_nO_{3n-2}$  perovskite-based homologues series was studied recently [1]. Presence of  $Pb^{2+}$  as A-cation and  $Fe^{3+}$  as B-cation allows coexistence of magnetic ordering and stereoactive lone electron pair.

A novel compound  $Pb_3Ba_2Fe_4SnO_{13}$  representing the  $n = 5$  member of the  $A_nB_nO_{3n-2}$  homologues series was synthesized in air at 800-980 °C. It was sintered for 80 hours with intermediate regrinding.

The crystal structure of this compound was solved using X-ray and neutron powder diffraction, electron diffraction and high-resolution transmission electron microscopy ( $a = 5.7768(8)$  Å,  $b = 4.0229(6)$  Å,  $c = 26.877(3)$  Å, S.G. *Ammm*). Crystal structure of  $Pb_3Ba_2Fe_4SnO_{13}$  can be derived from perovskite structure by slicing it with periodically spaced  $\frac{1}{2}[110]_p(101)_p$  crystallographic shear (CS) planes. The perovskite-like blocks are separated at the CS planes by chains of five-fold  $FeO_5$  polyhedra, which form pseudo-hexagonal tunnels. The tunnels are occupied by the  $Pb^{2+}$  cations, which have sufficient space to accommodate their lone electron pairs. Cation positions in the perovskite blocks are randomly occupied by  $Pb^{2+}/Ba^{2+}$  for the "A-positions" and  $Fe^{3+}/Sn^{4+}$  for the "B-positions" with a preference of  $Sn^{4+}$  to be located at the middle of the perovskite-like blocks.

Mössbauer spectroscopy revealed that the Fe oxidation state is "+3" with equal distribution of the Fe cations among the 6-fold and 5-fold coordinated positions, that confirms the refined structure.



[1] A. M. Abakumov et al., *Inorg. Chem.* 49, 9508 (2010).

**Keywords:** Perovskite, Iron, Lead

### MS67.P07

*Acta Cryst.* (2011) A67, C649

#### $Sn_{12}In_{19}(Se, S)_{41}$ and the $M_{15+N}S_{20+N}$ sliding series of complex In sulfides

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$Sn_{12}In_{19}(Se, S)_{41}$  was synthesized in a dry phase system Fe-Sn-Sb-In-S-Se at 600°C. Its crystal structure is monoclinic with  $a = 56.23(2)$ ,  $b = 3.920(1)$ ,  $c = 15.888(5)$  Å,  $\beta = 102.770(6)^\circ$ , space group  $C2/m$ , and  $Z = 2$ .  $R_1$  is 6.3% for 2339 unique reflections with  $F_o > 4\sigma(F_o)$ . There are 31 unique sites of Sn and In and 41 mixed sites of Se and S. It is a composite layer structure with two kinds of layers in regular alternation; together they underwent step-like modulation.

$Sn_{12}In_{19}(Se, S)_{41}$  is a member of a  $M_{15+N}S_{20+N}$  sliding series of closely related composite layer structures with alternating, periodically sheared pseudo-hexagonal and pseudotetragonal layers. The pseudotetragonal layers of this series are three atomic planes thick with two octahedra of In in the centre of "oval rods", surrounded by coordination prisms of Sn/Pb. All structures of a 'sliding series' consist of slabs with the same, fixed step-like configurations which include (parts of) both layer types. These slabs slide past one another, opening more and more an

additional space between the steps of two adjacent slabs. This space did not exist in the starting member of the series. Additional coordination polyhedra fill the opening and create chemical and structural differences between the consecutive members of the series. In the given series, the described sliding results in the pseudo-hexagonal layers, which are doubled for the length of one, two, etc. octahedra. The initial member has octahedron layers simply sheared, without overlap. A member with one-octahedron-long gap instead of overlap can be defined as well.

If the length of a not sheared interval of the pseudo-hexagonal layer is A, and that of the overlap is B, these layers can be described as A/B and, within a given series, by  $N = B$ . In the studied structure, the pseudo-hexagonal layers 7/2 alternate with 4/-1. The crystal structure of  $Sn_6In_{10}S_{21}$  [1] contains pseudo-hexagonal layers 7/2 alternating with 5/0 ( $N = 0, 2, 0, 2 \dots$ ).  $Bi_4In_8Pb_{16}S_{19}$  [2] and  $In_6^{3+}Sn_4^{4+}S_{19}$  [3] have pseudo-hexagonal layers 4/-1 ( $N = -1$ , whereas the present structure is  $N = -1, 2, -1, 2 \dots$ ).  $In_{10}Pb_6S_{21}$  [4] has 6/1, whereas the phase  $In_{11}Sn_{5.5}S_{22}$  [5] contains 7/2. This are members  $N = 1$  and  $N = 2$ , respectively. This scheme can continue with hypothetical members  $N = 3$  and, finally, up to  $N = 5$  with a complete doubling of the octahedral layer. The  $M_{15+N}S_{20+N}$  (or  $Me^{2+}_{5+N}Me^{3+}_{10}S_{20+N}$ ) sliding series is the principal family of complex In-based sulphosalts. A parallel series with less frequently sheared layers is known only as the  $In_{13.34}Pb_6S_{26} - In_{14}Sn_5S_{26}$  pair.

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**Keywords:** Sn-In sulfides, Pb-In sulfides, sliding series

### MS67.P08

*Acta Cryst.* (2011) A67, C649-C650

#### Ordering in lead-antimony oxide halides upon variation of chemical composition.

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Multinary oxyhalides of lead and bismuth form two structurally related families of layered fluorites (so-called Sillén phases), not in the last due to similarity of size and electronic structures of  $Pb^{2+}$  and  $Bi^{3+}$  ( $6s^2$ ). The principal difference lies in that Bi compounds exhibit mostly mixed-layer structures and  $Bi^{3+}$  can be substituted by a rather few ions while lead compounds demonstrate highly-ordered superstructures of just three or four structure types with partial substitution of  $Pb^{2+}$  by a much wider set of substituents, often with their own kind of environment. Most of the latter come from natural (mineral) sources.

The structural information on compounds  $[(Pb,Sb)_2(O,OH,F)_2][X]$  ( $X = Cl, Br, \text{ or } I$ ) adopting the simple  $Nd_2O_2Te$  (*anti*- $ThCr_2Si_2$ ) structure (or its ordered versions) remains contradictory while they are known for years.  $PbSbO_2Cl$  (known as a mineral nadorite) adopts an orthorhombic cation-ordered structure but a small stoichiometry shift to  $PbSbO_{2-x}Cl_{1-2x}$  is claimed to kill the ordering. The oxybromide  $PbSbO_2Br$  probably exists in both forms. In addition, there are oxyhydroxide minerals like  $Pb_{1.5}Sb_{0.5}O_{1.5}(OH)_{0.5}Cl$  where there is probably neither Pb/Sb nor O/OH ordering. In yet another group,  $Pb_2OFX$ ,  $O^{2-}$  and  $F^-$  are perfectly ordered. In the current study, we attempted to study the series more thoroughly, to find out any relationships between composition, synthesis conditions, and absence or existence of cation/anion ordering among lead – antimony oxo/fluoro-halides.

Our results have shown that ordered structure of  $PbSbO_2Br$  exists below 500°C while  $PbSbO_2I$  is always disordered. A simple stoichiometry shift to  $PbSbO_{2-x}X_{1-2x}$  does not produce the disordered