

## MS67.P01

*Acta Cryst.* (2011) A67, C647**Veblenite: a new ti-silicate related to hoh structures**

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Veblenite, ideally  $\text{KNa}(\text{Fe}^{2+}_5\text{Fe}^{3+}_4\text{Mn}_7)\text{Nb}_4(\text{Si}_2\text{O}_7)_2(\text{Si}_8\text{O}_{22})_2\text{O}_6(\text{OH})_{10}(\text{H}_2\text{O})_3$ , triclinic,  $P\bar{1}$ ,  $a$  5.3761(3),  $b$  27.5062(11),  $c$  18.6972(9) Å,  $\alpha$  140.301(3),  $\beta$  93.033(3),  $\gamma$  95.664(3)°,  $V$  1720.96(14) Å<sup>3</sup>, has no natural or synthetic analogues. It is a new mineral occurring at Ten Mile Lake, Seal Lake area, Labrador, Newfoundland, Canada, as red brown single laths and fibres included in feldspar. In the crystal structure of veblenite, M octahedra share common edges to form a wavy octahedral sheet parallel to (001).  $\text{SiO}_4$  tetrahedra share corners to form  $\text{Si}_2\text{O}_7$  groups and  $\text{Si}_8\text{O}_{22}$  ribbons. This is the first occurrence of an eight-membered Si-O ribbon in a mineral crystal structure. The Nb-dominant D octahedra,  $\text{Si}_2\text{O}_7$  groups and  $\text{Si}_8\text{O}_{22}$  ribbons share common vertices to form a heteropolyhedral (H) sheet. Two H sheets and an O sheet constitute an HOH block. Along [001], HOH blocks connect via common vertices of D octahedra and cations at the  $A(1,2)$  and  $B$  interstitial sites. In the intermediate space between two adjacent HOH blocks, two [100] channels of different size can be identified. A narrow channel of the width of an  $\text{Si}_2\text{O}_7$  group contains the  $A(1)$  site mainly occupied by K. A large channel has the width of four  $\text{Si}_2\text{O}_7$  groups ( $\text{Si}_8\text{O}_{22}$  ribbon) and contains  $A(2)$  sites partly occupied by K and  $\text{H}_2\text{O}$  groups.

The crystal structure of veblenite is related to several HOH structures where the O sheet is ideally composed of  $\text{Fe}^{2+}$  octahedra, such as jinshajiangite [1], niobophyllite [2] (astrophyllite group) and nafertisite [3]. Veblenite differs from those structures in the topology and chemistry of the H sheet. In jinshajiangite, the H sheet consists of ( $\text{Si}_2\text{O}_7$ ) groups and Ti-dominant octahedra. In niobophyllite, the H sheet is composed of ( $\text{Si}_4\text{O}_{12}$ ) astrophyllite ribbons [a double ribbon of ( $\text{Si}_2\text{O}_7$ ) groups] and Nb-dominant octahedra. In nafertisite, the H sheet is composed of ( $\text{Si}_6\text{O}_{17}$ ) ribbons [a triple ribbon of ( $\text{Si}_2\text{O}_7$ ) groups] and Ti-dominant octahedra. In veblenite, the H sheet is composed of ( $\text{Si}_2\text{O}_7$ ) groups (as in jinshajiangite), ( $\text{Si}_8\text{O}_{22}$ ) ribbons [a new type of a quadruple ribbon of ( $\text{Si}_2\text{O}_7$ ) groups which can be built of two astrophyllite ribbons] and Nb-dominant octahedra. The above reported setting is obtained from the reduced cell  $a$  5.3761(3),  $b$  17.7419(10),  $c$  18.6972(11) Å,  $\alpha$  97.991(1),  $\beta$  93.032(2),  $\gamma$  102.050(1)° thorough the transformation (1,0,0|0,1| $\bar{0}$ ,0,1). The chosen setting with a large  $\alpha$  is preferred in order to compare the structure topology of veblenite to those of jinshajiangite and niobophyllite.

[1] E. Sokolova, F. Cámara, F.C. Hawthorne, Y. Abdu, *European Journal of Mineralogy*, **2009**, *21*, 871-883. [2] F. Cámara, E. Sokolova, Y. Abdu, F.C. Hawthorne, *Canadian Mineralogist*, **2010**, *48*, 1-16. [3] G. Ferraris, G. Ivaldi, A.P. Khomyakov, S.V. Soboleva, E. Belluso, and A. Pavese, *European Journal of Mineralogy*, **1996**, *8*, 241-249.

**Keywords:** structure, layered, silicate

## MS67.P02

*Acta Cryst.* (2011) A67, C647**Hybrid inorganic-organic layered crystals constructed by oxide clusters and surfactant**

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Inorganic-organic hybrid layered crystals were successfully synthesized by using polyoxometalate anionic clusters and cationic surfactant. Such ionic crystals are a rare series of materials, and both inorganic and organic components can be flexibly selected to construct functional inorganic-organic hybrids.

Octamolybdate (Mo8) anions formed single crystals together with hexadecylpyridinium (C16py), and the crystal structures were revealed by X-ray diffraction analyses [1]. The crystals exhibited the alternate stacking composed of Mo8 layers and surfactant layers, and the Mo8 layers were sandwiched by the bilayer arrangements of the surfactant cations. The Mo8 anion has several isomers such as alpha-Mo8 or beta-Mo8, and the layered distance depended on the isomer structures of Mo8 at a variety from 1.86 to 3.75 nm.

The crystals of C16py-alpha-Mo8 and C16py-beta-Mo8 had different arrangement of Mo8 inorganic layers: each alpha-Mo8 was isolated by the inserted C16py cations, while beta-Mo8 formed one-dimensional infinite chain with sodium cations. In addition, there were two different types of crystals for C16py-beta-Mo8. One had a triclinic unit cell containing monolayers of the Mo8-chain. The other had a monoclinic unit cell with a long cell dimension ( $b = 7.5011$  nm), which contained the bilayers of the Mo8 chain. The layered periodicity of 3.75 nm (half of the  $b$  axis length) was the largest value for polyoxometalate-surfactant hybrid crystals previously reported. Such structural variety could contribute to the construction of functional inorganic-organic hybrid materials.

[1] T. Ito, K. Mikurube, Y. Abe, T. Koroki, M. Saito, J. Iijima, H. Naruke, T. Ozeki, *Chem. Lett.* **2010**, *39*, 1323-1325.

**Keywords:** layered, polyanion, surfactant

## MS67.P03

*Acta Cryst.* (2011) A67, C647-C648**Intercalated transition-metal dichalcogenides at different temperatures**

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Transition metal dichalcogenides ( $\text{MX}_2$ , M=transition metal and X=chalcogen) are of considerable interest due to layer-type structural properties. The transition metal has trigonal prismatic or octahedral coordination by six chalcogen atoms which is further connected to neighbouring coordination spheres to form a layered structure. Interaction between atoms within a slab are mainly covalent. Slab to slab interaction are weak, and in general are of the type of van der Waals interaction. Due to this weak interlayer interaction several different slab stacking sequences (crystal polytype) are possible. Intercalation compounds of transition metal dichalcogenides can be formed with a wide range of guest atoms or molecules including alkali metals and transition metals. The intercalated guest atom may be incorporated on octahedral or tetrahedral sites surrounded by chalcogen atoms in the van der Waals gaps. Intercalation of Cu atom in  $6R\text{-Cu}_x\text{M}_y\text{S}_2$  shows

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<sub>2</sub> 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.

[1] B. Harbrecht, G.Z. Kreiner, *anorg. allg. Chem.* **1989**, 572, 47-54.

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

## MS67.P04

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### Thermal studies of ammonium-cobalt-nickel phosphates, NH<sub>4</sub>[Co<sub>x</sub>Ni<sub>1-x</sub>PO<sub>4</sub>]·H<sub>2</sub>O

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Ammonium-metal(II) phosphates of general formula NH<sub>4</sub>M<sup>II</sup>PO<sub>4</sub>·H<sub>2</sub>O 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<sub>4</sub>CoPO<sub>4</sub>·H<sub>2</sub>O, 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<sub>4</sub>M<sup>II</sup>PO<sub>4</sub>·D<sub>2</sub>O (M<sup>II</sup> = Mn, Fe, Co, Ni) compounds. In 1999, Yakubovich *et al.* [4] have contributed with the first structure, for NH<sub>4</sub>CoPO<sub>4</sub>·H<sub>2</sub>O, obtained by single-crystal (X-ray diffraction) data. Apparently, all these layered compounds crystallize in the orthorhombic space group *Pmn*2<sub>1</sub>.

In a previous work, we introduced a new family of ammonium-cobalt-nickel phosphates, NH<sub>4</sub>[Co<sub>1-x</sub>Ni<sub>x</sub>PO<sub>4</sub>]·H<sub>2</sub>O (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.

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### 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<sub>n</sub>I<sub>n</sub>]-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<sub>2</sub>(μ-tp)(CH<sub>3</sub>CN)(μ-I)(μ<sub>3</sub>-I)]<sub>n</sub> (**1**) and [Cu<sub>2</sub>(μ-tp)(μ<sub>3</sub>-I)<sub>2</sub>]<sub>n</sub> (**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<sub>4</sub>I<sub>4</sub>] 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<sub>n</sub>I<sub>n</sub>] 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.

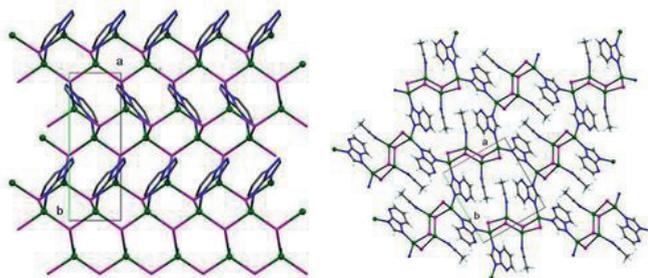


Figure 1. View of the 2D-networks of [Cu<sub>2</sub>(μtp)(CH<sub>3</sub>CN)(μI)(μ<sub>3</sub>-I)]<sub>n</sub> (**1**) (on the left) and [Cu<sub>2</sub>(μtp)(μ<sub>3</sub>-I)<sub>2</sub>]<sub>n</sub> (**2**) (on the right).

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

## MS67.P06

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

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