

determination was successful, providing important information on the characteristics of these materials.

In particular, the structure of ECS-2 (with R = phenylene) was solved by direct methods starting from high resolution synchrotron powder diffraction data [1]. It consists of a regular stacking of alternating inorganic and organic layers and can be classified as a clathrasil-like structure since the arrangement of the phenylene rings in the organic layers produces large cages not open to the exterior but able to clathrate ethanol molecules.

Still more interesting is the structure of ECS-3 (with R = phenylene as ECS-2, but synthesized in the presence of a mixture of Na and K ions), which was determined starting from electron diffraction data collected on sub-micrometer single crystals with the new Automated Diffraction Tomography (ADT) technique [2], [3]. The structure consists again in a regular stacking of inorganic and organic layers but, differently from ECS-2, the relative arrangement of the phenylene rings generates an open porosity, classifying this material as the first microporous aluminosilica-based hybrid organic-inorganic material [4].

For other ECS materials recently synthesized the structure determination is in progress and the results will be illustrated and discussed to provide a first overview of this interesting class of materials.

[1] G. Bellussi, A. Carati, E. Di Paola, R. Millini, W.O. Parker, Jr, C. Rizzo, S. Zanardi, *Microporous Mesoporous Mater.* **2008**, *113*, 252-260. [2] U. Kolb, T. Gorelik, C. Kübel, M.T. Otten, D. Hubert, *Ultramicroscopy* **2007**, *107*, 507-513. [3] U. Kolb, T. Gorelik, M.T. Otten, *Ultramicroscopy* **2008**, *108*, 763-772. [4] S. Zanardi, E. Montanari, E. Di Paola, R. Millini, G. Bellussi, A. Carati, C. Rizzo, M. Gemmi, E. Mugnaioli, U. Kolb, in *Proceedings of 16th International Zeolite Conference joint with the 7th International Mesostructures Materials Symposium*, Sorrento (Italy), **2010**, 1708-1709.

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## MS.67.2

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### Revision of the crystal chemistry of the astrophyllite group

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Until recently, there have been known seven structurally characterized astrophyllite-group minerals: astrophyllite, magnesiumastrophyllite, nalivkinite, niobophyllite, kupletskite, niobokupletskite, and kupletskite-(Cs), with the general formula  $A_2BC_7D_2(T_4O_{12})_2O_2(OH)_4X_{0-1}$ , where A = <sup>[5,12,13]</sup>(dominant K, Cs, Li, minor Rb, Pb, Na, Ca and □); B = <sup>[10]</sup>(dominant Na, minor Ca); C = <sup>[6]</sup>(dominant Fe<sup>2+</sup>, Mn<sup>2+</sup>, minor Fe<sup>3+</sup>, Na, Mg, Ca, Li, Zr and Zn); D = <sup>[5,6]</sup>(dominant Ti and Nb, minor Zr, Sn, Ta and Mg); T = <sup>[4]</sup>(dominant Si, minor Al) and X = dominant F, O, minor OH [1,2]. The characteristic feature of the astrophyllite structure is an (T<sub>4</sub>O<sub>12</sub>) ribbon that extends along [100]. The (Si<sub>4</sub>O<sub>12</sub>) astrophyllite ribbons share common vertices with D octahedra to form a heteropolyhedral (H) sheet. The octahedral (O) sheet is formed by the M(1-4) close-packed octahedra of the C-group. In the crystal structures of the astrophyllite-group minerals, the O sheet and two H sheets form an HOH block of composition C<sub>7</sub>D<sub>2</sub>(T<sub>4</sub>O<sub>12</sub>)<sub>2</sub>O<sub>2</sub>(OH)<sub>4</sub>X<sub>0-1</sub>. Linkage of two H sheets and a central O sheet is identical for all structures, except for magnesiumastrophyllite. Along [001], these HOH blocks connect *via* common X anions of D octahedra (except for magnesiumastrophyllite where the D atom is [5]-coordinated) and interstitial cations at the A and B sites.

In 2009, two new minerals of the astrophyllite group were structurally characterized: devitoite, [Ba<sub>6</sub>(PO<sub>4</sub>)<sub>2</sub>(CO<sub>3</sub>)]Fe<sup>2+</sup>·F

e<sup>3+</sup><sub>2</sub> (Si<sub>4</sub>O<sub>12</sub>)<sub>2</sub>O<sub>2</sub>(OH)<sub>4</sub>, [3], and sveinbergeite, Ca(Fe<sup>2+</sup>Fe<sup>3+</sup>)Ti<sub>2</sub>(Si<sub>4</sub>O<sub>12</sub>)<sub>2</sub>O<sub>2</sub>(OH)<sub>5</sub>(H<sub>2</sub>O)<sub>4</sub>, [4]. Discovery of these two minerals makes structural hierarchy of the astrophyllite group more complex. Here, I introduce an intermediate (I) block which comprises all atoms which occur between two adjacent HOH blocks. In seven astrophyllite-group structures, the I block comprises cations at the A and B sites. In devitoite and sveinbergeite, the I blocks are of different topologies and compositions, [Ba<sub>6</sub>(PO<sub>4</sub>)<sub>2</sub>(CO<sub>3</sub>)] and Ca(H<sub>2</sub>O)<sub>3</sub>, respectively.

In this talk, I revise the crystal chemistry of the astrophyllite group, explain why the topology of the HOH block in magnesiumastrophyllite is different from other eight structures, and predict new structure types based on a stable structural unit, an HOH block, and intermediate blocks of various topologies and chemical compositions.

[1] P.C. Piilonen, A.E. Lalonde, A.M. McDonald, R.A. Gault, A.O. Larsen, *Canadian Mineralogist* **2003**, *41*, 1-26. [2] F. Cámara, E. Sokolova, Y. Abdu, F.C. Hawthorne, *Canadian Mineralogist* **2010**, *48*, 1-16. [3] A.R. Kampf, G.R. Rossman, I.M. Steele, J.J. Pluth, G.E. Dunning, R.E. Walstrom, *Canadian Mineralogist*, **2010**, *48*, 29-40. [4] A.P. Khomyakov, F. Cámara, E. Sokolova, F.C. Hawthorne, *IMA* **2010-027**.

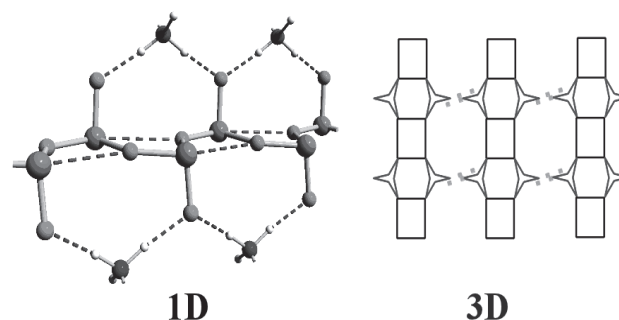
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### Ammonium polyoxoarsenates(III) – from columns to 3D structure

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Understanding how the forces driving supramolecular organisation in crystals balance one another is the key into rational development in the field of crystal engineering.

Reactions between arsenic(III) oxide with either ammonia or organic amines lead to the formation of hybrid inorganic-organic polyoxoarsenates(III). The following polyoxoarsenates(III) have been synthesized: ammonium (1), ethylenediammonium (2), benzylammonium (3), methylammonium (4) and ethanolammonium (5). The crystal structures of investigated compounds can be divided into three distinct levels reflecting the supramolecular organisation of entities in the structures.

Primary structure contains polyoxoarsenite chains decorated with ammonium cations. The inorganic polyanion is built of ψ-tetrahedra sharing two of their corners. The arsenic atom possesses distorted ψ-tetrahedral geometry, being surrounded by two bridging oxygen ligands, one terminal oxygen ligand and a stereoactive lone electron pair. Terminal oxygen ligands alternate on both sides of plane defined by arsenic atoms and bridging ligands. Such a chain conformation is stabilised by weak As...O interactions. Terminal ligands are spanned