

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.

Keywords: hybrid materials, layered, porous

MS.67.2

Acta Cryst. (2011) **A67**, C152

Revision of the crystal chemistry of the astrophyllite group

Elena Sokolova, *Department of Geological Sciences, University of Manitoba, Winnipeg, (Canada)*. E-mail: elena_sokolova@umanitoba.ca

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 = ^[5,12,13](dominant K, Cs, Li, minor Rb, Pb, Na, Ca and □); B = ^[10](dominant Na, minor Ca); C = ^[6](dominant Fe²⁺, Mn²⁺, minor Fe³⁺, Na, Mg, Ca, Li, Zr and Zn); D = ^[5,6](dominant Ti and Nb, minor Zr, Sn, Ta and Mg); T = ^[4](dominant Si, minor Al) and X = dominant F, O, minor OH [1,2]. The characteristic feature of the astrophyllite structure is an (T₄O₁₂) ribbon that extends along [100]. The (Si₄O₁₂) 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 C₇D₂(T₄O₁₂)₂O₂(OH)₄X₀₋₁. 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, [Ba₆(PO₄)₂(CO₃)]Fe²⁺·F

e³⁺₂ (Si₄O₁₂)₂O₂(OH)₄, [3], and sveinbergeite, Ca(Fe²⁺Fe³⁺)Ti₂(Si₄O₁₂)₂O₂(OH)₅(H₂O)₄, [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, [Ba₆(PO₄)₂(CO₃)] and Ca(H₂O)₃, 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**.

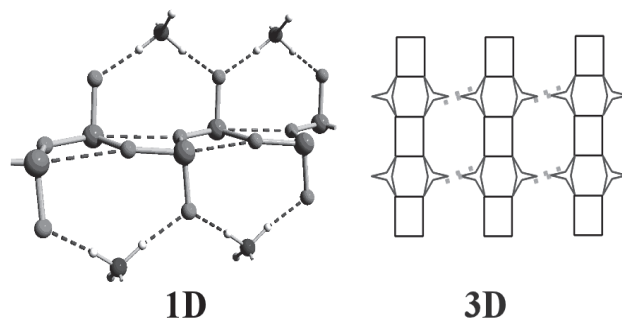
Keywords: layered, structure, prediction

MS.67.3

Acta Cryst. (2011) **A67**, C152-C153

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

Piotr A. Guńka, Maciej Dranka and Janusz Zachara *Warsaw University of Technology, Faculty of Chemistry, Department of Inorganic Chemistry and Solid State Technology, Warsaw (Poland)*. E-mail: piogun@ch.pw.edu.pl



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

by H–N–H hydrogen bridges which further stiffen inorganic chains. Cations are connected with polyanions via ionic interactions directed by hydrogen bonds i.e. ionic hydrogen bonds.

Neighbouring, electroneutral chains are linked into layers of secondary structure by N–H⋯O hydrogen bonds. They are formed between cations and terminal oxygen ligands in one boundary mode or between cations and bridging oxygen ligands in the other extreme. One of our structures (salt **5**) exhibits intermediate manner of interlayer connection with both bridging and terminal oxygen ligands involved in the formation of secondary structure.

The layers are connected into 3D, tertiary structure by a variety of linkers ranging from N–H⋯O hydrogen bonds in salt **1**, a –CH₂–CH₂– moiety in salt **2**, C–H⋯π and van der Waals interactions in salt **3**, O⋯H₂O⋯HOH⋯O bridges in salt **4** O–H⋯O bridges in salt **5**. This shows that the modification of organic moiety in cation leads to significant changes in the tertiary structure of investigated salts. Final 3D molecular organisation is a result of fine interplay between interactions constituting secondary and tertiary structure.

[1] P.A. Guńka, M. Dranka, J. Zachara, *CrystEngComm* **2011** (submitted).

Keywords: ammonium arsenite, supramolecular structure, weak interactions

MS.67.4

Acta Cryst. (2011) **A67**, C153

Complex topologies as a result of simple relationships between 2D and 3D actinide borates

Evgeny V. Alekseev,^{a,b} Shuao Wang,^{c,d} Thomas E. Albrecht-Schmitt,^{c,d} Wulf Depmeier,^a ^aDepartment of Crystallography, University of Kiel, Kiel, (Germany). ^bForschungszentrum Jülich GmbH, Institute for Energy and Climate Research (IEK-6), Jülich, (Germany). ^cDepartment of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, (USA). ^d Department of Civil Engineering and Geological Science, University of Notre Dame, Notre Dame, (USA). E-mail: e.alekseev@fz-juelich.de

Recently, we have found a very easy and productive method of actinide borate crystallization [1]. This method allowed us to synthesize more than 40 new actinide (Th, U, Np, Pu) phases, and to characterize them using methods like X-ray diffraction, UV-vis and MAS-NMR spectroscopy. With the only exception of Th borate [2], the structures of all the phases are based on complex actinide-borate sheets linked by BO₃ and/or BO₄ into 2D layered structures or 3D frameworks. The topologies of the oxoborate networks which incorporate the actinide atoms are quite diverse and complex. We have observed seven different topologies of 2D oxo-borate nets. Some of these nets are enantiomorphic and, thus, have different “left” or “right” configuration. Various stacking modes of such nets result in a significant number of structure types [3].

The structural complexity increases even more by insertion of BO₃ or BO₄ groups into the inter-sheets space. This kind of oxo-borate sheets modification can generate single or double layers, and 3D frameworks via poly-condensation of BO₂OH fragments [4]. The double layers can have between one and three BO₃ triangles within an inter-sheet space, and a total thickness of up to 2 nm [5, 6].

About 70% of actinide borates are non-centrosymmetric, because of the structure complexity of the layers and their possible different orientation. The lack of inversion allows for non-linear optical properties which, in fact, were shown to exist by measuring of SHG signals.

The layers can be functionalized via substitution of B–OH by B–F groups. This changes the structures dramatically as the substitution of terminal OH groups by F prevents the formation of hydrogen bond,

and thus the possibility of single layer condensation into double layers or 3D frameworks.

[1] S. Wang, E.V. Alekseev, J. Ling, S. Skanthakumar, L. Soderholm, W. Depmeier, T.E. Albrecht-Schmitt *Angew. Chem. Int. Ed.* **2010**, *49*, 1285–1288. [2] S. Wang, E.V. Alekseev, J. Diwu, W.H. Casey, B.L. Phillips, W. Depmeier, T.E. Albrecht-Schmitt *Angew. Chem. Int. Ed.* **2010**, *49*, 1057–1060. [3] S. Wang, E.V. Alekseev, J. Ling, G. Liu, W. Depmeier, T.E. Albrecht-Schmitt *Chem. Mater.* **2010**, *22*, 2155–2163. [4] S. Wang, E.V. Alekseev, J.T. Stritzinger, G. Liu, W. Depmeier, T.E. Albrecht-Schmitt *Chem. Mater.* **2010**, *22*, 5983–5991. [5] S. Wang, E.V. Alekseev, W. Depmeier, T.E. Albrecht-Schmitt *Inorg. Chem.* **2010**, *49*, 6690–6696. [6] S. Wang, E.V. Alekseev, J.T. Stritzinger, W. Depmeier, T.E. Albrecht-Schmitt *Inorg. Chem.* **2010**, *49*, 2948–2953.

Keywords: layered borates, framework, actinides

MS.67.5

Acta Cryst. (2011) **A67**, C153–C154

Temperature and moisture dependent studies on kanemite (NaSi₂O₄(OH)·3H₂O)

Volker Kahlenberg,^a Daniela Schmidmair,^a Daniel M. Töbrens,^a Jochem deWit,^b Ulrich J. Griesser,^b ^aUniversity of Innsbruck, Institute of Mineralogy and Petrography. ^bUniversity of Innsbruck, Institute of Pharmacy (Austria). E-mail: volker.kahlenberg@uibk.ac.at

Kanemite is a naturally occurring hydrated layer sodium silicate that was first discovered in evaporites at Kanem, Lake Chad. Apart from being a mineralogical curiosity, synthetic kanemite has been studied frequently due to its feasible applications as absorbent, catalyst support and precursor for the preparation of mesoporous or microporous materials.

Concurrently, two groups reported the orthorhombic crystal structure of kanemite (space group type *Pbcn*, a=4.946, b=20.510, c=7.277Å) [1,2]. The compound is based on negatively charged corrugated [Si₂O₄(OH)]-sheets which contain six-membered tetrahedral rings. Sodium cations are coordinated by six water molecules in form of distorted octahedra. They are sandwiched between the layers. The cationic and anionic sub-structures are linked by hydrogen bonding.

Our investigations on the thermal behaviour and moisture sorption of kanemite indicate a stepwise release of structural water with increasing temperature and a partial dehydration below 15% relative humidity (RH).

The moisture sorption isotherm at 25°C was started at 43% RH where the sample contains about 40% water. On lowering the relative humidity in 5% steps to 15% RH the water content is constant but decreases towards dryer conditions to about 20% water. In the sorption cycle the water content increases in a distinct step between 35 and 50% RH and then increases almost exponentially. The highest RH value (98% RH) was obtained by storing the material over saturated potassium sulphate solution in a semimicro hygrometer, where the sample takes up more than 12 mol water. In the desorption cycle, the water content drops down quickly at 90% RH and releases about 2 mol water between 90 and 50% RH. The original water content is completely retained after the desorption/sorption cycle.

In a N₂-atmosphere, thermogravimetric analysis shows a first dehydration step between 25°C and 110°C in which two water molecules per formula unit are expelled from the kanemite structure. With increasing the relative humidity this partially dehydrated material transforms back into kanemite. The remaining amount of one mol of structural water is released between 110°C and 250°C.

In-situ high temperature X-ray powder diffraction of kanemite