

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).

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

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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 enantiomorphous 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.

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

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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