

## Inorganic Compounds

**PS08.01.01 THE CRYSTAL STRUCTURE OF SODIUM AND EUROPIUM BORATE.** A.M. Agayev, G.K. Abdullayev, The Azerbaijani Academy of Oil, Prospekt Azadlik, 20, Baku, Azerbaijan.

Sodium and Europium borate  $\text{NaEuBO}_2(\text{OH})_2\text{OH}$  (I) was obtained under hydrothermal conditions in  $\text{Na}_2\text{O}-\text{Eu}_2\text{O}_3-\text{B}_2\text{O}_3-\text{H}_2\text{O}$  system at 400 °C. It is isomorphous with compounds  $\text{NaHoBO}_2(\text{OH})_2\text{OH}$ , crystals are yellow-white and has shortly prismatic habitus. The crystal structure was determined by single-crystal x-ray analysis (diffractometer, Mo radiation, 970 reflections, least square refinement with anisotropic approximation,  $R=0.053$ ). The cell dimensions are;  $a=5.213$ ,  $b=6.526$ ,  $c=6.235$  Å,  $\beta=114.8$ ,  $z=2$ ,  $d=4.929$  g/cm<sup>3</sup>, space group  $P2_1/m$ .

The crystal structure of I consists of isolated  $\text{BO}_2(\text{OH})_2$  3-tetrahedra ( $B-O=1.4861, 532$  Å) and coordination polyhedra of metallic cations. The sodium cations are inside the distorted becaped trigonal prisms formed by two O atoms and 6 OH groups ( $Na-O=2.213-2.654$  Å). The Europium cations are also inside the distorted eight coordinated polyhedra formed by four oxygens atoms and four OH groups ( $Eu-O=2.362-2.735$  Å). Each Na and Eu-Polyhedra form zig-zag chains along the axis b being connected through the general rib with the nearest symmetrically equivalent polyhedra. Such chains being associated by general summits and ribs of B-tetrahedra and hydrogen bonds between them, form the framework structure.

**PS08.01.02 NEW ONE-DIMENSIONAL CHANNEL STRUCTURES IN THE REDUCED Li-Ti-O SYSTEM.** By J. Akimoto\*, Y. Gotoh, and Y. Oosawa, National Institute of Materials and Chemical Research, Higashi, Tsukuba, Ibaraki 305, Japan.

The investigation of the reduced Li-Ti-O system has allowed new mixed-valence  $\text{Ti}^{3+}/\text{Ti}^{4+}$  compounds,  $\text{LiTi}_2\text{O}_4$  and  $\text{LiTi}_4\text{O}_8$ , to be isolated. Single crystals of these compounds were synthesized by a reaction of lithium metal and titanium dioxide at 1473 K in sealed iron vessels. The crystal structures were determined by singlecrystal X-ray diffraction method.

The framework of these compounds is built up from double-rutile-type  $\text{TiO}_6$  chains which are connected to each other by corner sharing.  $\text{LiTi}_2\text{O}_4$  has the orthorhombic ramsdellite-type structure, and is a high-temperature form of the spineltype  $\text{LiTi}_2\text{O}_4$ .  $\text{LiTi}_4\text{O}_8$  is an intergrowth phase of rutile and ramsdellite, which consists of  $[1 \times 1]$  and  $[1 \times 2]$ -type tunnel structures. Lithium atoms are occupied in the ramsdellite-type tunnel space in both compounds. The crystal data of these compounds are given in the following table:

$\text{LiTi}_2\text{O}_4$	orthorhombic Pbnm $a = 5.0356(6)$ , $b = 9.6377(8)$ , $c = 2.9484(7)$ Å
$\text{LiTi}_4\text{O}_8$	monoclinic C2/m $a = 14.1198(11)$ , $b = 2.9486(11)$ , $c = 4.9373(13)$ Å $\beta = 92.693(14)^\circ$

**PS08.01.03 RESPONSE TO CHANGES IN T, P OR CHEMISTRY: FRAMEWORK MECHANICS OF ALUMINOSILICATES.** Werner H. Baur, Institut für Kristallographie, Senckenberganlage 30, D-60054 Frankfurt am Main, Germany

Since *in situ* experiments under extreme conditions have become more common it is possible to follow up the detailed changes going on in the frameworks of porous materials. Such frameworks adapt to physical (temperature and/or pressure) and chemical (cation exchange) influences by changing the geometry of the T-O-T angles and T-O bonds and by undergoing phase transitions. Nevertheless, despite the adjustments in geometry some of the frameworks remain stable and even preserve approximately their overall dimensions. Frameworks formed by  $\text{TO}_4$  coordination tetrahedra are composed of rigid parts, the tetrahedra, and

of bridging O atoms serving as flexible hinges between the tetrahedra. A few tetrahedral frameworks are noncollapsible: their hinges antitotate, that is compression at one hinge necessitates tension at another hinge and vice versa (1). This happens to be true for the LTA and FAU types and for the feldspar framework. These frameworks do not collapse, even if no cations or sorbed molecules are present in their pores. On the other hand in collapsible frameworks the hinges corotate and compression or tension at all hinges is exerted simultaneously in the same sense. Collapse in such cases is stopped either (a) by the ions and molecules within the pores, when the framework begins to hug its filling, or else (b) when the collapse cannot proceed because the angles at the hinges T-O-T assume values which are too small to be compatible with the necessary bonding requirements [as is observed at 598 K in the dehydrated form of natrolite, metanatrolite, where Si-O-Al angles of  $114^\circ$  occur (2)]. The responses of the frameworks to change will be illustrated by examples, particularly stressing the mechanics of the feldspar type (3).

- (1) Baur, W. H. (1992). *J. Sol. State Chem.* **97**, 243-247
- (2) Baur, W. H. & Joswig, W. (1996) *N. Jahrb. Min. Mh.*, in the press
- (3) Baur, W. H. et al. (1996) *J. Solid State Chem.*, in the press

**PS08.01.04 CHROMYL COMPOUNDS IN THE SOLID STATE IN COMPARISON TO THEIR GAS PHASE STRUCTURES.** Horst Borrmann, Michael Wanitschek, Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1, D-70569 Stuttgart, Germany

Chromyl compounds, e.g. fluoride, chloride, and nitrate, are fascinating compounds mainly due to intense color, high volatility and high reactivity. Their crystal structures have been determined for the first time with high precision at low temperatures. As a main feature the  $\text{CrO}_2$  unit seems invariant with respect to kind and arrangement of the other ligands bonded to the Cr atom as indicated by the Cr=O distances being always very close to 158 pm and only minor changes of the OCrO angle occurring.

$\text{CrO}_2\text{F}_2$  ( $a = 565.93(4)$ ,  $b = 484.64(4)$ ,  $c = 911.42(7)$  pm,  $\beta = 93.001(6)^\circ$ ,  $P2_1/c$ ,  $Z = 4$  at 90 K) forms a layered structure by alternating corner- and edge-sharing of distorted octahedra via fluorine atoms.

$\text{CrO}_2\text{Cl}_2$  ( $a = 639.8(1)$ ,  $b = 495.4(1)$ ,  $c = 714.1(2)$  pm,  $\beta = 106.40(2)^\circ$ ,  $P2_1$ ,  $Z = 2$  at 138 K) is always obtained as a ruby-red glass upon cooling below its melting point at 177K. It turned out exceedingly difficult to crystallize such a glass. In contrast to the fluoride analogue  $\text{CrO}_2\text{Cl}_2$  forms a molecular structure with the tetrahedral molecules in a polar arrangement.

$\text{CrO}_2(\text{NO}_3)_2$  ( $a = 1070.7(2)$ ,  $b = 997.6(2)$ ,  $c = 548.65(9)$  pm, Pbcn,  $Z = 4$  at 90 K) proved to be an ideal link between fluoride and chloride. The structure is again built up from isolated molecules, but with the nitrate groups acting as bidentate ligands the coordination of the Cr atom is distorted octahedral like in the fluoride.

As the structures in the gas phase are known for all three molecules from excellent electron diffraction experiments this series of compounds is ideally suited for a detailed discussion of the bonding interaction.

Furtheron from the comparison with our results a redetermination of the crystal structure of  $\text{CrO}_3$  became necessary.

**PS08.01.05  $\text{YbCu}_{4.5}$  - A GIANT STRUCTURE DETERMINED BY SINGLE-CRYSTAL X-RAY DIFFRACTION AND HRTEM.** R. Cerny, Laboratoire de Cristallographie, University of Geneva, 24, quai Ernest Ansermet, CH-1211 Geneva 4, Switzerland

$\text{YbCu}_{4.5}$  crystallizes in one of the largest structures among intermetallic phases, having 7448 atoms per unit cell. It has monoclinic symmetry and its structure derives from the cubic  $\text{AuBe}_5$  type by introducing anti-phase boundaries and Cu-deficient shear planes parallel to  $\{hjh\}$  which lead to a nearly orthogonal  $\approx 7 \times 7 \times 6.5$  supercell having cell parameters  $a_s=48.961(20)$ ,  $b_s=48.994(4)$ ,  $c_s=45.643(4)$  Å,  $\beta=91.24(1)^\circ$ . A 4-dimensional structure analysis reveals a quasi-linear modulation of the atomic positions and occupancies