

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/cm³, 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, LiTi_2O_4 and LiTi_4O_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 TiO_6 chains which are connected to each other by corner sharing. LiTi_2O_4 has the orthorhombic ramsdellite-type structure, and is a high-temperature form of the spineltype LiTi_2O_4 . LiTi_4O_8 is an intergrowth phase of rutile and ramsdellite, which consists of [1x1] and [1x2]-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:

LiTi_2O_4	orthorhombic Pbnm $a = 5.0356(6)$, $b = 9.6377(8)$, $c = 2.9484(7)$ Å
LiTi_4O_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 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° 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 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.

CrO_2F_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.

CrO_2Cl_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 CrO_2Cl_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 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 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

of Yb and Cu along c_z . Based on this result and the high resolution transmission electron microscopy images a 3-dimensional model of the superstructure was constructed in space group $C2$ [1]. Yb was distributed on 336 (4c) sites, 7 (2b) sites and 7 (2a) sites, while Cu was distributed on 1519 (4c) sites. Three different types of Yb co-ordination occur in the structure with their relative abundancies 2:1:1 which is consistent with observed Mössbauer spectra. The Yb sites near the shear planes show Yb - Yb distances of the order of 3.6 Å which are presumably related to the formation of shear planes, and might be of relevance for the interpretation of the magnetic properties. The composition and calculated density of the model are consistent with their observed values. The calculated and observed X-ray structure factors agreed to $R = 12\%$. The structure of a related compound $\text{YbCu}_{3.5}$ can be predicted as having the same topology of plane defects as $\text{YbCu}_{4.5}$ but with a higher density of occurrence.

[1] R. Cerny, M. François, D. Jaccard, E. Walker, K. Yvon, V. Petricek, I. Cisarova, H.-U. Nissen and R. Wessicken; submitted to *J. Physics: Cond. Matter*

PS08.01.06 THE STRUCTURE OF COPPER(II) WITH 2-HYDROXYETHYL (PROPYL) IMINE -2-HYDROXY-1-BENZALDEHYDE. Yu.M. Chumakov, T.J. Malinowski, Institute of Applied Physics, Kishinev, 277028, Moldova, V. I. Tsapkov, N. M. Samus, Moldavian State University, Kishinev, Moldova

The various coordination compounds obtained by the interaction of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ with 2-hydroxyethyl (propyl) imine-2-hydroxy-1-benzaldehyde in function of pH of the medium and the nature of the proton acceptor reagent possess an antiseptic activity, which depends not only of the composition, but of the structure of the complex as well. In order to clarify this dependence the following complex compounds were synthesized and next analyzed by X-ray methods:

$\text{Cu}(\text{HL})\text{NO}_3$ [I], $\text{Cu}(3\text{-pic})(\text{HL})\text{NO}_3$ [II], $\text{Cu}(4\text{-pic})(\text{HL})\text{NO}_3$ [III], CuL [IV], CuL' [V], $\text{Cu}(\text{Py})(\text{HL})\text{NO}_3$ [VI], where $\text{H}_2\text{L} = 2\text{HOC}_6\text{H}_4\text{CHN}(\text{CH}_2)_2\text{OH}$, $\text{H}_2\text{L}' = 2\text{HOC}_6\text{H}_4\text{CHN}(\text{CH}_2)_3\text{OH}$.

It was determined, that the coordination polyhedron around the central atom in the compounds I - III is an extended tetragonal pyramid meanwhile the complex are polymers. The compound II is a dimer. The nitrate group serves in the polymer complexes as bridge-ligand, but in dimers this function fulfil the oxygen atom belonging to the phenol group, the nitrate group is three-dentate in I, monodentate in II and bidentate in III.

In IV the copper atom is coordinated fully by the deprotonated molecule H_2L through the oxygen atoms of phenol and alcohol and by nitrogen of the imine. The tetramer as cubane complex is formed in the complex compound. The surroundings of the central ion in V is a distorted square formed by oxygen atoms of the phenol and alcohol and of the nitrogen of the azometin $\text{H}_2\text{L}'$. The fourth corner of the square is occupied by the oxygen atom of the neighbouring complex CuL' coupled with the initial complex through the centre of symmetry.

PS08.01.07 AN INVESTIGATION INTO THE CRYSTAL STRUCTURE AND DISORDER OF PbZrO_3 . Corker, D. L., Glazer, A. M., Clarendon Laboratory, Physics Department, Oxford University, England

The following study reports a reinvestigation into the structure of lead zirconate, PbZrO_3 . Previously reported by Glazer *et al.* (1) in 1993, the crystal structure was determined in space group Pbam and said to exhibit a disorder in the oxygen sites such that the two oxygen substructures A and B were related by:

$$X_A, Y_A, Z_A \Rightarrow X_B, Y_B, Z_B + 0.5$$

This disorder, although agreeing with an earlier single-crystal X-ray diffraction study, disagrees with a neutron powder dif-

fraction analysis by Whatmore, in 1976 (2), where no indications of a disorder could be found.

To investigate this discrepancy further structural analysis is presented. This includes single-crystal X-ray diffraction, at both room and low temperature, and also neutron diffraction, although due to growth problems of large single crystals, the neutron analysis is restricted to that of powders only. If the disorder is false, then explanations of a disorder being exhibited are further cell doublings previously not recognised, twinning or possibly incorrect space group determination. Indeed, there has been much contradicting evidence over the space group determination and whether the structure is truly centrosymmetric. While there has been weak ferroelectricity reported by Dai *et al.* (3) which indicates a non-centrosymmetric space group, Scott and Burns (4), were unable to find neither piezoelectric or pyroelectric effects hence supporting the centrosymmetric classification Pbam.

There is also the possibility that the disorder is simply an artifact of pseudosymmetry. Whatever the space group, one of the main problems in an accurate structure determination is the strong pseudosymmetric character of the Pb and Zr sites and the relatively high scattering factors of the cations to the oxygens. Assuming nothing from previous determinations, an account is given of each of the stages used and pitfalls encountered in investigating all possibilities.

(1) Glazer, A. M., Roleder, K. & Dec, J. (1993). *Acta Cryst.* **B49**, p846

(2) Whatmore, R. PhD thesis, (1975). Univ. of Cambridge, England.

(3) Dai, X., Li, J. & Viehland, D. (1995). *Cond. Matter*, **51**, 5, 2651

(4) Scott, B. A. & Burns, G. (1972). *J. Am. Ceram. Soc.* **55**, 333

PS08.01.08 CONTRIBUTION TO THE STEREOCHEMISTRY OF MONOVALENT THALLIUM TO OXYGEN ATOMS. H. Effenberger, Institut für Mineralogie und Kristallographie, Universität Wien, Althanstrabe 14, A-1090 Wien, Austria

For Tl(I) atoms two principally different kinds of coordination spheres formed by oxygen atoms are known: (i) The Tl(I) atom is strongly covalently bound to a small number of neighbours with short Tl(I)—O bonds. In these cases usually two to four ligands with $2.50 \text{ \AA} < \text{Tl(I)—O} < 2.80 \text{ \AA}$ have been found to be arranged at one side of the Tl(I) atom. Additional ligands have definitely longer Tl(I)—O bonds starting by Tl(I)—O $> 3.00 \text{ \AA}$. These coordination figures are in accordance with expectations from the electron configuration of Tl(I) atoms with their lone-pair electrons. (ii) The Tl(I) atom is coordinated by a large number of O atoms with more or less equal Tl(I)—O bond lengths or at least without larger gap in the distribution of the distances. Regular polyhedra with up to 12 ligands are known. The Tl(I)—O bond lengths as a rule start with larger values as found for the type (i) coordinations. The type (ii) Tl(I) atoms sometimes replaces alkali or earth alkali atoms like K, Rb, Cs, and Ca or NH_4 . It is to be mentioned that transitions between these two principally different kinds of coordination figures are known. A similar crystal chemical behaviour shows e.g. Pb(II).

In connection with an investigation of the geometry of the coordination figures of the Tl(I) atoms three Tl(I) arsenates have been synthesized hydrothermally and their crystal structures were determined by single crystal X-ray diffraction methods: $\text{Tl(I)}_3(\text{AsO}_4)$ [$a = 8.517(3)$, $c = 5.233(2)$ Å, space group $\text{P}6_3/\text{m}$], $\text{Tl(I)}_2\text{Cu(I)}(\text{AsO}_4)$ [$a = 6.000(3)$, $b = 5.343(2)$, $c = 8.616(3)$ Å, $\beta = 98.05(3)^\circ$, space group $\text{P}2_1$], and $\text{Tl(I)}\text{Cu(II)}_2(\text{AsO}_4)(\text{AsO}_3\text{OH})$ [$a = 6.407(2)$, $b = 11.245(5)$, $c = 10.173(4)$ Å, $\beta = 98.64(2)^\circ$, space group $\text{P}2_1/\text{c}$]. All these compounds represent type (i) examples. In $\text{Tl}_3(\text{AsO}_4)$ the Tl(I)—O bond lengths are 2.527, 2.542 and 2.562 Å, in $\text{Tl}_2\text{Cu}(\text{AsO}_4)$ they are 2.487, 2.565 and 2.778 Å for Tl(1) and 2.509, 2.743, 2.749 and 2.847 Å for Tl(2), and in $\text{TlCu}_2(\text{AsO}_4)(\text{AsO}_3\text{OH})$ they are 2.565 and 2.640 Å, next Tl(I)—O distances are $\geq 3.0 \text{ \AA}$.