

structures but rather multiphase samples. However, partial substitution of O^{2-} (or X^-) by F^- , particularly with concomitant shift of Pb:Sb ratio from unity, results in suppression of cation ordering. The disordered and ordered compounds are clearly phase separated by composition. All three fluoride analogs of $Pb_{1.5}Sb_{0.5}O_{1.5}(OH)_{0.5}Cl$, $Pb_{1.5}Sb_{0.5}O_{1.5}F_{0.5}X$ ($X = Cl, Br, I$) were found to exist, with Pb:Sb and concomitantly O:F varying in relatively wide ranges. A very similar phase separation between ordered and disordered structures was also observed in systems $PbSb_{1-x}Bi_xO_2X$ ($X = Cl, Br$) with complete solubility upon $X = I$. It is curious to note that in the system $Pb_{1+x}Sb_{1-x}Bi_yO_{2+2x}F_xI$ where no ordering is observed, there exist two phase separated solid solutions with low and high concentration of fluorine. We conclude that ordering is suppressed when i) the atomic ratios (Pb:Sb, O:F, etc.) deviate from unity and ii) when voluminous anions like I^- are employed.

The structural similarity between layered oxyhalides and oxynitrates was also employed to give a new compound Pb_2OFNO_3 isostructural to Pb_2OFX ($X = Cl - I$). No analogies could unfortunately be traced between $MBiO_2NO_3$ and Sb compounds as Sb^{3+} is oxidized by NO_3^- at high temperatures.

Keywords: lead compounds, layered structures, ordering

MS67.P09

Acta Cryst. (2011) A67, C650

Synthesis and structure of two new layered silicate hydrates, RUB-52 and RUB-53

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Layered Silicate Hydrates (LSHs) are interesting materials which can be transformed into microporous materials by either condensating the layers to form zeolites or by silylation of layers to form Interlayer Expanded Zeolites (IEZ). Moreover, since LSHs are, in many cases, constructed from layers possessing the same topology as the layer-like building units of framework silicates it is instructive to compare these related materials.

RUB-52 and RUB-53 were obtained from hydrous reaction mixtures containing silica and diethyldimethyl ammonium (DEDMA) hydroxide or choline, respectively, as the structure directing agents (SDA). Mixtures were heated at 130°C or 100°C, respectively, for 15 d. Both materials were obtained as small, plate-like, colorless crystals. DTA-TG curves show a first rapid weight loss around 280°C (RUB-52) or 320°C (RUB-53) accompanied by an exothermic peak assigned to the burn off of the organic species. A further slow weight loss up to ca. 750°C indicates the release of carbon rich remains of the organic matter. During the DTA-TG measurement, the structure collapsed. In addition to a few signals attributed to protons of the SDA, the ¹H NMR spectra of RUB-52 and RUB-53 display a signal at ca. 15.8 ppm corresponding to strong hydrogen bonds with an O...O distance of about 2.45 Å. The ²⁹Si NMR spectra are typical for layer silicates comprising in both cases 5 signals of equal intensity which are separated into 3 sharp signals in the Q⁴ region and two broader signals assigned to Q³-type silicon.

The structures were solved ab initio from powder diffraction data by simulated annealing. Rietveld refinements converged to residual values $R_{\text{Bragg}} = 0.042$, $\chi^2 = 2.9$ (RUB-52) and $R_{\text{Bragg}} = 0.030$, $\chi^2 = 3.7$ (RUB-53).

RUB-52, $[N(CH_3)_2(CH_2CH_3)_2][H_2Si_{10}O_{22}]$, is triclinic (P-1) with $a_0 = 9.267$ Å, $b_0 = 12.499$ Å, $c_0 = 7.404$ Å, $\alpha = 98.09^\circ$, $\beta = 112.21^\circ$, $\gamma = 69.54^\circ$, $V_{\text{UC}} = 744$ Å³; RUB-53 is monoclinic (P2₁/c) with $a_0 = 7.315$ Å, $b_0 = 23.486$ Å, $c_0 = 9.544$ Å, $\beta = 115.97^\circ$, $V_{\text{UC}} = 1474$ Å³ and composition $[N(CH_3)_3(CH_2CH_2OH)]_4[H_4Si_{20}O_{44}]$.

The silicate layers are constructed from small [4²5⁴] composite building units which are interconnected to each other by additional oxygen atoms. This layer topology represents a new structure type. The layers are terminated by Si-OH as well as Si-O⁻ groups; intercalated DEDMA or choline cations compensate for the negative charge. In RUB-52 the layers are stacked in an AAA sequence while in RUB-53 stacking of layers follows an ABAB sequence. Structure analyses confirm the presence of strong intra-layer hydrogen bonds in both materials.

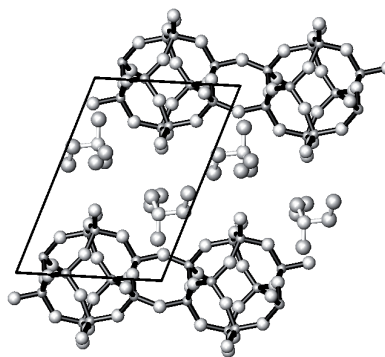


Fig. 1: The structure of RUB-52.

Keywords: layered, silicate, structure

MS67.P10

Acta Cryst. (2011) A67, C650-C651

Distribution of K⁺ and M⁺ ions in the alkali layer of (K⁺, M⁺)-β-ferrite (M: Rb, Na)

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(K⁺, M⁺)-β-ferrite (M: alkali ion) has a β-alumina type layer structure. This compound shows mixed alkali effect in ionic conductivity. We reported previously the distribution of K⁺ and Cs⁺ ions in (K⁺, Cs⁺)-β-ferrite [1]. It was confirmed that large Cs⁺ ions dominantly occupied Beavers Roth (BR) sites and that small K⁺ ions occupied both BR and mid-Oxygen (mO) sites in (K⁺, Cs⁺)-β-ferrite. Considering the occupancies of K⁺ and Cs⁺ ions, ionic radii and chemical composition, the distribution of K⁺ and Cs⁺ ions was determined. In this study, the structure refinement was performed for (K⁺, Rb⁺)-β-ferrite, in which the ionic radius of Rb⁺ is relatively close to that of K⁺. In addition, (K⁺, Na⁺)-β-ferrite including Na⁺ ions, of which ionic radius is smaller than that of K⁺, was also refined.

For (K_{0.3}Rb_{0.8})-β-ferrite, the structure refinement was performed based on two models; Rb⁺ and K⁺ occupied BR and mO sites, respectively (Model 1). Rb⁺ and K⁺ occupied both BR and mO sites (Model 2). The chemical compositions obtained from the structure refinement using Model 1 and Model 2 were comparable to that obtained by chemical analysis and the atomic displacement parameters (ADPs) were reasonable. This is because the difference of the ionic radius between K⁺ and Rb⁺ is relatively small, compared to the difference between K⁺ and Cs⁺. Table 1 shows the atomic coordinates and the isotropic ADPs in the alkali layers of (K_{0.3}Rb_{0.8})-β-ferrite using Model 1 and Model 2. The distributions of K⁺ and Rb⁺ in alkali layer were estimated; following the occupancies of K⁺ and Rb⁺, one alkali ion was put on every BR site, and then the residual alkali ions were put on mO sites, according to the chemical composition. The results were shown in Fig. 1. Furthermore, in (K_{0.8}Na_{0.7})-β-ferrite, Na⁺ occupied mO site and K⁺ occupied BR site. The distributions of K⁺ and Na⁺ were under consideration.

Table 1. Atomic coordinates and ADPs in $(K_{0.3}Rb_{0.8})\text{-}\beta\text{-ferrite}$.

(a) Model 1 ($R=0.0397$, $wR=0.1225$)

	site	occupancy	x	y	z	Uiso (Å)
O5	2c	1	1/3	2/3	1/4	0.021(2)
Rb1	6h	0.280(2)	0.6830(4)	0.3170(4)	1/4	0.0056(8)
K1	6h	0.099(9)	0.8824(15)	0.1176(15)	1/4	0.016(5)

(b) Model 2 ($R=0.0402$, $wR=0.1236$)

	site	occupancy	x	y	Z	Uiso (Å)
O5	2c	1	1/3	2/3	1/4	0.020(2)
Rb1	6h	0.263(4)	0.6829(4)	0.3171(4)	1/4	0.0055(8)
K1	6h	0.037(4)	0.6829(4)	0.3171(4)	1/4	0.0055(8)
Rb2	6h	0.015(8)	0.8826(15)	0.1174(15)	1/4	0.016(6)
K2	6h	0.065(8)	0.8826(15)	0.1174(15)	1/4	0.016(6)

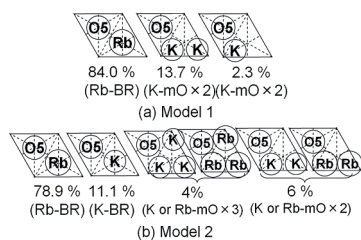


Fig.1 Distributions of K^+ and Rb^+ in $(K_{0.3}Rb_{0.8})\text{-}\beta\text{-ferrite}$.

[1] H. Watarai, K. Fujimoto, S. Ito, *ICC3 2010*, S1-P0245.

Keywords: structure refinement, mixed alkali beta-ferrite

MS67.P11

Acta Cryst. (2011) **A67**, C651

Structural analysis of a new complex containing tetrapropionatdirhodium units

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Rhodium dinuclear complexes with metal-metal bond with a variety of architectures, properties and different scientific approaches have been reported [1]. Although most of these compounds are based on discrete units, rhodium dimetallic species are currently used as building blocks to achieve an increasing number of coordination polymers with promising properties, mostly one-dimensional chains. However, many interesting arrangements based on dirhodium paddlewheel molecules can be obtained. In this abstract, we present a new dirhodium tetrapropionate with formula $\{K_2[Rh_2(O_2CET)_4(I)_2] \cdot H_2O\}$. In order to understand the structure of this compound a topological analysis has been carried out.

A good geometrical analysis of molecule-based structural types needs to answer, at least, two questions: the type of building blocks found in the structure, and the way in which these building blocks are connected. Sometimes, the resulting three-dimensional arrangement can be very complicated, and a conventional approach cannot clearly

explain the arrangement in the solid state. In these intricate structural types, it is often more illustrative to find the topological parameters that can describe the building blocks and explain their connectivity.

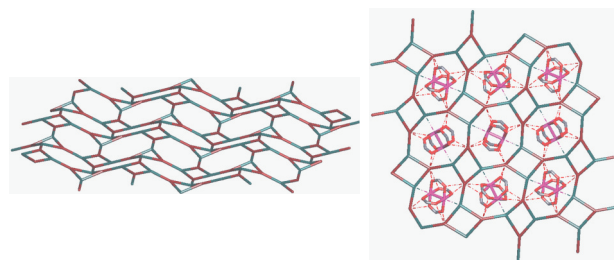


Figure 1. KI subnet (left) and simplified perpendicular view of a $\{K_2[Rh_2(O_2CET)_4(I)_2] \cdot H_2O\}_\infty$ layer (right).

Single crystal X-ray diffraction of $\{K_2[Rh_2(O_2CET)_4(I)_2] \cdot H_2O\}$ displays a complex arrangement of $[Rh_2(O_2CET)_4]$ paddlewheel molecules with the two axial positions occupied by two iodine atoms. However, the long Rh-I distance, which is higher than the sum of ionic radii, indicates the ionic nature of this interaction. The crystal structure can be described as a stacking of $\{K_2[Rh_2(O_2CET)_4(I)_2] \cdot H_2O\}_\infty$ layers parallel to the (-111) crystallographic plane. These layers consist of an undulated two-dimensional ionic network of KI, which can be topologically described as a 3-connected uninodal Shubnikov plane net (4.8^2). The dirhodium units are located inside the 8-member rings, displaying Rh-I and K-O ionic interactions with the inorganic framework. There are also weak hydrogen bonds between adjacent layers through the oxygen atoms from the water molecules bonded to the K^+ cations.

[1] F.A. Cotton, C.A. Murillo, R.A. Walton, *Multiple Bonds between Metal Atoms*, 2005.

Keywords: rhodium, coordination, crystallochemistry

MS67.P12

Acta Cryst. (2011) **A67**, C651-C652

Low temperature form of layer silicate RUB-15-LT, $[Si_{24}O_{48}(OH)_8][N(CH_3)_4]_8 \cdot 20H_2O$

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RUB-15 [1] is an interesting layer silicate with layers made up of 4- and 6-rings forming a puckered sheet of interconnected cups which point alternatively up and down. The cups can be described as one half of a sodalite cage with tetramethylammonium (TMA) cations intercalated between layers. Neighboring silicate layers are interconnected through additional hydrogen-bonded water molecules. This generates a 3-dim. bonding network consisting of layer like silicate ions and water molecules.

RUB-15 was synthesized at 130°C from a reaction mixture of SiO_2 / TMAOH / H_2O . Synchrotron powder diffraction data were collected between 295 and 150 K at HASYLAB, Hamburg to monitor the phase transition. For a structure analysis of RUB-15-LT a complete powder diffraction data set was collected at 150 K using a Bruker D8 diffractometer with $MoK\alpha$ radiation. To investigate hydrogen bonds 1H Solid-State MAS NMR spectra were recorded at RT on a Bruker ASX400 spectrometer.

RUB-15 shows a phase transition at ca. 200 K from ortho-rhombic to monoclinic symmetry. Upon cooling the unit cell volume shrinks from 2702.4 Å³ (295 K) to 2631.3 Å³ (150 K),