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 is 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 $Pb_{1+x}Sb_{1-x-y}Bi_yO_{2-x}F_xI$ 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 rations (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

**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 $^{29}Si$ 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 $Q^4$ region and two broader signals assigned to $Q^3$-type silicon.

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

RUB-52, $[N(CH_3)_2(CH_2CH_3)_2]_2[H_2Si_{10}O_{22}]$, is triclinic (P-1) with $a_0 = 9.267$ Å, $b_0 = 12.499$ Å, $c_0 = 7.404$ Å, $\alpha = 98.09°$, $\beta = 112.21°$, $\gamma = 69.54°$, $V_{UC} = 744$ Å$^3$; RUB-53 is monoclinic (P2$_1$/c) with $a_0 = 7.315$ Å, $b_0 = 23.486$ Å, $c_0 = 9.544$ Å, $\beta = 115.97°$, $V_{UC} = 1474$ Å$^3$ and composition $[N(CH_3)_3(CH_2CH_2OH)]_4[H_4Si_{20}O_{44}]$.

The silicate layers are constructed from small $[4^2 5^4]$ 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 pre- sence of strong intra-layer hydro- gen bonds in both materials.
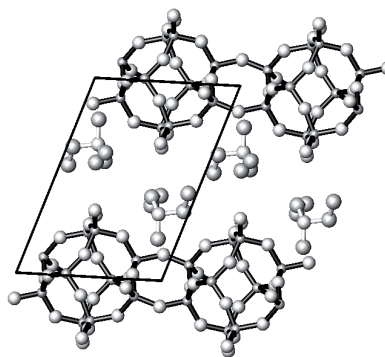


Fig.1: The structure of RUB-52.

**Keywords: layered, silicate, structure**

# MS67.P10

**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 Beevers 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.