Perovskite structure is able to accomodate a wide range of cations of different chemical nature and oxidation state and is flexible for various structure transformations and changes in stoichiometry. Combining the perovskite structure with different topologically suitable structure blocks would create perovskite-based homologues series.

The novel $A_nB_nO_{3n-2}$ perovskite-based homologues series was studied recently [1]. Presence of $Pb^{2+}$ as A-cation and $Fe^{3+}$ as B-cation allows coexistence of magnetic ordering and stereoactive lone electron pair.

A novel compound $Pb_3Ba_2Fe_4SnO_{13}$ representing the n = 5 member of the $A_nB_nO_{3n-2}$ homologues series was synthesized in air at 800-980 ˚C. It was sintered for 80 hours with intermediate regrinding.

The crystal structure of this compound was solved using X-ray and neutron powder diffraction, electron diffraction and high-resolution transmission electron microscopy ($a$ = 5.7768(8) Å, $b$ = 4.0229(6) Å, $c$ = 26.877(3) Å, S.G. *Ammm*). Crystal structure of $Pb_3Ba_2Fe_4SnO_{13}$ can be derived from perovskite structure by slicing it with periodically spaced $\frac{1}{2}[110]_p(1\,01)_p$ crystallographic shear (CS) planes. The perovskite-like blocks are separated at the CS planes by chains of five-fold $FeO_5$ polyhedra, which form pseudohexagonal tunnels. The tunnels are occupied by the $Pb^{2+}$ cations, which have sufficient space to accommodate their lone electron pairs. Cation positions in the perovskite blocks are randomly occupied by $Pb^{2+}/Ba^{2+}$ for the "A-positions" and $Fe^{3+}/Sn^{4+}$ for the "B-positions" with a preference of $Sn^{4+}$ to be located at the middle of the perovskite-like blocks.

Mössbauer spectroscopy revealed that the Fe oxidation state is "+3" with equal distribution of the Fe cations among the 6-fold an 5-fold coordinated positions, that confirms the refined structure.
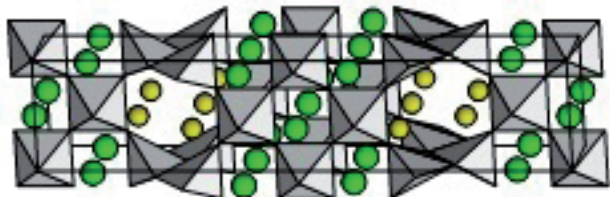


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**Keywords: Perovskite, Iron, Lead**

## MS67.P07

**$Sn_{12}In_{19}(Se, S)_{41}$ and the $M_{15+N}S_{20+N}$ *sliding series* of complex In sulfides**

Emil Makovicky,[a] and Dan Topa,[b]  [a]*Department of Geography & Geology, University of Copenhagen*; [b] *Department of Material Science, University of Salzburg*. E-mail: emilm@geo.ku.dk

**$Sn_{12}In_{19}(Se, S)_{41}$** was synthesized in a dry phase system Fe-Sn-Sb-In-S-Se at 600ºC. Its crystal structure is monoclinic with *a* 56.23(2), *b* 3.920(1), *c* 15.888(5) Å, *ß* 102.770(6)º, space group *C2/m*, and Z= 2. $R_1$ is 6.3% for 2339 unique reflections with $F_o > 4\sigma(F_o)$. There are 31 unique sites of Sn and In and 41 mixed sites of Se and S. It is a composite layer structure with two kinds of layers in regular alternation; together they underwent step-like modulation.

$Sn_{12}In_{19}(Se, S)_{41}$ is a member of a **$M_{15+N}S_{20+N}$ sliding series** of closely related composite layer structures with alternating, periodically sheared pseudohexagonal and pseudotetragonal layers. The pseudotetragonal layers of this series are three atomic planes thick with two octahedra of In in the centre of "oval rods", surrounded by coordination prisms of Sn/Pb. All structures of a 'sliding series' consist of slabs with the same, fixed step-like configurations which include (parts of) both layer types. These slabs slide past one another, opening more and more an

additional space between the steps of two adjacent slabs. This space did not exist in the starting member of the series. Additional coordination polyhedra fill the opening and create chemical and structural differences between the consecutive members of the series. In the given series, the described sliding results in the pseudohexagonal layers, which are doubled for the length of one, two, etc. octahedra. The initial member has octahedron layers simply sheared, without overlap. A member with one-octahedron-long gap instead of overlap can be defined as well.

If the length of a not sheared interval of the pseudohexagonal layer is A, and that of the overlap is B, these layers can be described as A/B and, within a given series, by N = B. In the studied structure, the pseudohexagonal layers 7/2 alternate with 4/-1. The crystal structure of $Sn_6In_{10}S_{21}$ [1] contains pseudohexagonal layers 7/2 alternating with 5/0 (N = 0, 2, 0, 2 ...). $Bi_4In_8Pb_{1.6}S_{19}$ [2] and $In^{3+}_6 Sn^{2+}_4 Sn^{4+}_2 S_{19}$ [3] have pseudohexagonal layers 4/-1 (N=-1, whereas the present structure is N = -1, 2, -1, 2 ....). $In_{10}Pb_6S_{21}$ [4] has 6/1, whereas the phase $In_{11}Sn_{5.5}S_{22}$ [5] contains 7/2. This are members N = 1 and N = 2, respectively. This scheme can continue with hypothetical members N = 3 and, finally, up to N = 5 with a complete doubling of the octahedral layer. The $M_{15+N}S_{20+N}$ (or $Me^{2+}_{5+N}Me^{3+}_{10}S_{20+N}$) sliding series is the principal family of complex In-based sulphosalts. A parallel series with less frequently sheared layers is known only as the $In_{13.34}Pb_6S_{26} - In_{14}Sn_5S_{26}$ pair.

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**Keywords: Sn-In sulfides, Pb-In sulfides, sliding series**

## MS67.P08

**Ordering in lead-antimony oxide halides upon variation of chemical composition.**

Arman A. Sadybekov, Dmitri O. Charkin, *Department of Chemistry, Moscow State University, Moscow (Russia)*. E-mail: big2ben@gmail.com

Multinary oxyhalides of lead and bismuth form two structurally related families of layered fluorites (so-called Sillén phases), not in the last due to similarity of size and electronic structures of $Pb^{2+}$ and $Bi^{3+}$ ($6s^2$). The principal difference lies in that Bi compounds exhibit mostly mixed-layer structures and $Bi^{3+}$ can be substituted by a rather few ions while lead compounds demonstrate highly-ordered superstructures of just three or four structure types with partial substitution of $Pb^{2+}$ by a much wider set of substitutents, often with their own kind of environment. Most of the latter come from natural (mineral) sources.

The structural information on compounds $[(Pb,Sb)_2(O,OH,F)_2][X]$ (X = Cl, Br, or I) adopting the simple $Nd_2O_2Te$ (*anti*-$ThCr_2Si_2$) structure (or its ordered versions) remains contradictory while they are known for years. $PbSbO_2Cl$ (known as a mineral nadorite) adopts an orthorhombic cation-ordered structure but a small stoichiometry shift to $PbSbO_{2+x}Cl_{1-2x}$ is claimed to kill the ordering. The oxybromide $PbSbO_2Br$ probably exists in both forms. In addition, there are oxy-hydroxide minerals like $Pb_{1.5}Sb_{0.5}O_{1.5}(OH)_{0.5}Cl$ where there is probably neither Pb/Sb nor O/OH ordering. In yet another group, $Pb_2OFX$, $O^{2-}$ and $F^-$ are perfectly ordered. In the current study, we attempted to study the series more thoroughly, to find out any relationships between composition, synthesis conditions, and absence or existence of cation/anion ordering among lead – antimony oxo/fluorohalides.

Our results have shown that ordered structure of $PbSbO_2Br$ exists below 500°C while $PbSbO_2I$ is always disordered. A simple stoichiometry shift to $PbSbO_{2+x}X_{1-2x}$ does not produce the disordered

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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**

Bernd Marler,[a] Zhaofei Li,[b] Guangmei Wang,[c] Hermann Gies,[a] [a]*Dept. of Geology, Mineralogy and Geophysics, University Bochum, (Germany).* [b]*Petrochemical Research Inst., PetroChina Co. Ltd., Beijing, (P. R. China).* [c]*Dept. of Inorganic Chemistry I, University Bochum, (Germany).* E-mail: bernd.marler@rub.de

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 $[4^25^4]$ 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.
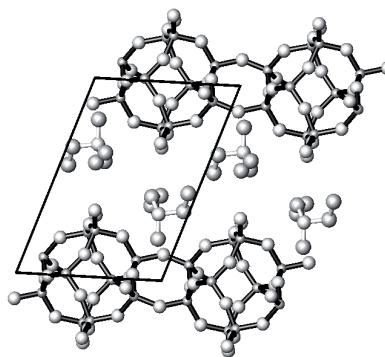


Fig.1: The structure of RUB-52.

**Keywords: layered, silicate, structure**

## MS67.P10

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

Hiroko Watarai, Kenjiro Fujimoto and Shigeru Ito, *Department of Pure and Applied Chemistry, Faculty of Science and Technology, Tokyo University of Science (Japan).* E-mail: ito@rs.noda.tus.ac.jp

($K^+$,$M^+$)-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.