Perovskite structure is able to accommodate 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 A₂B₂O₆₋₇, perovskite-based homologues series was studied recently [1]. Presence of Pb²⁺ as A-cation and Fe³⁺ as B-cation coexistence of magnetic ordering and stereoscopic lone electron pair.

A novel compound Pb₂Ba₂Fe₂Sn₄O₁₁, representing the n = 5 member of A₂B₂O₆₋₇, homologues series was synthesized in air at 800-980 °C. It was sintered for 8 hours with intermediate grinding. The crystal structure of this compound was solved using X-ray and neutron powder diffraction, electron diffraction and high-resolution transmission electron microscopy (a = 5.776(8) Å, b = 4.0229(6) Å.

Crystal structure of Pb₂Ba₂Fe₂Sn₄O₁₁ can be derived from perovskite structure by slicing it with periodically spaced [½, 1101, 1101] crystallographic shear (CS) planes. The perovskite-like layers are separated at the CS planes by chains of five-fold FeO₆ polyhedra, which form pseudohexagonal tunnels. The tunnels are occupied by the Pb²⁺ cations, which have sufficient space to accommodate their lone electron pairs. Cation positions in the perovskite blocks are randomly occupied by Pb²⁺/Bi³⁺ for the “A-cations” and Fe³⁺/Sn⁴⁺ for the “B-potations” with a preference of Sn⁴⁺ 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 and 5-fold coordinated positions, that confirms the refined structure.

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 Sn₄In₃Sn₂[1] contains pseudohexagonal layers 7/2 alternating with 5/0 (N = 0, 2, 0, 2,...). Bi₄In₉Pb₂Sn₄[2] and InSn₄⁺Sn⁵⁺Sn⁶⁺[3] have pseudohexagonal layers 4/-1 (N=-1), whereas the present structure is N = -1, 2, -1, 2...). In₉Pb₃Sn₄[4] has 6/1, whereas the phase In₉Sn₄Sn₂[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 M₄Sn₉Sn₂Sn₄(n=5) (or Me²⁺Sn₉Sn₂Sn₄(n=5) sliding series is the principal family of complex In-based sulfosalts. A parallel series with less frequently sheared layers is known only as the In₉Sn₄Sn₂Sn₄ pair.


Keywords: Perovskite, Iron, Lead

MS67.P08

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

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Multinary oxihalides of lead and bismuth form two structurally related families of layered fluorides (so-called Sillén phases), not in the last due to similarity of size and electronic structures of Pb²⁺ and Bi³⁺ (6s²). The principal difference lies in that Bi compounds exhibit mostly mixed-layer structures and Bi²⁺ 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 Pb²⁺ by a much wider set of substituents, often with their own kind of environment. Most of the latter come from natural (mineral) sources.

The structural information on compounds [(PbSb)(O,OH,F)][X] (X = Cl, Br, or I) adopting the simple Nd₂O₆Te (anti-ThCr₁Si₁) structure (or its ordered versions) remains contradictory while they are known for years. PbSbO₃CI (known as a mineral nadorite) adopts an orthorhombic cation-ordered structure but a small stoichiometry shift to PbSbO₃CI₁₋ₓ is claimed to kill the ordering. The oxybromide PbSbO₃Br probably exists in both forms. In addition, there are oxy-hydroxide minerals like Pb₁₋ₓSnₓO₃(OH)Cl₁₋ₓ where there is probably neither Pb/Sb nor O/OH ordering. In yet another group, Pb₂OFₓ, O²⁻ 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/hydroxohalides.

Our results have shown that ordered structure of PbSbO₃Br exists below 500°C while PbSbO₃I is always disordered. A simple stoichiometry shift to PbSbO₂ₓSnₓ₋ₓ does not produce the disordered

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

MS67.P07


Sn₄In₅(Se, S)₄ and the M₄Sn₉Sn₂Sn₄ₙ(n=5) sliding series of complex In sulfides

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Sn₄In₅(Se, S)₄ was synthesized in a dry phase system Fe-Sn-Sb-In-S-Se at 600°C. Its crystal structure is monoclinic with a = 56.23(2), b = 3.920(1), c = 15.844(5) Å, β = 102.770(6)°, space group C2/n, and Z = 2. R₁ is 6.3% for 2339 unique reflections with F > 4σ(F). 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.

Sn₄In₅(Se, S)₄ is a member of M₄Sn₉Sn₂Sn₄ₙ(n=5) 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.
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 a few signals attributed to protons of the SDA, the building units of framework silicates it is instructive to compare these related materials.

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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 Beever 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⁺,Rb⁺)-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⁺, Rb⁺)-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, respectively. The results were shown in Fig. 1. Furthermore, in (K⁺,Na⁺)-β-ferrite, Na⁺ occupied mO site and K⁺ occupied BR site. The distributions of K⁺ and Na⁺ were under consideration.