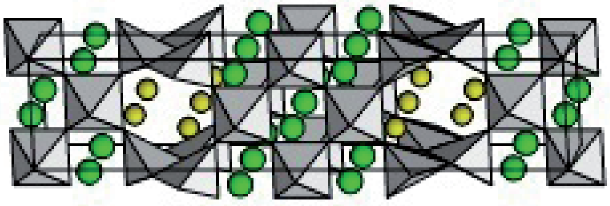
Perovskite structure is able to accomodate a wide range of cations of different chemical nature and oxidation state and is flexible for various structure transformations and changes in stoichiometry. Combining the perovskite structure with different topologically suitable structure blocks would create 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 ½$[110]_p(1\,01)_p$ 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

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

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$Sn_{12}In_{19}(Se, S)_{41}$ 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, β 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 $In^{3+}{}_6Sn^{2+}{}_4Sn^{4+}{}_2S_{19}$ [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

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

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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