Six different Sb\textsuperscript{3+-}O-F compounds have previously been reported. Two are orthorhombic, designated as L- and M-SbOF\textsubscript{3},\textsuperscript{1} one is cubic denoted as H-SbOF, one is glass\textsuperscript{2} and the remaining two phases are monoclinic denoted as α-Sb\textsubscript{2}O\textsubscript{6}F\textsubscript{2} and β-Sb\textsubscript{2}O\textsubscript{6}F\textsubscript{2}.\textsuperscript{3} One more compound, Sb\textsubscript{2}OF\textsubscript{4}, is theoretically predicted from the Sb\textsubscript{2}OF\textsubscript{6} phase diagram, however, it is not yet found experimentally. All the Sb-O-F compounds show framework type of structures. The main structural unit consists of different kinds of SbO\textsubscript{E}, SbO\textsubscript{FE}, SbF\textsubscript{E}, SbOF\textsubscript{E}, SbO\textsubscript{E} polyhedral units, where Sb\textsuperscript{3+-} is equipped with a lone-electron-pair, E.

H-, L-, M- and the amorphous form of SbOF are synthesized by solid state reactions at different temperatures from mixtures of SbF\textsubscript{5} and SbO\textsubscript{2} (1:1 ratio). The compounds α-Sb\textsubscript{2}O\textsubscript{6}F\textsubscript{2} and β-Sb\textsubscript{2}O\textsubscript{6}F\textsubscript{2} were synthesized in an aqueous solution of NH\textsubscript{4}F and SbF\textsubscript{5} with molar ratio of 0.05:1.\textsuperscript{4} Synthesis via hydrothermal techniques havenot previously not been reported for these compounds.

In this study Sb\textsubscript{2}OF\textsubscript{4}, a new Sb\textsuperscript{3+-}O-F compound, has been synthesized by hydrothermal techniques. We have also synthesized Y\textsubscript{2}Sb\textsubscript{2}O\textsubscript{6}F by introducing YF\textsubscript{3} as one of the reactants. The structural characterization is made from single crystal data will be extensively discussed. Single crystals of the two previously known compounds M-SbOF\textsubscript{3} and α-Sb\textsubscript{2}O\textsubscript{6}F\textsubscript{2} were also synthesized by the same technique differing from the previously known solid state synthesis. A comparison is made with previously reported compounds in the Sb\textsuperscript{3+-}O-X system (X = F, Cl, Br, I).
MS15-P3 Mixed alkali/alkaline earth trielides of the BaAl₄-type structure: A combined synthetic, crystallographic and theoretical case study for the ‘coloring’ in polar intermetallics

Martha Falk¹, Carolin Meyer¹, Matthias Kledt¹, Caroline Röhr¹

¹. Institut für Anorganische und Analytische Chemie, Universität Freiburg
email: martha@almandine.chemie.uni-freiburg.de

The ‘coloring’ [1], the distribution of different atoms $M$ among the apical/basal site of the pyramids in the BaAl₄-type (d), has already been extensively investigated for hundreds of ternary TM/p-block compounds (cf. references in [2-4]). Concerning the electronic stability the optimized ‘bond energy’ of 14 ve/fu is sufficiently proven [5,6], even though the structure type occurs from 12 to almost 15 ve/fu. Using metallic $M$ and ionic $A$° radii, the ratio $r_M^{\text{apical}}/r_A^{\text{basal}}$ of the BaAl₄-type ranges from 0.89 to 1.04 [4].

The ‘coloring’ of the $M$ anion by the triels, which differ both in size and electronegativity $\chi$, have been systematically investigated for the Ba series (Al/Ga/In), SrGa₄ to SrAl₄ (+In, [7]) (14 ve/fu) as well as for the Ga-containing K/Rb tetraindides (13 ve/fu). Carefully performed powder/single crystal structure analysis of distinct compounds (black symbols) reveal the ThCr₂Si₂ ordering only ($I\bar{4}/mmm$), no indications towards the CaBe₂Ge₂ or other 1:1:3 ordering variants are observed.

The calculated (FP-LAPW DFT) Bader volumes ($V_{BB}^{M}$) of the binary trielides indicate no significant size differences for $M_a$ and $M_b$, but a substantial more negative charge ($q$) of $M_a$, due to the larger Coulomb interaction $M_a—A$. Accordingly, all Ga-phases show a strong preference for the electronegative Ga to occupy the $M_a$ site (red curves in (a) and (b)). The preference is more restrictive for shorter $A—M_a$ contacts, i.e. smaller $r_A$ (e.g. difference Sr/Ba in (a)). The calculated ‘coloring energy’ ([5], $\Delta E_{\text{tot}}^{\text{CaAl_b^2Ga_a^2}\Rightarrow\text{CaGa_b^2Al_a^2}}$, 0.46 eV) is by far larger than the difference of the $M_a—M_a$ bond energies for Al/Ga (0.14 eV).

For mixed Al/In compounds (c) the $M$ distribution changes with $r_A$. For smaller Sr with higher ‘site energy’ $A—M_a$ in with larger $\chi$ occupies the $M_a$ site. In contrast, for $A=$Ba the less electronegative element Al occupies this site. This change of the site preference could be verified by the calculations. It is a striking example for the important contribution of Coulomb interactions in the lattice energy of polar intermetallics.