

## MS15 Minerals and materials

## MS15-P2 New topology of cesium aluminum borophosphate: synthesis, crystal structure and IR-spectroscopy investigation

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MS15-P1 Synthesis and characterization of  $\text{Sb}_3\text{O}_4\text{F}$ ,  $\text{Y}_{0.49}\text{Sb}_{2.51}\text{O}_4\text{F}$ , and other Sb-O-F compoundsSk Imran Ali<sup>1</sup>, Mats Johansson<sup>2</sup>

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Six different  $\text{Sb}^{3+}$ -O-F compounds have previously been reported. Two are orthorhombic, designated as L- and M-SbOF,<sup>1</sup> one is cubic denoted as H-SbOF, one is glass<sup>1</sup> and the remaining two phases are monoclinic denoted as  $\alpha\text{-Sb}_3\text{O}_3\text{F}_5$ ,  $\beta\text{-Sb}_3\text{O}_3\text{F}_5$ .<sup>2</sup> One more compound,  $\text{Sb}_3\text{O}_4\text{F}$ , is theoretically predicted from the  $\text{Sb}_3\text{F}_4\text{-Sb}_2\text{O}_3$  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  $\text{SbO}_3\text{E}$ ,  $\text{SbO}_2\text{FE}$ ,  $\text{SbF}_4\text{E}$ ,  $\text{SbOF}_3\text{E}$ ,  $\text{SbO}_2\text{E}$  polyhedral units, where  $\text{Sb}^{3+}$  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  $\text{Sb}_3\text{F}_4$  and  $\text{Sb}_2\text{O}_3$  (1:1 ratio). The compounds  $\alpha\text{-Sb}_3\text{O}_3\text{F}_5$  and  $\beta\text{-Sb}_3\text{O}_3\text{F}_5$  were synthesized in an aqueous solution of  $\text{NH}_4\text{F}$  and  $\text{SbF}_3$  with molar ratio of 0.05:1.<sup>1</sup> Synthesis via hydrothermal techniques haven't previously not been reported for these compounds.

In this study  $\text{Sb}_3\text{O}_4\text{F}$ , a new  $\text{Sb}^{3+}$ -O-F compound, has been synthesized by hydrothermal techniques. We have also synthesized  $\text{Y}_{0.49}\text{Sb}_{2.51}\text{O}_4\text{F}$  by introducing  $\text{YF}_3$  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 and  $\alpha\text{-Sb}_3\text{O}_3\text{F}_5$  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  $\text{Sb}^{3+}$ -O-X system (X = F, Cl, Br, I).

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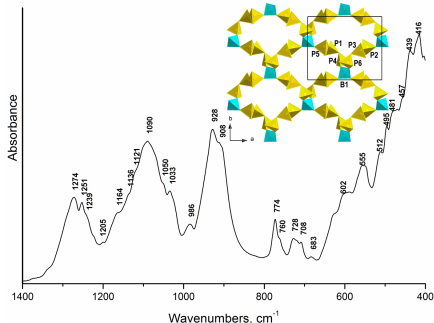
**Keywords:** Hydrothermal synthesis, Transition metal oxo-halides, Single crystal X-ray diffraction

Borophosphates have received much attention because of their fascinating structural architectures and potential applications in sorption, catalysis, optics and ion exchange. An open-framework cesium aluminum borophosphate,  $\text{CsAl}_3\text{BP}_6\text{O}_{20}$ , with novel topology of layered anionic borophosphate partial structure was synthesized by solid state reaction method. The crystal structure was determined from single-crystal X-ray data ( $R_p = 0.043$ ): S.G. *Pbca*,  $a = 11.815(2)$ ,  $b = 10.042(2)$ ,  $c = 26.630(4)$  Å,  $Z = 8$ ,  $V = 3159.5(10)$  Å<sup>3</sup>. The structure contains the 16-member ring borophosphate layers stacked along [001] (Fig.1) and interconnected by aluminum octahedra. The resulting three-dimensional framework is characterized by channels running parallel to [021] and [100] directions formed by six- and five-membered rings, respectively. Cs ions reside within these channels. The topological relations between the  $\text{CsAl}_3(\text{P}_3\text{O}_{10})_2$  [1] and  $\text{CsAl}_2\text{BP}_6\text{O}_{20}$  structures are discussed.

The MID-FTIR spectrum (Fig.1) of new borophosphate corresponds well to revealed crystal structure. Its interpretation can be made on the basis of characteristic vibrations of  $\text{PO}_2$ ,  $\text{PO}_3$  and  $\text{BO}_4$  groups, P-O-P and B-O-P bridges. The high frequency bands between 1280–1230  $\text{cm}^{-1}$  are attributed to the antisymmetric vibrations of O-P-O bonds  $\nu_2(\text{PO}_2)$ . The bands in the region 1205 – 1150  $\text{cm}^{-1}$  are assigned to symmetrical vibrations of O-P-O bonds  $\nu_1(\text{PO}_2)$ . The bands in the region from 1140 to 930  $\text{cm}^{-1}$  belong to the asymmetrical stretching vibrations of  $\text{PO}_2$ ,  $\text{PO}_3$  and  $\text{BO}_4$  units. Strong bands at 930–900  $\text{cm}^{-1}$  and weak bands at 775–680  $\text{cm}^{-1}$  can be, respectively, attributed to the antisymmetric and symmetric stretching vibrations of P-O-P and B-O-P bridges. The low-frequency region (650–400  $\text{cm}^{-1}$ ) is quite complex: bending vibrations of  $\text{PO}_3$  and  $\text{BO}_4$  units and Al-O stretching vibrations contribute to the absorption in the 650–450  $\text{cm}^{-1}$  region.

The  $\text{CsAl}_3\text{BP}_6\text{O}_{20}$  presents a first example of borophosphates with anionic partial structure containing the triphosphate groups and characterizing by B:P equal to 1:6.

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**Figure 1.** The 2D borophosphate anionic partial structure and infrared absorption spectrum of  $\text{CsAl}_2\text{BP}_6\text{O}_{20}$ .

**Keywords:** New topology of borophosphate, solid state reaction method

## MS15-P3 Mixed alkali/alkaline earth trielides of the $\text{BaAl}_4$ -type structure: A combined synthetic, crystallographic and theoretical case study for the 'coloring' in polar intermetallics

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The 'coloring' [1], the distribution of different atoms  $M$  among the apical/basal site of the pyramids in the  $\text{BaAl}_4$ -type (d), has already been extensively investigated for hundreds of ternary  $\text{TM}p$ -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  $A^{n+}$  radii, the ratio  $r_M:r_A$  of the  $\text{BaAl}_4$ -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),  $\text{SrGa}_4$  to  $\text{SrAl}_4$  (+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  $\text{ThCr}_2\text{Si}_2$  ordering only ( $I4/mmm$ ), no indications towards the  $\text{CaBe}_2\text{Ge}_2$  or other 1:1:3 ordering variants are observed.

The calculated (FP-LAPW DFT) Bader volumes ( $V_{\text{BB}}$ ) 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  $A-M$  contacts, i.e. smaller  $r_A$  (e.g. difference Sr/Ba in (a)). The calculated 'coloring energy' ([5],  $\Delta E_{\text{tot}}^{\text{coloring}} \text{CaAl}^b_2\text{Ga}^a_2 \Leftrightarrow \text{CaGa}^b_2\text{Al}^a_2$ , 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  $r$ : For smaller Sr with higher 'site energy'  $A-M_a$ , In with larger  $\chi$  occupies the  $M_a$  site. In contrast, for  $A=\text{Ba}$  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.

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