

MS15 Minerals and materials

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

Vladislava I. Belik¹, Larisa V. Shvanskaya¹, Elena Y. Borovikova¹

I. M.V. Lomonosov Moscow State University

email: vladislava.belik@mail.ru

Chairs: Frederic Hatert, Roland Nilica

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 Ali¹, Mats Johansson²

1. Post-doc research fellow, Stockholm University S-10691 Stockholm Sweden

2. Prof., Department of Materials and Environmental Chemistry, Stockholm University S-10691 Stockholm Sweden

email: skimran1984@gmail.com

Six different Sb^{3+} -O-F compounds have previously been reported. Two are orthorhombic, designated as L- and M-SbOF,¹ one is cubic denoted as H-SbOF, one is glass¹ and the remaining two phases are monoclinic denoted as $\alpha\text{-Sb}_3\text{O}_3\text{F}_5$, $\beta\text{-Sb}_3\text{O}_3\text{F}_5$.² 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 SbO_3E , SbO_2FE , SbF_4E , SbOF_3E , SbO_2E polyhedral units, where 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 Sb_3F_4 and Sb_2O_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 NH_4F and SbF_3 with molar ratio of 0.05:1.¹ 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 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 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 Sb^{3+} -O-X system (X = F, Cl, Br, I).

[1] A. S. Astrom, *Acta chem. Scand.*, 1971, **25**, 1519–1520.

[2] A. A. Udovenko, L. A. Zemnukhova, E. V. Kovaleva and G. A. Fedorishcheva, *Russ. J. Coord. Chem.*, 2004, **30**, 618–624.

[3] A. V. Kalinchenko, F. V., Borzenkova, M.P., and Novoselova, *Zh. Neorg. Khim.*, 1983, **28**, 2426.

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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, $\text{CsAl}_2\text{BP}_6\text{O}_{20}$, 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, $Z = 8$, $V = 3159.5(10)$ Å³. 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 PO_2 , PO_3 and BO_4 groups, P-O-P and B-O-P bridges. The high frequency bands between 1280–1230 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 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 cm^{-1} belong to the asymmetrical stretching vibrations of PO_2 , PO_3 and BO_4 units. Strong bands at 930–900 cm^{-1} and weak bands at 775–680 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 cm^{-1}) is quite complex: bending vibrations of PO_3 and BO_4 units and Al-O stretching vibrations contribute to the absorption in the 650–450 cm^{-1} region.

The $\text{CsAl}_2\text{BP}_6\text{O}_{20}$ presents a first example of borophosphates with anionic partial structure containing the triphosphate groups and characterizing by B:P equal to 1:6.

[1] Lesage J., Guesdon A., Raveau B. // *J. Solid State Chem.* 2005. V. 178. P. 1212.