

FA2-MS17-T04

Crystal growth, crystal structure and thermal expansion of a new layered borate $\text{Ba}_2\text{Bi}_3\text{B}_{25}\text{O}_{44}$.

Stanislav Filatov, Sergey Krivovichev, Rimma Bubnova^b, Maria Krzhizhanovskaya, Anna Egorysheva^c, Sergey Volkov^{a,b}. ^a*Department of Crystallography, St. Petersburg State University, Russia.* ^b*Grebenshchikov Institute of Silicate Chemistry, Russian Academy of Sciences, St. Petersburg, Russia.* ^c*Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences, Moscow, Russia.*
E-mail: filatov.stanislav@gmail.com

Triangulation of the $\text{BaO-Bi}_2\text{O}_3\text{-B}_2\text{O}_3$ system at 600° [1] presents four stable compounds: BaBiBO_4 , $\text{BaBi}_2\text{B}_4\text{O}_{10}$, $\text{Ba}_3\text{BiB}_3\text{O}_9$, and $\text{BaBiB}_{11}\text{O}_{19}$. For the last five years three ternary borates were structurally characterized in $\text{BaO-Bi}_2\text{O}_3\text{-B}_2\text{O}_3$ system: BaBiBO_4 [2] and $\text{BaBi}_2\text{B}_4\text{O}_{10}$ [3] and $\text{Ba}_3\text{BiB}_9\text{O}_{18}$ [4]. Here we report synthesis, crystal structure and thermal expansion of another ternary compound $\text{Ba}_2\text{Bi}_3\text{B}_{25}\text{O}_{44}$ discovered in the $\text{BaO-Bi}_2\text{O}_3\text{-B}_2\text{O}_3$. Single crystals of $\text{Ba}_2\text{Bi}_3\text{B}_{25}\text{O}_{44}$ were grown from a melt of non-stoichiometric composition close to $\text{BaBiB}_{11}\text{O}_{19}$. The crystal structure of $\text{Ba}_2\text{Bi}_3\text{B}_{25}\text{O}_{44}$ was solved by direct methods and refined to $R1 = 0.030$. The compound is trigonal, space group $R\bar{3}m$, $a = 7.8514(16)$, $c = 46.203(14)$ Å, $V = 2466.6(10)$ Å³. The structure is based on the complicate B–O layers bonded by Bi–O octahedra. The B–O layer is parallel to (001) and is composed of two symmetrically equivalent sublayers from triborate rings composed of two tetrahedra and triangle. Two sublayers are connected through partly disordered triborate rings composed of triangles only. Ba atoms are located in the voids within the borate layer. Thermal expansion of $\text{Ba}_2\text{Bi}_3\text{B}_{25}\text{O}_{44}$ prepared by solid state reactions has been investigated by X-ray powder diffraction in air in temperature range from 20 to 700 °C. It is anisotropic with the maximal expansion along a axis and near the zero in the perpendicular direction. Low expansion between the layers is explained by the strong bonding of layers through the BiO_6 octahedra. The studies are supported by the Russian Found the Basic Research (project # 08-03-00232).

[1] Egorysheva et al., *Russ. J. Inorg. Chem.*, 2006, 51(12) 1956-1960. [3] Bubnova et al., *J. Solid State Chem.*, 2007, 180, 596–603. [4] Cai et al., *Mater. Res. Bull.*, 2009, 44(12), 2211-2216.

Keywords: boron compounds, single-crystal diffraction, high-temperature powder diffraction

FA2-MS17-T05

Transition metal compounds with the CrVO_4 -type structure under pressure. E. Stavrou^a, I.

Efthimiopoulos^a, S. M. Souliou^a, J. Law^a, R. K. Kremer^a, G. V. Vajenine, K. Syassen^a, M. Hanfland^b.
^a*MPI-FKF, Stuttgart, Germany.* ^b*ESRF, Grenoble, France.*
E-mail: e.stavrou@fkf.mpg.de

Ternary CrVO_4 -type materials crystallize in the orthorhombic space group Cmc. Characteristic structural features are the mixed coordination [Cr (Ti) and V (P) cations are octahedrally and tetrahedrally coordinated, respectively, by O anions] and

the fact that octahedra form edge-sharing chains. Compounds that crystallize in this structure at ambient or at high pressure have been the subject of extensive studies, for two main reasons. First, different magnetic properties [1] arise from isolated chains of edge-sharing octahedra. Second, the Cmc structure is intermediate between quartz-like ABO_4 structures with only four-fold coordinated cations and structures with both cations in six-fold coordination [2-4]. Because of the close connection to quartz alike under pressure, a HP study of CrVO_4 -structure compounds is attractive from the structural systematics point of view. In this study we investigate the effect of pressure on the structural and vibrational properties of CrVO_4 -type materials, specifically the prototype CrVO_4 itself and TiPO_4 , using both high-resolution angle-dispersive x-ray powder diffraction and Raman spectroscopy. In the case of CrVO_4 , from x-ray powder diffraction data, we see reversible first-order phase transitions to new crystalline phases at ~4 and ~40 GPa. Raman mode frequencies indicate an increase of coordination of V already at the very first transition, presumably to six-fold. From the above results the Cmc \rightarrow P2/m \rightarrow P2/c (wolframite) phase route is concluded. The equations of state and internal structural parameters for all phases are also determined. For TiPO_4 we have also identified, only by Raman, two ‘precursor’ transitions, presumably hidden superstructures of Cmc, before we see clear indications for sixfold coordinated phosphorous appearing near 45 GPa. A related structural model is presented.

[1] H.-J. Koo and M.-H. Whangbo, *Inorg. Chem.* 42, 5932, 2003 and references therein. [2] J. Pellicer-Porres, A. M. Saitta, A. Polian, J. P. Itie, M. Hanfland, *Nature Materials*. 6, 698, 2007. [3] D. Errandonea, F. J. Manjón, *Prog. Mat. Science*, 53, 711, 2008. [4] M.P. Pasternak, G.K. Rozenberg, A.P. Milner, M. Amanowicz, T. Zhou, U. Schwarz, K. Syassen, R.D. Taylor, M. Hanfland, K. Brister, *PRL* 79, 4409 (1997).

Keywords: Phase Transitions, High-pressure, CrVO_4 -type structure