Crystal growth, new layered structure and thermal expansion of a novel layered borate Ba$_3$Bi$_3$B$_{25}$O$_{44}$. Stanislav Filatov, Sergey Krivovichev, Rimma Bubnova$^a$, Maria Krzhizhanovskaya, Anna Egorysheva$^a$, 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.

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Triangulation of the BaO–Bi$_2$O$_3$–B$_2$O$_3$ system at 600°C [1] presents four stable compounds: BaB$_2$O$_4$, Ba$_2$B$_2$O$_7$, Ba$_3$BiB$_9$O$_{18}$, and BaBi$_4$O$_{15}$. For the last five years three ternary borates were structurally characterized in BaO–Bi$_2$O$_3$–B$_2$O$_3$ system: BaB$_2$BO$_4$ [2] and BaBi$_2$B$_4$O$_{10}$ [3] and Ba$_3$BiB$_9$O$_{18}$ [4]. Here we report synthesis, crystal structure and thermal expansion of another ternary compound Ba$_3$Bi$_3$B$_{25}$O$_{44}$ discovered in the BaO–Bi$_2$O$_3$–B$_2$O$_3$ system. Single crystals of Ba$_3$Bi$_3$B$_{25}$O$_{44}$ were grown from a melt of non-stoichiometric composition close to BaBi$_2$B$_4$O$_{10}$. The crystal structure of Ba$_3$Bi$_3$B$_{25}$O$_{44}$ was solved by direct methods and refined to $R_1 = 0.030$. The compound is trigonal, space group $R-3m$, $a = 7.851(16)$ Å, $c = 46.203(14)$ Å, $V = 2466.6(10)$ Å$^3$. The structure is based on the complex O layers bounded 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 Ba$_3$Bi$_3$B$_{25}$O$_{44}$ was 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).

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

Transition metal compounds with the CrVO$_4$-type structure under pressure. E. Stavrou$^{a,b}$, I. Efthimiopoulos$^a$, S. M. Souliou$^a$, J. Law$^a$, R. K. Kremer$^b$, G. V. Vajenie, K. Syassen$^c$, M. Hanfland$^b$.

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Ternary CrVO$_4$-type materials crystallize in the orthorhombic space group Cmcm. 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 Cmcm structure is intermediate between quartz-like ABO$_3$ 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 alikes 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 Cmcm $\rightarrow$ 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 Cmcm, before we see clear indications for sixfold coordinated phosphorous appearing near 45 GPa. A related structural model is presented.


Keywords: Phase Transitions, High-pressure, CrVO4-type structure