

Structural peculiarities of bismuth-containing $R\text{Fe}_3(\text{BO}_3)_4$ ($R = \text{Ho}, \text{Y}, \text{Sm}, \text{Nd}$)

E. Smirnova¹, O. Alekseeva¹, A. Dudka¹, I. Verin¹, V. Artemov¹, D. Khmelenin¹, I. Gudim², K. Frolov¹, I. Lyubutin¹

¹FSRC «Crystallography and Photonics» RAS, Leninskiy Prospekt 59, Moscow, 119333 Russia

²Kirensky Institute of Physics of the Siberian Branch of the RAS, Akademgorodok 50, Krasnoyarsk, 660036 Russia

esmi@ns.crys.ras.ru

Rare-earth iron borate $R\text{Fe}_3(\text{BO}_3)_4$ crystals are studied worldwide lately owing to their perspective magnetoelectric and multiferroic properties [1]. A major part of these single crystals was grown by flux method using $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ as a solvent [2, 3]. In this work temperature-dependent structural behavior of $R\text{Fe}_3(\text{BO}_3)_4$ ($R = \text{Ho}, \text{Y}, \text{Sm}, \text{Nd}$) single crystals were studied by X-ray structure analysis. The chemical composition was verified by X-ray energy-dispersive elemental analysis. Additional structure information was obtained by Mössbauer spectroscopy on ^{57}Fe nuclei.

Bi atoms entered the composition of all the crystals during the growth process and the final compositions of single crystals studied are $\text{Ho}_{0.96}\text{Bi}_{0.04}\text{Fe}_3(\text{BO}_3)_4$, $\text{Y}_{0.95}\text{Bi}_{0.05}\text{Fe}_3(\text{BO}_3)_4$, $\text{Sm}_{0.93}\text{Bi}_{0.07}\text{Fe}_3(\text{BO}_3)_4$, and $\text{Nd}_{0.91}\text{Bi}_{0.09}\text{Fe}_3(\text{BO}_3)_4$.

Unit cell parameters for $R = \text{Ho}, \text{Y}, \text{Nd}$ were measured over 30–500 K. Parameters a, b of the crystals with $R = \text{Ho}, \text{Y}$ are descending with temperature lowering, whereas a, b parameters of Nd-crystal do not change strongly. A sharp jump of a, b for $R = \text{Ho}$ and Y was registered demonstrating presence of structural phase transition. At the same time, c (T) dependence has the similar character for all three crystals ($R = \text{Ho}, \text{Y}, \text{Nd}$) – c parameter decreases with lowering temperature to 80–100 K and then grows smoothly down to 30 K.

Structure of $\text{Ho}_{0.96}\text{Bi}_{0.04}\text{Fe}_3(\text{BO}_3)_4$, $\text{Y}_{0.95}\text{Bi}_{0.05}\text{Fe}_3(\text{BO}_3)_4$, $\text{Sm}_{0.93}\text{Bi}_{0.07}\text{Fe}_3(\text{BO}_3)_4$, and $\text{Nd}_{0.91}\text{Bi}_{0.09}\text{Fe}_3(\text{BO}_3)_4$ was determined at several temperatures in 90–500 K temperature range to study temperature-dependent structure peculiarities, in particular, changes during the structural phase transition for $R = \text{Ho}, \text{Y}$. The temperature of the phase transition $T_{str} = 365$ K for $R = \text{Ho}$ and $T_{str} = 370$ K for $R = \text{Y}$ was stated on the basis of systematic absences analysis and temperature dependence of a, b parameters. Inclusion of Bi atoms with a larger ionic radius leads to T_{str} lowering in comparison with powder samples without Bi [4]. The structure of the compounds with $R = \text{Ho}, \text{Y}$ was refined in sp. gr. $R32$ above T_{str} and in sp. gr. $P3_121$ below it. Structure of crystals with $R = \text{Sm}, \text{Nd}$ belongs to sp. gr. $R32$ at all temperatures studied. There is a slight steady decrease of specific distanced in $(R, \text{Bi})\text{O}_6$ trigonal prisms, FeO_6 octahedra, BO_3 triangles and Fe–Fe helicoidal chains with temperature lowering in sp. gr. $R32$. When going to lower-symmetry sp. gr. $P3_121$ (for $R = \text{Ho}, \text{Y}$) and with further temperature decreasing non-uniform changes in the bond lengths are observed. Equivalent atomic displacement parameters U_{eq} decrease with temperature lowering. However, U_{eq} of oxygen atoms O1 and O2 as well as ones of boron atoms B2 and B3 (sp. gr. $P3_121$ labels) are highly sensitive to a structural phase transition, demonstrating fluctuations around T_{str} .

Debye (T_D) and Einstein (T_E) characteristic temperatures for cations in the crystals with $R = \text{Ho}, \text{Y}, \text{Sm}, \text{Nd}$ were calculated. Both T_D and T_E values are close for the same type of cations. T_D and T_E for R and Fe atoms in sp. gr. $R32$ are close to the corresponding values in sp. gr. $P3_121$, and there is a significant change in T_D, T_E values for B atoms after a phase transition.

Gamma-resonance measurements on ^{57}Fe nuclei showed that the hyperfine parameters of the Mössbauer spectra correspond to Fe^{3+} ions in an octahedral oxygen environment. Quadrupole splitting Δ temperature dependence demonstrates complex behavior and is in good agreement with X-ray diffraction results.

[1] Kadomtseva, A.M., Popov, Yu F., Vorob'ev, G.P. et. al. (2010) *Low Temp. Phys.* **36**, 511.

[2] Bezmaternykh, L. N., Kharlamova, S. A. & Temerov, V. L. (2004) *Crystallogr. Rep.* **49** (5), 855.

[3] Gudim, I.A., Eremin, E.V., Temerov, V.L. (2010) *J. Cryst. Growth.* **312**, 2427.

[4] Hinatsu, Y., Doi, Y., Ito, K., Wakeshima, M. & Alemi, A. (2003) *J. Solid State Chem.* **172**, 438.

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