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Multifunctional $R\mathrm{Fe_3(BO_3)_4}$ Materials: Quality Control

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Rare-earth iron borates with general formula $R\mathrm{Fe_3(BO_3)_4}$ (R = Y, Pr-Er) have a structure of the natural mineral huntite (SG $R32$). Their magnetic properties are governed by the presence of two interacting magnetic subsystems – Fe^{3+} and R^{3+} ones. The magnetic structure of $R\mathrm{Fe_3(BO_3)_4}$ changes as a function of temperature, external magnetic field and substitutions in the rare-earth subsystem. Compounds belonging to this family display a considerable magnetoelectric coupling and their electric (magnetic) properties can be controlled by the magnetic (electric) field.

Iron borates with an ionic radius of R smaller than that of Sm undergo a structural phase transition into the space group $P3_121$ at the temperature T_S inversely proportional to the ionic radius of R^{3+}. $\mathrm{EuFe_3(BO_3)_4}$ has the lowest T_S. T_S=88K and T_S=58K were reported for powder samples prepared by solid-phase synthesis [1] and for a single crystal [2], respectively. In the present work we study how and why the method of sample growth influences structural, magnetic, and spectroscopic properties of $\mathrm{EuFe_3(BO_3)_4}$. We compare optical spectra of $\mathrm{EuFe_3(BO_3)_4}$ crystals grown by flux-melting technique using (i) $\mathrm{Bi_2Mo_3O_{12}}$ and (ii) $\mathrm{Li_2WO_4}$ based fluxes. The spectra clearly evidence T_S=58K for the sample (i) and T_S=83K for the (ii) one, whereas T_N=34K for both samples. Obviously, lower T_S for the sample (i) is connected with entering of a "big" Bi^{3+} ion from the flux into positions of Eu^{3+} [3]. Our estimate gives 7±2 % for Bi concentration in the sample (i). Bi impurity manifests itself also by a presence of extra lines in the spectra, due to Eu^{3+} located near Bi impurities. These data allowed us to estimate the Bi^{3+} concentrations in a number of rare-earth iron borates, grown using Bi-containing flux. In all investigated materials (R=Dy, Ho, Tb, Gd) the concentration of bismuth was in the range 3-10%. These results form a basis for a correct description of magnetic and magnetoelectric properties of $R\mathrm{Fe_3(BO_3)_4}$ and for improvement of growth technologies not only of iron borates but also of other crystals grown by flux-melting technique.

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