===== **MAGNETISM** =====

Magnetic and Magnetoelectric Properties of the $Tb_{0.75}Ho_{0.25}Fe_3(BO_3)_4$ Ferroborate

N. V. Volkov[a, b], E. V. Eremin[a, b]*, V. L. Temerov[a], and I. A. Gudim[a]

[a] *Kirensky Institute of Physics, Siberian Branch, Russian Academy of Sciences, Akademgorodok 50–38, Krasnoyarsk, 660036 Russia*

[b] *Siberian Federal University, pr. Svobodnyi 79, Krasnoyarsk, 660041 Russia*

* e-mail: eev@iph.krasn.ru

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Abstract—Single crystals of the $Tb_{0.75}Ho_{0.25}Fe_3(BO_3)_4$ ferroborate have been grown by the group method from a solution−melt based on bismuth trimolybdate. The magnetic and magnetoelectric properties of the ferroborate single crystals have been investigated in the temperature range from 4.2 to 300 K and in magnetic fields up to 9 T. Magnetically, this material is an antiferromagnet with the Néel temperature $T_N = 38.8$ K and easy-axis anisotropy. The magnitude of the magnetoelectric polarization has been found to be more than 1.5−2.0 times greater than the sum of the polarizations induced by the magnetic field for the ferroborates $TbFe_3(BO_3)_4$ and $HoFe_3(BO_3)_4$ taken in the corresponding shares.

1. INTRODUCTION

In recent years, trigonal rare-earth oxyborates $RMe_3(BO_3)_4$ (where R = Y, La−Lu; Me = Fe, Al, Cr, Ga, Sc) have been intensively studied by many Russian and foreign research groups [1−7]. In the case of borates with two magnetic subsystems (ferroborates $RFe_3(BO_3)_4$), it has been established that they belong to multiferroics [1, 3, 7]. Ferroborates have a rhombohedral structure described by the space groups $R32$ or $P3_121$. Below the Néel temperature $T_N = 30−40$ K, the spins of Fe^{3+} ions are antiferromagnetically ordered, while the rare-earth subsystem remains disordered down to temperatures of the order of the 1 K, but, owing to the $f−d$ exchange, it has an influence on the magnetic anisotropy of ferroborates. The orientation of the magnetic moments of iron ions with respect to the crystallographic axes is determined by the type of rare-earth ion: ferroborates have an easy-axis antiferromagnetic structure, when the spins of iron ions are aligned along the trigonal axis c (R = Dy, Tb, Pr) [2], or an easy-plane structure, when the iron spins are ordered in the ab plane perpendicular to the c axis of the crystal (R = Nd, Sm, Eu, Er, Y) [2]. Moreover, the ferroborates $GdFe_3(BO_3)_4$ and $HoFe_3(BO_3)_4$ can undergo a spontaneous spin-reorientation transition from the easy-axis antiferromagnetic structure to the easy-plane structure.

In this regard, it is of interest to investigate changes in the magnetic anisotropy and magnetoelectric properties of ferroborates with substituted compositions, where there are two types of rare-earth ions that stabilize the structures with different types of magnetic anisotropy, which presumably will provide a wider variety of the observed effects and, possibly, their enhancement. For example, in [8], it was shown that the maximum value of the polarization in $Ho_{1-x}Nd_xFe_3(BO_3)_4$ ferroborates is greater than that in pure $HoFe_3(BO_3)_4$. In our previous study [9], we carried out the experimental and theoretical investigations of the magnetic and magnetoelectric properties of $Ho_{1-x}Nd_xAl_3(BO_3)_4$ ferroborates and, on this basis, analyzed the possible reasons for a decrease in the magnetic field induced polarization, which allowed us to make the conclusion about the influence exerted on the magnetoelectric properties of oxyborates with the huntite structure by the crystal field parameters of the rare-earth ion.

This study is devoted to the synthesis and experimental investigation of new substituted ferroborates $Tb_{0.75}Ho_{0.25}Fe_3(BO_3)_4$, as well as to the comparison of their magnetic and magnetoelectric properties with those of the $HoFe_3(BO_3)_4$ and $TbFe_3(BO_3)_4$ compounds.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Single crystals of the $Tb_{0.75}Ho_{0.25}Fe_3(BO_3)_4$ ferroborate were grown from a solution−melt based on bismuth molybdate [10] $(100 − n)$ wt % $[Bi_2Mo_3O_{12} +$

$2.5B_2O_{33} + 0.5[0.75Tb_2O_3 + 0.25Ho_2O_3) + n$ wt % $Tb_{0.75}Ho_{0.25}Fe_3(BO_3)_4$. For $n = 23$, the ferroborates had the saturation temperature $T_{sat} \approx 962°C$ with the concentration dependence $dT_{sat}/dn \approx 12°C/wt$ %. The crystals were grown from a solution−melt 120 g in weight on seeds in the crystal growth mode with a decrease in the temperature at a rate of $1-2°C/day$. After the completion of the growth process, crystals from 4 to 6 mm in size were lifted up above the solution−melt and cooled to room temperature at a rate of no higher than $100°C/h$.

The magnetic properties of the grown single crystals were investigated on a Quantum Design PPMS vibrating-sample magnetometer in the temperature range from 4.2 to 300 K and in magnetic fields up to 9 T. For measurements of the magnetoelectric polarization, epoxy resin electrodes with a conductive filler were applied on the faces of the studied sample prepared in the form of a plane-parallel plate (planes of the faces were perpendicular to the a axis). The charge induced on the sample due to the magnetoelectric effect was measured with an electrometer Keithley 6517B. The magnetic field was applied along the crystallographic twofold axis, i.e., the a axis, and along the b axis perpendicular to the a axis and the c axis.

3. RESULTS AND DISCUSSION

3.1. Structural Transition

It is known that, with a decrease in the temperature, ferroborates $RFe_3(BO_3)_4$ (R = Eu, Gd, Tb, Dy, Ho, Y, Er) undergo the structural transition $R32 \rightarrow P3_121$, the temperature of which increases with a decrease in the ionic radius of the rare-earth ion [11]. This transition is accompanied by anomalies in dielectric properties, thermal expansion, heat capacity, polarization, etc. [2]. The ferroborates grown according to the technology used in this work have different temperatures of the structural transition: $T_s = 92$ K for $TbFe_3(BO_3)_4$ [12] and $T_s = 387$ K for $HoFe_3(BO_3)_4$ [13]. Taking into account the shares of the Tb^{3+} and Ho^{3+} ions, the structural transition in the $Tb_{0.75}Ho_{0.25}Fe_3(BO_3)_4$ compound is expected to occur at 240 K.

The temperature dependences of the magnetic field induced polarization as a function of the direction of the magnetic field $\Delta P_{aa}(T)$ and $\Delta P_{ab}(T)$ are shown in Fig. 1. It can be seen from this figure that, in the temperature range from 220 to 260 K, the two dependences exhibit anomalies that can be attributed to the structural transition $R32 \rightarrow P3_121$.

The coincidence of the calculated structural transition temperature with the experimentally determined value of T_s indicates that then Tb^{3+} and Ho^{3+} ions are present in the crystal in accordance with the specified concentration. It is worth noting that the phase transition is not homogeneous and consists of several peaks.
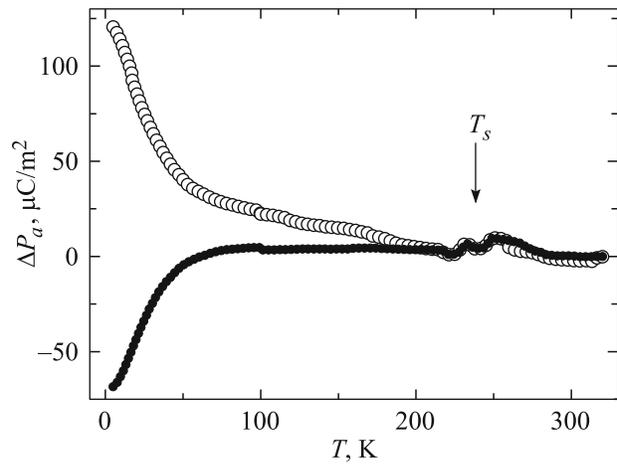

Fig. 1. Temperature dependences of the longitudinal magnetoelectric polarization ΔP_a along the a axis measured in a magnetic field of 9 T for magnetic field orientations $\mathbf{B} \parallel \mathbf{a}$ (open circles) and $\mathbf{B} \parallel \mathbf{b}$ (closed circles).

Apparently, this is associated with the uneven distribution of the Tb^{3+} and Ho^{3+} ions in the matrix of the crystal. Possibly, this unevenness of the distribution is typical of ferroborates, For example, the magnetic phase diagram of $Nd_{1-x}Dy_xFe_3(BO_3)_4$ ferroborates could be described only after the introduction of two magnetic subsystems with different exchange interaction constants [14].

3.2. Magnetic Properties

The temperature and field dependences of the magnetization of the $Tb_{0.75}Ho_{0.25}Fe_3(BO_3)_4$ ferroborates measured in the direction of the magnetic field along the c axis $M_c(T)$ and $M_c(H)$, as well as the dependences measured along the a axis $M_a(T)$ and $M_a(H)$, are shown in Figs. 2 and 3. It can be seen from Fig. 2 that, during cooling in the range from 300 K to the Néel temperature T_N, the magnetization $M_c(T)$ in a magnetic field $B = 0.1$ T increases in accordance with the hyperbolic law, whereas with a decrease in the temperature in the range $T < T_N$ ($T_N = 38.8$ K), it decreases monotonically and tends to zero.

The curve $M_c(T)$ resembles in shape the curve for $TbFe_3(BO_3)_4$; i.e., along direction of the c axis, the magnetic properties are predominantly determined by the terbium ion. This is indicated by the field dependences of the magnetization $M_c(H)$, which suggest that there is a spin-flop transition. The same transition from the easy-axis to canted state in the magnetic field directed along the c axis is observed in the $TbFe_3(BO_3)_4$ ferroborate. However, owing to the fact that the number of Tb^{3+} ions in this compound is smaller by a quarter, the spin-flop transition is shifted toward lower magnetic fields (Fig. 3a).
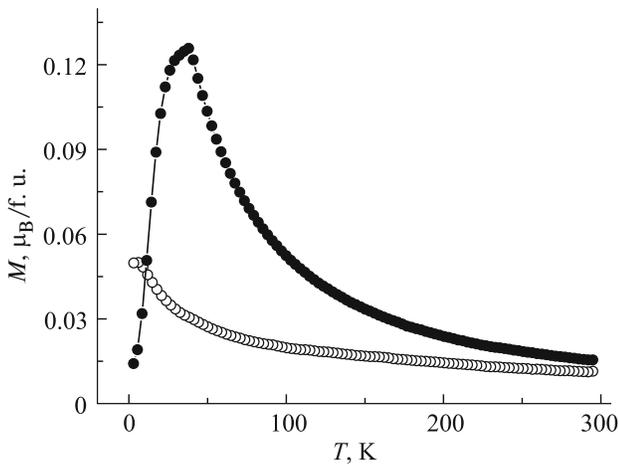
Fig. 2. Temperature dependences of the magnetization of the $Tb_{0.75}Ho_{0.25}Fe_3(BO_3)_4$ ferroborate single crystals measured in a magnetic field of 0.1 T for magnetic field orientations $\mathbf{B} \parallel \mathbf{c}$ (closed circles) and $\mathbf{B} \perp \mathbf{c}$ (open circles).

Since the Tb^{3+} ion is highly anisotropic (i.e., it is almost an Ising ion [12]) with the easy-axis anisotropy, the influence on the magnetic anisotropy of the $Tb_{0.75}Ho_{0.25}Fe_3(BO_3)_4$ ferroborate in the direction of the magnetic field along the *a* axis should be exerted only by the Ho^{3+} ion. However, the observed magnetic properties in the direction of the *a* axis are slightly more intricate. In contrast to the $HoFe_3(BO_3)_4$ ferroborate, the $Tb_{0.75}Ho_{0.25}Fe_3(BO_3)_4$ compound does not undergo a spin-reorientation transition from the easy-axis to easy-plane state with an increase in the temperature, as follows from the temperature and field dependences of the magnetization $M_a(T)$ and $M_a(H)$ (Figs. 2 and 3b).

Thus, we can state that, magnetically, the $Tb_{0.75}Ho_{0.25}Fe_3(BO_3)_4$ ferroborate is described in the framework of the model of a classical two-sublattice antiferromagnet with an easy-axis anisotropy.

3.3. Magnetoelectric Properties

The field dependences of the magnetoelectric polarization $\Delta P_{aa}(H)$ and $\Delta P_{ab}(H)$ at different temperatures and different directions of the magnetic field are shown in Fig. 4. It can be seen from this figure that the magnitude of the magnetoelectric effect reaches $100 \ \mu C/m^2$ (at $T = 5$ K, $B = 9$ T), and the character of the curves differs from that observed for both the $TbFe_3(BO_3)_4$ and $HoFe_3(BO_3)_4$ ferroborates. In contrast to the case of the $HoFe_3(BO_3)_4$ compound, there are no low-field features associated with the spin-flip transition induced by a magnetic field. From the comparison of the considered ferroborate with the $TbFe_3(BO_3)_4$ compound, it follows that, in our case, all the curves $\Delta P_{aa}(H)$ are positive, while the curves
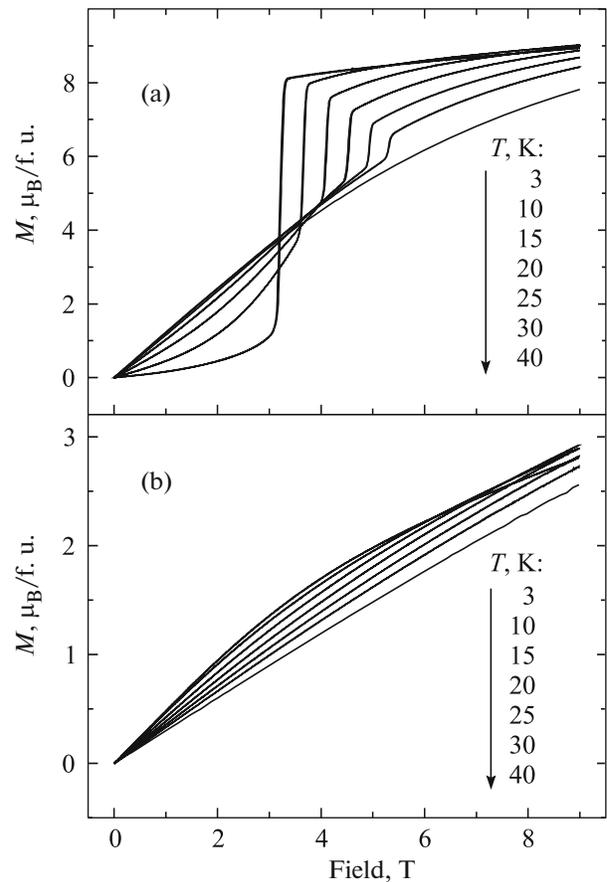

Fig. 3. Field dependences of the magnetization of the $Tb_{0.75}Ho_{0.25}Fe_3(BO_3)_4$ ferroborate single crystals measured at different temperatures for magnetic field orientations (a) $\mathbf{B} \parallel \mathbf{c}$ and (b) $\mathbf{B} \perp \mathbf{c}$.

$\Delta P_{ab}(H)$ are negative, whereas in the case of the $TbFe_3(BO_3)_4$ ferroborate, this is true only for temperatures $T > 50$ K. It should be noted that the shape of the obtained curves most closely resembles the dependences $\Delta P_{aa}(H)$ and $\Delta P_{ab}(H)$ for paramagnetic oxyborates with the huntite structure (see, for example, [6, 7]).

As regards the magnitude of the magnetoelectric effect, it turned out that the simple addition of the values with the corresponding shares of the $TbFe_3(BO_3)_4$ and $HoFe_3(BO_3)_4$ ferroborates does not give the coincidence with the experimentally determined values.

For the direction of the magnetic field $\mathbf{H} \parallel \mathbf{a}$, the magnetoelectric effect in $HoFe_3(BO_3)_4$ is approximately equal to $\Delta P_{aa} = 160 \ \mu C/m^2$ ($B = 9$ T and $T = 5$ K) [15], whereas for $TbFe_3(BO_3)_4$, it is $\Delta P_{aa} = 5 \ \mu C/m^2$ ($B = 9$ T and $T = 5$ K) [16]. If we assume that the contribution to the magnetoelectric effect is introduced by holmium and terbium ions in equal shares, then for our compound it should be equal to $\Delta P_{aa} = \delta P_{ab}(Ho) \cdot 0.25 + \Delta P_{aa}(Tb) \cdot 0.75 \cong 45 \ \mu C/m^2$, which
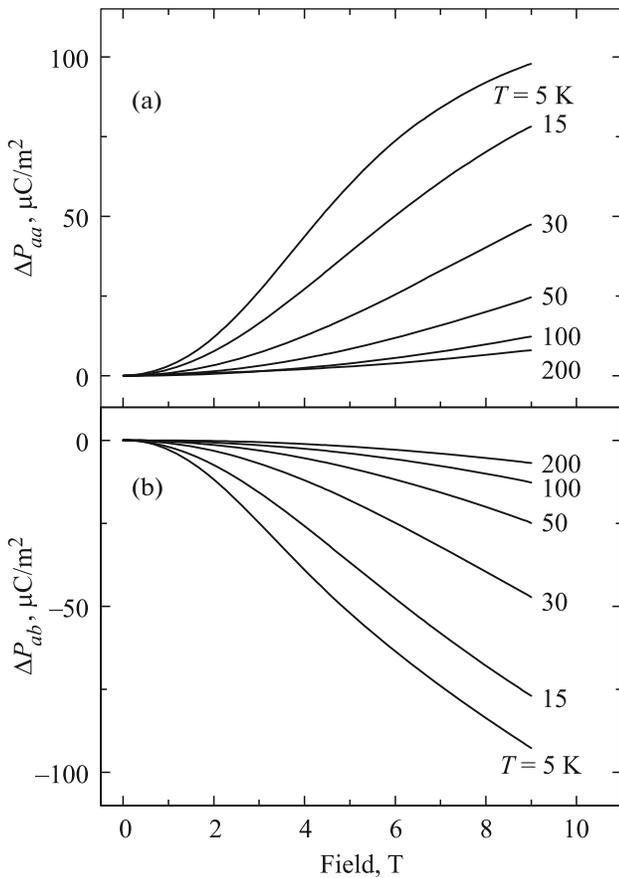
Fig. 4. Field dependences of the longitudinal magneto-electric polarization ΔP_a measured at different temperatures for magnetic field orientations (a) $\mathbf{B} \parallel \mathbf{a}$ and (b) $\mathbf{B} \parallel \mathbf{b}$.

is more than two times less than that observed in the experiment (Fig. 4a).

For the direction of the magnetic field $\mathbf{H} \parallel \mathbf{b}$, we have $\Delta P_{ab}(\mathrm{HoFe_3(BO_3)_4}) = 260 \ \mu\mathrm{C/m^2}$ [15] and ΔP_{ab} $(\mathrm{TbFe_3(BO_3)_4}) = -5 \ \mu\mathrm{C/m^2}$ [16]. In this case, $\Delta P_{ab} = \Delta P_{ab}(\mathrm{Ho}) \cdot 0.25 + \delta P_{ab}(\mathrm{Tb}) \cdot 0.75 \cong 65 \ \mu\mathrm{C/m^2}$, which is approximately 1.5 less than that observed in the experiment (Fig. 4b).

Thus, we can state that the magnitude of the magnetoelectric effect in the $\mathrm{Tb_{0.75}Ho_{0.25}Fe_3(BO_3)_4}$ compound is higher than the expected value. Most likely, this is associated with the change in the energy structure of the rare-earth ion due to local distortions. In other words, the crystal field parameters for $\mathrm{Tb^{3+}}$ and $\mathrm{Ho^{3+}}$ ions in the $\mathrm{Tb_{0.75}Ho_{0.25}Fe_3(BO_3)_4}$ compound apparently change as compared to the crystal field parameters of these ions in the unsubstituted ferroborates $\mathrm{TbFe_3(BO_3)_4}$ and $\mathrm{HoFe_3(BO_3)_4}$. Possibly, this is caused by the increase of local distortions in the studied ferroborate due to the uneven distribution of $\mathrm{Tb^{3+}}$ and $\mathrm{Ho^{3+}}$ ions.

4. CONCLUSIONS

The $\mathrm{Tb_{0.75}Ho_{0.25}Fe_3(BO_3)_4}$ ferroborate was grown by the group method from a solution−melt based on bismuth trimolybdate. The magnetic and magnetoelectric properties of the ferroborate were investigated in the temperature range from 4.2 to 300 K and in magnetic fields up to 9 T.

It was found that, in the temperature dependence of the polarization $\Delta P_a(T)$, there is an anomaly in the temperature range from 220 to 260 K, which we attributed to the structural transition $R32 \rightarrow P3_121$.

Magnetically, the $\mathrm{Tb_{0.75}Ho_{0.25}Fe_3(BO_3)_4}$ ferroborate is an antiferromagnet with the Néel temperature $T_N = 38.8$ K. The field and temperature dependences of the magnetization indicate that the ferroborate is well described as a classical two-sublattice antiferromagnet with an easy-axis anisotropy.

The investigation of the magnetoelectric properties demonstrated that the magnitude of the direct magnetoelectric effect is approximately 1.5−2.0 times greater than the sum of the polarizations with the corresponding shares of $\mathrm{TbFe_3(BO_3)_4}$ and $\mathrm{HoFe_3(BO_3)_4}$. Most likely, this is associated with the change in the energy structure of the rare-earth ions $\mathrm{Tb^{3+}}$ and $\mathrm{Ho^{3+}}$ due to local distortions.

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