CRYSTAL
GROWTH

Melt−Solution Synthesis and Magnetic Properties of SmFe$_{2.8}$Sc$_{0.2}$(BO$_3$)$_4$ Ferroborate

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

[a] *Kirensky Institute of Physics, Federal Research Center "Krasnoyarsk Scientific Center," Siberian Branch, Russian Academy of Sciences, Krasnoyarsk, 660036 Russia*

[b] *Siberian Federal University, Krasnoyarsk, 660041 Russia*

[c] *Siberian State University of Science and Technologies, Krasnoyarsk, 660037 Russia*

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

Abstract—Single crystals of SmFe$_{2.8}$Sc$_{0.2}$(BO$_3$)$_4$ ferroborates are grown in melt−solutions based on bismuth trimolybdate. The magnetic properties of grown single crystals are studied. The presence of long-range magnetic order in these crystals is found.

INTRODUCTION

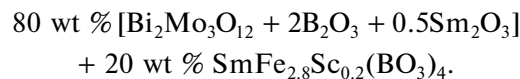The multiferroic properties of trigonal rare-earth oxiborates RM_3(BO$_3$)$_4$ (R = Y, La−Lu, M = Fe, Al, Cr, Ga, Sc) have been intensively studied in the last years [1, 2]. It was recently found [3] that aluminoborates RAl$_3$(BO$_3$)$_4$, which were previously of interest mainly due to their optical and magnetooptical properties, have giant values of magnetoelectric polarization. The value of magnetoelectric polarization in HoAl$_3$(BO$_3$)$_4$ is record for multifferoics: being measured along the crystallographic axis a, with field applied in the perpendicular direction b, it amounts to $\Delta P_{ab}(B_b) = -5240$ μC/m^2 at $T = 5$ K in a field of 9 T [4]. This value exceeds many times the known maximum values of magnetoelectric polarization, including those for ferroborates. An enhancement of the magnetoelectric effect is also observed when Fe^{3+} ions in HoFe$_3$(BO$_3$)$_4$ are replaced with Ga^{3+} ions [5].

In this regard, it is of interest to study other subclasses of borates, for example, with Sc^{3+} ions in the subsystem of small cations. Since the strongest magnetoelectric effect was observed in samarium SmFe$_3$(BO$_3$)$_4$ ferroborate [6], the study of samarium SmSc$_3$(BO$_3$)$_4$ scandoborate is most interesting. However, since melt−solution synthesis of SmSc$_3$(BO$_3$)$_4$ meets certain difficulties, we applied the method of subsequent replacement in the small-radius cation of well-known ferroborate SmFe$_3$(BO$_3$)$_4$.

In this paper, we report the results of studying the melt−solution technique for growing SmFe$_{2.8}$Sc$_{0.2}$(BO$_3$)$_4$ single crystal and its magnetic properties.

GROWTH OF SmFe$_{2.8}$Sc$_{0.2}$(BO$_3$)$_4$ SINGLE CRYSTALS

The growth was performed from a melt−solution based on bismuth trimolybdate solvent of the following composition:

$$80 \text{ wt \%} [\text{Bi}_2\text{Mo}_3\text{O}_{12} + 2\text{B}_2\text{O}_3 + 0.5\text{Sm}_2\text{O}_3]$$
$$+ 20 \text{ wt \% SmFe}_{2.8}\text{Sc}_{0.2}(\text{BO}_3)_4.$$

A solution−melt of mass 150 g was prepared at $T = 1000°$C in a platinum cylindrical crucible (diameter $D = 100$ mm, height $H = 90$ mm) by melting a mixture of Bi$_2$O$_3$, MoO$_3$, B$_2$O$_3$, Sm$_2$O$_3$, Fe$_2$O$_3$, and Sc$_2$O$_3$ oxides in a ratio determined by the aforementioned formula. The crucible was placed in a crystallization furnace, where the temperature decreases from the crucible bottom with a vertical gradient of 1−2°C/cm. The melt−solution was homogenized at $T = 1000°$C for 24 h. Stirring was performed to maintain homogeneity.

Ranges of stability of SmFe$_{2.8}$Sc$_{0.2}$(BO$_3$)$_4$ crystals and the ratios of melt−solution components were determined by direct phase probing. The saturation temperature was determined with an error of ±2°C using probe crystals, which were obtained previously from the same melt−solution under the conditions of spontaneous nucleation on a rotating platinum rod holder. The metastable-zone width $\Delta T_{\text{met}} \approx 12°$C was defined as the maximum supercooling at which nucleation was absent during a 20-h exposure.

To obtain seeds of SmFe$_{2.8}$Sc$_{0.2}$(BO$_3$)$_4$ crystals, we used the method for limiting the number of seeds by nucleation in a thin melt−solution layer. In this case, after determining the crystallization parameters, a rod
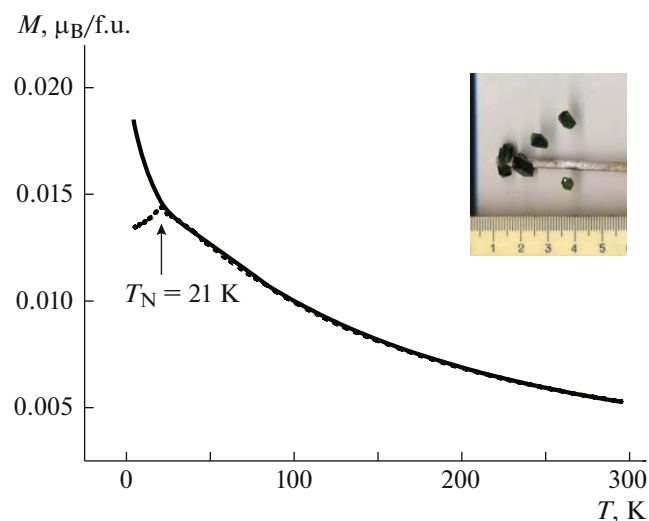
Fig. 1. Temperature dependences of the magnetization of oxiborate $SmFe_{2.8}Sc_{0.2}(BO_3)_4$ with huntite structure, which were measured in a magnetic field of 0.1 T directed along the crystallographic axis c (solid line) and, in the basal plane, along the axis a (dotted line). The photograph of grown crystals is shown in the inset.

was immersed in the melt−solution at the homogenization temperature, and rotation with a speed of 40 rpm was switched on. Two hours later the melt−solution temperature was reduced to 5−7°C below the saturation temperature. Two more hours later the rod was lifted to the colder zone of furnace chamber (with a temperature 10−15°C below the saturation temperature). In this case, only few nuclei were formed in a thin melt−solution layer remaining on the rod. The number of nuclei is small, because the concentration of crystal-forming oxides reduces drastically in the small volume of retained melt−solution layer. The nucleation lasted 1 h. Then the rod was immersed again in the melt−solution, and seeds were grown up for 24 h. Then the rod was took out from the furnace. The remnants of melt−solution were removed by boiling in a 20% aqueous solution of nitric acid. Grown seed crystals were removed from the rod and used in further growth of large crystals.

Four high-quality seeds were fixed on the platinum rod holder, which was suspended above the melt−solution at the homogenization temperature. The holder was immersed in the melt−solution at $T = T_{sat} + 7°C$, and then reverse rotation with a period 1 min and speed $\omega = 30$ rpm was switched on. The temperature was reduced to $T = T_{sat} - 7°C$ 15 min after. Then the melt−solution temperature was reduced with an accelerated rate of 1−3°C/day, so that the crystal growth rate did not exceed 0.5 mm/day. The growth continued for 9−10 days. After the growth, the holder with crystals was lifted above the melt−solution surface and cooled to room temperature with a rate not higher more than 100°C/h. As a result, crystals with a size of 5−7 mm were obtained.

MAGNETIC PROPERTIES

Figure 1 shows the temperature dependences of magnetization of $SmFe_{2.8}Sc_{0.2}(BO_3)_4$ single crystals. The magnetization was measured in a magnetic field of 0.1 T, directed along the c axis ($M_{\parallel}(T)$), and in the basal plane along the second-order axis a ($M_{\perp}(T)$). It can be seen that, despite the substitution of non-magnetic Sc^{3+} ions for magnetic Fe^{3+} ions, the compound still preserves a long-range magnetic order with a Neel temperature $T_N = 21$ K. This value is less than that in pure $SmFe_3(BO_3)_4$ ($T_N = 31$ K [3]). The presence of Sc^{3+} ions with such concentration is insufficient for implementing a transition to the paramagnetic state.

In the paramagnetic region, the magnetization is isotropic and obeys the Curie−Weiss law. The experimentally found paramagnetic Curie temperature turned out to be $\theta = -113$ K, which is less than that for $SmFe_3(BO_3)_4$ ($\theta = -131$ K [6, 7]). The negative sign is indicative of antiferromagnetic exchange interaction in the compound. It can be seen that Curie paramagnetic temperature is also lower. This fact indicates antiferromagnetic interaction of Sm^{3+} ions with the nearest iron ions Fe^{3+}.

CONCLUSIONS

$SmFe_{2.8}Sc_{0.2}(BO_3)_4$ single crystals were grown in melt−solution based on bismuth trimolybdate, and their magnetic properties were studied. The compound was found to preserve long-range magnetic order. The values of Neel and paramagnetic Curie temperatures were determined: $T_N = 21$ K and $\theta = -113$ K, respectively.

REFERENCES

1. Y. Hinatsu, Y. Doi, K. Ito, et al., J. Solid State Chem. **172**, 438 (2003).
2. A. K. Zvezdin, S. S. Krotov, A. M. Kadomtseva, et al., JETP Lett. **81** (6), 272 (2005).
3. K.-C. Liang, R. P. Chaudhury, B. Lorenz, et al., Phys. Rev. B **83**, 180417(R) (2011).
4. A. I. Begunov, A. A. Demidov, I. A. Gudim, and E. V. Eremin, JETP Lett. **97** (9), 528 (2013).
5. N. V. Volkov, I. A. Gudim, E. V. Eremin, et al., JETP Lett. **99** (2), 67 (2014).
6. A. A. Mukhin, G. P. Vorob'ev, V. Yu. Ivanov, et al., JETP Lett. **93** (5), 275 (2011).
7. A. A. Demidov, D. V. Volkov, I. A. Gudim, et al., JETP **116** (5), 800 (2013).
   https://doi.org/10.1134/S1063776113050038

Translated by D. Churochkin