Flux growth of MBO_3 (M=Fe, Ga, In, Sc, Lu) single crystals

S.G. Ovchinnikov, V.V. Rudenko *

Kirensky Institute of Physics, Federal Research Center KSC SB RAS, Akademgorodok 50, bld. 38, Krasnoyarsk 660036, Russia

A B S T R A C T

The temperatures for saturation of the MBO_3 (M=Fe, Ga, In, Sc, Lu) compounds in the M_2O_3–B_2O_3– (70 PbO–30 PbF_2, wt%) solvents are determined. The growth rates of $FeBO_3$ and $GaBO_3$ crystal faces as functions of the flux supercooling are obtained. It is demonstrated that the bulk $FeBO_3$ and $GaBO_3$ crystals can be grown in a narrow flux supercooling range using a controlled seeding technique. The MBO_3 (M=In, Sc, Lu) crystals in the form of (111) plates are synthesized by spontaneous crystallization.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

This work devoted to the development of a flux technique for growing large MBO_3 (M = Fe, Ga, In, Sc, Lu) crystals that have been carried out at the Laboratory of Resonance Properties of Magnetically Ordered Media and the Laboratory of Physics of Magnetic Phenomena of the Kirensky Institute of Physics (Krasnoyarsk). Previously, large bulk $FeBO_3$ crystals have been grown by Die et al. [1] using gas transport and by Bezmaternykh et al. [2] using the flux technique. In [2], the borate-lead solvent was used, the composition of which significantly differs from that of the solvent used by us. A part of the results reported here was published in [3–5].

The $FeBO_3$ crystals hold a particular position among borate compounds. Although the iron borate crystals are well-studied, they still attract attention of researchers as suitable objects for refining various magnetic models. The $FeBO_3$ crystals have a simple rhombohedral lattice with trigonal syngony (calcite structure), sp. gr. $R\bar{3}c$, high Neel temperature (348 K), narrow antiferromagnetic resonance lines, and a series of isostructural diamagnetic analogs. Using the iron borate crystals, Dmitrienko et al. determined for the first time the sign and value of vector components in the Dzyaloshinski−Moriya interaction [6]. In addition, these crystals are interesting for femtosecond magnetooptics. Recently, Kalashnikova et al. [7] observed the effect of pulse excitation on interacting magnetic moments in $FeBO_3$ by the linearly polarized light.

The large high-quality $FeBO_3$ single crystals are widely used in modern synchrotron techniques. In particular, in an ID28 beamline at the European Synchrotron Radiation Facility (ESRF) in Grenoble (France), the $FeBO_3$ single crystals are used as monochromators for X-ray synchrotron radiation with an energy resolution of 10 neV for Mössbauer spectroscopy of extremely small (micron) samples.

The modern requirements of the large high quality $FeBO_3$ single crystals cannot be satisfied by the technology described early in [3]. Recently we have optimized the temperature regimes that results in the strong decreasing of the growth rate and allows us to obtain large качественных crystals.

Using the technique for growing MBO_3 (M=Ga, In, Sc, Lu) diamagnetic crystals [4,5], the samples with the Fe^{3+} impurity were obtained. Electron spin resonance study of the isostructural diamagnetic analogs of MBO_3 (M=Ga, In, Sc, Lu) with the trivalent iron impurity allowed us to quantitatively describe the anisotropy in the magnetically concentrated $FeBO_3$ crystal [8].

The important parameters of the controlled crystal synthesis are the dependence of saturation temperature T_S on equilibrium concentration of the dissolved crystal phase and the dependence of the number of crystallization centers formed on a crystal holder and crystal face growth rates on the flux supercooling (ΔT).

2. Experimental

The experiments were carried out in a shaft furnace equipped with a flux mixer. The temperature was maintained accurate to 0.1 °C by an RTN-3N regulator. A platinum-platinum/rhodium

thermocouple was used to control temperature.

The solubility of all MBO$_3$ compounds under study was investigated using the same technique. As an example, we take the GaBO$_3$ compound, whose solubility was investigated at temperatures of 780 – 860°C. The initial Ga$_2$O$_3$, B$_2$O$_3$, PbO, and PbF$_2$ reagents were weighted for GaBO$_3$ contents of 24.7, 25.0, and 25.6 wt% in the GaBO$_3$–(47.7B$_2$O$_3$–36.6–PbO–15.7PbF$_2$, wt%) pseudo-binary system and fused in a 75 cm^3 platinum crucible. The weight was 150 g. Then, the crucible was placed in a furnace heated to 1150°C and held until complete dissolution of the oxides. After that, the temperature was rapidly decreased to 700°C and the crucible was held at this temperature for 2–4 h. Then, the final temperature T_S was set for 24 h. During exposure at 700, 1150, and T_S°C, the flux was mixed (dynamic mode). After exposure at T_S, the crucible was removed from the furnace and quenched in air. The crystal phase was separated from the flux in the (10–20)% aqueous solution of nitric acid. The obtained crystal phase was weighted and studied by X-ray diffraction analysis. Taking into account the weight of the initial components and obtained crystal product, the equilibrium GaBO$_3$ concentration required for the flux saturation at T_S was calculated.

To determine the number of crystallization centers and growth rates of the FeBO$_3$ crystal faces as functions of ΔT, we used the following technique. The Fe$_2$O$_3$ (22.5 g), B$_2$O$_3$ (232.4 g), PbO (136.6 g), and PbF$_2$ (58.5 g) reagents were fused in a 225 cm^3 platinum crucible. When the oxides were completely dissolved at 1000°C, the temperature was rapidly decreased and the required flux supercooling ΔT was specified on the basis of the solubility curves. Note that the flux saturation temperature T_S can differ within two nominally identical compositions and is refined using a test-seed technique. The flux was held at the specified ΔT value for 24 h in the dynamic mode. Crystal centers were formed on a mixer, in particular, due to the temperature gradient along its axis. After exposure, the crystal holder (mixer) was removed from the furnace, the number N of crystallization centers was counted, and the crystal diameter in the (111) plane (d) and in the [111] direction (L) was measured. Then, the parameter $\delta = (L/d)$ averaged over all crystals was determined for the specified supercooling.

The largest grown crystal was used to determine the face growth rates. The largest crystal was assumed to be held at specified ΔT for 24 h. This is a good approximation, since the number of centers forming on the mixer is relatively large. Since the flux evaporation loss was insignificant, the same composition was repeatedly used.

3. Results and discussion

Figs. 1–5 presents the MBO$_3$ (M=Fe, Ga, In, Sc, Lu) solubility curves [3–5]. We note that in this work, dependence at Figs. 1–5 were processed using least square method, compared to [3–5]. In Fig. 6, open circles show the crystal habitus parameter $\delta = (L/d)$ as a function of the flux supercooling and closed circles, the number of FeBO$_3$ crystallization centers formed on the mixer at the specified flux supercooling. The character of distribution of the FeBO$_3$ crystal face growth rates with ΔT leads to the fact that the bulk samples can be grown at certain flux supercooling values. This can be clearly seen in Fig. 6.

3.1. Growing the FeBO$_3$ bulk crystals from the Fe$_2$O$_3$–B$_2$O$_3$–(70PbO+30PbF$_2$ wt%) flux by controlled synthesis

The charge containing Fe$_2$O$_3$ (22.5 g), B$_2$O$_3$ (232.4 g), PbO (136.6 g), and PbF$_2$ (58.5 g) was fused in a 225 cm^3 platinum crucible at a temperature of 850 °C. Then, the crucible was placed in a furnace heated to 1000 °C and the charge was mixed with a rotational
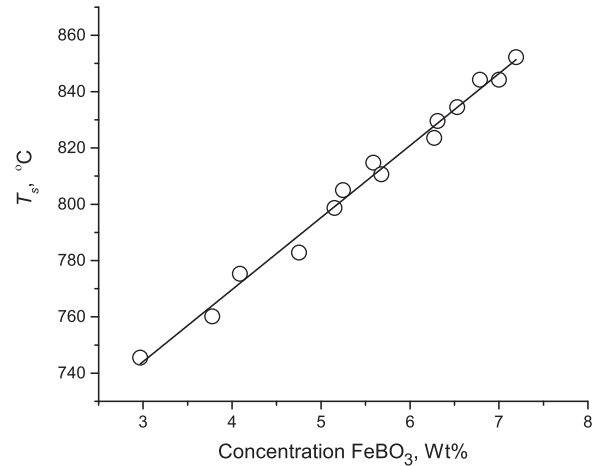

Fig. 1. Solubility of FeBO$_3$ in the (53.3B$_2$O$_3$–32.7PbO–14.0PbF$_2$, wt%) pseudo-binary system.
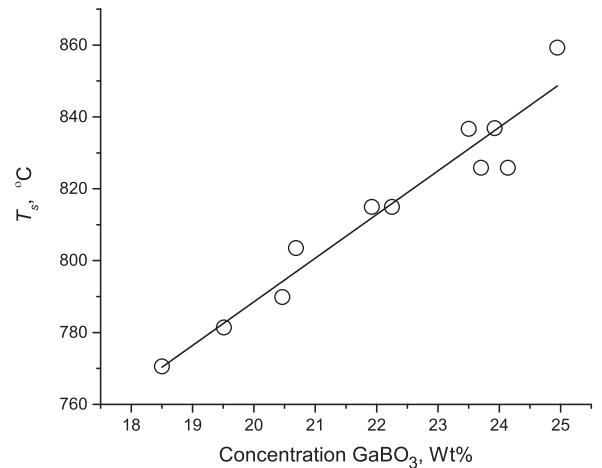

Fig. 2. Solubility of GaBO$_3$ in the (47.7B$_2$O$_3$–36.6PbO–15.7PbF$_2$, wt%) pseudo-binary system.
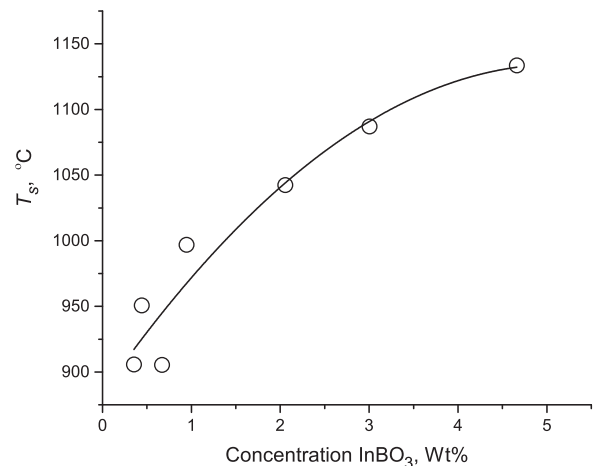

Fig. 3. Solubility of InBO$_3$ in the (41.3B$_2$O$_3$–41.1PbO–17.6PbF$_2$, wt %) pseudo-binary system.

speed of 60 rmp until complete dissolution of the charge. After that, the flux saturation temperature T_S was determined by a test-seed technique. A certain supercooling ($(8 – 10)$°C was specified, the charge was mixed for 24 h, and then the number of crystallization
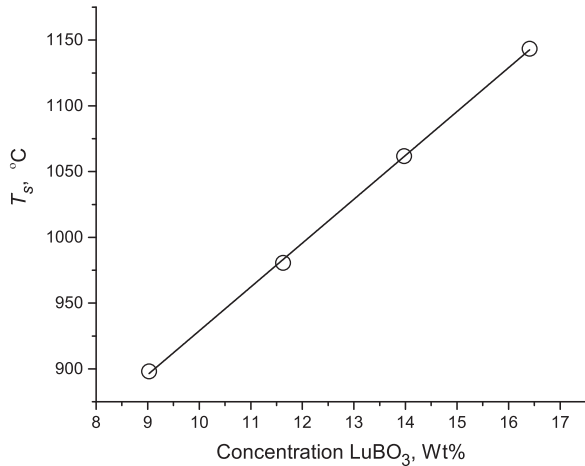
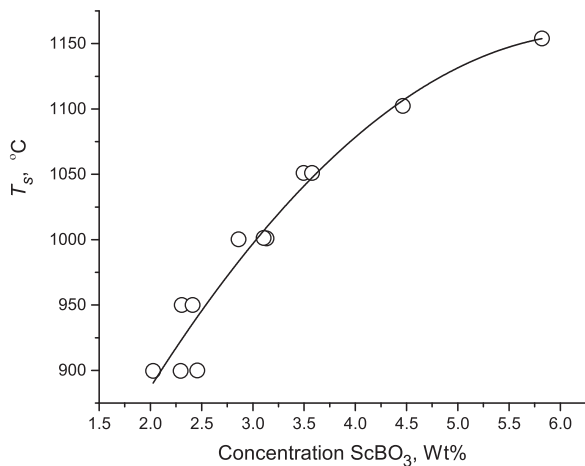**Fig. 4.** Solubility of LuBO₃ in the (37.7B₂O₃–43.6PbO–18.7PbF₂, wt %) pseudo-binary system.

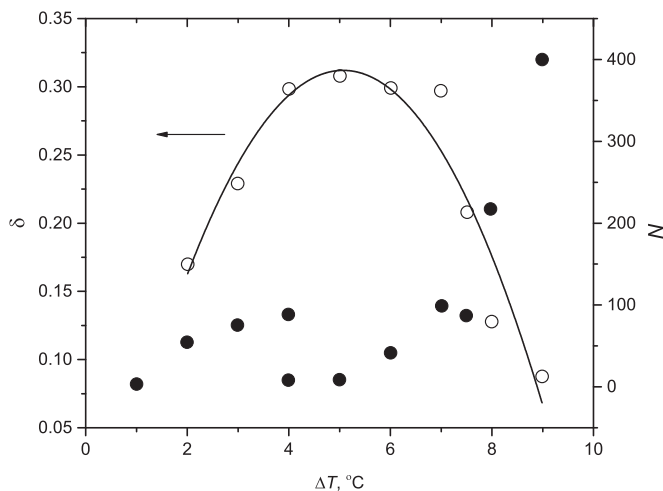**Fig. 5.** Solubility of ScBO₃ in the (41.1B₂O₃–41.2PbO–17.7PbF₂, wt %) pseudo-binary system.

Fig. 6. Dependence of the crystal habitus parameter $\delta=(L/d)$, where L is the average crystal size along the [111] direction and d is the average diameter in the (111) plane, on the flux supercooling. Closed circles show the number N of crystallization centers formed on the mixer at the flux supercooling ΔT.

centers was counted. These experiments were repeated for several times for the given composition until the number of centers on the mixer became 10–15. The last experiment was repeated at the obtained supercooling and then the temperature was increased by (3–

5)°C. At this temperature, further nucleation of crystals on the mixer is improbable. After that, the temperature was decreased according to the law calculated using the expression from [9].

According to [9], the current flux temperature T_t at the instant of time t is

$$T_t = T_S - \Delta T - \left[m(1 - C_0)G_1 \right]/(G_0 - G_1)$$

where $T_S = 863\ °C$ is the flux saturation temperature, ΔT is the flux supercooling (5–7 °C in this experiment), which was kept constant during the synthesis; $m = \Delta T_S/\Delta C = 27 \cdot 10^2\ °C$ is the solubility curve slope; $C_0 = 0.0718$ is the FeBO₃ concentration in zero instant of time; $G_0 = 450\ g$ is the initial flux weight; $G_1 = 2prNV_{(111)}^2\ V_{[111]}t^3$ is the weight of disk-shaped crystals forming during the synthesis; $\rho = 4.28\ g/cm^3$; $N \approx 10\text{–}20$; $V_{(111)} = 6 \cdot 10^{-4}\ cm/h$; $2V_{[111]} = 2 \cdot 10^{-4}\ cm/h$; and t is the time (in hours) counted from the moment corresponding to $T_0 = 858\ °C$ ($\Delta T = 5\ °C$).

In this expression for the temperature drop with time, G_1 in the denominator is negligible as compared with G_0. The final current temperature expression for calculating the growth regime for the FeBO₃ crystals is

$$T_t \approx \left(858 - 10^{-7}t^3 \right)°C,$$

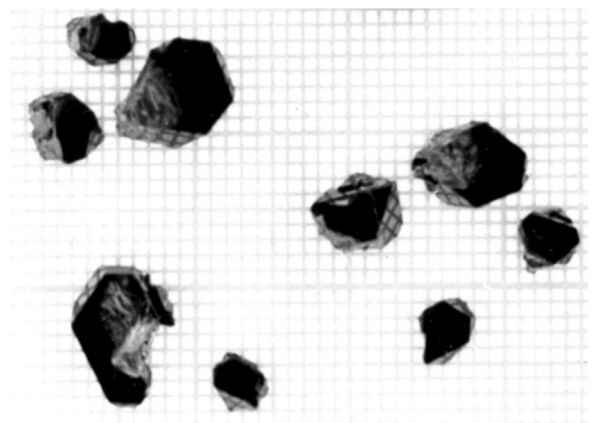where t – time in hours. The temperature was decreased to 850 °C.

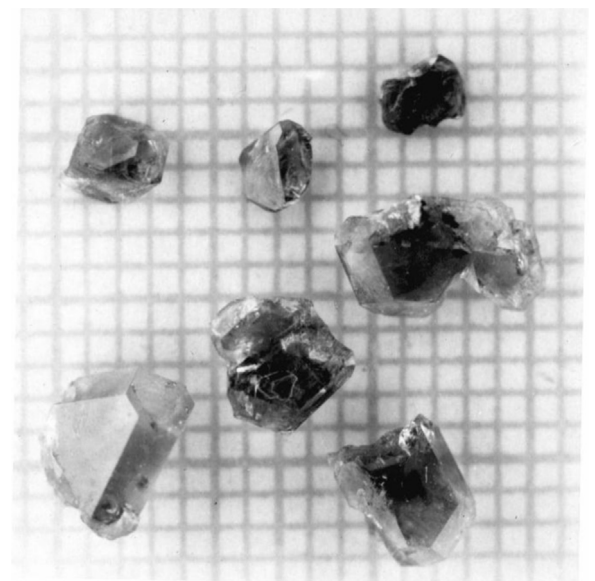**Fig. 7.** FeBO₃ crystals grown by the controlled synthesis. The scale factor is 1 mm.

Fig. 8. GaBO₃ crystals grown by controlled synthesis. The scale factor is 1 mm.

Fig. 7 shows a photograph of the obtained crystals. The scale factor is 1 mm.

3.2. Growing the GaBO₃ bulk crystals from the Ga₂O₃–B₂O₃–(70PbO+30PbF₂ вес.%) flux by controlled synthesis

3.2. Growing the $GaBO_3$ bulk crystals from the Ga_2O_3–B_2O_3–($70PbO+30PbF_2$ вес.%) flux by controlled synthesis

A technique for preparing crystallization of the $GaBO_3$ bulk samples is analogous to that used for iron borate. The crystal growth rates in the [111] direction are $V_{[111]} = 3 \cdot 10^{-4}$ cm/h and, in the (111) plane, $V_{(111)} = 6 \cdot 10^{-4}$ cm/h at a supercooling of $\Delta T = 15$ °C ($T_0 = 830$ °C) in the dynamic mode. The rotational speed of the mixer is 60 rpm.

When the number of crystallization centers on the mixer attained ~ 10, the experiment was repeated under the same conditions. Then, the temperature was rapidly increased to $T_0 = 835$ °C ($\Delta T = 10$ °C). At such supercooling values, the nucleation on the mixer is almost missing. After that, the temperature was decreased in the regime calculated analogously to the case of iron borate. Here, the following parameters were used: $T_S = 845$ °C, $\Delta T = 10$ °C (kept constant during the synthesis), $m = 11.43 \cdot 10^2$ °C, $C_0 = 0.2425$, $G_0 = 300$ g, $G_1 = 2\pi\rho N V_{(111)}^2 V_{[111]} t^3$ (weight of a solid phase precipitated during the growth of disk-approximated crystals), $\rho = 5$ g/cm³, $N = 10$, $V_{(111)} = 6 \cdot 10^{-4}$ cm/h, and $2 V_{[111]} = 6 \cdot 10^{-4}$ cm/h; time t in hours was counted from the instant of time corresponding to $T_0 = 835°$ C. The final expression for T_t is

$$T_t \approx \left(835 - 10^{-7} t^3\right)° C,$$

The temperature was decreased to 825 °C. After the synthesis, 10–15 large crystals with maximum sizes of $5 \times 5 \times 2.5$ mm³ were found on the mixer (Fig. 8).

3.3. Growing the MBO₃ (M=In, Lu, Sc) crystals from the M₂O₃–B₂O₃– (70PbO+30PbF₂ wt.%) flux by spontaneous crystallization

3.3. Growing the MBO_3 (M=In, Lu, Sc) crystals from the M_2O_3–B_2O_3– ($70PbO+30PbF_2$ wt.%) flux by spontaneous crystallization

The $InBO_3$, $LuBO_3$, and $ScBO_3$ crystals were grown by spontaneous crystallization from the flux using the following technique. The initial reagents In_2O_3 (5.3 g), B_2O_3 (60.6 g), PbO (58.9 g), and PbF_2 (25.2 g); Lu_2O_3 (20.6 g), B_2O_3 (51.0 g), PbO (54.9), and PbF_2 (23.5 g); and Sc_2O_3 (5.2 g), B_2O_3 (61.1 g), PbO (58.6 g), and PbF_2 (25.1 g) were fused in 75-cm³ platinum crucibles at a temperature of about 900 °C. The crucibles were covered with platinum covers and placed in a furnace. The temperature in the furnace was rapidly increased to 1200 °C and held for 5 h. Then, the temperature was rapidly decreased to 1080 °C and held for 4 h. After that, the temperature was rapidly increased to 1135 °C and then decreased to 950 °C with a pitch of 1°/h. Photographs of the obtained $InBO_3$, $LuBO_3$, and $ScBO_3$ crystals are presented in Fig. 9a, b, and c, respectively.

The described technological regimes can be used for growing the MBO_3 (M=In, Lu, Sc) crystals in the form of hexagonal plates. However, to solve some experimental problems, bulk samples are often required. The experiments reported in this study are insufficient to develop a technique for synthesis of such crystals. Nevertheless, our physicochemical investigations can be used in further refining of the regimes for obtaining high-quality MBO_3 (M=In, Lu, Sc) bulk crystals.

4. Conclusions

The large high-quality bulk $FeBO_3$ crystals can be used in synchrotron radiation facilities. The diamagnetic bulk and plate MBO_3 (M=Ga, In, Lu, Sc) samples with the paramagnetic Fe^{3+} impurity fabricated using the pure crystal technique can be used in electron
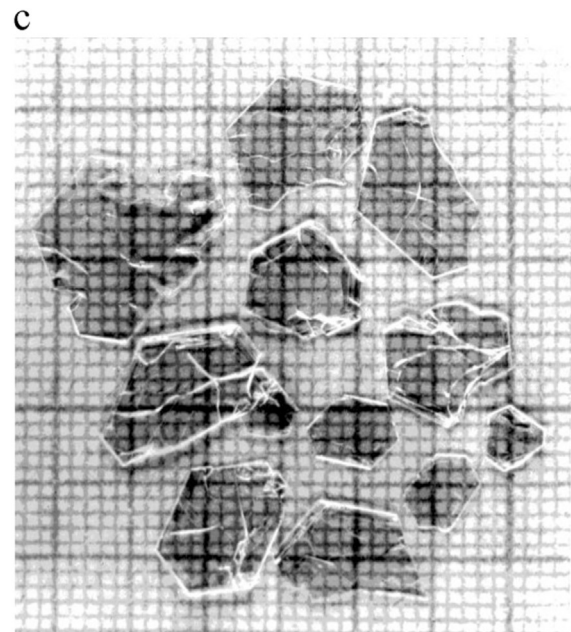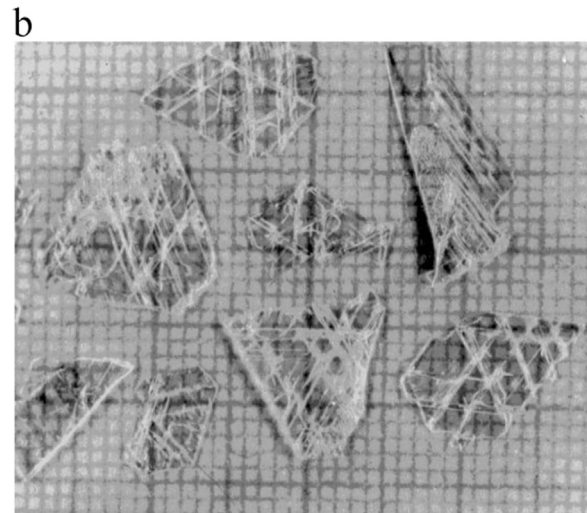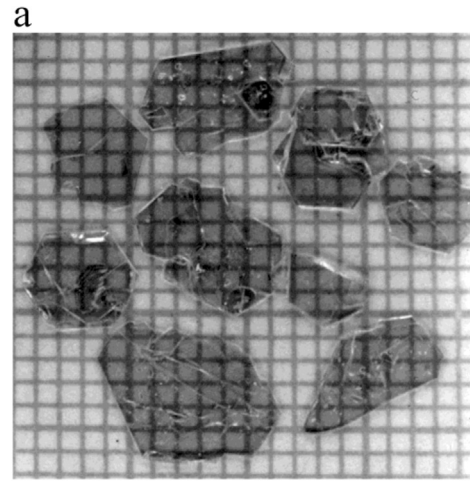
Fig. 9. a. $InBO_3$ crystals grown by spontaneous crystallization. The scale factor is 1 mm. b. $LuBO_3$ crystals grown by spontaneous crystallization. The scale factor is 1 mm. c. $ScBO_3$ crystals grown by spontaneous crystallization. The scale factor is 1 mm.

spin resonance experiments (see, for example [8],). The electron spin resonance study made it possible to quantitatively describe the magnetic anisotropy in the $FeBO_3$ crystals [8].

Acknowledgements

References

[1] R. Die, A. Raubar, F. Friedrich, J. Cryst. Growth 29 (1975) 225–233.
[2] L.N. Bezmaternykh, V.G. Maschenko, V.A. Chikhachev, V.S. Bliznyakov, Authors certificate no.1059029. Published in bulletin no. 45 (1983).
[3] G.A. Petrakovskii, V.V. Rudenko, V.M. Sosnin, G.N. Stepanov, Acta Phys. Hung. 61 (1987) 243–246.
[4] V.V. Rudenko, Crystallogr. Rep. 40 (1995) 347–348.
[5] V.V. Rudenko, Inorg. Mater. 34 (1998) 1253–1254.
[6] V.E. Dmitrienko, et al., Nat. Phys. 10 (2014) 202–206.
[7] A.M. Kalashnikova, et al., Phys. Rev. Lett. 99 (2007), 167205-1 – 167205-4.
[8] S.G. Ovchinnikov, V.V. Rudenko, Phys.-Uspekhi 57 (2014) 1180–1198.
[9] O.M. Konovalov, S.N. Li Fun-ga, Izv. Akad. Nauk Ussr. Fiz. 35 (1971) 1227–1228.