Synthesis of composite single crystal structures on the basis of iron borate for fundamental studies and practical applications

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Abstract. Composite single crystal structures based on iron borate FeBO$_3$, namely diamagnetically diluted iron-gallium Fe$_{1-x}$Ga$_x$BO$_3$ and iron-aluminium Fe$_{1-x}$Al$_x$BO$_3$ borates with low $x$-values, as well as doped GaBO$_3$:Ni single crystals with Ni 0.1-0.01 mass %, have been synthesized using modified flux growth technique. Two technological modes that allowed improving the quality of the samples have been developed: crystallization in (1) open and (2) closed crucibles. Thin magnetic film of iron borate on a diamagnetic gallium borate substrate have been synthesized by liquid-phase epitaxy route.

1. Introduction

Iron borate FeBO$_3$ is a unique “transparent magnet” that combines a spontaneous magnetization at room temperature and transparency in the visible region of the spectrum [1]. It possesses a calcite structure with spatial symmetry group $D_{3d}^4$. From the standpoint of magnetic structure, FeBO$_3$ is a two-sublattice easy-plane trigonal antiferromagnet with weak ferromagnetism [1]. Its magnetic state is quite sensitive to external magnetic fields, pressures, temperature, etc. This fact makes FeBO$_3$ of a great interest for possible practical applications and fundamental research, see e.g. [2-8]. Such crystals can be used as elements of magnetic memory, magneto-optical and magnetoacoustic transducers, sensors of weak magnetic fields, pressure and temperature.

The isomorphous substitution of a part of Fe$^{3+}$ ions by ions of other metals makes it possible to modify the physical properties of iron borate and form new ones. For instance, diamagnetically diluted crystals Fe$_{1-x}$Ga$_x$BO$_3$ allow fine-tuning such characteristics as a magnetocrystalline anisotropy, exchange and Dzyaloshinskii-Moriya interaction, the Neel temperature, etc [9-12]. Decreasing of the latter one is extremely important for applications of iron borate based crystals as a unique monochromators for synchrotron Mössbauer spectroscopy [13-16]. In this case extremely strict requirements are imposed on the quality of these crystals. Meanwhile, diamagnetic dilution decreases a degree of structural perfection [16] that leads to the necessity of testing different diamagnetic ions and modification of a standard procedure of crystal synthesis.

In doped FeBO$_3$:Ni single crystals photomagnetic properties are observed, namely, a light-induced dynamic instability and photomagnetic memory [17]. The microscopic nature of these properties is still under the question. In order to elucidate this issue we propose to synthesize and study by Electron Paramagnetic Resonance GaBO$_3$ single crystals with a small admixture of Ni. In these materials Ni ions are located in the diamagnetic matrix of Ga ions; this matrix is isostructural to Fe one in FeBO$_3$. Thus, paramagnetic Fe ions “do not interfere” studying the magnetic state of Ni.
For obtaining abovementioned single crystals, the flux growth technique seems to be the most appropriate [1, 12, 15, 18-20]. This is due to the fact that it allows obtaining crystals that are of a better structural quality than those obtained by gas phase technique [15]. Moreover, flux growth technique allows obtaining single crystals in the form of thin basal plates that is crucial for applications in synchrotron Mössbauer spectroscopy [15].

One more outstanding object for fundamental studies and practical applications is thin magnetic film of FeBO$_3$ on diamagnetic substrate. Such composite structure will make it possible to carry out fundamental studies of the nature of surface magnetism in FeBO$_3$ and can be considered as a magnetic memory element [2].

The aim of the present work is to synthesize composite single crystal structures based on iron borate: Fe$_{1-x}$Me$_x$BO$_3$ (Me = Ga, Al) single crystals with low $x$ and doped GaBO$_3$:Ni single crystals with Ni 0.1-0.01 mass % using developed by us (in order to improve the quality of the crystals) modified flux growth technique, as well as thin epitaxial films of FeBO$_3$ on diamagnetic GaBO$_3$ substrate using liquid-phase epitaxy (LPE) route.

2. Experimental details

The standard procedure of flux growth technique includes the following steps [15, 20]:

1. preparing the charge by mixing reagents weighed in predetermined ratios;
2. obtaining a homogeneous solution melt in a metallic crucible by successively adjoining small portions of the charge to a metallic crucible at 870 °C;
3. slow cooling of the solution-melt down to room temperature in according to predetermined temperature mode;
4. extraction of the synthesized crystals from the crucible by boiling in 20 % solution of HNO$_3$.

In order to obtain Fe$_{1-x}$Me$_x$BO$_3$ (Me = Ga, Al) and GaBO$_3$:Ni single crystals, crystallizations were carried out in the Me$_2$O$_3$ (Me = Ga, Al)–Fe$_2$O$_3$–B$_2$O$_3$–PbO–PbF$_2$ and NiO–Ga$_2$O$_3$–B$_2$O$_3$–PbO–PbF$_2$ systems, respectively.

It should be noted that for crystals with different compositions the development of specific charge compositions and temperature modes has been required.

During the standard procedure of flux growth technique cooling of the synthesized crystals occurs in the solution melt that leads to mechanical stresses and destruction of the crystals. We have substantially modified the process of extraction of synthesized crystals from a crystallization setting. As a result, two technological modes have been developed: (1) crystallization in open and (2) closed crucibles. During the first one, the synthesis has been carried out using a seed holder that was extracted with the synthesized crystals before solidification of the solution-melt. In the latter mode the solution-melt was drained from a crucible at high temperatures immediately after finishing of crystal growth. Both modes required the modernization of crystallization setting.

Using a seed holder made it possible to synthesize thin magnetic film of iron borate on a diamagnetic gallium borate substrate. In this case, the seed crystal is GaBO$_3$, and a thin film of FeBO$_3$ is synthesized by LPE route. This route for synthesizing thin films makes it possible to obtain films on two surfaces of substrate crystal [21]. A technique for fixing the substrate crystal to a seed holder that allows obtaining a thin film of FeBO$_3$ on one surface of GaBO$_3$ single crystal has been developed. For this purposes a platinum fixing mask was used.

3. Results and discussion

The synthesized iron borate FeBO$_3$ and gallium borate GaBO$_3$ single crystals, diamagnetically diluted crystals Fe$_{1-x}$Ga$_x$BO$_3$ and Fe$_{1-x}$Al$_x$BO$_3$ with contents of Ga and Al in the charge 0.05 (in what follows, the value of $x$ is mentioned as in the charge) and GaBO$_3$:Ni single crystals are shown in Figure 1. Our preliminary X-ray fluorescence studies have shown the presence of Ga and Al in Fe$_{1-x}$Ga$_x$BO$_3$ and Fe$_{1-x}$Al$_x$BO$_3$ crystals, respectively, as well as Ni in GaBO$_3$:Ni. Crystals have the form of thin hexagonal plates with the dimensions of 3 mm in the basal plane and up to 400 µm in the perpendicular direction. Charge compositions used in the synthesis are shown in Table 1. Iron borate
FeBO$_3$ single crystals have been synthesized using crystallization in closed crucible, *vide supra*. Other crystals from these series have been obtained using open crucible synthesis. The synthesized gallium borate GaBO$_3$ single crystals have been used as a substrate for thin films of FeBO$_3$, see Figure 1d. The GaBO$_3$ single crystal was immersed into the homogeneous solution-melt at a temperature of 800 - 825 °C for 0.5 - 3 hours that makes it possible to obtain films of different thicknesses.

![Figure 1](image1.png)

Figure 1. Optical microscope pictures of: (a) GaBO$_3$, Fe$_{1-x}$Ga$_x$BO$_3$ with $x=0.05$ and FeBO$_3$ single crystals (from left to right), (b) Fe$_{1-x}$Al$_x$BO$_3$ single crystals with $x=0.05$, (c) GaBO$_3$:Ni single crystals and (d) electron microscope pictures of FeBO$_3$ film (grey) on GaBO$_3$ substrate (light grey), chip shows the film and the substrate in depth.

Table 1. Charge compositions used for synthesis of composite single crystal structures based on iron borate.

|           | Fe$_2$O$_3$ | Ga$_2$O$_3$ | Al$_2$O$_3$ | NiO | B$_2$O$_3$ | PbO | PbF$_2$ |
|-----------|-------------|-------------|-------------|-----|------------|-----|--------|
| FeBO$_3$  | 5.7         | -           | -           | -   | 51.3       | 29.3| 13.7   |
| GaBO$_3$  | -           | 18.6        | -           | -   | 42.4       | 27.3| 11.7   |
| FeBO$_3$(film) | 4.91 | -           | -           | -   | 58.32      | 25.12| 11.65  |
| Fe$_{1-x}$Ga$_x$BO$_3$ | $x=0.05$ | 5.39       | 0.34        | -   | 51.23      | 29.31| 13.73  |
| Fe$_{1-x}$Al$_x$BO$_3$ | $x=0.05$ | 5.54       | 0.19        | -   | 51.23      | 29.31| 13.73  |
| GaBO$_3$:Ni | -   | 18.597     | -           | 0.003| 42.43      | 27.32| 11.65  |
| Ni 0.1-0.01 mass % | - | 18.597 | - | | 42.43 | 27.32 | 11.65 |
Typical temperature mode used in synthesizing iron borate based single crystals is shown in Figure 2 and includes following steps:

1. furnace heating;
2. homogenization of the solution-melt;
3. sharp temperature dropping in order to avoid appearance of spurious phases;
4. slow cooling in order to provide nucleation and crystal growth (at the end of this step crystals are extracted from the crucible);
5. furnace cooling and switching it off.

It should be noted that temperature mode has been modified for obtaining crystals with definite compositions during synthesis in opened and closed crucibles.

![Figure 2](image-url)

**Figure 2.** Typical temperature mode used in synthesizing iron borate based single crystals.

4. Conclusions
A standard procedure of flux growth technique has been modified. Namely, we have substantially modified the process of extraction of synthesized crystals from the solution-melt before the solidification of the latter. Thus, two technological modes of synthesis: in opened and closed crucibles are developed. Iron borate based composite single crystal structures, \( \text{Fe}_{1-x}\text{Ga}_x\text{BO}_3 \), \( \text{Fe}_{1-x}\text{Al}_x\text{BO}_3 \) and \( \text{GaBO}_3:\text{Ni} \), as well as epitaxial film of \( \text{FeBO}_3 \) on diamagnetic \( \text{GaBO}_3 \) substrate have been synthesized using developed techniques. Fundamental studies of the synthesized structures allow one to get insight in the magnetic properties of trigonal magnets, moreover, these properties can be fine-tuned that opens up great opportunities for the practical application of such materials.

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