

Synthesis of composite structures on the basis of GaBO₃ and FeBO₃ trigonal crystals

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Abstract. Film of iron borate FeBO₃ is of a great interest as a model object for various scientific studies and is a promising material for practical applications in different branches of experimental science and engineering. Thin magnetic films of FeBO₃ on GaBO₃ single crystal substrate were prepared by a liquid phase epitaxy route. In order to observe a mechanism of film formation we have carried out optical microscopy studies. X-ray diffraction analysis has confirmed the existence of the FeBO₃ layer on the GaBO₃ substrate.

1. Introduction

Iron borate, FeBO₃, is one of the most interesting dielectric magnetic materials. This is due to a unique set of its properties: magnetic, magneto-acoustic, optical, magneto-optical, resonance, etc, see e.g. [1-6]. From the viewpoint of magnetic properties FeBO₃ is an easy-plane transparent antiferromagnet with a weak ferromagnetism, the Néel temperature being 348 K. It has a rhombohedral calcite structure with D_{3d}⁶ space group [7]. Due to the features of the magneto-crystalline structure, characteristics of a thin near-surface layer of iron borates radically differ from those of the volume [8, 9]. We assume that thin iron borate magnetic films are appropriate objects to study the effects of surface magnetism by magneto-optics techniques. Thus the aim of the present work is to develop synthesis technique and to prepare FeBO₃ films on a single crystal optically transparent diamagnetic substrate. To achieve this goal it is necessary to:

- choose and prepare a high-quality single crystal to be used as a substrate for synthesis a thin layer of iron borate;
- choose the synthesis technique, determine charge compositions and temperature modes for obtaining iron borate films.

Iron borates can be grown by two routes: (i) from the gas phase and (ii) from the solution in the melt. The first technique allows to synthesize bulk crystals [10], and the second one to obtain thin hexagonal plates [11, 12]. For the purposes of the present work substrates of a high structural perfection are required. The solution in the melt technique has proved to be most appropriate to synthesize required single crystals of a high quality [12, 13]. Thus it should be used for the preparation of the substrate. As a most promising technique for synthesizing thin iron borate films a liquid phase epitaxy (LPE) has been selected.



In the present work we develop synthesis technique, obtain composite structures on the basis of iron borate crystals, carry out optical microscopy and X-ray diffraction (XRD) studies of the synthesized samples.

2. Experimental

Gallium borate GaBO_3 single crystals have been used as a substrate to synthesize thin iron borate film. The GaBO_3 solution in the melt crystallization was carried out in the $\text{Ga}_2\text{O}_3 - \text{B}_2\text{O}_3 - \text{PbO} - \text{PbF}_2$ system.

Iron borate FeBO_3 film has been synthesized by LPE in the $\text{Fe}_2\text{O}_3 - \text{B}_2\text{O}_3 - \text{PbO} - \text{PbF}_2$ system.

The charge compositions and temperature modes for both crystallizations have been chosen based on the results of differential thermal analysis and probe method [12].

Control of temperature mode of crystallization was carried out using laboratory-developed microprocessor system. Experiments can be performed in a temperature range from room temperature to 1150°C , maintaining the accuracy of the temperature $\pm 0.2^\circ\text{C}$.

In order to study steps and to determine a mechanism of film formation we have carried out studies using optical microscope.

The unit cell parameter c [7] of the film have been determined by means of XRD analysis with a DRON-3 diffractometer using monochromatic copper radiation ($K \lambda_{\text{Cu}} = 1.54051 \text{ \AA}$).

3. Results and discussions

One of the most important conditions for a successful synthesis of a magnetic film is a selection and preparation of an appropriate substrate. Gallium and iron borates, GaBO_3 and FeBO_3 , both have calcite structure with space group D_{3d}^6 [14], therefore, their unit cells are identical. According to the Royer-Freidel, a fusion of two crystals in a regular orientation is possible if the corresponding parameters of unit cells will not differ by more than 15%. Table 1 shows the comparative characteristics of GaBO_3 and FeBO_3 structures.

Table 1. Comparative characteristics of GaBO_3 and FeBO_3 structures

Crystal	Space group	Crystal system	Unit cell parameters in the hexagonal system [15]	The difference in the parameters
FeBO_3	D_{3d}^6	trigonal	$a = 4.62 \text{ \AA}$	$\Delta a = 1.29 \%$ $\Delta c = 2.13 \%$
GaBO_3			$c = 14.49 \text{ \AA}$	
			$a = 4.56 \text{ \AA}$	
			$c = 14.18 \text{ \AA}$	

As one can see from Table 1, the unit cell parameters of gallium and iron borates differ from each other by no more than 2%. It makes GaBO_3 a promising candidate for use as a substrate for the magnetic film FeBO_3 .

The synthesis of the GaBO_3 substrate starts with a charge preparation; fusing the charge in a crucible at 900°C in the muffle furnace and setting of the crucible with the solution melt in the growing furnace. Crystallization has been carried out according to predetermined temperature mode. It consists of the following steps:

- heating of the furnace;
- homogenization of the solution melt at 950°C during 24 hours (At the beginning of this step a seed holder was dipped and rotated in the solution melt. During the homogenization it served as a mixer.);
- sharp, with a rate of 280°C per hour, lowering the temperature down to 810°C in order to avoid the emergence of “parasitic” phases, such as Ga_3BO_6 ;

- slow, with a rate of 0.3°C per hour, lowering the temperature down to 760 °C for nucleation and GaBO₃ crystal growth (At the end of this step the seed holder with the synthesized crystals was extracted from the solution melt, see Figure 1a. These crystals on the holder will be used as a substrate for the FeBO₃ film.);
- cooling of the furnace.

The sizes of the crystals are in the range of 1 to 3 mm in the cross section and 0.01 to 0.06 mm thick. The synthesized GaBO₃ samples are suitable for use as a substrate for the FeBO₃ film.



Figure 1. The seed holder with almost transparent GaBO₃ single crystals (a), and green online film of FeBO₃ on the GaBO₃ substrate (b).

For the LPE synthesis of the FeBO₃ film, first, we have to prepare a solution melt. For this purpose we have used the same procedure as for GaBO₃ synthesis, *vide supra*. After setting the crucible with solution melt for FeBO₃ in the growing furnace the general crystallization procedure was as follows:

- heating of the furnace;
- homogenization of the melt at 950°C during 24 hours;
- sharp, with a rate of 260°C per hour, lowering the temperature down to 810-835°C in order to avoid the emergence of “parasitic” phases, such as Fe₃BO₆ and α-Fe₂O₃ (During this step a seed holder with GaBO₃ substrate (was prepared earlier and shown in Figure 1a) was dipped in the solution melt at 835°C.);
- keeping the temperature 820°C during 0.5-3 hours;
- slow, with a rate of 3°C per hour, lowering of the temperature down to 800°C (At the end of this step the seed holder has been extracted from the crucible, see Figure 1b. As one can see, GaBO₃ crystals became green.);
- cooling of the furnace.

The second one important condition for the successful epitaxial synthesis is to choose appropriate temperature modes. Crystallization regimes suitable for obtaining epitaxial film of FeBO₃ were determined empirically. We have carried out a series of crystallizations with and without rotation of the seed holder, testing different temperatures modes and time of keeping the seed holder at 820°C. Figure 2 shows optical microscope pictures of the obtained samples. As one can see from Figure 2a, microcrystals of iron borate (0.006 - 0.012 mm in cross section) have the same orientation on the surface of a gallium borate. This indicates that the FeBO₃ film grows copying the GaBO₃ substrate structure. Analysis of Figure 2 allows concluding that the mechanism of the film formation is island growth [16]. Our preliminary XRD studies of the synthesized samples have allowed determining a value of the hexagonal parameter $c=14.48\pm 0.01$ Å of the film. This value is in a good accordance with those previously determined for the FeBO₃ crystal, see Table 1, that confirms the existence of the FeBO₃ layer on the GaBO₃ substrate. The detailed results on our XRD studies will be published elsewhere. The obtained epitaxial film of iron borate, see Figure 1b and 2d, has a thickness of 0.003 to 0.006 mm.

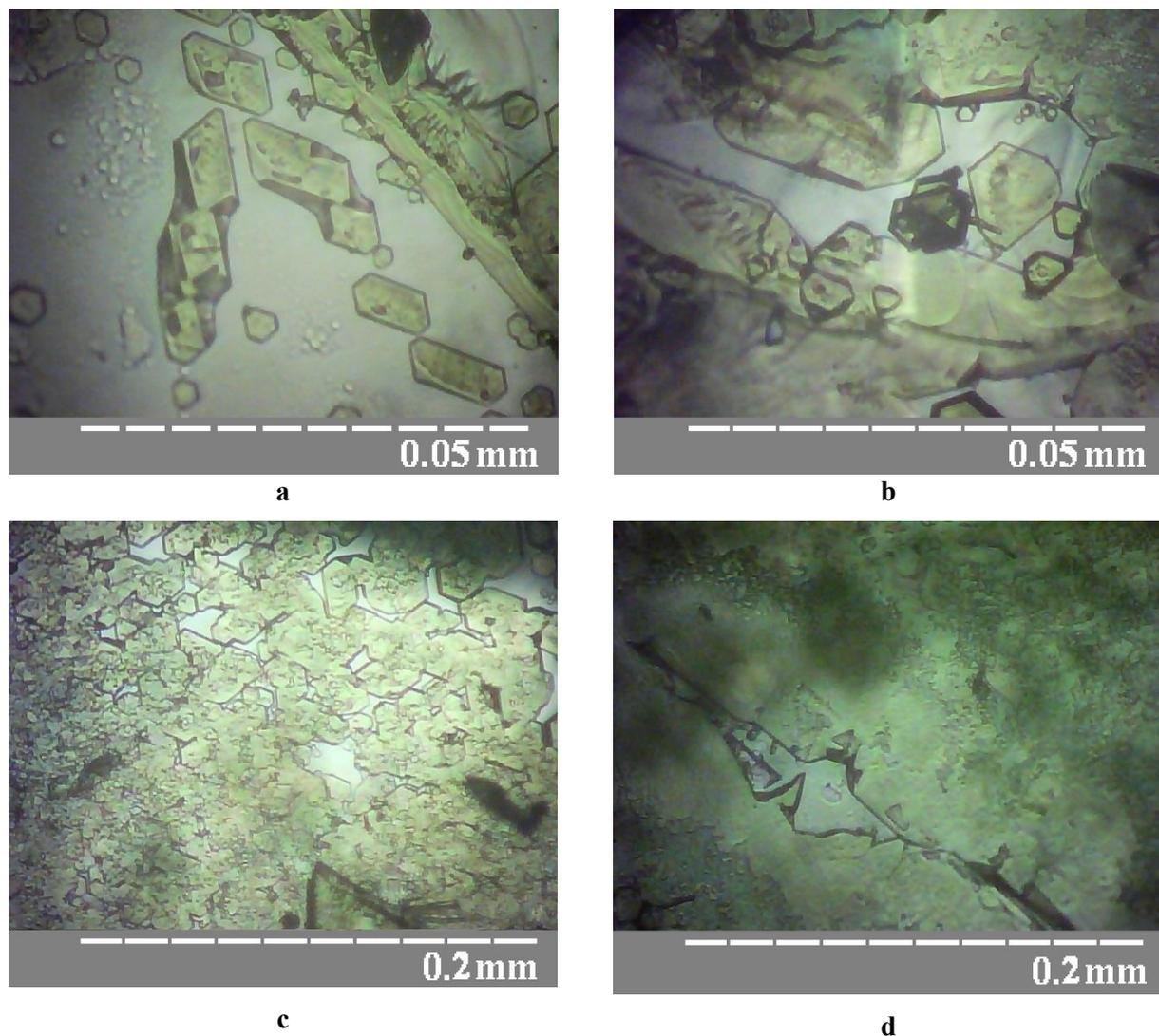


Figure 2. Optical microscope pictures showing different stages of a formation of the FeBO₃ film: a coalescence of islets (a), a formation and filling of channels (b), a process of accretion of individual sections of the film FeBO₃ (c), a final stage of the formation of the film of iron borate on the GaBO₃ substrate (d).

4. Conclusions

As a result, we have developed synthesis technique and obtained the film of FeBO₃ on the diamagnetic substrate using LPE technique. We have succeeded in the selection and preparation of the single crystal for the substrate. It is shown that gallium borate GaBO₃ is an appropriate material for this purpose. In the framework of the present work a series of the experiments has been carried out in order to determine crystallization regimes suitable for the film FeBO₃ growth.

The optical studies of the prepared composite structures have allowed us to study in details different stages of the film formation and to conclude that the growth mechanism is island growth. The XRD analysis of the obtained samples confirms the existence of the iron borate film on the GaBO₃ substrate.

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