Journal of Magnetism and Magnetic Materials 417 (2016) 338–343

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Iron borate films: Synthesis and characterization

S. Yagupov [a], M. Strugatsky [a,*], K. Seleznyova [a,b], Yu. Mogilenec [a], E. Milyukova [a], E. Maksimova [a], I. Nauhatsky [a], A. Drovosekov [c], N. Kreines [c], J. Kliava [b]

[a] Physics and Technology Institute, Crimean Federal V.I. Vernadsky University, 4 Vernadsky Avenue, Simferopol 295007, Russia
[b] LOMA, UMR 5798 Université de Bordeaux-CNRS, 33405 Talence cedex, France
[c] P.L. Kapitza Institute for Physical Problems RAS, 2 ul. Kosygina, Moscow 119334, Russia

ARTICLE INFO

Article history:
Received 12 April 2016
Received in revised form
5 May 2016
Accepted 27 May 2016
Available online 30 May 2016

Keywords:
Iron borate film
Liquid phase epitaxy
Electron microscopy
Energy-dispersive spectroscopy
X-ray diffraction
Electron magnetic resonance

ABSTRACT

We report the first successful synthesis of iron borate films. $FeBO_3$ films on $GaBO_3$ single crystal substrates have been prepared by a liquid phase epitaxy route. In order to determine optimal crystallization regimes, a series of experiments has been carried out. Electron microscope studies have allowed monitoring different phases of the film formation. The compositions of the film and of the substrate have been determined by energy-dispersive spectroscopy. X-ray diffraction analysis has allowed an accurate determination of a mismatch between the lattice parameters of the film and of the substrate. Electron magnetic resonance studies of the $FeBO_3$ film confirm the existence of magnetic ordering. The values of the effective Dzyaloshinskii field as well as the Néel temperature are in good accordance with those previously determined for $FeBO_3$ single crystal.

1. Introduction

The research interest in iron borate $FeBO_3$ is mainly due to its remarkable magnetic, magneto-acoustical, optical, magneto-optical, resonance, etc., characteristics, e.g., see [1–6]. In particular, iron borate can be categorized as a "transparent magnet", combining transmission windows in visible spectral range with room temperature magnetic ordering. From the standpoint of magnetic properties, $FeBO_3$ is an easy-plane antiferromagnet with weak ferromagnetism and the Néel temperature $T_N \approx 348$ K. The AFMR studies of $FeBO_3$ were carried out in a wide range of temperatures and frequencies [6]. From the standpoint of crystalline structure, $FeBO_3$ is a rhombohedral calcite-type crystal of space group D_{3d}^6 [7].

In contrast to conventional ferromagnets, in iron borate the surface magnetocrystalline anisotropy, caused by symmetry breaking in the surrounding of near-surface iron ions [8], is not suppressed. This is due to the fact that the demagnetizing field, proportional to weak ferromagnetic vector, is small and the anisotropy in the basal plane, (0001) in hexagonal coordinate system, is weak [7]. Consequently, the magnetic characteristics of a thin (0.01–0.1 μm) near-surface layer of iron borate drastically differ from those in the volume. Such effects were studied both experimentally using magneto-optic Kerr effect [9] and theoretically [9,10]. Another interesting effect is that surface magnetocrystalline anisotropy stimulates the formation of bubble magnetic domains in the near-surface layer of iron borate [9]. From the standpoint of practical applications, the surface of iron borate single crystals can be considered as a magnetic memory element analogous to thin-film magnetic materials containing cylindrical magnetic domains. Undoubtedly, thin $FeBO_3$ magnetic films deposited on a diamagnetic transparent substrate are appropriate for studying surface magnetism using not only the Kerr effect [9] but also the Faraday effect. In particular, in very thin (less than 0.1 μm) iron borate films one can study "pure" surface magnetic effects, not altered by volume magnetism.

In $FeBO_3$ single crystals having the shape of basal plates, interesting magneto-acoustic effects were found, related to magnetic structure of this crystal [2,11]. The magnetization in this case follows quasi-statically natural longitudinal [2] and transversal [11] acoustic modes. In very thin $FeBO_3$ film, one can expect the emergence of forced magnetic oscillations at frequencies approaching the natural magnetic oscillation frequency, i.e. the AFMR frequency, resulting in promising new effects.

The aim of the present work is to develop the synthesis technique, to obtain and to characterize $FeBO_3$ films on a diamagnetic substrate. As the substrate we have used gallium borate, $GaBO_3$, single crystal. This material is isostructural with $FeBO_3$; besides, it is also transparent in the visible range, albeit diamagnetic [12]. Both crystals have similar lattice parameters: in iron borate

* Corresponding author.
E-mail address: strugatsky@crimea.edu (M. Strugatsky).

http://dx.doi.org/10.1016/j.jmmm.2016.05.098
0304-8853/

$a=4.626$, $c=14.493$, and in gallium borate $a=4.568$, $c=14.182$ Å (in the hexagonal coordinate system). As one can see, the relative difference between the corresponding parameters for both crystals is less than 2%, while the structure of deposited film is known to reproduce that of substrate if this difference does not exceed ca. 14% [13]. Thus, $GaBO_3$ crystal seems to be the best candidate to be used as substrate for depositing $FeBO_3$ film.

A successful depositing of a high-quality film requires using a high-quality substrate. On the basis of our previous studies on synthesis of iron-based borate crystals, e.g., see [12,14], we have concluded that high-quality samples can be obtained by the solution in the melt technique. Thus, this technique has been used for synthesizing the substrate, and for depositing the $FeBO_3$ film in these conditions, the liquid phase epitaxy (LPE) technique appears to be optimal.

During the sample synthesis, different phases of the film formation and compositions of the film and the substrate have been monitored by electron microscopy and energy-dispersive spectroscopy (EDS), respectively. The lattice parameters of the film and of the substrate have been measured by X-ray diffraction (XRD). The magnetic characteristics of the film, such as the Dzyaloshinskii field H_D and T_N, have been determined by means of electron magnetic resonance (EMR).

2. Synthesis of the film

The synthesis of $FeBO_3$ film by the LPE technique includes the following steps:

(i) Choosing appropriate charge compositions and temperature modes;
(ii) Preparing a high-quality $GaBO_3$ substrate;
(iii) LPE synthesis of the $FeBO_3$ film on the substrate.

The crystallizations in the steps (ii) and (iii) were carried out with Ga_2O_3–B_2O_3–PbO–PbF_2 and Fe_2O_3–B_2O_3–PbO–PbF_2 solution melts, respectively. The most appropriate charge compositions, determined by differential thermal analysis method, are shown in Table 1 [12,14].

The synthesis of the $GaBO_3$ single crystal – the substrate – has recently been described by some of the present authors [12].

The synthesized $GaBO_3$ crystals are shown in Fig. 1. For comparison, we also show previously synthesized $FeBO_3$ single crystals [14]. Both $GaBO_3$ and $FeBO_3$ crystals have the shape of hexagonal plates with the dimensions of 3–7 mm in the basal plane and 0.05–0.1 mm in thickness. Note that gallium borate is colorless while iron borate is green.

The operating mode used to deposit $FeBO_3$ film by the LPE route was as follows: the $GaBO_3$ substrate was placed into a metallic supporting cone perforated with small holes and maintained during 30 min in a crucible containing the solution melt for $FeBO_3$ synthesis, see Table 1. The corresponding temperature mode is shown in Fig. 2. It includes the following stages: (i) heating of the furnace, (ii) homogenization of the solution melt, (iii) fast temperature dropping in order to avoid the emergence of spurious phases, e.g., Fe_3BO_6, (iv) nucleation and film growth and

Table 1
Charge compositions (in mass %) used for synthesizing $GaBO_3$ substrate and $FeBO_3$ film.

	Ga_2O_3	Fe_2O_3	B_2O_3	PbO	PbF_2
$GaBO_3$ substrate	18.6	0	42.4	27.3	11.7
$FeBO_3$ film	0	5.8	51.2	29.3	13.7

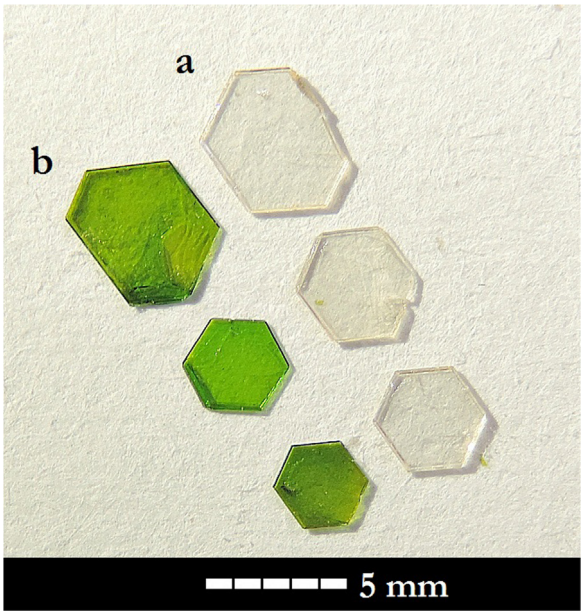

Fig. 1. $GaBO_3$ (a) and $FeBO_3$ (b) single crystals synthesized by solution in the melt technique. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

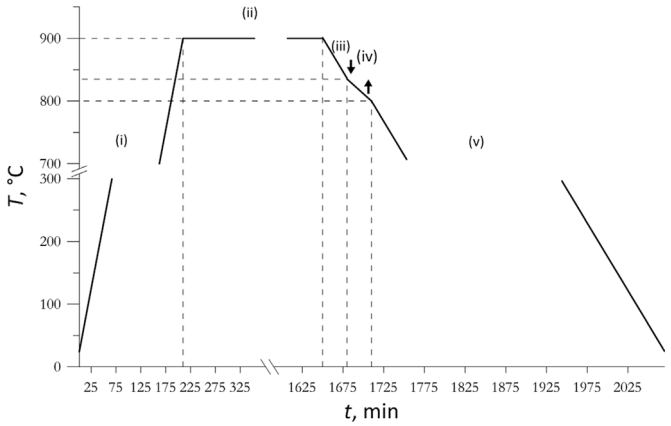

Fig. 2. Temperature mode used in synthesizing $FeBO_3$ film, see the text for details.

(v) cooling the furnace. The moments when the cone with the substrate has been immersed in and extracted from the solution melt are indicated by arrows. Due to the perforation, during the immersion the solution melt was filling the cone and bathing the whole substrate. During the extraction, the solution melt was withdrawn through the holes back into the crucible, and the synthesized sample (substrate with deposited film) remained in the cone, see Fig. 3. As one can see in online version, after the crystallization the sample surface becomes light green, as characteristic of iron borate.

3. Characterization of the synthesized samples

3.1. Electron microscopy

$FeBO_3$ film formation has been monitored by electron microscopy using REM 106 and field emission SEM JSM-7800F microscopes.

The film formation in this system occurred following the epitaxial island growth mechanism. Consecutive stages of the film growth are shown in Fig. 4. Conventionally, it can be divided into