Synthesis and structural characterization of Fe$_{1-x}$Me$_x$BO$_3$
(Me = Al, Sc) single crystals

Yu Mogilenec, K Seleznıyova, S Yagupov, K Selezev, I Nauhatsky, E Maksimova and M Strugatsky

Physics and Technology Institute, V.I. Vernadsky Crimean Federal University, Simferopol, Crimea

E-mail: mogilenecya@cfuv.ru

Abstract. Fe$_{1-x}$Me$_x$BO$_3$ (Me = Al, Sc) single crystals have been synthesized by flux growth technique using Bi$_2$O$_3$-PbO-PbF$_2$ solvent and approach of identical synthesis conditions. The contents of the diamagnetic ions Me in the initial charge of both compositions were equal, $x_{\text{charge}}=0.05$. The exact contents and crystal lattice parameters of the synthesized crystals were determined by X-ray fluorescence analysis and X-ray diffraction, respectively.

1. Introduction

The creation of new materials with predetermined properties allows one to improve modern technologies, as well as to develop completely new scientific approaches for solving fundamental problems of solid-state physics. One of the most advanced ways to fine-tune different properties of existing materials is the isomorphous substitution method.

Iron borate, FeBO$_3$, is a two-sublattice easy-plane trigonal antiferromagnet with weak ferromagnetism [1]. It possesses a calcite-type structure of $R\bar{3}c$ space group and has several isostructural diamagnetic analogues MeBO$_3$ (Me = Ga, Al, Sc, In), where Me$^{3+}$ ions occupy the same structural positions as Fe$^{3+}$ ions in FeBO$_3$ [2-4]. Undoubtedly, using diamagnetically diluted Fe$_{1-x}$Me$_x$BO$_3$ single crystals, in which a part of paramagnetic iron ions is isomorphically substituted by diamagnetic ions, is suitable for studying the nature of the magnetic properties of pure FeBO$_3$ [5, 6]. This approach allows one to study different mechanisms that stand behind certain properties of the crystal, as well as to create materials with predetermined characteristics. For instance, the partial isomorphous substitution of Fe$^{3+}$ by Ga$^{3+}$ in FeBO$_3$ crystals (with the formation of Fe$_{1-x}$Ga$_x$BO$_3$ crystals) allows one to study the transformation of magnetic properties under the transition from magnetically ordered to diamagnetic state, as well as modifies such magnetic characteristics of FeBO$_3$ as the Dzyaloshinskii-Moriya field and the Νéel temperature [6, 7]. The major drawback of such isomorphic substitutions is that impurity ions significantly reduce the degree of the structural perfection of the crystals [8]. Thus, the search for new technological approaches for synthesizing Fe$_{1-x}$Me$_x$BO$_3$ single crystals with different diamagnetic ions that would have a negligible influence on structural perfection is of paramount importance.

In the present work, it is proposed to synthesize Fe$_{1-x}$Me$_x$BO$_3$ single crystals with low contents of Al$^{3+}$ and Sc$^{3+}$ ions that allow a slight decreasing the Νéel temperature in comparison with pure FeBO$_3$. Such diamagnetically diluted high-perfection crystals are of great importance for further practical applications in synchrotron technologies of a new generation [9]. The ionic radii of sixfold-coordinated Fe$^{3+}$, Al$^{3+}$ and Sc$^{3+}$ are 0.645, 0.535 and 0.745 Å, respectively [10]. Complete
isomorphism is possible if the ionic radius of an impurity ion differs by no more than 15% from those of substituted ion [11]. In our case, the difference is up to 20% that probably indicates limited isomorphism. Moreover, in as much as the ionic radius of Al$^{3+}$ is smaller concerning the ionic radius of Fe$^{3+}$, and Sc$^{3+}$ is larger; the probability of Fe/Al substitutions is bigger than that of Fe/Sc. In order to check this assumption, we propose (i) to synthesize Fe$_{1-x}$Me$_x$BO$_3$ (Me = Al, Sc) single crystals with a fixed contents of the diamagnetic ions in the charge, $x_{\text{charge}}$, under identical synthesis conditions; (ii) to determine and analyze the exact crystal composition and crystal structure.

2. Experimental
The synthesis of Fe$_{1-x}$Me$_x$BO$_3$ single crystals was carried out by the flux growth technique using a boron-lead solvent: B$_2$O$_3$ - PbO - PbF$_2$ [12]. This technique allows one to obtain iron borate based single crystals in the form of hexagonal plates of high structural perfection.

It is supposed to obtain crystals with low $x$-values, thus, the charge composition and temperature mode of crystallization for the synthesis of pure FeBO$_3$ were chosen as the initial [13]. The extraction of the synthesized crystals from the cooled crucibles was carried out by boiling in a 20% solution of nitric acid.

The exact contents of aluminium and scandium in the synthesized crystals have been determined using X-ray fluorescence analysis (XRF) analysis with a high-power benchtop sequential wavelength dispersive X-ray fluorescence spectrometer Rigaku Supermini200.

The crystal phase and parameters of the crystal lattice of the synthesized crystals were determined by X-ray diffraction (XRD) analysis with a diffractometer using cobalt radiation Co Kα in the angle range of $10^\circ < 2\theta < 130^\circ$ with the step of 0.01°.

3. Results and discussion
Charge compositions, see Table 1, were calculated in such a way that the contents of the diamagnetic ions in the charge, $x_{\text{charge}}$ = 0.05 and is the same for synthesizing Fe$_{1-x}$Me$_x$BO$_3$ (Me = Al, Sc) single crystals.

| Table 1. Charge compositions used for synthesizing Fe$_{1-x}$Me$_x$BO$_3$ (Me = Al, Sc) single crystals with $x_{\text{charge}}$ = 0.05 |
|----------------------------------|---|---|---|---|---|---|
|                                | Al$_2$O$_3$ | Sc$_2$O$_3$ | Fe$_2$O$_3$ | B$_2$O$_3$ | PbO | PbF$_2$ |
| Fe$_{1-x}$Al$_x$BO$_3$          | 0.19 | -  | 5.54   | 51.23 | 29.31 | 13.73 |
| Fe$_{1-x}$Sc$_x$BO$_3$          | -    | 0.25 | 5.48   |        |      |        |

The conditions of the preparation of the solution-melts – dehydration of the reagents, homogenization – were identical for both compositions; and both crucibles had the same shape and volume. In order to reduce the influence of such external factors as evaporation of the solvent and contamination of the solution-melt, the growth crucibles were covered with lids. The uniformity of the temperature modes of crystallization was ensured by placing crucibles into a uniform temperature zone of the growth furnace close to each other.

The main functional element of the laboratory-developed crystallization setting is a resistance furnace СИЮ/1 1.3/12-H11. Its construction provides a gradient-free zone inside the furnace shaft about 5-7 cm in height. Software control of the temperature mode of crystallization was provided by a precision controller ТЕРМОДАТ-19Е5. The temperature mode of crystallization used in synthesizing Fe$_{1-x}$Me$_x$BO$_3$ single crystals is shown in Figure 1. It includes the following steps: (1) heating the furnace; (2)-(7) isothermal exposures with subsequent sharp temperature drops (homogenization of the solution melt); (8) exposure at 830°C during 180 min; (9) cooling down to 760°C with a speed of
0.1°C/h (nucleation and crystal growth); (10) exposure at 760°C during 60 min; (11) cooling down and switching off the furnace.

Figure 1. Temperature mode of crystallization used in synthesizing Fe_{1-x}Me_xBO_3 single crystals with x_{charge} = 0.05

As a result of crystallization, transparent green single crystals have been obtained, see Figure 2. They possess a typical for FeBO_3 hexagonal shape – plates with dimensions up to 5 mm in the basal plane and up to 40 µm in the perpendicular direction. Optical microscopy studies of the synthesized crystals have shown that Fe_{1-x}Sc_xBO_3 crystals possess much more visible defects than Fe_{1-x}Al_xBO_3 single crystals, cf. Figure 2.

Figure 2. Synthesized (a) Fe_{1-x}Al_xBO_3 and (b) Fe_{1-x}Sc_xBO_3 single crystals with x_{charge} = 0.05.

The existence of concentration and convection flows in the solution-melt during crystallization leads to the fact that the contents of the diamagnetic ions in the synthesized crystals, x_{crystal}, differ from those in the initial charge, x_{charge}. Moreover, x_{crystal} differs for crystals extracted from the same
crucible [5]. XRF studies of the synthesized crystals have shown that the contents of the diamagnetic ions are within the following limits: 0.06 ≤ \( x_{\text{crystal}} \) ≤ 0.22 for \( \text{Fe}_{1-x}\text{Al}_x\text{BO}_3 \) and 0.05 ≤ \( x_{\text{crystal}} \) ≤ 0.07 for \( \text{Fe}_{1-x}\text{Sc}_x\text{BO}_3 \) single crystals. It can be explained by the fact that \( \text{Al}^{3+} \) ion possesses smaller with respect to \( \text{Fe}^{3+} \) radius, thus, enters the overall crystal structure \( \text{FeBO}_3 \) more easily than \( \text{Sc}^{3+} \) that possesses a larger one.

\( \text{Fe}_{0.94}\text{Al}_{0.06}\text{BO}_3 \) and \( \text{Fe}_{0.94}\text{Sc}_{0.06}\text{BO}_3 \) crystals with the same values of \( x_{\text{crystal}} \), were selected for detailed structural studies. Powder XRD patterns of these crystals are shown in Figure 3. XRD analysis has shown that the synthesized crystals have a rhombohedral calcite-type structure.

Isomorphous substitution of iron with aluminium or scandium produces a slight shift of the XRD peaks from their positions in pure \( \text{FeBO}_3 \).

![Figure 3. Powder XRD patterns of \( \text{Fe}_{0.94}\text{Al}_{0.06}\text{BO}_3 \) (a, bottom curve, red online), \( \text{Fe}_{0.94}\text{Sc}_{0.06}\text{BO}_3 \) (b, bottom curve, blue online) and \( \text{FeBO}_3 \) (a, b, top curves, black) crystals. Miller’s indices of \( \text{FeBO}_3 \) crystals are indicated on the figures. Insets show a slight shift of XRD peaks.](image)

The hexagonal lattice parameters \( a \) and \( c \) for \( \text{Fe}_{0.94}\text{Al}_{0.06}\text{BO}_3 \) and \( \text{Fe}_{0.94}\text{Sc}_{0.06}\text{BO}_3 \) single crystals, as well as the percentage of the lattice parameter shifts, \( \varepsilon_a \) and \( \varepsilon_c \), are shown in Table 2. As one can see, the diamagnetic ion with a larger ionic radius with respect to \( \text{Fe}^{3+} \) leads to increasing lattice parameters, and vice versa, smaller ionic radius leads to decreasing lattice parameters.

|               | \( a, \text{Å} \)   | \( \varepsilon_a, \% \) | \( c, \text{Å} \)   | \( \varepsilon_c, \% \) |
|---------------|---------------------|--------------------------|---------------------|--------------------------|
| \( \text{FeBO}_3 \) | 4.6247(1)           | -                        | 14.4813(3)          | -                        |
| \( \text{Fe}_{0.94}\text{Al}_{0.06}\text{BO}_3 \) | 4.6245(1)          | -0.004                   | 14.4810(3)          | -0.002                   |
| \( \text{Fe}_{0.94}\text{Sc}_{0.06}\text{BO}_3 \) | 4.6397(3)          | 0.324                    | 14.5814(10)         | 0.691                    |
4. Conclusion
We have succeeded in obtaining Fe$_{1-x}$Me$_x$BO$_3$ (Me = Al, Sc) single crystals with $x_{\text{charge}}=0.05$ using the flux growth technique. We have applied identical synthesis conditions for both compositions.

The XRF analysis has revealed a certain dispersion of the contents of diamagnetic ions in the crystals extracted from the same crucible. The aluminium content in the synthesized Fe$_{1-x}$Al$_x$BO$_3$ crystals is much higher than in the charge, while the scandium content in the Fe$_{1-x}$Sc$_x$BO$_3$ crystals almost coincides with the initial one in the charge.

Crystal structure and lattice parameters of Fe$_{0.94}$Al$_{0.06}$BO$_3$ and Fe$_{0.94}$Sc$_{0.06}$BO$_3$ single crystals have been determined using XRD analysis. It was shown that the synthesized crystals have a rhombohedral calcite-type structure. It was found that the lattice parameters of the Fe$_{0.94}$Al$_{0.06}$BO$_3$ crystal are smaller, and the lattice parameters of the Fe$_{0.94}$Sc$_{0.06}$BO$_3$ crystal are larger than those of pure FeBO$_3$. X-ray diffraction and topography studies of the crystal structure perfection are in progress and will be published elsewhere.

Acknowledgement
The reported study was funded by RFBR, project number 19-32-90054 (crystal synthesis and X-ray studies) and 19-29-12016 (modernization of the crystallization setting).

References
[1] Diehl R, Jantz W, Nolang B I and Wettling W 1984 Current Topics in Materials Science vol 11, ed E Kaldis (New-York: Elsevier) p 241
[2] Santamaria-Perez D, Gomis O, Sans J A, Ortiz H M, Vegas A, Errandonea D, Ruiz-Fuertes J, Martiez-Garcia D, Garcia-Domene B, Pereira A L J, et al. 2014 Journal of Physical Chemistry C 118 pp 4354-4361
[3] Ovchinnikov S G and Rudenko V V 2016 Journal of Crystal Growth 455 pp 55-59
[4] Lukin S N, Rudenko V V, Seleznov V N and Tsintsadze G A 1980 Fiz. Tverd. Tela 22 pp 51-56
[5] Strugatsky M, Seleznynova K, Yagupov S, Drobosekov A and Kliava J 2017 Journal of Magnetism and Magnetic Materials 442 pp 417-422
[6] Seleznynova K, Strugatsky M, Yagupov S, Mogilenec Yu, Drobosekov A, Kreines N, Rosa P and Kliava J 2019 Journal of Applied Physics 125 pp 223905
[7] Kamzin A S, Ol'khovik L P and Snetkova E V 2003 Physics of the Solid State 45(11) pp 2128-2130
[8] Snegirev N, Mogilenec Yu, Seleznynova K, Nauhatsky I, Strugatsky M, Yagupov S, Kulikov A, Zolotov D, Marchenkov N, Frolov R and Lyubutin I 2019 IOP Conf. Ser.: Mater. Sci. Eng. 525 pp 012048
[9] Smirnova K, Snegirev N, Lyubutin I, Starchikov S, Artemov V, Lyubutina M, Yagupov S, Strugatsky M, Mogilenec Yu, Seleznynova K and Alekseeva O 2020 Acta Cryst. B 76 pp 1100-1108
[10] Shannon R D 1976 Acta Cryst. A 32 pp 751-767
[11] Goldschmidt V M 1954 Geochemistry ed A Muir (Oxford: Clarendon Press) p 730
[12] Yagupov S, Strugatsky M, Seleznynova K, Maksimova E, Nauhatsky I, Yagupov V, Milyukova E and Kliava J 2015 Applied Physics A 121 pp 179-185
[13] Yagupov S, Strugatsky M, Seleznynova K, Mogilenec Yu, Snegirev N, Marchenkov N, Kulikov A, Eliovich Yan, Frolov K, Ogarkova Yu and Lyubutin I 2018 Crystal Growth and Design 18 pp 7435-7440