Ferro-gallium borate single crystals for nuclear resonance synchrotron experiments

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Ferro-gallium borate single crystals for nuclear resonance synchrotron experiments

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Abstract. A series of ferro-gallium borate $Fe_{1-x}Ga_xBO_3$ single crystals was synthesized by a flux growth technique. The ratio of elements in crystals was determined by X-ray fluorescence analysis. The degree of structural perfection was studied by high-resolution X-ray diffraction techniques. These crystals are of a great interest for modern synchrotron experiments. It is established that diamagnetic impurity affects the degree of structural perfection of the samples.

1. Introduction

In traditional Mössbauer spectroscopy used in a laboratory, the γ-radiation from a radioactive source is uniformly distributed over the sphere (in 4π) and only a small part of it falls on the sample under study. Therefore, it takes a long time to accumulate a high-quality spectrum with a good signal-to-noise ratio. In this situation, the possibility of using high-intensity focused synchrotron radiation seems to be the most effective and optimal solution. Especially, it is critical for the experiments under extreme condition, such as high pressure studies in diamond anvil cells, where the sample size is very small [1]. This technique is called Synchrotron Mössbauer Spectroscopy (SMS) and it has recently been implemented at the ESRF (Grenoble, France) [2] and Spring-8 (Tsukuba, Japan) [3] synchrotron radiation facilities. The key element of the SMS scheme is an iron borate $FeBO_3$ single crystal, designed for the final monochromatisation of the synchrotron radiation with energy corresponding to Mössbauer resonance at the ^{57}Fe nuclei. In this case extremely high requirements are imposed on the structural perfection of single crystals [4].

The energy spectrum of the radiation reflected from $FeBO_3$ consists of several lines due to magnetic hyperfine splitting of the ^{57}Fe nuclear levels, which considerably complicates spectroscopic measurements [5]. This make it necessary to heat the crystal near the Néel temperature (~348.5 K), where the energy spectrum of the reflected radiation collapses into a single line [6]. However, heating, combined with highly ionized radiation, can lead to a degradation of the structural perfection of the crystal- monochromator. One of the possible solution to this problem could be a controlled decrease of the Néel temperature by isomorphous substitution of a part of paramagnetic iron ions in $FeBO_3$ with diamagnetic gallium ions [7-9]. Pure iron borate single crystals can be synthesized by vapor deposition

and flux growth techniques [10]. Using vapor deposition technique, bulk single crystals of iron borate can be obtained [11]. The flux growth technique allows obtaining single crystals with the shape of hexagonal basal plates. Such crystals have high structural perfection [12]. Thus, for the purposes of the present work the flux growth technique has proved to be the most appropriate. However, it is required to determine the degree of structural perfection of ferro-gallium borate ($Fe_{1-x}Ga_xBO_3$) single crystals.

The purpose of the present work is to synthesize the series of $Fe_{1-x}Ga_xBO_3$ single crystals and determine the degree of their structural perfection by high-resolution X-ray diffraction (HRXRD) techniques.

2. Synthesis of $Fe_{1-x}Ga_xBO_3$ single crystals

Single crystals $Fe_{1-x}Ga_xBO_3$ were synthesized by the flux growth technique. Crystallizations were carried out in the Ga_2O_3–Fe_2O_3–B_2O_3–PbO–PbF_2 system. The crystal-forming reagents are Fe_2O_3, Ga_2O_3 and B_2O_3, whereas PbO, PbF_2, and B_2O_3 serve as solvents. A typical composition of the reagents (in wt %) is as follows: Fe_2O_3 + Ga_2O_3 (5.73), B_2O_3 (51.23), PbO (29.31), and PbF_2 (13.73). Technological steps of the flux growth technique are: preparing of the charge, obtaining a homogeneous solution melt in a platinum crucible, slow cooling of the solution melt and extracting of synthesized crystals [13]. The synthesized crystals have the shape of hexagonal plates with the dimensions up to 5 mm in the basal plane and about 60 μm in thickness. Examples of the synthesized single crystals are shown in Figure 1.

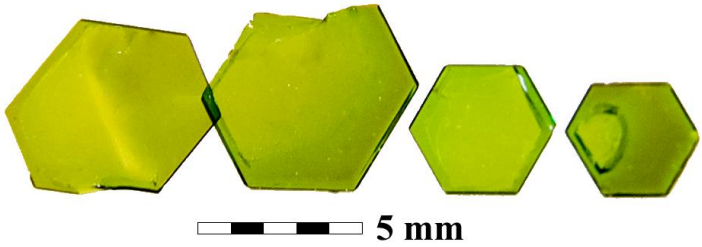

Figure 1. Examples of synthesized single crystals.

3. Characterization of the synthesized $Fe_{1-x}Ga_xBO_3$ single crystals.

The exact contents of Fe and Ga in the synthesized $Fe_{1-x}Ga_xBO_3$ single crystals were determined by X-ray fluorescence analysis (XRF) using Rigaku Supermini200 spectrometer. Studied crystals were fixed using a platinum diaphragm with a 4 mm hole. This made it possible to study crystals with different surface areas. The results of measurements are shown in Table 1.

Table 1. Gallium contents in $Fe_{1-x}Ga_xBO_3$ single crystals *vs.* gallium contents in charge.

x in charge	*x* in crystal
0.05	0.03
0.4	0.32
0.75	0.69
0.8	0.73
0.9	0.82

To determine the degree of structural perfection of $Fe_{1-x}Ga_xBO_3$ single crystals, the HRXRD techniques were used.

The double-crystal diffraction rocking curves (DRCs) were measured using an in-house diffractometer, the experimental scheme of which was described in detail in [14]. The scans were carried out in Bragg (for X-ray reflection) geometry for reflection 0012 with a Bragg angle in the range of 17.08° - 17.47° and extinction length L_{ext} in the range of 10.5 - 9.0 μm depending on the Ga contents (for x between 0 and 1). The local area of single crystals was illuminated by an X-ray beam, limited by an incidence slit with dimensions of 0.1×4 mm^2. A Mo X-ray tube ($K\alpha_1$ characteristic line with λ = 0.70932 Å) and a symmetric Si (110) monochromator tuned to the 220 reflection were used.

The X-ray topography studies of $Fe_{1-x}Ga_xBO_3$ single crystals were carried out using an in-house experimental setup «DITOM-M» [15]. The scheme of this setup is shown in Fig. 2. Radiation from conventional X-ray tube with a Mo anode was monochromatised using an asymmetrically cut Si (111) crystal (asymmetry coefficient $\beta \sim 10$), which also provided a beam of sufficient width to measure the whole sample in Laue (for X-ray transmission) geometry. Further adjustment of the beam size was achieved by slits. The acquisition was performed using a CCD camera with a 9 μm pixel size. The monochromator–sample and the sample–detector distances were about 1000 mm and 30 mm, respectively. Exposures were at least 45 minutes. The reflection 300 with a Bragg angle in the range of 15.40° - 15.61° and L_{ext} = 99.9 - 82.3 μm (for x between 0 and 1) was used.

The 2D-topograms were obtained at two various modes:

- Integrate mode is the scan along DRC (ω - scan). It is sensitive to structural features and defects in the sample volume [16].
- Static mode is the intensity acquisition at a fixed angular position at the DRC slope. This mode is sensitive to Bragg angle variation and deformations in the crystal lattice [16].

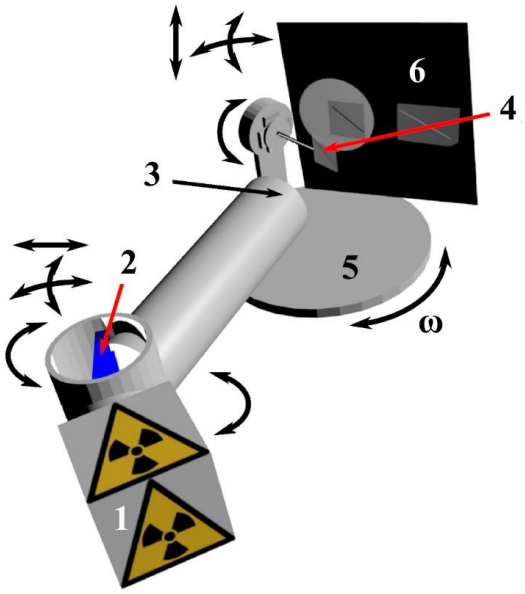

Figure 2. The scheme of «DITOM-M» setup: (1) X-ray source tube, (2) monochromator crystal, (3) tube collimator with the system of slits, (4) crystal under study, (5) goniometer and (6) CCD.

Figure 3 and Figure 4 shows double-crystal DRCs of of $Fe_{1-x}Ga_xBO_3$ single crystals with x = 0.0, 0.03, 0.32 and 1.0. The values of the half-width (FWHM) of DRCs are about 10 angle seconds for pure $FeBO_3$ and $GaBO_3$ crystals (Figure 3a,b). The DRCs for perfect pure crystals were calculated in accordance with the dynamic theory of diffraction taking into account the structural factor of the crystals, the instrumental function of the experimental scheme with allowance for the dispersion effect

[17, 18]. The calculated curves are in good agreement with the experimental data, which testifies the high perfection of the pure crystals.

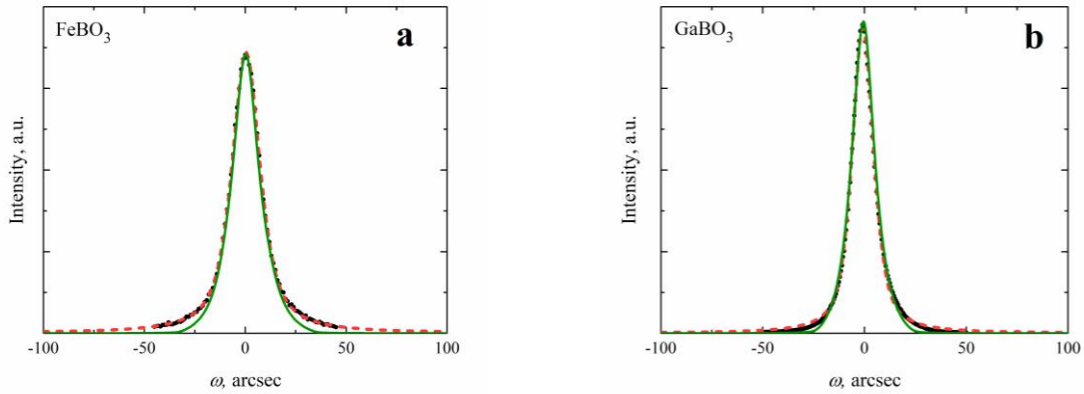

Figure 3. (Color online) Experimental (dotted), calculated (solid green lines) and fitted using pseudo-Voigt profile (dashed red lines) double-crystal DRCs of $FeBO_3$ and $GaBO_3$ single crystals. Reflection 0012 in Bragg geometry was used.

The DRCs of ferro-gallium borate $Fe_{1-x}Ga_xBO_3$ single crystals consist of several broadened peaks (Figure 4a,b). The existence of several peaks can be explained by defects in the crystal structure, for example, crystalline blocks. Due to different ionic radii of Ga and Fe, isomorphous substitution should lead to a distortion of crystal structure, which leads to a broadening of the rocking curves with respect to pure crystals.

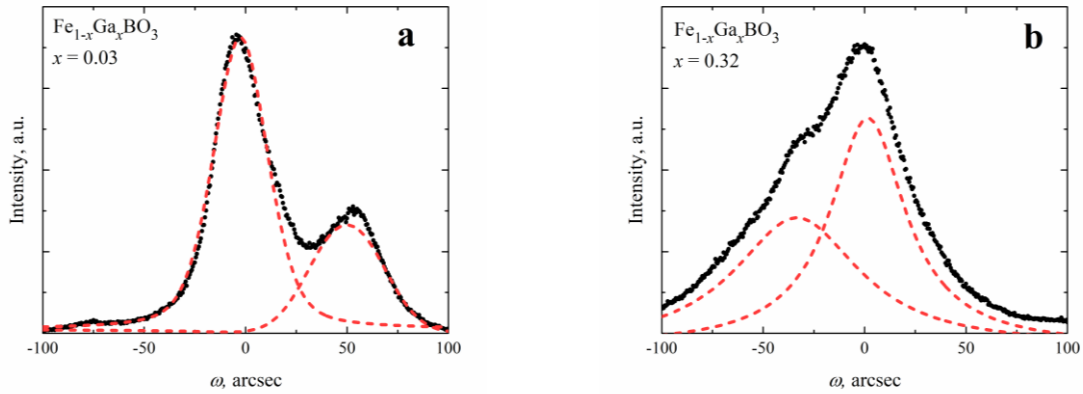

Figure 4. (Color online) Experimental (dotted) and fitted using pseudo-Voigt profile (dashed red lines) double-crystal DRCs of $Fe_{1-x}Ga_xBO_3$ single crystals. Reflection 0012 in Bragg geometry was used.

The X-ray topograms of $FeBO_3$ and $Fe_{1-x}Ga_xBO_3$ with x = 0.73 single crystals are shown in Figure 5. The absence of intensity contrast in the integrate scanning mode indicates the absence of growth steps and macroscopic structural defects, such as cracks and dislocations in both crystals [16]. However, the intensity contrast in the static mode for $Fe_{1-x}Ga_xBO_3$ single crystal with x = 0.73 is associated with mechanical strains [16]. The distribution of the mechanical strains can be caused by a non-uniform distribution of the iron/gallium contents over the crystal. It should be noted that the distribution of the mechanical strains does not exactly follow the distribution of the impurity contents.

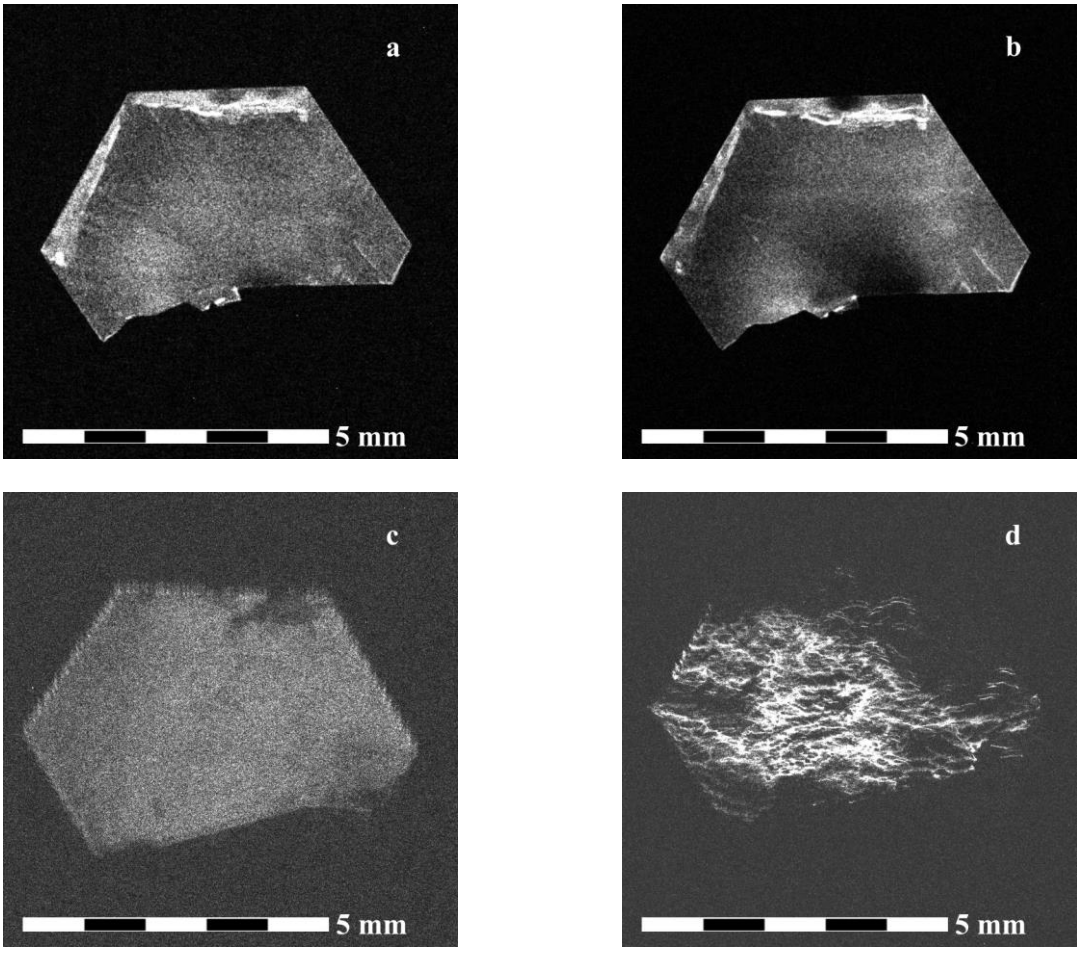

Figure 5. X-ray topograms of $FeBO_3$ (a, b) and $Fe_{1-x}Ga_xBO_3$ with x = 0.73 (c, d) single crystals, taken with integrate (a, c) and static (b, d) scanning modes. Reflection 300 in Laue geometry was used.

4. Conclusion

The series of iron borate based single crystals $Fe_{1-x}Ga_xBO_3$ was synthesized and studied by XRF and HDXRD techniques. Double-crystal diffraction rocking curves of pure $FeBO_3$ and $GaBO_3$ crystals are in excellent agreement with the calculated curves for perfect crystals. However, the DRCs of the crystals with mixed compositions $Fe_{1-x}Ga_xBO_3$ are broadened with respect to pure crystals. This can be explained by different ionic radii of Ga and Fe, and random distribution of gallium in the crystal lattice. Isomorphous substitution should lead to a distortion of crystal structure and to appearance of mechanical strains in ferro-gallium borate crystals.

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