Microstructure, XRD and Mössbauer spectroscopy study of Gd doped BiFeO₃

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Abstract

The results of fabrication process and characterization of Bi₁₋ₓGdₓFeO₃ (x = 0.05, 0.07, 0.10) ceramics are reported in the paper. The samples were prepared by standard solid state reaction method from the mixture of oxides: Bi₂O₃, Fe₂O₃ and Gd₂O₃. The influence of Gd substitution on the microstructure and density of Bi₁₋ₓGdₓFeO₃ was studied. Phase composition and structure of the obtained samples were investigated by X-ray diffraction. It turns out that the Bi₁₋ₓGdₓFeO₃ solid solutions with x = 0.05 and 0.07 crystallize in trigonal structure characteristic of BiFeO₃ compound. For the sample with x = 0.1, beside the major trigonal phase, 6% of orthorhombic phase typical for GdFeO₃ was detected. Hyperfine interaction parameters were studied by Mössbauer spectroscopy. Mössbauer results proved that the spin cycloid characteristic of BiFeO₃ compound gradually disappears when substituting Gd³⁺ ions at the Bi³⁺ sites.

Keywords: BiFeO₃, Gd³⁺ doping, solid state method, X-ray diffraction, Mössbauer spectroscopy

I. Introduction

Multiferroics are the class of materials that possess at least two of the properties among ferroelectricity, ferromagnetism and ferroelasticity in the same phase [1,2]. The magnetostrictive coupling between magnetic and electrical orders in these multiferroics enables to control magnetic polarization by applying electric field and vice versa [3]. Multiferroic materials attract particular interest in view of both fundamental physics and realizing multifunctional devices used in information storage, spintronics, sensors and other fields [4,5].

Bismuth ferrite BiFeO₃ is one of the widely studied materials which exhibits ferroelectric and antiferromagnetic properties at room temperature in the same phase. Bismuth ferrite has high Curie (Tᵣ ≈ 1103 K) and Néel (Tᵥ ≈ 643 K) temperatures [6,7]. The crystal structure of bismuth ferrite is described by the rhombohedral space group R₃c, which allows antiphase octahedral tilting and ionic displacements from the centrosymmetric positions along the [001]H direction [8]. As it is well known, bismuth ferrite is a G-type antiferromagnet due to superexchange interaction of neighbouring Fe³⁺ ions [9]. Each Fe³⁺ ion is located inside oxygen octahedron. In the second coordination sphere there is 8 Bi³⁺ ions while the third sphere is occupied by 6 Fe³⁺ ions with spins antiparallel with respect to the spin of the central Fe³⁺ ion. In fact, magnetic moments of two neighbouring Fe³⁺ ions are not strictly antiparallel but they are canted due to the Dzialoshynskii-Moriya interaction [10]. Thus, weak ferromagnetic moment arising from incomplete compensation of sublattices should appear. However, there is spin cycloid with period of 620 Å superimposed on the canted antiferromagnetic order which cancels out the weak ferromagnetic moment [7].
There is a lot of scientific research available on BiFeO$_3$ based materials. Lomanova et al. [11] reported the possibility of Bi$_2$Fe$_4$O$_9$ and Bi$_{23}$Fe$_{30}$O$_{69}$ formation during BiFeO$_3$ synthesis and this was shown to be dependent upon the quality of the initial reagents. In recent years, many attempts have been made to modify the structure of BiFeO$_3$ by suitable substitution of some rare earth ions. Doping of BiFeO$_3$ with rare earth ions at A-site proved to be an effective way to improve its ferroelectric properties [12,13] as well as A-site doping with ions of smaller radius influencing the Fe–O–Fe bond angle, giving a more insulating character to bismuth ferrite [14,15]. Doping of B-site is also another effective way to reduce the leakage current in BiFeO$_3$ and to improve its multiferroic properties [16,17].

In this paper, Gd-doped BiFeO$_3$ ceramics were synthesized by solid-state reaction method. Microstructure and chemical composition tests were carried out using a scanning electron microscope. Investigations of microstructure, crystalline structure and magnetic properties of the obtained materials were performed using X-ray diffraction (XRD) and $^{57}$Fe Mössbauer spectroscopy (MS).

II. Experimental procedure

Gd-doped BiFeO$_3$ powders having the formula Bi$_{1-x}$Gd$_x$FeO$_3$ ($x = 0.05, 0.07, 0.10$) were prepared by the conventional solid state reaction route. High purity Bi$_2$O$_3$, Fe$_2$O$_3$ and Gd$_2$O$_3$ (99.99%) powders were weighed according to the stoichiometry, mixed and milled in a planetary mill for $t = 24$ h with zirconia-yttria balls (ZrO$_2$-Y$_2$O$_3$, with the diameter of $d = 10$ mm) in polyamide cup containing ethyl alcohol (Poch, 96%). In the next step, the ground and dried powders were uniaxially cold pressed by a hydraulic press at $P = 60$ MPa in a steel matrix into disks with a diameter of $d = 23$ mm. The compacts were placed in corundum crucibles, stacked and separated from each other with Al$_2$O$_3$ alumina ballast (Poch, 99.9%) so that they did not touch the crucible and each other. The samples were heated using temperature rate of 5 °C/min up to $T = 800$ °C for $t = 3$ h. The temperature and duration of the reaction were determined as the optimal conditions for gadolinium doped bismuth ferrite, resulting in the densest Bi$_{1-x}$Gd$_x$FeO$_3$ samples with the lowest content of secondary phases. The solid-phase reaction that occurs during the synthesis can be written by the following equation:

$$1 - \frac{x}{2} \text{Bi}_2\text{O}_3 + \frac{x}{2} \text{Gd}_2\text{O}_3 + \frac{1}{2} \text{Fe}_2\text{O}_3 \rightarrow \text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$$ (1)

After synthesis, the compacts were placed in a porcelain mortar and ground thoroughly. The pre-ground powders were again milled with zirconia-yttria balls in a planetary mill for $t = 24$ h in polyamide containers containing ethyl alcohol. After drying the powders were pressed into discs $d = 10$ mm in diameter, at pressure of $P = 30$ MPa. Air sintering was carried out at $T = 880$ °C for $t = 3$ h. The whole process is schematically presented in Fig. 1.

The microstructure and chemical composition of the final ceramics were examined with a scanning electron microscope (SEM, JSM - 7100F) operating at 15 kV and equipped with an energy dispersive spectrometer (EDS, NORAN Vantage). EDS spectrum, which is dependent on the number of counts as a function of radiation, makes it possible to identify the elements contained in the tested material. The density of the obtained ceramics was calculated from the geometry and the mass of the sample.

X-ray diffraction measurements were made on a X’Pert Pro diffractometer. A Cu-Kα X-ray wavelength $\lambda = 0.154$ nm was used. Phase and structural analyses of the X-ray diffraction patterns of Bi$_{1-x}$Gd$_x$FeO$_3$ powders were carried out using HighScore Plus program equipped with PDF2 crystallographic database.

The samples were also analysed using Mössbauer spectroscopy. A POLON spectrometer working in range utilization mode was used. As a source of gamma quanta with energy $E = 14.4$ keV, $^{57}$Co nuclei embedded in the Rh crystal matrix were used.

III. Results and discussion

XRD patterns of the Bi$_{1-x}$Gd$_x$FeO$_3$ solid solutions are shown in Fig. 2. Phase analysis of the diffractograms revealed that beside the major BiFeO$_3$-like phase small amounts of parasitic Bi$_2$Fe$_4$O$_9$ and Bi$_{23}$Fe$_{30}$O$_{69}$ phases exist. The most intensive peaks from these phases were stored in discs $d = 10$ mm in diameter, at pressure of $P = 30$ MPa. Air sintering was carried out at $T = 880$ °C for $t = 3$ h. The whole process is schematically presented in Fig. 1.

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revealed 11.1% of orthorhombic Pnma phase and 88.9% of rhombohedral R3c phase for the BiFeO$_3$ solid solutions. The quantitative phase analysis showed that the content of the major BiFeO$_3$ phase is 89.0, 91.4 and 95.1 wt.% for $x = 0.05$, $x = 0.07$ and $x = 0.10$, respectively. However, in the case of the sample with $x = 0.1$ small amount (6 wt.%) of orthorhombic Pnma phase characteristic of GdFeO$_3$ compound was detected. This can be evidenced e.g. by appearance of small peaks in the vicinity of $2\theta = 22.5^\circ$, $32.1^\circ$ and $46.3^\circ$ of $2\theta$ angle (see the right panel in Fig. 2) which correspond to the (101), (121) and (202) plains of Pnma structure. Thus, it may be supposed that the gradual transformation from R3c to Pnma structure starts for about 10% of Gd-doping of BiFeO$_3$. This result agrees well with data published by Guo et al. [18]. They revealed 11.1% of orthorhombic Pnma phase and 88.9% of R3c phase for the Bi$_{0.93}$Gd$_{0.07}$FeO$_3$ solid solution prepared by sol-gel method. It was shown by Ablat et al. [19] that single Pnma phase was obtained for $x > 0.15$ when the samples were prepared by solid state reaction method. The detailed structural parameters derived from the Rietveld refinement of XRD patterns are summarized in Table 1. The data for the undoped BiFeO$_3$ taken from Ref. [20] were included for comparison. Gradual decrease of lattice parameters $a$, $b$, $c$ and the volume of unit cell, $V$, can be clearly observed. This is the result of partial substitution of larger Bi$^{3+}$ ions (ionic radius in VIII coordination $r_{Bi} = 1.17$ Å) by smaller Gd$^{3+}$ ions ($r_{Gd} = 1.053$ Å in VIII coordination) [1].

SEM micrographs of the Bi$_{1-x}$Gd$_x$FeO$_3$ ceramics are shown in Fig. 3. The procedure of recording sample images was random selection of fields distributed over the entire surface of the tested ceramics. The microstructure is characterized by a compact, non-porous structure with well-developed grains. A slight increase in grain size is visible along with the increase in gadolinium concentration in the obtained materials.

Based on the density studies, it can be stated that the increase in gadolinium concentration resulted in decreased density, which are as follows: 7.353, 7.028 and 6.712 g/cm$^3$ for the Bi$_{0.95}$Gd$_{0.05}$FeO$_3$, Bi$_{0.93}$Gd$_{0.07}$FeO$_3$ and Bi$_{0.9}$Gd$_{0.1}$FeO$_3$ ceramics, respectively.

EDS spectra of the Bi$_{1-x}$Gd$_x$FeO$_3$ ceramics are shown in Fig. 4 and the theoretical and experimental contents of elements (calculation for simple oxides) are given in Table 2. The results prove that the chemical composition of the produced ceramics has been preserved.

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<td>Pnma</td>
<td>5.628</td>
<td>7.797</td>
<td>5.433</td>
<td>238.5</td>
<td>6</td>
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Table 1. Structural parameters of Bi$_{1-x}$Gd$_x$FeO$_3$ derived from the Rietveld refinement of XRD patterns (Å denotes relative content of a phase).
Figure 3. SEM micrographs of the fracture surface of sintered samples: a) Bi$_{0.95}$Gd$_{0.05}$FeO$_3$, b) Bi$_{0.93}$Gd$_{0.07}$FeO$_3$ and c) Bi$_{0.9}$Gd$_{0.1}$FeO$_3$

Figure 4. EDS spectra of Bi$_{1-x}$Gd$_x$FeO$_3$ ceramics

The measurement uncertainty is small and the largest discrepancy is ±3.58%. The EDS study confirmed both the quantitative and qualitative chemical composition of the produced Bi$_{1-x}$Gd$_x$FeO$_3$ ceramics. The analysis also showed the purity of the samples tested and excluded the presence of foreign elements and impurities.

Figure 5 shows room-temperature $^{57}$Fe-Mössbauer spectra measured for the studied Bi$_{1-x}$Gd$_x$FeO$_3$ solid solutions. It is well known that ferro- and antiferromagnetic materials show six-line Mössbauer patterns (sex- tets) due to the Zeeman splitting of $^{57}$Fe nuclear levels caused by the hyperfine magnetic field (HMF). On the other hand, paramagnetic phases show single line or doublet. Single line corresponds to the transition between excited nuclear state of $^{57}$Fe (spin $I = \frac{3}{2}$) and ground state (spin $I = \frac{1}{2}$). Doublet occurs when electric field gradient (EFG) is present at $^{57}$Fe nucleus site [21]. As it can be seen in Fig. 5 the spectra consist of six-line part connected with antiferromagnetic BiFeO$_3$- like structure and small paramagnetic doublets D1 and D2 arising due to the parasitic Bi$_2$Fe$_4$O$_9$ and Bi$_{25}$FeO$_{40}$ phases. The total contribution of paramagnetic part to the whole spectrum is 17.5%, 11.5% and 8.3% for the samples with $x = 0.05$, 0.07 and 0.1, respectively. One can note that these are significantly higher values than the contributions derived from XRD patterns analysis: 11%, 8.6%, 4.9%. This can be explained in terms of different probabilities of recoilless absorption of 14.4 keV gamma radiation for the Bi$_{1-x}$Gd$_x$FeO$_3$ solid solution and parasitic phases. It is obvious that the probability will be higher for Bi$_2$Fe$_4$O$_9$ compound as it contains four Fe ions per formula unit (proportion of Fe and Bi ions 2:1) while the Bi$_{1-x}$Gd$_x$FeO$_3$ sample contains one Fe ion (proportion of Fe and Bi ions approximately 1:1).

Distortion in perovskite crystal structure occurs either through displacement of central cations from their centrosymmetric position or from the rotation of oxygen octahedral [22]. In BiFeO$_3$ both of them occur simultaneously leading to the lowering of the crystal symmetry from cubic to rhombohedral and break of inversion symmetry of perovskite cell. Oxygen octahedra rotates in the opposite way in adjacent chemical cells joint by the line along [111] pseudocubic direction which is also the direction of polarization vector $P$. Moreover, iron ions are displaced along the same polar [111] direction and

Table 2. Theoretical and experimental contents of elements (calculation for simple oxide) for Bi$_{1-x}$Gd$_x$FeO$_3$ ceramics

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<thead>
<tr>
<th>Sample</th>
<th>Content from EDS [%]</th>
<th>Theoretical content [%]</th>
<th>Content error [%]</th>
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<td>Gd$_2$O$_3$</td>
<td>Fe$_2$O$_3$</td>
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<td>Bi$<em>{0.9}$Gd$</em>{0.1}$FeO$_3$</td>
<td>68.154</td>
<td>5.891</td>
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Figure 5. Mössbauer spectra measured for Bi$_{1-x}$Gd$_x$FeO$_3$ solid solutions. The components S1 and S2 come from Bi$_{1-x}$Gd$_x$FeO$_3$ solid solution and paramagnetic doublets D1 and D2 are due to Bi$_2$Fe$_4$O$_9$ and Bi$_{25}$FeO$_{40}$ parasitic phases.

The magnetic part of the spectra shown in Fig. 5 was fitted in approximation of two-sixtet model (S1 and S2) as explained above. The derived hyperfine parameters are summarized in Table 3 and compared with the data obtained by other authors for the undoped BiFeO$_3$. The fitted sextets are characterized by two distinct $B_{hf}$ values differing by $\Delta B_{hf}$ and two values of $2\varepsilon$ with opposite signs. This result is consistent with the data reported by others [24,28]. By analysing the shape of the magnetic part of the spectra one can note two effects: asymmetry of the spectra reflected by different amplitudes of 1st and 6th line (see parameter $\Delta A_{16}$ in Table 3) and inhomogeneous lines broadening (e.g. different widths of lines $\Gamma_1$ and $\Gamma_6$). As widely discussed in Ref. [31] the line broadenings and spectral asymmetry in the spiral magnetic phase of BiFeO$_3$ are due to different causes: the broadenings arise from the slight modulation of the hyperfine energies as the magnetic moment rotates with respect to the principal axis of the EFG tensor, and the asymmetry stems from an intrinsic anisotropy of the magnetic hyperfine interaction at a site with trigonal symmetry. Thus, the spectra presented in Fig. 5 confirm existence of cycloidal spin ordering in the studied samples. The increase of the Gd dopant concentration leads to the reduction of the spectra asymmetry as evidenced by the drop of $\Delta A_{16}$ parameter and disappearance of inhomogeneous lines broadening ($\Gamma_1$ and $\Gamma_6$, much different for the sample with $x = 0.05$, but comparable for the sample with $x = 0.1$). Moreover, the difference between the
HMF fields of the two sextets, $\Delta B_{hf}$, significantly decreases reaching as little as 0.09 T for the sample with $x = 0.1$. Hence, we conclude that the increasing amount of Gd in the structure of BiFeO$_3$ causes gradual destruction of spin cycloid as proved by disappearance of inhomogeneous lines broadening. Besides, the reduction of spectral asymmetry $\Delta A_{16}$ and drop of the difference between two values of HMF, $\Delta B_{hf}$, can be accounted for structural changes in the rhombohedral lattice. It can be supposed that increase of Gd concentration causes change of distortion of FeO$_6$ octahedral structure thus, the two iron sites become more equivalent as evidenced by the drop of $\Delta B_{hf}$. This conclusion is supported by findings of Xiao et al. [27], although it needs further investigations. The values of isomer shift $\delta$ ($-0.37 \text{ mm/s}$) confirm that only trivalent iron ions in high spin state are present in the structure of Bi$_{1-x}$Gd$_x$FeO$_3$.

IV. Conclusions

Conventional solid state reaction route and sintering at 880 °C were successfully adopted for preparation of Bi$_{1-x}$Gd$_x$FeO$_3$ (for $x = 0, 0.05, 0.07, 0.1$) ceramics. An addition of gadolinium affects the grain size and causes a slight increase in grains in the materials obtained. XRD studies revealed that the Bi$_{1-x}$Gd$_x$FeO$_3$ solid solutions with $x = 0.05$ and $0.07$ have rhombohedral R3c structure characteristic of BiFeO$_3$ compound. For the sample with $x = 0.1$, beside the major R3c phase, $6\%$ of orthorhombic Pnma phase characteristic of GdFeO$_3$ compound was detected. It was shown that increase of Gd dopant concentration leads to the reduction of unit cell volume. Mössbauer spectroscopy was applied for investigation of hyperfine interaction parameters of the samples and confirmed phase composition deduced from XRD patterns analysis. Mössbauer investigations proved that the studied solid solutions exhibit aniferromagnetic BiFeO$_3$-like magnetic structure with cycloidal modulation of spins arrangement. Substitution of increasing amounts of Gd$^{3+}$ ions causes systematic change of FeO$_6$ octahedral distortion and gradual destruction of the spin cycloid.

References

11. N.A. Lomanova, V.V. Gusarov, “Influence of synthesis temperature on BiFeO$_3$ nanoparticles formation”,

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<th>Sample</th>
<th>Component</th>
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<th>$\Delta B_{hf}$ [T]</th>
<th>$C$ [%]</th>
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