MgFe$_2$O$_4$ phase effect on magnetic properties of BiFeO$_3$ in ceramic composites of (1-x) BiFeO$_3$–x MgFe$_2$O$_4$

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Abstract. A two-stage ceramic technology was used for producing a family of (1-x) BiFeO$_3$–x MgFe$_2$O$_4$ heterophase systems. The study of the magnetic hysteresis loop revealed the presence of a ferrimagnetic response. The experimentally obtained concentration and temperature dependences of the magnetic permeability made it possible to consider the influence of the BiFeO$_3$ phase on the magnetic response of the studied samples.

1. Introduction

In recent years, there has been an increased need for technologies related to the creation and improvement of elements that combine the advantages of non-volatile magnetic memory, low power consumption and high-speed electrical information processing systems [1]. To solve this problem, one could use magnetoelectric multiferroics in which the magnetic state is varied by applying an electric field [2], which could significantly improve energy efficiency.

One of the promising multiferroics now is the bismuth ferrite BiFeO$_3$ (BF). The main advantage of this material is high Curie and Neel temperatures ($T_C = 1083$ K, $T_N = 643$ K). In bismuth ferrite, all types of magnetoelectric interactions described in [3] take place. The main BF problem is the absence of the bulk magnetic moment. This is caused by spatial modulation of the magnetization with a period of 62 nm [4, 5], which leads to a "zero" magnetoelectric response. Attempts to eliminate this disadvantage used various methods to destroy the spin cycloid: applying high magnetic fields (~ 200 kOe) [6], doping of BF with rare-earth and transition metals [7], preparing solid solutions based on BF [8-10], and so on.

In this paper, the magnetoelectric ordering of the BF was attempted by creating a heterophase system, where the ferrimagnetic compound MgFe$_2$O$_4$ was chosen as the second phase. Thus, the aim of this work is to study the magnetic properties of the ceramic heterophase system of (1-x) BiFeO$_3$–x MgFe$_2$O$_4$ at various magnesium ferrite contents ($x = 0.01; 0.05; 0.1; 0.15; 0.2$).

2. Experiment

The initial components of the (1-x) BiFeO$_3$–x MgFe$_2$O$_4$ system were obtained by ceramic technology from simple oxides of Bi$_2$O$_3$, Fe$_2$O$_3$ and MgO (99.5%) previously dried and then mixed in a stoichiometric ratio. Synthesis of BiFeO$_3$ was carried out in two stages with intermediate grinding. The first stage included annealing at $T_1 = 800$ °C for 10 hours. After that, the sample was ground and re-pressed to complete the synthesis. The second stage of synthesis was carried out at $T_2 = 800$ °C for
5 hours. MgFe$_2$O$_4$ was synthesized at 1100 °C for 48 hours. The obtained samples of the initial components (BiFeO$_3$, MgFe$_2$O$_4$) were crushed and ground, after which their powders were mixed in a ratio calculated by the mole fraction $x$, and pressed in the form of tablets. Samples of (1-$x$) BiFeO$_3$ - $x$ MgFe$_2$O$_4$ ($x = 0.01, 0.05, 0.1, 0.15$ and $0.2$) were sintered at 850 °C for 4 hours. The samples were coated with silver electrodes by firing a silver paste.

X-ray diffraction analysis was performed on a Bruker D2 Phaser diffractometer using Cu K$_\alpha$ radiation. Micrographs of the samples of the investigated magnetoelectric composites were obtained using a scanning electron microscope (JEOL 6510 4V).

The magnetic hysteresis loops were obtained using a vibrating magnetometer. For temperature measurements of magnetic permeability, a copper wire with high-temperature insulation was wound on a ceramic (Al$_2$O$_3$) tube. The samples were placed inside the tube. The inductance of the coil was detected with an E7-20 immittance meter. The magnetic permeability was calculated using the formula for a solenoid.

### 3. Results and discussion

X-ray diffraction analysis of the synthesized samples (figure 1) revealed that apart from the cases of $x = 1$ (magnesium ferrous spinel) and $x = 0$ (bismuth ferrite), the system is a two-phase structure. This proves the presence of the reflexes inherent in both MgFe$_2$O$_4$ and BF on the X-ray patterns for all the compositions. As the content of one of the components of the heterophase structure increases, the intensity of its reflexes increases, while the intensity of the reflexes of the other component decreases. It is established that the cubic phase corresponding to MgFe$_2$O$_4$ has a symmetry group $Fd\bar{3}m$ and a lattice parameter $a = 8,369 \, \text{Å}$.

In the samples with $x = 0$ (BF), three phases were detected: the main rhombohedral phase (with lattice parameters $a = 5,563 \, \text{Å}; c = 13,829 \, \text{Å}$) corresponding to BF with the symmetry group R3c; the orthorhombic Bi$_2$Fe$_4$O$_9$ phase with lattice parameters $a = 7,936 \, \text{Å}, b = 8,418 \, \text{Å}, c = 5,985 \, \text{Å}$ and the spatial symmetry group Pbam; and the cubic Bi$_2$O$_3$ phase with a lattice parameter $a = 10,119 \, \text{Å}$ and the symmetry group I23. According to the literature data, the presence of secondary phases in bismuth ferrites is associated with the instability of the main phase at the synthesis temperature and the incongruent melting temperature near it. In our case, a ceramic material containing 71% of the BF phase was obtained.

As seen in figure 1, no other phases appear in the system under study with the increase in the MgFe$_2$O$_4$ content. The content of the magnesium ferrite phase increases, while the content of secondary phases in BiFeO$_3$ decreases. Thus, the system under study is not a solid solution but a two-phase system consisting of BiFeO$_3$ and MgFe$_2$O$_4$ – a magnetoelectric composite.

It is known from the literature that doping of BiFeO$_3$ ceramics leads to a variation in the average grain size that affects its physical properties. Therefore, to reveal the effect of the composition on the average grain size, the grain structure on the cleavage of the samples of the (1-$x$) BiFeO$_3$ - $x$ MgFe$_2$O$_4$ composite was determined using a scanning electron microscope (figure 2).

One can see that in all cases the grain size does not exceed 10 μm. The concentration dependence of the average grain size is presented in figure 3. As can be seen, even a small content of the MgFe$_2$O$_4$ phase leads to a significant decrease in the grain size. It is possible that the addition of the synthesized MgFe$_2$O$_4$ powder alters the sintering mode of the composite samples. The number of defects pinning the interphase boundaries and hindering the growth of grains in the process of high-temperature recrystallization increases. Therefore, the average grain size decreases with increasing magnesium ferrite content.

The dependence of the magnetization $J$ on the amplitude of the magnetic field intensity $H$ (figure 4) shows that the magnetization $J$ in the "pure" BF is almost independent of $H$, since bismuth ferrite has an antiferromagnetic ordering. However, even a small addition of MgFe$_2$O$_4$ leads to a nonlinear response, which increases with increasing $x$. 


We note that magnesium ferrite itself, being a ferrimagnet, has a similar nonlinear behavior $J(H)$. In order to understand whether the magnetization of the BF phase makes any contribution to the magnetic response of the entire composite, we have studied the concentration dependence of the

![Figure 1. XRD patterns for the composite system of $(1-x)$BiFeO$_3$ – $x$ MgFe$_2$O$_4$ at $x = 0; 0.01; 0.05; 0.1; 0.15; 0.2$ and $1.0$ (bottom to top) at room temperature. * - BiFeO$_3$ phase, Δ – MgFe$_2$O$_4$ phase](image1.png)

![Figure 2. Morphology of the surface of composite samples of $(1-x)$ BiFeO$_3$ - $x$MgFe$_2$O$_4$, at $x = 0$ (a); 0.01(b); 0.1 (c); 0.15 (d) and 1.0 (e).](image2.png)

![Figure 3. Average grain size dependence on the MgFe$_2$O$_4$ content, calculated from microphotographs.](image3.png)
magnetic permeability of the composite. This dependence was obtained using two different methods: magnetic loops (the initial part of the magnetization curve) and the coil inductance measurement (figure 5).

Figure 4. Dependences of the magnetization on the magnetic field strength for the composite of (1-\(x\)) BiFeO₃ – \(x\) MgFe₂O₄.

Figure 5. Dependences of the magnetic permeability of (1-\(x\)) BiFeO₃ – \(x\) MgFe₂O₄ on the content of the MgFe₂O₄ component:
1 – experimental data obtained from measurements of inductance; 2 – experimental data obtained from magnetic loops; 3 – dependence calculated according to the Luang formula; 4 – dependence calculated using the K. Lichtenecker formula.

Figure 5 shows that the experimental dependences \(\mu(x)\) obtained using two different methods coincide with each other quantitatively and qualitatively, which indicates the reliability of the experimental data. As the content of the magnesium ferrite phase increases, the magnetic permeability of the composite increases. The analysis of the obtained dependence was carried out as follows. The studied composite is a particulate one (figure 2), where BF plays the role of a matrix, and statistically distributed magnetic granules of MgFe₂O₄ serve as filler. Then, if the phases of BF and MgFe₂O₄ do not interact with each other, the effective permeability of the composite can be calculated using the Luang formula:

\[
\mu_{\text{eff}}^{1/3} = (1-x)\mu_{\text{BF}}^{1/3} + x\mu_{\text{Mg}}^{1/3},
\]

or the K. Lichtenecker formula:

\[
\mu_{\text{eff}} = \mu_{\text{BF}}^{1-x} \mu_{\text{Mg}}^x,
\]

where \(\mu_{\text{eff}}\) is the magnetic permeability of the composite, \(\mu_{\text{BF}}\) is the magnetic permeability of BiFeO₃, and \(\mu_{\text{Mg}}\) is the magnetic permeability of MgFe₂O₄.

It follows from formulas (1) and (2) that the increase in the content of the ferrimagnetic MgFe₂O₄ phase should lead to the growth of the magnetic permeability of the composite (figure 5, curves 3 and 4). However, as can be seen in figure 5, the experimental data lie much higher than the curves calculated by mixing formulas, which indicates the effect of the magnetic subsystem of magnesium ferrite on bismuth ferrite, leading to a partial suppression of the spin-modulated ordering of the
magnetic moment in BF. Such influence can be explained as follows. During high-temperature sintering, the magnesium ions migrate from the MgFe$_2$O$_4$ phase to the BF phase, and the bismuth ions ($r_{Bi}^{3+} = 0.096$ nm) are replaced by magnesium ions ($r_{Mg}^{2+} = 0.066$ nm) in the BiFeO$_3$ lattice, which leads to a variation in the exchange interaction determining the magnetic ordering in BiFeO$_3$. To test this assumption, the temperature dependences of the magnetic permeability were studied (figure 6), which made it possible to observe a shift of the temperature of the magnetic transition in BF as a function of the MgFe$_2$O$_4$ phase content.

![Figure 6](image_url)  

**Figure 6.** Temperature dependences of the magnetic permeability for the composites at different MgFe$_2$O$_4$ contents. On the inset: Dependence of the magnetic transition temperature in BF on the MgFe$_2$O$_4$ content.

A sharp decrease in the magnetic permeability in the temperature range from 350 °C to 400 °C can be observed in figure 6, which is associated with a magnetic phase transition. We note that the form of the dependences obtained for $x < 1$ is characteristic of an antiferromagnetic substance and can be associated only with BiFeO$_3$. Thus, the Neel temperature in BiFeO$_3$ increases with the addition of magnesium ferrite, as shown in the inset of figure 6.

The increase in the Neel temperature can be explained in the following way: as the ions of Bi$^{3+}$ are replaced by smaller Mg$^{2+}$ ions, the volume of the unit cell decreases. This leads to a change in the energy of the exchange interaction and requires a greater thermal energy for magnetic disordering. Therefore, the Neel point shifts toward higher temperatures.

4. Conclusions

An attempt was made to suppress the spin-modulated structure of BiFeO$_3$ by creating a heterophase system of $(1-x)$ BiFeO$_3$-$x$ MgFe$_2$O$_4$ at $x = 0.01; 0.05; 0.1; 0.15$ and $0.2$. X-ray diffraction analysis made it possible to establish the presence of the main phases and a small number of secondary phases, the appearance of which is associated with the synthesis of BiFeO$_3$. A study of the morphology of the surface showed that the average grain size of the samples studied decreases with the increase of
MgFe$_2$O$_4$ content, which leads to a decrease in the content of secondary phases. Measurements of magnetic properties allow us to conclude that a ferrimagnetic response in BiFeO$_3$ appears. An analysis of the concentration and temperature dependences of the magnetic permeability indicates a partial suppression of the spin-modulated structure in BiFeO$_3$.

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