Low-temperature phase transition in bismuth ferrite films substituted by manganese

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Abstract. Measurements of the capacitance and tangent of dielectric loss angle, impedance and resistance, magnetization in a magnetic field of 8.6 kOe BiMnₓFe₁₋ₓO₃ films in the temperature range 80-600 K were carried out. The anomalies of the dielectric properties are explained in the Debye model and correlate with changes in the magnetic moment versus temperature.

1. Introduction

Materials with magnetoelectric properties are promising for technological applications in spintronics, sensor technology, information storage and recording devices [1-4]. Magnetically ordered crystals with antiferromagnetic ordering – multiferroic bismuth ferrite [5] were chosen as model objects of study. Today, bismuth ferrite BiFeO₃ or briefly (BFO) is one of the most popular compounds, based on which new magnetoelectric materials are created, it has high temperatures electrical (Tc = 820 C) and magnetic (TN = 370 C) ordering [6]. Below 180 K, an increase in the reciprocal lattice vector of the film surface was found, which is absent in the bulk of the single crystal [7].

The main feature of this phase transition is a sharp change in volume without actually changing the symmetry. According to the authors of this work, the phase transition was observed due to the complexity of the phase diagram of the BiFeO₃ compound, which is very sensitive to even small changes, such as surface tension or deformation of the local field around vacancies and defects. The peculiarity of this compound BiFeO₃ is that it should not be considered as a homogeneous material. Structural, electrical, and magnetic properties of the surface layer differs from the bulk. The anomaly found at the 200K is attributed to the spin-glass state formation [8].

Increasing the ferroelectric and magnetic moment is achieved by substitution of iron into BiFeO₃ by manganese [9]. Studies on these compounds prove the presence of structural distortions. With an increase in the concentration of substitution, the residual magnetization is about 15 times higher than the magnetization for a pure sample of BiFeO₃ and is explained by the suppression of the cycloid spin structure and an increase in the angle of angularity of antiferromagnetically ordered spins [10].

The goal of the study is to establish the effect of the substitution of manganese ions on the low-temperature phase transition in BiMnₓFe₁₋ₓS films.
2. Results and Discussion

The bismuth ferrite solid solution films were formed by the burst-mode deposition of the preliminary synthesized solid solutions onto object glasses. The precursors used were powders with a grain size from 0.1 to 0.3 mm. The deposition was performed in a UVN-71P-2 vacuum facility. The pressure in a reaction chamber during deposition was $10^{-3}$ Pa. The tantalum evaporator temperature was kept at a level of ~2000°C. The substrates were placed at a distance of 10 cm from the evaporator. The substrate temperature ranged between 250–300°C. The films were 1240-nm-thick and had geometric sizes of $13 \times 17$ mm.

The magnetic moment of the film was measured by the Faraday method in a magnetic field of 8.6 kOe [11, 12]. Figure 1 shows the temperature dependences of the magnetic moment for two compositions. As in bulk samples, the magnetic moment increases and reaches a maximum value at $x = 0.05$, then decreases by half. This is due to the destruction of the spin cycloid and the formation of antiferromagnetic order G type.

Below room temperature, the magnetization has an inflection point at $T = 245$ K and $T = 218$ K for concentrations $x = 0.05$ and 0.15. The temperature of the magnetic phase transition is in the high-temperature region of 560–580 K.

The substitution of iron for manganese forms electrically inhomogeneous states, including regions with local electric polarization. The electrically inhomogeneous states were established by impedance spectroscopy [13, 14]. We measured the active (real part $Z'$) and reactive (imaginary part $Z''$) of the resistance using an AM-3028 component analyzer and determined full impedance $Z = Z' + iZ''$ of the films in the frequency range of $\omega = 0.1–1000$ kHz at temperatures of 80–400 K. The imaginary part of the impedance (figure 2) measured at frequencies of 0.1–1000 kHz is described well by the function $\text{Im}Z = 1/\omega C$ with the capacitance increasing upon heating.

![Figure 1](image.png)

**Figure 1.** Magnetization thin films BiMnxFe1-xO3 for $x=0.05$ (1), 0.15 (2) versus temperature.
The carrier transport mechanism can be established from the frequency and temperature dependences of the conductivity. The power dependence of the conductivity \( \sigma(\omega) = C \omega^s \) is indicative of the hopping conductivity \( s=1 \); in particular, it is attributed to electron hoppings between electrically inhomogeneous states in the film, which are caused by spin polaron pinning over the localized states with phonons involved [15]. With increasing temperature, a smooth transition from a linear dependence associated with the Coulomb glass regime for interacting electrons to a quadratic dependence in the Fermi glass mode for noninteracting electrons is observed. Thus, at \( T = 380 \) K index \( s = 1.6 \). Below 220-240 K, Coulomb glass is realized. The capacity of the BiMn\(_x\)Fe\(_{1-x}\)O\(_3\) film for \( x = 0.05 \) undergoes small gaps at temperatures \( T = 214 \) K and \( T = 244 \) K with a wide maximum of the tangent of dielectric loss angle (figure 3).

**Figure 2.** The real part \( Z' \) (a) and full impedance \( Z \) (b) of the films BiMn\(_x\)Fe\(_{1-x}\)O\(_3\) for \( x=0.05 \) on the frequency at \( T=300 \) K(1), 340 K (2), 380 K (3).

**Figure 3.** Capacity (a) and tangent of angle (b) dielectric loss of thin films BiMn\(_x\)Fe\(_{1-x}\)O\(_3\) for \( x=0.05 \) at frequencies \( \omega = 1 \) kHz (1), 5 kHz (2), 10kHz (3), 50kHz (4), 100kHz (5), 300kHz (6).
The independence of jump $C(T, \omega)$ temperature on frequency indicates the possibility of a first-order phase transition. Dielectric losses are associated with energy transfer to the magnetic and ferroelectric systems. The transition temperature interval shifts to high temperatures ($278$–$316 \text{ K}$) with an increase in the concentration of substitution for manganese ions (figure 4). At $T = 176 \text{ K}$, a dynamic transition at high frequencies was determined (figure 4b).

![Figure 4](image_url)

**Figure 4.** Capacity (a) and tangent of angle of dielectric loss (b) thin films BiMn$_x$Fe$_{1-x}$O$_3$ for $x = 0.15$ at frequencies $\omega = 1 \text{ kHz}$ (1), $5 \text{ kHz}$ (2), $10 \text{ kHz}$ (3), $50 \text{ kHz}$ (4), $100 \text{ kHz}$ (5), $300 \text{ kHz}$ (6).

### 3. Conclusion

In the low-temperature region, anomalies of magnetic and dielectric properties were found in thin films BiMn$_x$Fe$_{1-x}$O$_3$. A jump in the capacity and the loss tangent for the composition with $x = 0.2$ is established. Perhaps these anomalies are associated with the pinning of lattice polarons and the formation of a Coulomb gap with the spectrum of impurity electronic excitations.

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