Regulating the BiMn_xFe_{1-x}O₃ film conductivity upon cooling in magnetic and electric fields

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Regulating the $BiMn_xFe_{1-x}O_3$ film conductivity upon cooling in magnetic and electric fields

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ABSTRACT

The magnetic and electrical properties of the $BiFe_{1-x}Mn_xO_3$ (x = 0.05, 0.15) films in the temperature range of 80-600 K have been investigated. The Curie temperature (Tc) of the films has been determined. A decrease in the conductivity of the films with x = 0.05 upon cooling in an electric field from the temperatures T < Tc has been found. This effect has been described in the model of decreasing quantum well (domain wall) density and the tunneling coefficient drop. A decrease in the conductivity of the $BiFe_{1-x}Mn_xO_3$ film by more than an order of magnitude upon cooling from high temperatures in a magnetic field has been established. The experimental data are interpreted using the magnetic-field-induced magnetic structure variation and exchange splitting of the impurity subband.

Keywords: Multiferroic, Curie temperature, conductivity, cooling in magnetic field

Introduction

There still has been a lack of understanding of the interplay between the electron transport and ferroelectric polarization [1-3], which is caused by the formation of domain walls and crystallographic defects. Multiferroic materials can contain domains of two interrelated types, ferroelectric and magnetic [4-7]. A typical example of multiferroics is $BiFeO_3$. It is well known that BFO is G-type antiferromagnet and each Fe^{3+} spin is surrounded by six canted antiparallel spins on the nearest Fe neighbors which allow net magnetic moment [8, 9]. The weak ferromagnetism in BFO powder samples was observed to depend on the DM interactions and also on the single-ion anisotropy [10]. When iron ions are substituted by manganese ions, the magnetization increases and hysteresis is observed with small remanent magnetization. Ferroelectric ordering exists in an orthorhombic structure and disappear into a tetragonal one at a concentration of x = 0.2 in $BiMnFeO_3$ [11].

The conductivity in BFO was regulated by magnetic and ferroelectric domain walls that is higher than the domain conductivity by several orders of magnitude and the activation energy in the electron excitation spectrum is lower than in the bulk by 10-20% [12]. In [12], the local conductivity of domains and domain walls in thin films containing mainly the 71° domain walls was examined. The measurements performed at room and high temperatures revealed the conductivity implemented via the 71° domain walls. Mainly n-type carriers are involved in the conductivity.

To control the film conductivity, it is necessary to create materials with the strong magnetoelectric coupling [13, 14], which is achieved as a result of substitution of Fe by Mn ion within one crystal structure ($0< x <0.2$). A change in the magnetic and electrical state is also possible due to electronic phase separation caused by manganese ions. For concentration of Mn x= 0.167 in ($BiMn_{0.167}Fe_{0.833}O_3$) the ground state of BMFO is found to be antiferromagnetic with magnetization of 1.0000 μ_B/cell [15]. According to group theory, the 3d orbitals of the transition metal in rhombohedral BFO (C3v symmetry) are split into a1, 1e and 2e, where 1e and 2e denote lower-lying and higher-lying

e states, respectively [16]. Manganese ions yield the gap states, half of which are filled with electrons (half-filled) [16].

At temperatures below the magnetic transition, electron droplets with magnetization are formed. Diffusion of droplets slows with decreasing temperature and they freeze in the lattice. At small concentration of Mn the unoccupied O-2p state appears just above the valence band, with a ligand hole in the O-2p state. In Mn substituted films, a random distribution of the electric potential is realized with potential wells filled with electrons and holes. Therefore, the conductivity of the films will depend on the prehistory of exposure to electric and magnetic fields.

The aim of this study was to determine the conductivity of a bismuth ferrite film upon cooling in magnetic and electric fields in a magnetically ordered state.

1. Results and Discussion

Bismuth ferrite films were formed by depositing the previously synthesized solid solutions onto object glasses by flash evaporation. The optically determined film thickness was 440 nm. According to the X-ray diffraction analysis, the films have a rhombohedral crystal structure (Fig. 1).

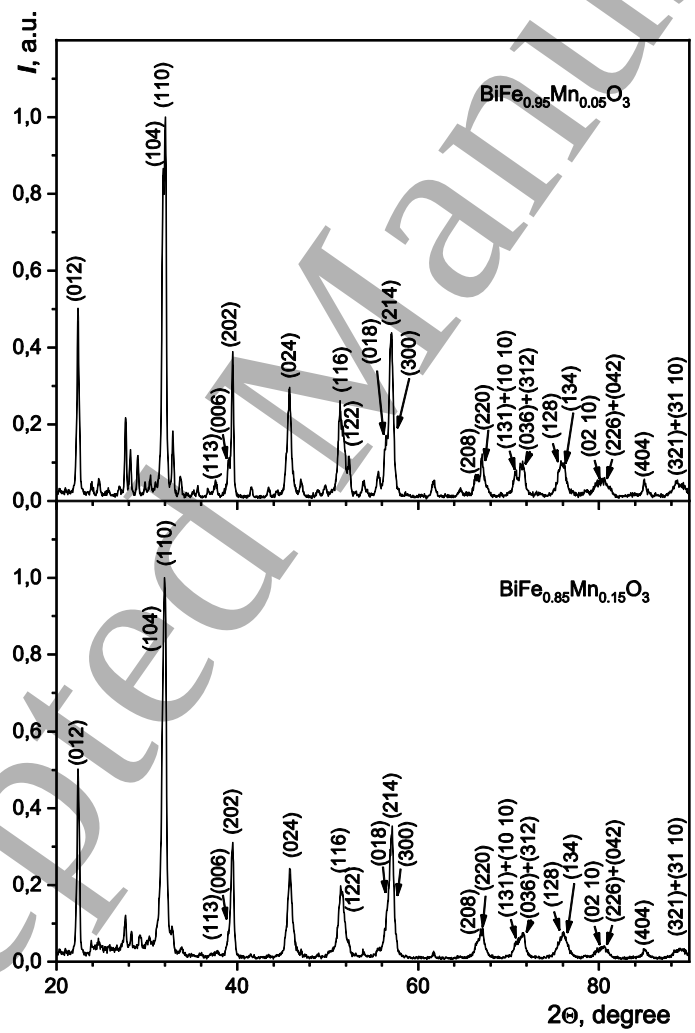

Fig. 1. X-ray for $BiFe_{1-x}Mn_xO_3$ with x=0.05 (a), x=0.15 (b).

The magnetic moment of the films was measured by the Faraday method in a magnetic field of H = 8.6 kOe (Fig. 2). For $BiFeO_3$, the magnetic susceptibility has a peak at the Néel temperature and decreases stepwise above 634 K (Fig. 2a), which is typical for magnets with an incommensurate magnetic structure. Substitution of Fe for Mn causes spin polarization in the $BiFe_{1-x}Mn_xO_3$ film (x = 0.05, 0.15) [16]. The magnetization of the film on temperature is qualitatively described in the molecular field approximation $m = m_0 (1-T / T_c)^{1/2}$ with T_c = 560 K for two compositions (Fig. 2b). Above room temperature, the experimental magnetization magnitudes exceed the theoretical ones. This

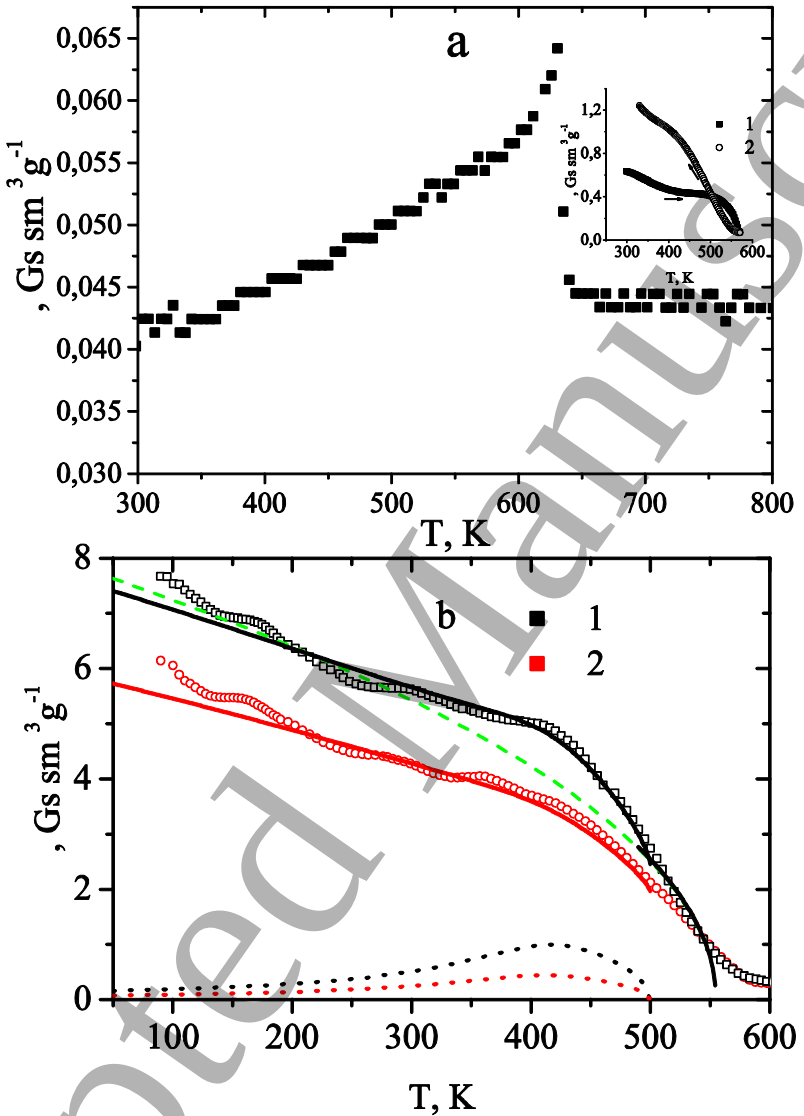

Fig. 2. The magnetization of $BiFe_{1-x}Mn_xO_3$ films in a magnetic field H = 8.6 kOe at x =**0 (a);** 0.05 (1), 0.15 (2) **(b)** on the temperature. The magnetization describes by the functional dependence (1) (dotted line) and summation magnetization (solid line) (2). In the insert: heating (1) and cooling (2) of the $BiFe_{0.15}Mn_{0.85}O_3$ precursor in a magnetic field H = 1.6 kOe.

may be due to the formation of electron phase separation and with nonuniform magnetic structure (ferron) [17]. In films with rhombohedral symmetry, magnetic anisotropy is a power function of magnetization. The anisotropy axes are randomly distributed in the film. Below 300 K, the magnetic moments are frozen, and they tend to line up in the direction of the external magnetic field at the heating. Ferron magnetization (M_F) disappears at a critical temperature T_{cF}. The temperature dependence of magnetization can be described in model of ferromagnetic with a random distribution of anisotropy fields.

We estimate magnetic susceptibility using the model of a superparamagnetic in the presence of the applied magnetic field H and the anisotropy field H_A. The energy of superparamagnetic particles is presented as $W = M_F\ H\ \cos\theta + M_F\ H_A\cos(\gamma - \theta)$, where the angle θ specifies the direction of the magnetic moment with respect to the applied magnetic field and γ is the angle between the directions of the applied magnetic field and the anisotropy field. The equilibrium direction of the magnetic moment is determined by the expression $tg\theta = H_A\sin\gamma/(H + H_A\cos\gamma)$. Longitudional magnetic susceptibility at $\gamma=\pi/2$ has the form:

$$X^Z = M_F \times \cos(\theta) = M_F / \left(H \times \sqrt{(1+(H_A/H)^2)} \right) \quad (1)$$

Ferron magnetization is represented as a power function $M_F = m_{0F}(1-T/T_{cF})^{1/2}$. The anisotropy field also has a power -law temperature dependence, $H_A = K(1 - T/T_{cF})^n$. The experimental data are fitted better by the curve corresponding to the exponent n = 2. We depict the resulting magnetization in the form of a homogeneous part $M = m_0\ (1-T / T_c)^{1/2}$ and a nonuniform:

$$M_{res} = m_0 \times \sqrt{(1-T/T_c)} + m_{0F} \times \sqrt{(1-T/T_{cF})} / \sqrt{(1+(K\times(1-T/T_{cF})^2/H)^2)} \quad (2)$$

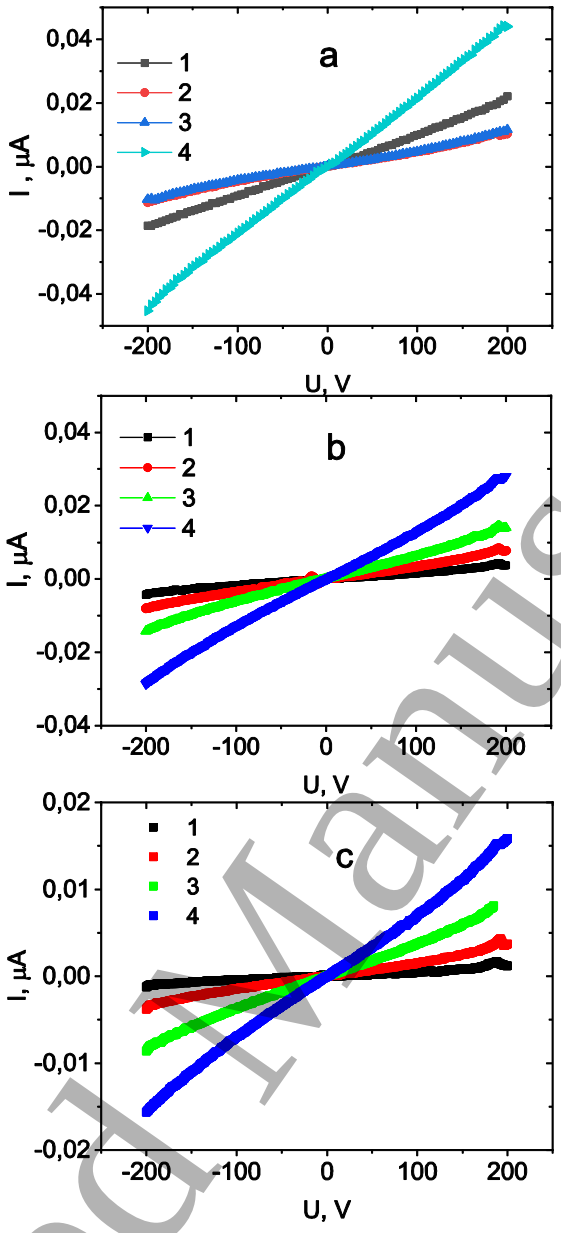

Fig. 3. I-V characteristic film $BiFe_{1-x}Mn_xO_3$ with x=0.05 atT=300 K(1), cooling at E=900 V/cm from 350 K to 300 K (2), in magnetic field H=1 kOe (3), at T=340 K (4) (a); I-V characteristic film at T=300 K (1), 340 K(2), 380 K(3), 420 K (4) at the heating (b), cooling at E=900 V/cm (c).

The experimental data on the magnetization are rather well fitted by function (2) with T_{cF} =500 K and Tc=560 K (Fig 2b).

The magnetization of powder precursors used in film fabrication exhibits the temperature hysteresis. In the inset in Fig. 2, the magnetizations of the $BiMn_{0.15}Fe_{0.85}O_3$ solid solution before heating and upon cooling in a magnetic field of H=1.6 kOe differ by a factor of two. In this concentration range, $BiMn_{0.15}Fe_{0.85}O_3$ is magnetically inhomogeneous. The magnetic structure is degenerate in the spontaneous magnetic moment direction and the degeneracy of these regions is eliminated by an external magnetic field. The substitution of iron for manganese ions shifts the magnetic phase transition toward lower temperatures.

We determine the film resistance and conductivity mechanism from the *I-V* characteristics measured before and after cooling in an electric field of E = 900 V/cm and in a magnetic field of H =1

kOe. Figure 3 shows the *I-V* characteristics for the films with x = 0.05. Cooling from 350 K in electric field doubles the resistance at 300 K. The repeated cooling in a magnetic field of H = 1 kOe changes the resistance by about 1% (Fig. 3a). The heating and cooling processes are illustrated in Figs. 3b and 3c. The film resistance increases by a factor of three upon cooling from 450 K to room temperature in an electric field. In the films with x = 0.05, the Ohm's law is fulfilled both upon heating and upon cooling. The conductivity is implemented by the impurity states.

The LDA calculation of the $[Bi_{16}(Fe_{15}Mn)O_{48}]$ cluster with the rhombohedral R3 symmetry showed the formation of impurity subband located above the valence band by 0.9 eV [16]. The film contains charged vacancies. Cooling of the $BiFe_{0.85}Mn_{0.15}O_3$ film from 350 K in an electric field sharply increases the resistance: $\Delta R = R(\text{cooling})/R(\text{heating}) = 2$ at T = 340 K, $\Delta R(T = 320\ K) = 4$, and $\Delta R(T = 300\ K) = 12$ (Fig. 4). Cooling in a magnetic field leads to a decrease in the current and an increase in the resistance in several times as compared with the values for cooling in an electric field: $\Delta R(T = 320\ K) = 6$ and $\Delta R(T = 300\ K) = 50$. Annealing in a magnetic field from 450 K increases the room-temperature resistance by an order of magnitude: $\Delta R(T = 300\ K) = 15$.

The conductivity is described using a model of space-charge limited currents and the quadratic Mott law [19] for $BiMn_xFe_{1-x}O_3$:

$$j = \frac{9}{8}\tau_\mu \sigma_0 \mu \frac{U^2}{L^3}, \quad (3)$$

where j is the current density, τ_μ is the Maxwell relaxation time, σ_0 is the electrical conductivity in the bulk of the material in the absence of carrier injection, μ is the carrier mobility, U is the applied voltage, and L is the sample thickness. In Fig. 4, the experimental *I-V* characteristic are described well by Eq. (3) for the films with x = 0.15 at U > 30 V.

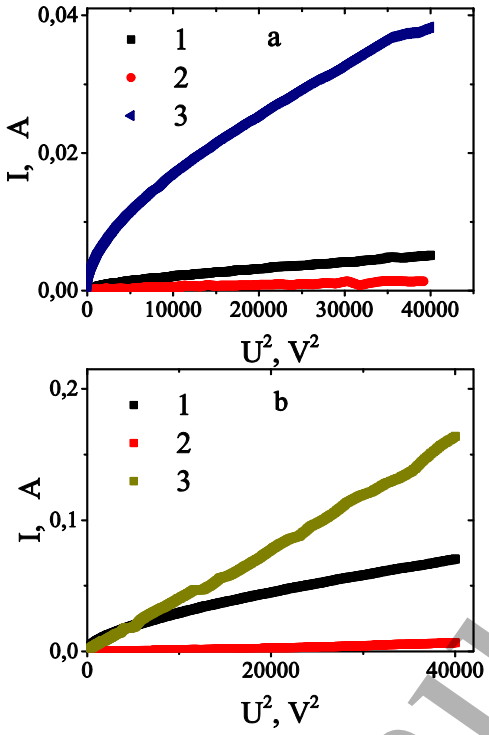

Fig. 4. I-V characteristic film $BiFe_{1-x}Mn_xO_3$ with x=0.15 cooling at E=900 V/cm from 350 K to 300 K (1), in magnetic field H=1 kOe (2), at T=340 K (3) (a); I-V characteristic film at T=300 K (1), cooling in magnetic field H=1 kOe from 450 K to 300 K (2), at T=420 K (3) cooling at E=900 V/cm (b).

2. Model

Depending on the manganese concentration, two mechanisms of the film prehistory effect on the resistive properties can work. Transport properties are determined by anionic oxygen vacancies and a partially filled eg shell when Mn^{3+} ions substitute with Fe^{3+}. In disordered semiconductors with two types of current carriers, the conductivity is determined by the location of the mobility edge of current carriers in the region of electrons or holes [19]. Holes are positively charged and are described by spinless charge transfer operators. Therefore, the influence of a magnetic field on the conductivity in a magnetically ordered region is insignificant. For small concentration the hopping conductivity mechanism dominate; in particular, it is attributed to hole hoppings over the localized states. The topology of potential wells can be varied by changing the direction of electric polarization by an external electric field. The coefficient of electron tunneling between potential wells is $D = D_0\exp(-2\beta l)$, where β determines the level position in a potential well and l is the distance between wells. As the l value doubles, the tunneling coefficient decreases by an order of magnitude and, as the distance triples, the resistance decreases by two orders of magnitude. This model qualitatively describes the experimental data.

The films with x = 0.15 have the mobility edge of current carriers in the region of electrons formed by Mn ions. Upon cooling in a magnetic field the structural magnetic factor with the ferromagnetic ordering increases. The impurity band forms from the cationic t2g states with the strong exchange coupling between localized and delocalized electron spins; the value of interaction is about the Hund's exchange integral: J ~ 1 eV. The exchange splitting of the impurity subband is $\Delta E = J\ s <S> g\mu_B \sim 0.1$ eV for a magnetic moment of $<S> g\mu_B = 0.1\ \mu_B$, which is 2% of the saturation magnetization. The resistance variation with an increase in the magnetization by a factor of two is $\Delta R = \exp(\Delta E/kT) = 25$.

3. Conclusions

Substitution of iron ions by manganese in $BiMn_xFe_{1-x}O_3$ films leads to an inhomogeneous magnetic structure containing regions with a weak ferromagnetic moment. Upon cooling of the $BiMn_{0,05}Fe_{0,95}O_3$ film in an electric field from the temperatures corresponding to reorientation of ferron magnetization, the film resistance multiply grows. The magnetic field increases the resistance by about 1%. The conductivity of the film with x = 0.15 is described by the Mott law with a bulk charge. The correlation of the magnetization and resistance growth upon cooling in a magnetic field was established. The annealing of the $BiMn_xFe_{1-x}O_3$ film in a magnetic field increases the film resistance by an order of magnitude as compared with the initial state. This effect was explained by the sd exchange splitting of the impurity subband and a decrease in the electron density of states at the chemical potential level.

Acknowledgments

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