Photo- and magnetic-field-induced conductivity change in the BiFe1-xCoxO3 films

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Abstract. The magnetic and electrical properties of the polycrystalline BiFe1-xCoxO3 films have been investigated in the temperature range of 80‒600 K and magnetic fields of up to 12 kOe. The photocurrent and the diode effect induced by the blue light laser illumination at room temperatures have been established. The ohmic conductivity has been determined from the I‒V characteristics and the conductivity growth in a magnetic field has been observed. The deviation of the temperature dependence of the magnetization from the power law below room temperature has been found.

1. Introduction
Recently, multiferroics have been intensively investigated due to the presence of the magnetic and ferroelectric order in them [1, 2]. The interaction between the magnetic and electric subsystems in these materials makes it possible to control the electric polarization by a magnetic field and govern the magnetic characteristics by an electric field [3‒7]. This offers the opportunity of increasing the storage density and making the memory nonvolatile. The inclusion of defect states into multiferroics can change their conductivity and the latter can be controlled by domain walls [8, 9] in an electric field. The conductivity of semiconductors can be governed by a magnetic field, even in the paramagnetic state [10‒15]. In the magnetically ordered state, the conductivity over defect states depends on the type of a magnetic order [16‒19].

According to the results of the LDA calculation [20], cobalt-substituted bismuth ferrite forms impurity states near the valence band. As the substitution concentration increases, the electron density in the t2g shell grows; this leads to the degeneracy, which can be eliminated by the strong electron correlations [21] or the orbital ordering of electrons. This leads to the conductivity change, which was observed in semiconductors with the orbital ordering [22‒26]. The coexistence of the magnetoelectric effect and conductivity makes it possible to manipulate the current by magnetic and electric fields [27‒28].

Substitution of holmium and strontium ions for bismuth in the BiFeO3 compound [29, 30] causes the metal-type conductivity of the material. The formation of defect states in the oxygen subsystem ensures the hopping-type conductivity. Substitution of 3d metals for iron ions leads to the partial filling of the impurity band and increases the conductivity. In [31], the IR radiation-induced diode effect in the BiMnxFe1–xO3 films was found, which is related to the asymmetry of quantum wells and band bending at the film surface.
In the BiMexFe\textsubscript{1-x}O\textsubscript{3} (Me = Mn, Co, V) films, areas with the electric polarization can be retained and the conduction channels controlled by magnetic and electric fields can exist. An internal electric field creates the prerequisites for the photocurrent and photoinduced effects [32].

The aim of this study is to investigate the possibility of the illumination and magnetic-field control of the current in the BiCoFeO\textsubscript{3} films with electron doping obtained by replacing trivalent iron by cobalt ions with an additional electron in the t\textsubscript{2g} shell.

2. Experimental part and discussion

The cobalt-doped bismuth ferrite films were synthesized from the BiFe\textsubscript{0.8}Co\textsubscript{0.2}O\textsubscript{3} solid solution precursors on object glasses by the ignition technique. Sputtering was performed in a vacuum system at a pressure of 10\textsuperscript{−3} Pa in the reaction chamber; the temperature of a tantalum evaporator was kept around 2000°C. The substrate temperature was varied within 250–300°C. The film was 13 × 17 mm in size and 980 nm thick. According to the X-ray diffraction data, the BiFe\textsubscript{1-x}Co\textsubscript{x}O\textsubscript{3} (BFCO) compound has a rhombic structure (R3c sp. gr.) with crystal lattice parameters of a = b = 0.558 nm and c = 1.380 nm (figure 1). The X-ray diffraction patterns contain, along with the reflections of the main BFCO phase, the reflections of Bi\textsubscript{x}FeO\textsubscript{39} with a 5% sillenite structure, which is paramagnetic.

![Figure 1. XRD pattern of the BiCo\textsubscript{0.2}Fe\textsubscript{0.8}O\textsubscript{3} at T=300K.](image)

Figure 2 shows the temperature dependence of the magnetization measured in a magnetic field of 8.6 kOe by the Faraday method. Upon heating, the magnetization smoothly increases, passes through a maximum at 360 K, and tends to zero at 600 K, which was attributed by us to the occurrence of a magnetic phase transition. Above 300 K, the temperature behavior of the magnetization is satisfactorily described in the molecular field approximation by the power law \( M = M_0(1 - T/T_c)^{1/2} \) with \( T_c = 600 \) K. The deviation from the theoretical power dependence observed below 300 K is possibly due to the noncollinear arrangement of spins caused by the competition of exchange interactions between the spins of iron ions and the cobalt spins. The more than half-filling of the t\textsubscript{2g} shell facilitates the ferromagnetic exchange in cobalt clusters. The degenerate state occurring in the t\textsubscript{2g} shell can be eliminated by the orbital ordering, the formation of which leads to a change in the magnetic structure [33]. The degeneracy
elimination by the Jahn–Teller channel causes the formation of a strong electron–phonon interaction, which leads to the four-spin interaction and a decrease in the magnetic moment on a site [34–40].

![Figure 2](image2.png)

Figure 2. Temperature dependence of the magnetization for the BiCo0.2Fe0.8O3 film in a magnetic field of \( H = 8.6 \) kOe. Fitting function \( M = M_0 \left(1 - \frac{T}{T_c}\right)^{1/2} \) (dotted line).

We establish the effect of light on the resistive characteristics and current from the I–V characteristics measured without light and under laser illumination in the blue range at a wavelength of 405 nm. The I–V characteristics are linear up to 400 K; upon further heating, they become nonlinear (figure 3). This is related to the impurity states formed by cobalt ions and oxygen vacancies, which contribute to the conductivity. At low voltages, the carriers injected from the electrodes fill shallow traps. As the voltage increases (\( U > U_c \)), the shallow traps are filled and the transitions of electrons (holes) to the higher-lying vacant states start contributing to the resistance. Under illumination, the current slightly (by 2–5%) grows. The voltage dependence of the photocurrent is shown in figure 4.

![Figure 3](image3.png)

Figure 3. VAX of the BiCo0.2Fe0.8O3 film without illumination (1,3,5,7) and with \( \lambda = 405 \) nm (2,4,6,8) at \( T = 300 \) K (1,2), 360 K (3,4) (a), \( T = 420 \) K (5,6), 450 K (7,8) (b).

At temperatures of up to 360 K, the relative current variation \( (I IR - I(0)/I(0)) \) increases with a decrease in the external electric field; above this temperature, it is almost voltage-independent (figure 4). In the film with the high \( (x = 0.2) \) cobalt concentration, an impurity subband is formed from manganese ions. The top of the valence band and the bottom of the conduction band change in space with the smooth band bending caused by structural defects and oxygen vacancies. When the film is illuminated by light
quanta with an energy of $h\nu = 3$ eV, the majority carriers are holes in the valence band and electrons in the conduction band. The low photocurrent is explained by the disappearance of the electric polarization. The photocurrent is proportional to the density of carriers passed from the valence to conduction band upon absorption of a photon. At room temperature, the photocurrent asymmetry and the diode effect are 3%; above 360 K, they vanish.

We find the effect of the magnetic field on the conductivity from the field dependence of the conductivity at constant temperatures (figure 5). As the temperature of the magnetic phase transition is approached, the conductivity increases in a magnetic field. The increase in the conductivity is caused by electrons hoppings over iron ions. The hopping probability increases when the magnetic moments are parallel and decreases at other magnetization directions. The magnetic field dependence of the conductivity is described within the ferron model [41] as

$$\delta \sigma = \frac{\sigma(H) - \sigma(0)}{\sigma(0)}$$

for film BiCo0.2Fe0.95O3 at (1)300K, (2)330K, (3)360K and (4)390K. The solid line shows fitting by Eq. (1).
(σ(H) − σ(0))/σ(0) = 1 − exp(−BHξ/k_BT) \tag{1}

In the BiCo\textsubscript{x}Fe\textsubscript{1-x}O\textsubscript{3} (x = 0.05) film, the voltage dependence of the current is linear (figure 6a). In a magnetic field of 12 kOe, the current and conductivity increase. The magnetic field dependence of the conductivity shown in figure 6b is satisfactorily described within the electron hopping model with regard to the spin polarization. Since the distance between cobalt ions at x = 0.05 is much shorter than for the composition with x = 0.2, an increase in the potential barrier leads to a decrease in the effect of the magnetic field on the conductivity. The two methods for measuring the conductivity lead to the conductivity growth in a magnetic field upon approaching the temperature of the magnetic phase transition.

Figure 6. I-V characteristics measured in zero magnetic field and 12 kOe field for BiCo0.05Fe0.95O3 film at T = 300K (1), 340K (2), 380K (3). Insert: temperature dependence of magnetoconductivity \( \delta_H = \frac{\delta(0) - \delta(H)}{\delta(0)} \). b) field dependence of normalized resistance at 300K (1), 320K (2) and 360K (3). The fitting functions by equation (1) (solid line).

3. Conclusions
In the BiFe\textsubscript{1-x}Co\textsubscript{x}O\textsubscript{3} (x = 0.2) films, the photo-effect and the weak diode effect at room temperatures were found. A linear voltage dependence of the current below 400 K was observed. The conductivity growth in a magnetic field at the two cobalt concentrations was established; it was found that the effect of the magnetic conductivity increases with the concentration. The conductivity growth was explained using the model of electron hoppings over ferrons with regard to the spin polarization of electrons.

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