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Synthesis and Magnetic Properties of Polycrystalline Films of $Co_xFe_yCr_{3-x-y}O_4$ and $Cr_2O_3/CoFe_2O_4$ Multiferroics

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Abstract—Magnetic properties of first obtained polycrystalline films of $FeCr_2O_4$, $CoCr_2O_4$, and $CoFe_{0.5}Cr_{1.5}O_4$ multiferroics and films of a $Cr_2O_3/CoFe_2O_4$ composite multiferroic have been studied. In particular, magnetization curves and temperature dependences of the magnetic moment of the samples were measured in the temperature range 4.2–300 K in fields of up to 10 kOe. It was shown that the Curie point of a multiferroic depends on its cation composition. It was found that an exchange bias of the hysteresis loop exists in films of the $Cr_2O_3/CoFe_2O_4$ composite multiferroic at temperatures below the Néel point of Cr_2O_3 (330 K).

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The interest in multiferroics is due to their unusual physical properties caused by the simultaneous existence of ferromagnetic and ferroelectric kinds of ordering and by the interaction between them [1]. Thin-film multiferroics open up new opportunities for their analysis and application in devices of functional electronics [2].

Ionic compounds in a variable-composition system with a chemical formula $Co_xFe_yCr_{3-x-y}O_4$ exhibit widely diverse magneto-optic [3], magnetic [4–7], and electrical properties [5, 8], which makes these compounds exceedingly interesting for scientific and applied research. Multiferroic properties have been comparatively recently discovered in the spinels $CoCr_2O_4$, $CoFe_{0.5}Cr_{1.5}O_4$ [5], and $FeCr_2O_4$ [8]. Multiferroics based on spinels are among the rare materials in which multiferroic properties are observed in the magnetic-ordering region. It is known that the $CoCr_2O_4$ spinel, exhibiting a unique conical spiral magnetic structure [6], is the first example of a multiferroic with spontaneous magnetization and magnetic-field-dependent electric polarization. Below the Curie point $T_c = 94$ K in $CoCr_2O_4$ and $T_c = 80$ K in $FeCr_2O_4$, there exists a collinear ferrimagnetic ordering, and a long-range helicoidal magnetic order arises at a temperature $T \approx 27$ K in $CoCr_2O_4$ and at $T \approx 38$ K in $FeCr_2O_4$. It has been shown that electric polarization exists both in the helicoidal magnetic phase and in the collinear ferrimagnetic phase [5, 8]. The $CoFe_{0.5}Cr_{1.5}O_4$ multiferroic differs from $CoCr_2O_4$ in a higher Curie point (175 K) and lower temperature of transition to the spiral magnetic structure [15]. The temperature range in which the spontaneous electric polarization exists in the former coincides, as also it does in the latter, with the magnetic-ordering region. Film-type multiferroics with a Cr_2O_3 antiferromagnetic exhibiting a magnetoelectric effect are also of interest. The bias field is switched in structures of this kind under the effect of an electric field, which opens up new opportunities of practical applications [2].

This communication presents the results of a study of the first obtained polycrystalline films of $FeCr_2O_4$, $CoCr_2O_4$, and $CoFe_{0.5}Cr_{1.5}O_4$ multiferroics and of a composite multiferroic in the form of a $Cr_2O_3/CoFe_2O_4$ double-layer structure.

Polycrystalline films were synthesized under the conditions of solid-phase reactions in metal/oxide layered structures at temperatures of 820–920 K [3]. We have shown previously that solid-phase reactions may occur in structures of this kind in both the isothermal annealing and self-propagating high-temperature synthesis (SHS) regimes [3].

Solid-phase synthesis of $FeCr_2O_4$, $CoCr_2O_4$, and $CoFe_{0.5}Cr_{1.5}O_4$ films was performed by chemical reactions of the type

$$Fe + Cr_2O_3 + 1/2O_2 = FeCr_2O_4, \quad (1)$$

$$Co + Cr_2O_3 + 1/2O_2 = CoCr_2O_4, \quad (2)$$

$$Co + 0.5Fe + 0.75Cr_2O_3 + 1.25O_2 = CoFe_{0.5}Cr_{1.5}O_4. \quad (3)$$

The reactants in reactions (1) and (2) have the form of layers in the Cr_2O_3/Fe and Cr_2O_3/Co film structures, respectively, and those in reaction (3) have the form of layers in the Cr_2O_3/Co/Fe structure. The metal layers were deposited in the order Cr, Co, Fe onto fused silica plates by thermal evaporation in vacuum (residual pressure 5×10^{-4} Pa, substrate temperature 470 K). Prior to deposition of Co and Fe layers, the Cr layer was oxidized at a temperature of 820–870 K in air in the technological chamber.

The solid-phase reactions in these film structures were carried out in the isothermal annealing mode at temperatures of 820–920 K in air. As a result, polycrystalline films of multiferroics with a thickness of 150–200 nm were formed.

To obtain the $Cr_2O_3/CoFe_2O_4$ structure, the following procedure was performed. Cr_2O_3 films were formed on the quartz substrate as described above. Then, Co and Fe layers were deposited. The cobalt ferrite $CoFe_2O_4$ film was formed under solid-phase reaction conditions in the SHS mode at an initiation temperature of 620 K:

$$Co + Fe + Cr_2O_3 + O_2 = CoFeO_4 + Cr_2O_3. \quad (4)$$

The chemical composition and the thickness of the films were monitored by X-ray fluorescence analysis. The crystal structure was examined by X-ray phase analysis. The magnetic properties of the films were measured with a Quantum Design MPMS-XL installation at temperatures in the range from 4 to 300 K in a magnetic field of up to 10 kOe and with a Nano MOKE 2 magneto-optic magnetometer.

The X-ray diffraction patterns of $FeCr_2O_4$, $CoCr_2O_4$, and $CoFe_{0.5}Cr_{1.5}O_4$ multiferroic films contain only spinel reflections. Figure 1a shows the X-ray diffraction pattern of a $CoCr_2O_4$ film. The X-ray diffraction pattern of $Cr_2O_3/CoFe_2O_4$ multiferroic films, shown in Fig. 1b, confirms that Cr_2O_3 and $CoFe_2O_4$ are formed.

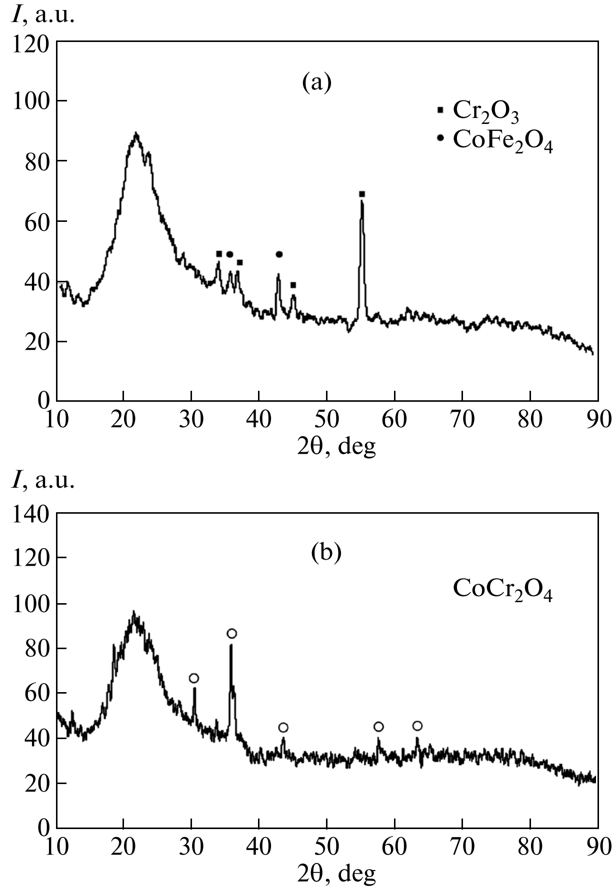

Fig. 1. X-ray diffraction patterns of (a) $Cr_2O_3/CoFe_2O_4$ and (b) $CoCr_2O_4$ multiferroic films.

Measurements of the magnetization curves of the polycrystalline $FeCr_2O_4$ and $CoCr_2O_4$ films with a magneto-optic magnetometer in the temperature range from 4.2 to 300 K demonstrated that ferromagnetic curves appear at a temperature of 90 K for $CoCr_2O_4$ films and at 70 K for $FeCr_2O_4$ films. The coercive force is 2000 and 1500 Oe, respectively.

The temperature dependence of the magnetization of the films was measured on an MPMS-XL installation in the temperature range of 10–300 K. The nature of the temperature dependences for $CoCr_2O_4$ and $FeCr_2O_4$ qualitatively coincides with that of the corresponding dependences for bulk polycrystals [5, 8]. The Curie points of the $CoCr_2O_4$ and $FeCr_2O_4$ films are 80 and 100 K, respectively.

The magnetization curve of the polycrystalline $CoFe_{0.5}Cr_{1.5}O_4$ multiferroic film obtained on the MPMS-XL installation is shown in Fig. 2a. The temperature dependence of the saturation magnetization measured in a field of 10 kOe is shown in Fig. 2b. The observed dependence has the classical form. In this case, the Curie point exceeds the corresponding value for the bulk polycrystalline $CoFe_{0.5}Cr_{1.5}O_4$ by approximately 100 K [5]. If it is assumed that the films obtained are composed of a single-phase ferrimagnetic, then the distinction of our results (comparatively high Curie point) may be due to the fact that the bulk polycrystalline samples and our films are obtained at different synthesis temperatures. In particular, the temperature at which films were synthesized in our experiments (820–920 K) is substantially lower than the synthesis temperature of the polycrystalline samples obtained in [5, 7]. Attention should be given to the bend point at low temperatures (~20 K) in the curve describing the temperature dependence of the magnetic moment, which coincides with the temperature at which there appear the short-range order in the conical spiral magnetic phase and anomalies of the dielectric constant of $CoFe_{0.5}Cr_{1.5}O_4$ multiferroic [5].

The films of the $Cr_2O_3/CoFe_2O_4$ composite multiferroic are exchange-coupled antiferromagnetic–ferrimagnetic (AF–FM) films. It is known that the exchange-coupled AF–FM systems exhibit such phenomena as the exchange bias. To observe the exchange bias, we measured magnetization curves $M(H)$ in cool-

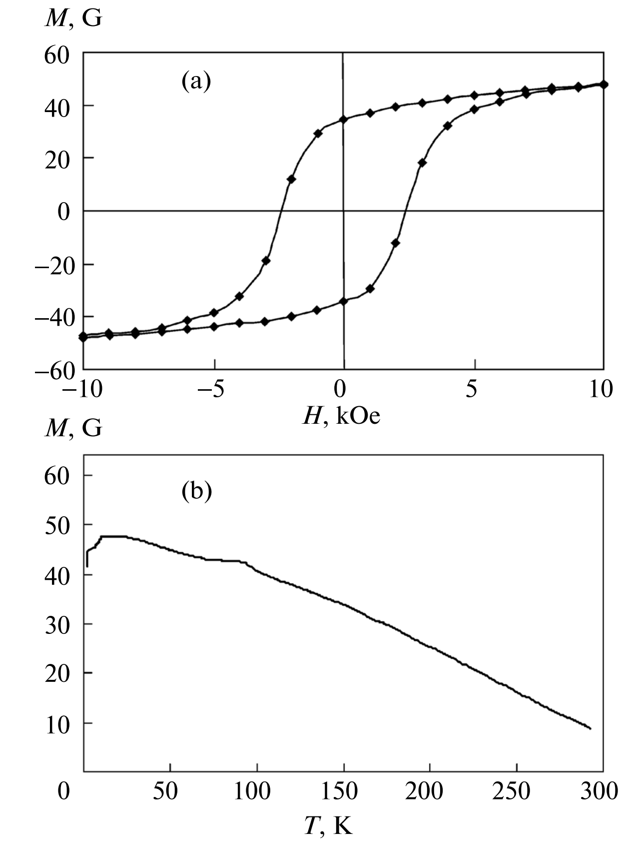

Fig. 2. (a) Magnetization curves and (b) temperature dependences of the saturation magnetization of $CoFe_{0.5}Cr_{1.5}O_4$ multiferroic film.

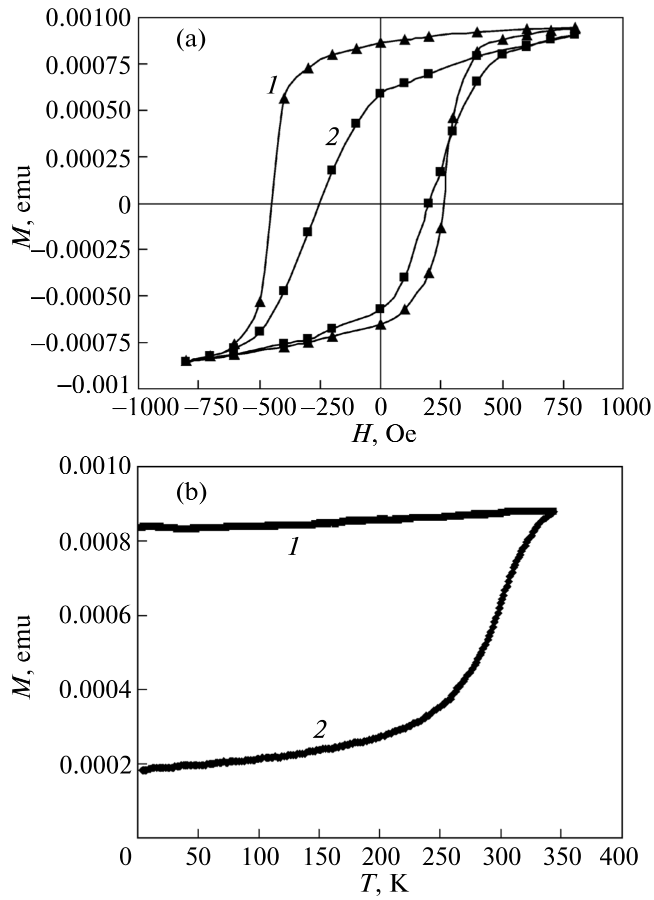

Fig. 3. (a) Magnetization curves and (b) temperature dependences of the magnetic moment of a $Cr_2O_3/CoFe_2O_4$ polycrystalline film.

ing from the Néel point of Cr_2O_3 (310 K) to 4 K. The samples were cooled in two modes: without a magnetic field (zero-field-cooled, ZFC) and in a 1-kOe field (field-cooled, FC). The magnetic field was applied along a chosen in-plane direction.

It is known that the exchange-bias field depends on various factors, including the thicknesses of the AF and FM layers. In our case, the thicknesses of the Cr_2O_3 and $CoFe_2O_4$ layers were 80 and 150 nm, respectively. The magnetic measurements confirmed the existence of the exchange coupling in the $Cr_2O_3/CoFe_2O_4$ double-layer structure. Figure 3a shows the magnetization curves obtained with a SQUID magnetometer at a temperature of 4.2 K. It can be seen that the FC-curve (*1*) is shifted toward negative magnetic fields. The exchange-bias field is 90 Oe. The temperature dependences of the magnetic moment for two cooling modes shown in Fig. 3b [(*1*) FC and (*2*) ZFC] make it possible to determine the Néel point of the Cr_2O_3 layer (330 K).

Let us note the main results of the study. The method of solid-phase synthesis in metal/oxide layered structures was used to obtain for the first time polycrystalline films of the $FeCr_2O_4$, $CoCr_2O_4$, $CoFe_{0.5}Cr_{1.5}O_4$, and $Cr_2O_3/CoFe_2O_4$ multiferroics. The magnetic properties of polycrystalline films of the multiferroics were also studied for the first time in a wide temperature range. It was shown that the Curie point of a multiferroic depends on its cation composition. It was found that doping of $CoCr_2O_4$ with Fe ions substantially expands to higher temperatures (up to 300 K) the temperature range in which the ferrimagnetism exists in $CoFe_{0.5}Cr_{1.5}O_4$ and can thereby extend the temperature range of the magnetic-field-dependent electric polarization [5]. An exchange bias of the hysteresis loop upon cooling in a magnetic field from a temperature below the Néel point of Cr_2O_3 (330 K) was observed in films of the $Cr_2O_3/CoFe_2O_4$ composite multiferroic. The magnetic properties of the polycrystalline multiferroic films obtained in the study qualitatively coincide with the corresponding properties of bulk single crystals and polycrystals.

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