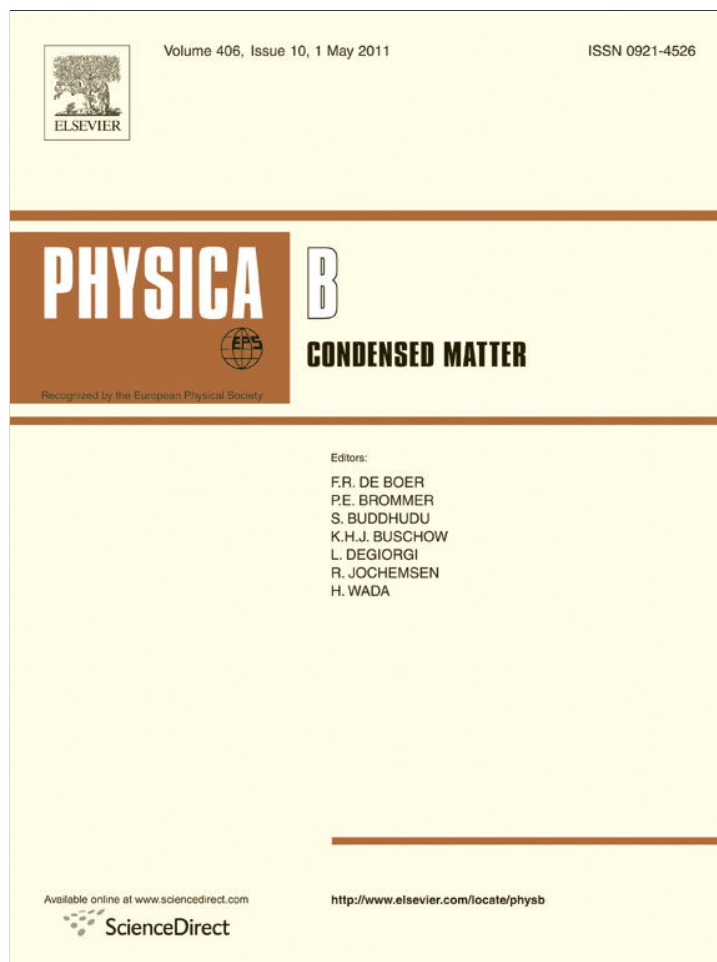


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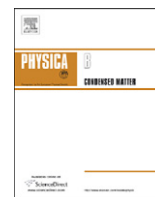


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## The multiferroic properties of $\text{Bi}(\text{Fe}_{0.95}\text{Co}_{0.05})\text{O}_3$ films

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### ABSTRACT

$\text{Bi}(\text{Fe}_{0.95}\text{Co}_{0.05})\text{O}_3$  films were prepared on conductive indium tin oxide (ITO)/glass substrates by chemical solution deposition. Well saturated polarization hysteresis loop has been observed with a remnant polarization value of about  $22 \mu\text{C}/\text{cm}^2$  at room temperature. Weak ferromagnetism with saturation magnetization of about  $3 \text{ emu}/\text{cm}^3$  was observed at room temperature. The clear observation of both room temperature ferroelectric and ferromagnetic properties suggests the potential multiferroic applications of  $\text{Bi}(\text{Fe}_{0.95}\text{Co}_{0.05})\text{O}_3$ .

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### 1. Introduction

Multiferroic materials possess the magnetoelectric (ME) effect which allows the coupling between polarization and magnetization, making them promising candidates for applications in memories, spintronics and magnetoelectric sensor devices [1]. For most multiferroic materials, the temperature for the coexistence of the ferroelectricity and magnetism, thus the mutual control between them remains very low.  $\text{BiFeO}_3$  is one of the rare multiferroic materials with both ferroelectricity (Curie temperature  $T_c \sim 1103 \text{ K}$ ) and magnetism (Neel temperature  $T_N \sim 643 \text{ K}$ ) above room temperature (RT) [2]. Large ferroelectric polarization with remnant polarization  $P_r$  of  $\sim 60 \mu\text{C}/\text{cm}^2$ , which is close to the theoretical value, has been reported in the high quality epitaxial  $\text{BiFeO}_3$  films and single crystals [3,4]. However,  $\text{BiFeO}_3$  has a superimposed incommensurate cycloid spin structure with a periodicity of about 64 nm [5]. This structure cancels the macroscopic magnetization and inhibits the observation of the linear ME effect [6].

RT ferromagnetism and ferroelectricity are required in one material for the daily multiferroic applications. Efforts have been devoted to enhance the RT ferromagnetism and suppress the leakage current by ion substitution in  $\text{BiFeO}_3$  [7,8]. In our previous study, Co was used to substitute Fe sites in  $\text{BiFeO}_3$ , enhanced RT ferromagnetism with saturate magnetization of  $1.9 \text{ emu}/\text{g}$  has also been observed in  $\text{Bi}(\text{Fe}_{0.95}\text{Co}_{0.05})\text{O}_3$  ceramics [9]. Furthermore, the

enhanced RT ferromagnetism in Co-doped  $\text{BiFeO}_3$  is due to the large lattice distortion on Fe sites due to Co substitution from the Raman spectra [10]. In this paper, we prepared the  $\text{Bi}(\text{Fe}_{0.95}\text{Co}_{0.05})\text{O}_3$  films by chemical solution deposition, well-shaped ferroelectric hysteresis loop with weak ferromagnetism at RT are presented to further demonstrate the possible multiferroic applications of  $\text{Bi}(\text{Fe}_{0.95}\text{Co}_{0.05})\text{O}_3$ .

### 2. Experimental details

$\text{Bi}(\text{Fe}_{0.95}\text{Co}_{0.05})\text{O}_3$  films were deposited onto conductive indium tin oxide (ITO)/glass substrates by chemical solution deposition. The precursor were prepared by dissolving  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (1:0.95:0.05 in molar ratio) in acetic acid and methanol. No excess Bi was added, due to the low temperature preparation [11]. Ethylene glycol was added to adjust the viscosity. Citric acid was added as the chelating agent. The  $\text{Bi}(\text{Fe}_{0.95}\text{Co}_{0.05})\text{O}_3$  films were deposited onto the substrates by spin coating at 4000 rpm for 30 s. The wet films were pyrolyzed at  $400 \text{ }^\circ\text{C}$  for 10 min in  $\text{O}_2$  and annealed at  $525 \text{ }^\circ\text{C}$  for 5 min in  $\text{N}_2$ . These steps were repeated several times to increase film thickness. Then the films were annealed finally at  $525 \text{ }^\circ\text{C}$  for 30 min in  $\text{N}_2$  for achieving better crystallinity. The X-ray diffraction (XRD) with  $\text{Cu K}\alpha$  radiation was used for the phase analysis. The structures of the samples were studied by scanning electron microscope (SEM) and scanning probe microscope (SPM). The magnetization of  $\text{Bi}(\text{Fe}_{0.95}\text{Co}_{0.05})\text{O}_3$  was measured by a vibrating sample magnetometer (VSM) integrated in a physical property measurement system (PPMS-9, Quantum Design). A Precision

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Premier II ferroelectric tester (Radiant Technologies) was used to detect the ferroelectric and leakage properties.

### 3. Results and discussions

Fig. 1 shows the XRD pattern of  $\text{Bi}(\text{Fe}_{0.95}\text{Co}_{0.05})\text{O}_3$  film. Except for the diffraction peaks corresponding to ITO/glass marked by stars, all other the diffraction peaks can be indexed to the rhombohedral perovskite structure (R3c) as  $\text{BiFeO}_3$ . The lattice constants calculated from the XRD pattern are  $a=5.577 \text{ \AA}$  and  $c=13.785 \text{ \AA}$ . Interestingly, the intensity of (0 1 2) peak is much stronger than other peaks, which is in contrast to the bulk  $\text{BiFeO}_3$  that the (1 1 0) peak exhibits the strongest intensity. This indicates the  $\text{Bi}(\text{Fe}_{0.95}\text{Co}_{0.05})\text{O}_3$  film on ITO/glass has high (0 1 2) orientation. Fig. 2(a) shows the surface morphology by SPM. The film shows some columnar structure with grain size of about 400 nm. The surface roughness is about 3 nm, indicating the film surface is rather flat. As shown from the cross-sectional SEM

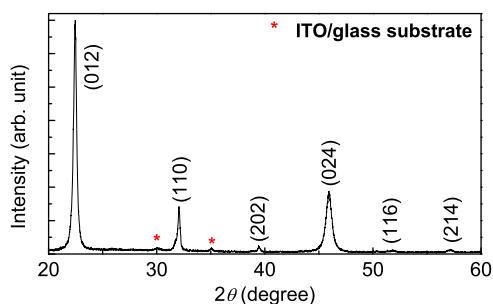


Fig. 1. XRD pattern of  $\text{Bi}(\text{Fe}_{0.95}\text{Co}_{0.05})\text{O}_3$  film, the stars mark the diffraction peaks from ITO/glass substrate.

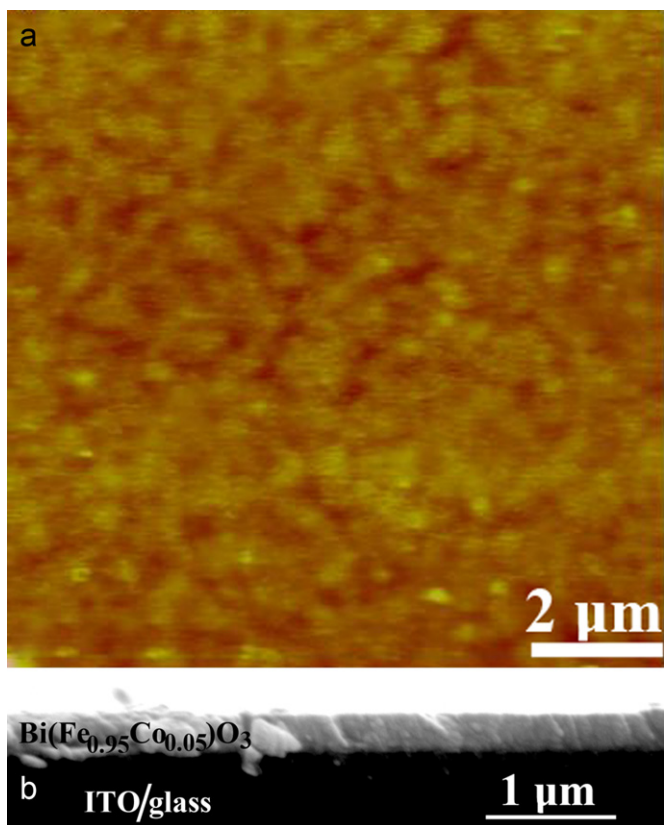


Fig. 2. (a) Surface morphology image by SPM, (b) the cross-sectional SEM image of  $\text{Bi}(\text{Fe}_{0.95}\text{Co}_{0.05})\text{O}_3$  film.

image of the film, it can be clearly seen that the film is very dense without any pores or cracks. The thickness of the film is about 240 nm and very uniform.

Fig. 3 shows the polarization–electric field ( $P$ – $E$ ) hysteresis loop of the  $\text{Bi}(\text{Fe}_{0.95}\text{Co}_{0.05})\text{O}_3$  film measured at RT with frequency  $f$  of 5 kHz. It can be clearly seen that well-shaped and saturated  $P$ – $E$  hysteresis loop has been obtained. The remnant polarization ( $P_r$ ) is about  $22 \mu\text{C}/\text{cm}^2$ . This value is comparable to the  $\text{Bi}(\text{Fe}_{0.95}\text{Mn}_{0.05})\text{O}_3$  film prepared by spin coating [12]. Due to the (0 1 2) orientation of our film, the inferred full saturation polarization along [0 0 1] direction is close to  $38 \mu\text{C}/\text{cm}^2$ . The coercive field ( $E_c$ ) is about 330 kV/cm, which is larger than the reported value of 180 kV/cm for the epitaxial  $\text{BiFeO}_3$  film [3] and 15 kV/cm for the  $\text{BiFeO}_3$  single crystal [4], but comparable to  $\text{Bi}(\text{Fe}_{0.9}\text{Mn}_{0.1})\text{O}_3$  film by spin coating (322 kV/cm) [12].

The local piezoelectric coefficient  $d_{33}$  was measured by the SPM at RT. The piezoelectric hysteresis loop has been clearly observed, as shown in Fig. 4. The remnant out-of-plane  $d_{33}$  of about 4 pm/V is rather smaller than the 70 pm/V for epitaxial  $\text{BiFeO}_3$  film and about 15–30 pm/V for Mn doped  $\text{BiFeO}_3$  films [3,12]. With the film thickness of 240 nm, the coercivity from the piezoelectric hysteresis loop is calculated to be about 320 kV/cm, which coincides well with the value from the  $P$ – $E$  loop.

Fig. 5(a) shows the leakage current ( $J$ ) vs. electric field ( $E$ ) characteristics measured at RT and 93 K. It should be noted that the  $\text{Bi}(\text{Fe}_{0.95}\text{Co}_{0.05})\text{O}_3$  film is easy to breakdown when a high electric field is applied. As can be seen, one spot on the is breakdown after applying  $E$  of 224 kV/cm, while the breakdown field increases to 298 kV/cm at 93 K. To understand the leakage mechanism, we concentrate on the  $J$ – $E$  curve below the breakdown field. The leakage current at RT is close to  $10^{-4} \text{ A}/\text{cm}^2$ , which is about 2 orders lower than the reported leakage current ( $10^{-2} \text{ A}/\text{cm}^2$ ) of 6% Co doped  $\text{BiFeO}_3$  film and the annealed  $\text{BiFeO}_3$  film [13,14]. The low leakage current further demonstrates the high quality of our  $\text{Bi}(\text{Fe}_{0.95}\text{Co}_{0.05})\text{O}_3$  films.

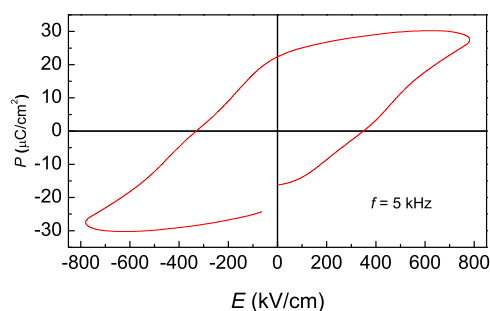


Fig. 3.  $P$ – $E$  loop of  $\text{Bi}(\text{Fe}_{0.95}\text{Co}_{0.05})\text{O}_3$  film measured at RT with frequency of 5 kHz.

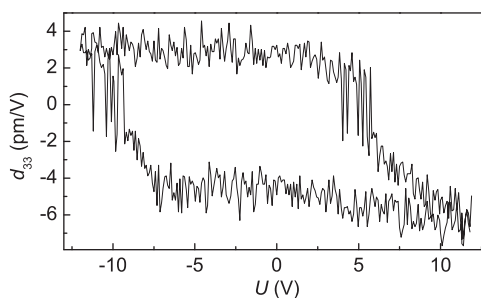


Fig. 4. Dependence of  $d_{33}$  on the applied voltage of  $\text{Bi}(\text{Fe}_{0.95}\text{Co}_{0.05})\text{O}_3$  film measured at RT by SPM.

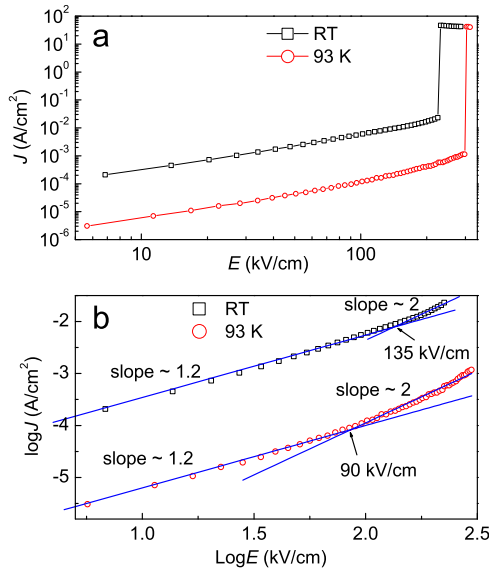


Fig. 5. (a)  $J$ – $E$  curves measured at RT and 93 K, (b)  $\log J$  vs.  $\log E$  at RT and 93 K.

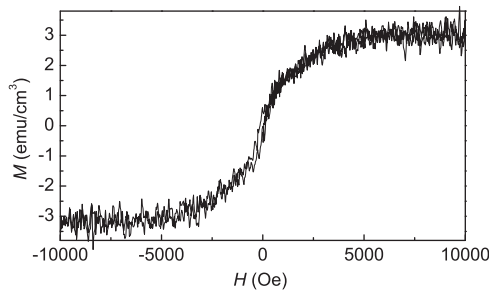


Fig. 6. RT magnetic hysteresis loop of  $\text{Bi}(\text{Fe}_{0.95}\text{Co}_{0.05})\text{O}_3$  film.

Fig. 5(b) shows the  $\log J$  vs.  $\log E$  characteristics for the  $\text{Bi}(\text{Fe}_{0.95}\text{Co}_{0.05})\text{O}_3$  film before the breakdown at RT and 93 K. As can be seen, in the higher electric field range, the plot of  $\log J$  and  $\log E$  is linear and the slope is 2, in agreement with the space-charge-limited current (SCLC) behavior [14]. At lower electric field, the  $\log J$  and  $\log E$  is also linear, however the slope is about 1.2, which is close to 1 and can be attributed to mainly the Ohmic contact. SCLC originates from the density of free carriers due to the carrier injection,  $n_i$ , and become dominant when  $n_i$  is larger than the volume-generated free carriers,  $n_v$  [14].  $n_i$  increases with increasing electric field. The conduction will change from Ohmic contact to SCLC at transition electric field  $E_t$  when  $n_i > n_v$ .  $E_t$  is about 135 kV/cm at RT, and decreases to 90 kV/cm at 93 K. This is due to the decrease of  $n_v$  with decreasing temperature, thus lower  $E_t$  is needed for  $n_i$  to exceed  $n_v$ .

The magnetic hysteresis loop of the  $\text{Bi}(\text{Fe}_{0.95}\text{Co}_{0.05})\text{O}_3$  film is shown in Fig. 6. The diamagnetic signal from ITO/glass substrate has been subtracted. The film exhibits weak ferromagnetism with saturation magnetization ( $M_s$ ) of about 3  $\text{emu}/\text{cm}^3$ . The shape of the hysteresis loop is similar to the previous reported Co doped  $\text{BiFeO}_3$  [13] and Mn doped  $\text{BiFeO}_3$  films [12], but  $M_s$  is smaller than that of Co doped  $\text{BiFeO}_3$  [13]. It must be noted that  $\text{CoFe}_2\text{O}_4$  might exist as an impurity and contribute to the observed ferromagnetism in Co doped  $\text{BiFeO}_3$  [15]. As shown in Fig. 1,

no peaks corresponding to  $\text{CoFe}_2\text{O}_4$  can be observed, thus the observed weak ferromagnetism can be attributed to the intrinsic properties of  $\text{Bi}(\text{Fe}_{0.95}\text{Co}_{0.05})\text{O}_3$ . As discussed before, the observed ferromagnetism in  $\text{Bi}(\text{Fe}_{0.95}\text{Co}_{0.05})\text{O}_3$  is attributed to the enhanced structure distortion on Fe sites by Co substitution and the suppression of the spiral spin structure [9,10]. The structure distortion is not only influenced by the ion substitution, but also by the stress induced by the substrate. The smaller magnetization observed in our  $\text{Bi}(\text{Fe}_{0.95}\text{Co}_{0.05})\text{O}_3$  film might be due to a different substrate, and further confirmed that the structural distortion plays an important role in enhancing the ferromagnetism in  $\text{BiFeO}_3$ . Thus further studies are needed to carefully tune the structural distortion in  $\text{BiFeO}_3$  to enhance the room temperature ferromagnetism.

#### 4. Conclusions

We have prepared  $\text{Bi}(\text{Fe}_{0.95}\text{Co}_{0.05})\text{O}_3$  films on conductive ITO/glass substrates by chemical solution deposition. The film has high (0 1 2) orientation. Well saturated polarization hysteresis loop has been observed with remnant polarization value of about 22  $\mu\text{C}/\text{cm}^2$  at RT. The inferred full saturation polarization along [0 0 1] direction is about 38  $\mu\text{C}/\text{cm}^2$ . Weak ferromagnetism with saturation magnetization of about 3  $\text{emu}/\text{cm}^3$  was observed at RT. The clear observation of both ferroelectric and ferromagnetic properties suggests the potential multiferroic applications of  $\text{Bi}(\text{Fe}_{0.95}\text{Co}_{0.05})\text{O}_3$ .

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