

Room temperature magnetic-field manipulation of electrical polarization in multiferroic thin film composite $\text{BiFeO}_3/\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$

Zhenxiang Cheng and Xiaolin Wang*

Institute for Superconducting and Electronic Materials, University of Wollongong, NSW 2522, Australia

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The electrical polarization in an epitaxially BiFeO_3 film grown on $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3/\text{SrTiO}_3$ is observed to be enhanced greatly by a magnetic field at room temperature. The simultaneous ferromagnetic order and ferroelectric polarization shown by the BiFeO_3 film causes the strong coupling of the magnetic and ferroelectric domains in the BiFeO_3 films. It was proposed that the activation energy for the electrical polarization domains switching is reduced by the application of a magnetic field. As a result, the electrical polarization that can be switched by an electrical field is increased by the magnetic field.

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Increasing attention has been recently focused on the multiferroic materials, which exhibit simultaneous ferroelectric and ferromagnetic behaviors, because of both their intriguing physical origin and their great potential for multifunctional applications, for instance, in controlling the magnetic order parameter via electric field in a switchable manner, and vice versa.^{1–5} Several composite materials, consisting of separate piezoelectric and magnetic phases, have been reported to show magnetoelectric coupling at room temperature.^{6–8} However, room temperature single phase multiferroic materials are very limited in number, due to the chemical incompatibility between magnetism and conventional ferroelectricity.^{9,10} Among the few room-temperature single-phase multiferroic materials reported so far, BiFeO_3 (BF) has the greatest potential for practical application. This is because BiFeO_3 is the only known perovskite oxide that exhibits both G -type antiferromagnetism (weak magnetism from canted spins or parasitic ferromagnetism such as $\alpha\text{-Fe}_2\text{O}_3$) and ferroelectricity at room temperature (with $T_N \sim 643$ K and $T_C \sim 1103$ K).^{11–14} The polarization and magnetization in BiFeO_3 single crystal are quite small, which seems to be a strong obstacle to practical application. However, recent studies on BiFeO_3 have confirmed the existence of a large ferroelectric polarization, as well as a large magnetization moment, in a strained structure formed through epitaxial growth on SrRuO_3 buffered SrTiO_3 (STO) substrate.¹⁵ This result has also been confirmed by theoretical predictions in terms of first-principles calculations.¹⁰ Another obstacle to the practical application of BiFeO_3 is that this compound has a serious electrical leakage problem, most likely as a result of sample defects and nonstoichiometry. However, this problem could be solved by an improved fabrication process for thin films, for example, by reduced oxygen pressure, and composition modification in the ceramics.^{16–19} Besides all the achievements that have occurred in terms of materials processing techniques, another important achievement is the direct observation of the electrical control of antiferromagnetic domains in epitaxially grown BiFeO_3 films on STO at room temperature.^{20–22} Using piezoforce microscopy and x-ray photoemission electron microscopy, high-resolution images of both antiferromagnetic and ferroelectric domain structures of (001)-oriented BiFeO_3 films were detected.²⁰ A clear correlation was observed between the ferroelectric and

antiferromagnetic domains, indicating a strong coupling between the two types of order. Thus, antiferromagnetic domain switching induced by ferroelectric polarization switching has been observed. However, the reverse phenomenon, that is, ferroelectric polarization domain switching by a magnetic field, has not been reported so far for BiFeO_3 . In this paper, we present for the first time magnetic field assisted electrical polarization in BiFeO_3 thin film.

The thin film samples in this work were deposited using a pulsed laser deposition system (PLD). Third harmonic generation of a Nd:YAG laser with a wavelength of 355 nm and a repetition rate of 10 Hz was used. BiFeO_3 ceramics with 5% excess bismuth and stoichiometric $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ (LCMO) ceramics, synthesized by solid state reaction were used as targets. A LCMO layer was deposited on (100) oriented SrTiO_3 (STO) single crystal substrate at a temperature of 720 °C with a dynamic oxygen pressure of 200 mtorr. After the deposited film was cooled down to room temperature and reheated again, a BF layer was then deposited on the LCMO film at 600 °C at a dynamic oxygen pressure of 50 mtorr. After deposition, the double layer film was cooled down to room temperature in a half hour. The phase and structure of the films was determined by x-ray diffraction (XRD) using $\text{Cu } K\alpha$ radiation. The surface morphology of the as-deposited films was scanned by an atomic force microscope (AFM) in tapping mode. A Pt upper electrode with an area of 0.007 85 mm² was deposited by magnetron sputtering through a metal shadow mask. The thickness of the films was obtained through observation of the cross section of the film under a high resolution scanning electron microscope (SEM); the BF and LCMO layers are each about 300 nm. Magnetic properties of the sample were investigated on a Quantum Design magnetic properties measurement system (MPMS). The ferroelectric properties were measured by an aixACCT EASY CHECH 300 ferroelectric tester. During the measurement of the polarization-electrical field loop (P-E loop), a static magnetic field of 1000 Oe was applied along the film normal.

The θ - 2θ XRD pattern of the double layered thin film is shown in Fig. 1. Epitaxial growth of LCMO along its (010) direction on (001) STO substrate was confirmed, since no trace of diffraction from other directions was observed. The BF layer on LCMO shows a tetrahedral structure, which is

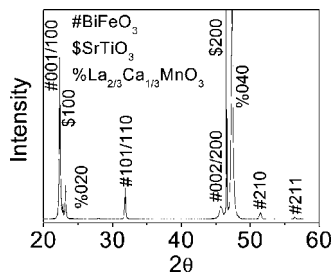


FIG. 1. The θ - 2θ x-ray diffraction pattern of the $\text{BiFeO}_3/\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ double layer thin film on SrTiO_3 , indicating epitaxial growth of the $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ film along its (010) direction on (100) SrTiO_3 , and preferred growth of the tetragonal BiFeO_3 film along its (001) direction.

different from the bulk rhombohedral structure. To compare with the diffraction pattern of the ceramic sample, preferred growth of BF along its (001) direction was observed on the LCMO buffer layer. The growth habit of the tetragonal BF and LCMO can be easily explained by the diffraction positions of the STO (100), LCMO (010), and BF (001) peaks, and the epitaxial growth relationship of the faces mentioned above was obtained.

A typical surface morphology of the as-grown BF films is shown in Fig. 2. It was found that the maximum grain size can reach up to 300 nm, while the average grain size is less than 200 nm. The surface is quite smooth with a root-mean-square roughness of less than 8 nm.

Figure 3 shows magnetization hysteresis loops (M-H loops) of the BF/LCMO thin film composite measured at 300 K and 10 K. The composite is ferromagnetic at both room temperature and 10 K. It is known that BiFeO_3 is antiferromagnetic below its Néel temperature of 643 K, and its weak ferromagnetism is from the breaking of the long spiral structure of the tilted antiferromagnetic arrangement of spins

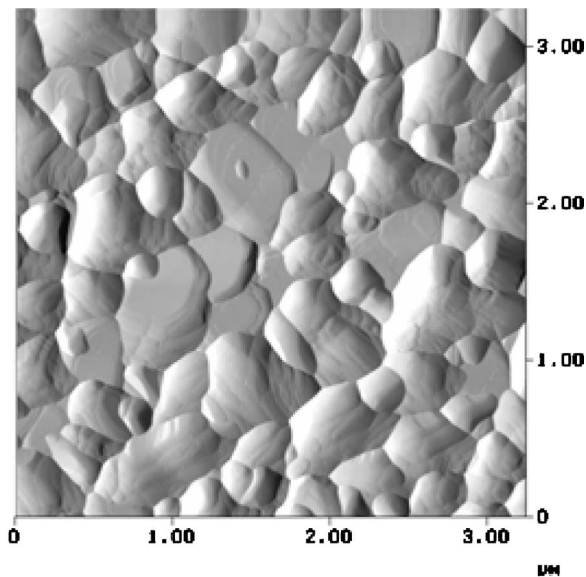


FIG. 2. Surface morphology of BiFeO_3 film on $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3/\text{SrTiO}_3$ in a $3.2 \times 3.2 \mu\text{m}^2$ area scanned by atomic force microscope (AFM) in tapping mode.

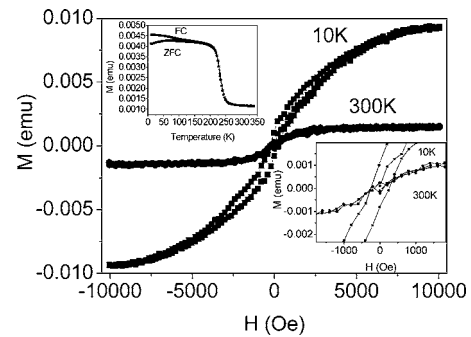


FIG. 3. Magnetization hysteresis loops of $\text{BiFeO}_3/\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ double layer composite measured at 10 K and 300 K. The inset is the FC-ZFC magnetization curve at 1000 Oe.

in the thin film. The LCMO is paramagnetic at room temperature, which is far above its ferromagnetic T_C of 250 K. This is also proved by the field-cooled and zero field-cooled (FC-ZFC) measurements of the magnetic susceptibility, shown in the inset of the figure. So the ferromagnetism shown by the thin film composite at room temperature is from the BF layer, while both the LCMO and the BF contribute to the magnetization at 10 K. This indicates that both component layers in the BF/LCMO composite maintain their own ferromagnetism, revealing a good interfacial compatibility of the two materials.

Figure 4 shows electrical polarization-electrical field (P-E) hysteresis loops of a Pt/BF/LCMO capacitor measured at different maximum applied voltages. The remanent polarization ($2P_r$) values of the capacitor measured at maximum voltages of 10 V and 14 V are 5.4 and $7.3 \mu\text{C}/\text{cm}^2$, respectively, which is below the value after the sample is completely switched. However, the complete switching of the polarization was hindered by electrical leakage, which might be caused by oxygen vacancy ionic conductivity. After a 1000 Oe magnetic field was applied, the P-E loops were measured again.

A comparison of the polarization measured with and without magnetic field applied is plotted in Fig. 5. It was found that the loops were tilted up by the magnetic field, revealing an increase in the saturated polarization (P_s , with the P at the maximum voltage here denoted by P_s , although the polarization is not completely switched). For example, the P_s values

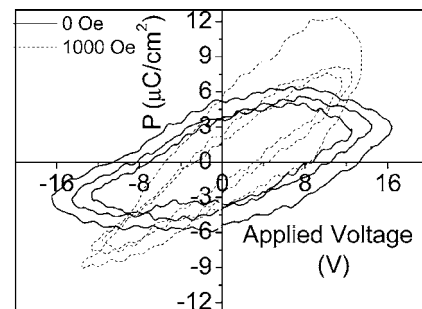


FIG. 4. Polarization-electrical field hysteresis loops measured at different applied voltages and zero magnetic field (solid line) and at a magnetic field of 1000 Oe (dotted line) (H is along the film surface normal).

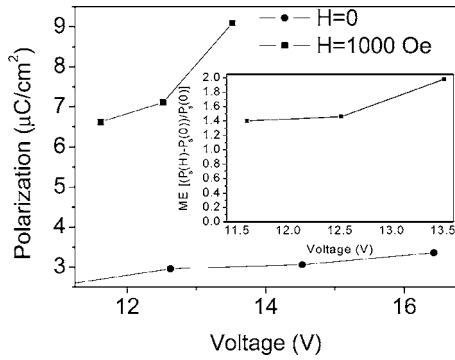


FIG. 5. Comparison of polarization of Pt/BiFeO₃/La_{2/3}Ca_{1/3}MnO₃ capacitor measured without magnetic field applied and with a 1000 Oe magnetic field applied. Inset figure is the ME effect in terms of $[P_s(H) - P_s(0)]/P_s(0)$.

at a maximum applied voltage of 13 V are 2.6 $\mu\text{C}/\text{cm}^2$ and 7.6 $\mu\text{C}/\text{cm}^2$ when no magnetic field and a 1000 Oe static magnetic field were applied, respectively. An ME effect of 196% in terms of P_s enhancement, defined as $[P_s(H) - P_s(0)]/P_s(0)$, was obtained at 1000 Oe magnetic field. However, it was found that P_r remains almost unchanged under the magnetic field. It is worth indicating that the ME effect defined here should include the contribution from the possible linear and high rank ME effect due to the structure change of BiFeO₃ thin film and unique polarization hysteresis loop measurement under a magnetic field.²³

To elucidate the origin of the observed ME effect in our double layer thin film composite, the magnetoresistance (MR) behavior of the bottom electrode was examined. It was found that the bottom LCMO electrode has good conductivity, but no MR effect was observed at room temperature. This is also in accordance with the magnetic measurements on the sample, that is, LCMO is paramagnetic above its T_C of 250 K.^{24,25} So, any effect from the bottom electrode could be ruled out. The origin of the ME effect in the BF/LCMO thin film composite is believed to come from the intrinsic properties of the multiferroic BF layer. The ME effect in BF has been confirmed using first-principles density functional theory calculations.^{9,10} The Dzyaloshinskii-Moriya interaction, leading to the canting of the magnetic moments and the appearance of macroscopic magnetization, is a result of polar distortion in BF. As a result, the magnetization is strongly coupled to the ferroelectric polarization, and the reversal of the ferroelectric polarization by an electric field will be accompanied by the reversal of the macroscopic magnetization. This is proved by the direct observation of the switching behavior of the antiferromagnetic domains in BF in response to an electrical field at room temperature.²⁰ The observation also showed that antiferromagnetic domains and ferroelectric domains were present in the same domain area, which means that the vectors of the ferroelectric domains and antiferromagnetic domains are strongly coupled together no matter how the ferroelectric domains or antiferromagnetic domains are switched.

In BF thin film with a suppressed long-wavelength spiral structure, the “easy magnetization plane,” where individual spin vectors fall in the G -type antiferromagnetic order, is perpendicular to the polarization direction.¹⁹ When a switching electrical field is applied, the switching of the ferroelectric polarization will couple to the ferroelastic strain, which will cause the reorientation of the antiferromagnetic spins according to the above relationship between the electrical polarization and antiferromagnetic vectors. However, the opposite method of control in BiFeO₃, that is, electrical polarization domain switching by a magnetic field, has not been reported. Probably it is technically difficult to realize the switching of electrical polarization only by a magnetic field. Our sample reveals that the magnetic field facilitates the electrical polarization switching by an electrical field, but the electrical polarization may not be switched by such a magnetic field alone. The M-H loops of our sample reveal the weak ferromagnetic magnetization behavior of the sample under a magnetic field of 1000 Oe (shown in the inset of Fig. 2 in the bottom-right corner). The ferromagnetic magnetization of the BF thin film is a process involving the recanting of the antiferromagnetic spins. However, the antiferromagnetic vector may not be switched by such a small magnetic field. When a switching electrical field was applied, the switching of the ferroelectric polarization will cause the reorientation of the antiferromagnetic spins. So part of the energy will be consumed by the switching of antiferromagnetic domains.

When a magnetic field is applied, it helps the recanting of the spin by facilitating the antiferromagnetic domain switching. In such a way, the activation energy for the switching of the electrical polarization domains is reduced. As a result, the electrical polarization that could be switched by an electrical field is increased by a magnetic field. Thus, the P-E loops for our BF films are tilted up in a high electrical field by a magnetic field.

In summary, we have grown BF thin film on LCMO epitaxially grown on a STO substrate. Both ferromagnetic and ferroelectric properties were demonstrated by the BF film. We observed for the first time that the electrical polarization in BiFeO₃ films can be enhanced greatly by magnetic field at room temperature. Due to the fact that both magnetic and ferroelectric domains are strongly coupled together in the BF films, we proposed that the activation energy for the electrical polarization domains switching is reduced by the application of a magnetic field. As a result, the electrical polarization that can be switched by an electrical field is increased by the magnetic field. Further experimental work in the future will be focused on the temperature and magnetic field dependence of the ME effect, thus it is expected that this explanation will acquire more evidence.

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*Corresponding author. Electronic address: xiaolin@uow.edu.au

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