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Weak ferromagnetism in La-doped $BiFeO_3$ multiferroic thin films

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$Bi_{1-x}La_xFeO_3$ thin films ($x = 0.0, 0.3, 0.5$) were grown on glass substrates by thermal physical vapor deposition. The monoclinically distorted crystal structure of the films was revealed by x-ray diffraction at room temperature. Field and temperature (up to 1000 K) dependences of magnetization were studied. Saturation of the room temperature magnetic hysteresis loop has been observed at magnetic field above 0.15 T, demonstrating the weak ferromagnetic nature of the thin films. Our magnetic force microscopy results show clearly the presence of magnetic domains in BFO thin films. These structural and magnetic properties suggest the absence of magnetic spiral spin structure in monoclinically distorted BFO-based thin films. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4730896]

I. INTRODUCTION

Ferromagnetoelectric materials (multiferroics) are compounds with coexistence of long-range magnetic and electric order parameters in the same phase.[1,2] The coupling between the spontaneous polarization and spontaneous magnetization can be used for developing a novel memory media which combine the advantages of ferroelectric random access memories (FeRAMs) and magnetic random access memories (MRAMs) in the form of non-volatile magnetic storage bits that are switched by an electrical field.[3]

Among the several classes of multiferroics, $BiFeO_3$ (BFO) has already attracted the greatest attention[4,5] for its room temperature multiferroic properties. In this compound the ferroelectric Curie temperature is about 1098 K and the antiferromagnetic Neel temperature is about 643 K.[4] Bulk bismuth ferrite can be described as a rhombohedrally distorted ferroelectric perovskite with *R3c* space group. The unit cell parameters are $a = 3.96$ Å, $\alpha = 89.76°$.[4] The antiferromagnetic ordering of bulk BFO corresponds to a spiral spin structure with an incommensurate long-wavelength period of 62 nm, resulting in the suppression of net magnetization.[6] The lack of saturation and remanent magnetization appears to be the main obstacles for the wide practical applications and hence make bulk BFO less interesting for potential use in magnetic device research.

Recently, it has been shown that the spiral modulated spin structure can be suppressed by fabricating BFO in thin film form.[7,8] BFO thin films have been successfully made by many researchers using pulsed laser deposition (PLD),[7–9] metalorganic chemical vapor deposition,[10] chemical solution deposition,[11,12] sol-gel,[13] etc. The value of remanent magnetization of bismuth ferrite thin film has reached $M_r \sim 8$ emu/g at room temperature.[7] The origin of ferromagnetism in epitaxial BFO films is not clear yet and, despite extensive study on this subject, there are still many diverse scenarios discussed in the literature.[7–16] Wang *et al.*[7] first proposed spin canting due to epitaxial constraint resulting from the lattice mismatch between the film and substrate, as a possible mechanism of the weak ferromagnetism in BFO thin films. Eerenstein *et al.*[14] and Chang *et al.*[9] suggested that ferromagnetism originated from the presence of a substantial fraction of the Fe^{2+} ions. In this case, ferrimagnetic alignment of Fe^{3+} and Fe^{2+} ions may give rise to a net magnetization. At the same time further development of these materials using Bi-site doping with rare-earth elements is of prime interest. In this paper we investigate the magnetic properties of Bi_{1-x} La_xFeO_3 (BLFO) thin films as a function of external magnetic field and temperature. The $BiFeO_3$–$LaFeO_3$ solid solutions with perovskite-like structure are typical magnetoelectric materials which exhibit the coexistence of antiferromagnetic and ferroelectric orders.[1,2]

II. EXPERIMENTAL DETAILS

BLFO ($x = 0.0, 0.3, 0.5$) thin films of 90 nm thickness were grown on SiO_2-glass substrates using a thermal physical vapor deposition method in a UVM-71 R-2 vacuum divice.[17] In this method, container with previously synthesized BLFO powder is placed at an angle of 20° to horizontal axis and is connected to the Ta evaporator by the groove. After the container has been shaken, a small amount of the powder (~10 mg) is moved to the Ta evaporator through the groove. The temperature of Ta evaporator was around 2300 K. Glass substrate was placed at a distance of 100 mm from the heater which enabled to keep the substrate temperature at 570 K during deposition. The chamber pressure was about 10^{-3} Pa.

The crystal structure was studied at room temperature by x-ray diffraction (XRD) using a Siemens D 5000 diffractometer with CuK_α ($\alpha = 1.5418$ Å) radiation. The surface morphological study of the films was carried out by scanning electron microscopy (SEM, Hitachi S-3000 N) and atomic

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force microscopy (AFM, XE-100 Park systems). The elemental composition was determined using ARL QUANTRIS Emission Mass Spectrometer Thermo (CCD). The magnetization hysteresis (M-H) loops were measured using an automated vibrating sample magnetometer (VSM, Oxford instruments). For the measurements of magnetization as a function of temperature, the device[17] based on the ponderomotive method was used. The ponderomotive method consists in measurement of the mechanical force acting upon the sample being studied in a nonuniform magnetic field. In order to study the magnetic domain structure of BFO based thin films, magnetic force microscopy (MFM) measurements were done at room temperature using an Autoprobe M5 setup (VEECO Instruments).

III. RESULTS AND DISCUSSION

Figure 1 shows typical SEM (a) and AFM (b) images of the BLFO thin films deposited on glass substrate. The one-dimensional cross section scan of the surface profile is also plotted in Fig. 1(b). As it can be seen, La-doped BFO thin films are quite rough. The surface morphology of the film consists of hills and craters and has a RMS surface roughness (Rq) of approximately 42.4 nm and the average height roughness (Ra) of 34.4 nm (see Fig. 1(b)). As seen in Fig. 1(a), the round-like outgrowths reaching the size of 2 μm were also formed on the surface of BLFO thin films. The x-ray fluorescence spectroscopy (XRF) was used for the element analysis of these hillocks. Figure 2 indicates that the outgrowths on the surface of the BFO film correspond to the Bi-rich phase in contrast to the black background. These outgrowths may originate from unreacted bismuth oxide during deposition. The absence of spurious Fe_2O_3 phase in BLFO thin films was also confirmed by XRF.

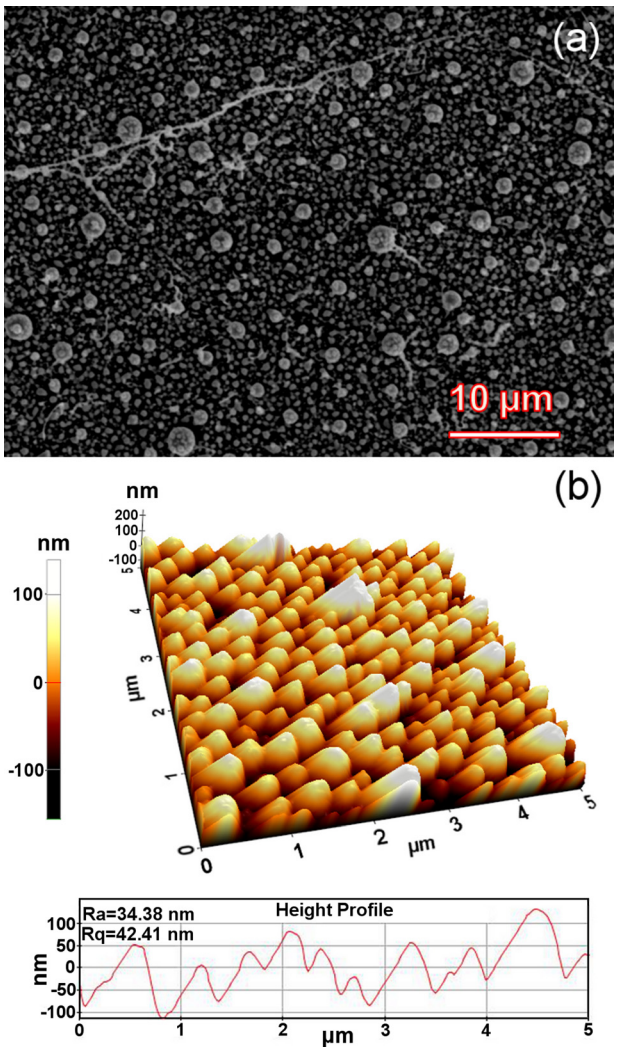

FIG. 1. (a) SEM and (b) AFM images of the $Bi_{0.5}La_{0.5}FeO_3$ thin film.

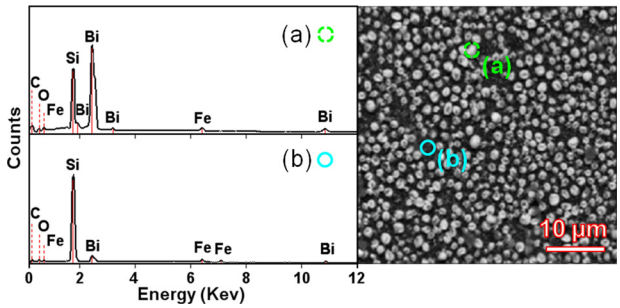

FIG. 2. Energy dispersive XRF spectrum taken at (a) the outgrowth (white spots) and (b) the plain surface (dark regions) of the $BiFeO_3$ thin film.

Figure 3 shows the XRD data obtained at room temperature for the BLFO thin films. The diffraction peaks of the BLFO thin films have a slight shift as compared to those of undoped BFO caused by the La substitution of Bi atoms. This may result from a slight difference in ionic radii between Bi^{3+} (1.03 Å) and La^{3+} (1.032 Å) ions.[18] However, the phase structure of the BLFO thin films does not change with increasing La concentration, which is consistent with other report.[19] In contrast, analysis of the XRD patterns of the source BLFO powders revealed that the lattice symmetry gradually changes from rhombohedral (*R3c*) to orthorhombic (*Pnma*) when Bi atoms are substituted by La. Singh *et al*. in his work on the La doping of BFO films observed structural changes upon doping.[20]

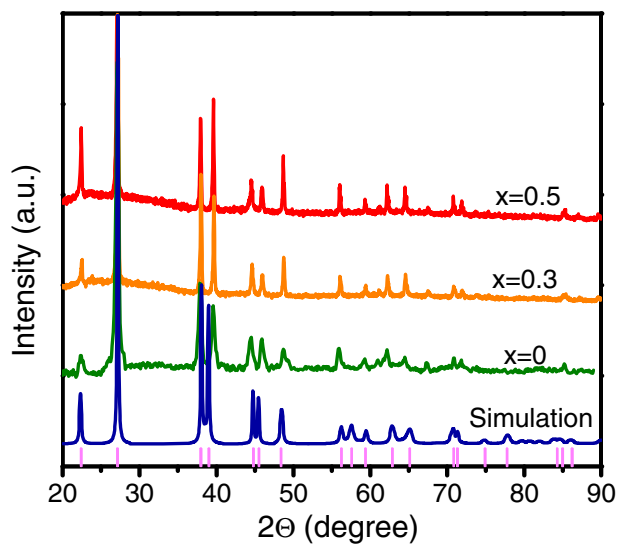

FIG. 3. XRD patterns of the $Bi_{1-x}La_xFeO_3$ (x = 0, 0.3, 0.5) thin film samples. The three upper curves are experimental data, and the bottom one is a calculated spectrum. Lower ticks denote monoclinic $P2_1/m$ structure.

XRD data modeling was performed using Endeavour 1.2 XRD pattern processing software[21] in order to analyze the crystal structure of the BLFO thin films (Fig. 3). The peak positions and intensities were found to be compatible with the monoclinic ($P2_1/m$ space group) phase. Moreover, the absence of impurity phases that are commonly formed along with the BFO, such as Bi_2O_3, Fe_2O_3, and $Bi_2Fe_4O_9$, was confirmed. Thereby we can suggest that the BLFO films have monoclinically distorted perovskite structure with lattice constants $a = 3.37$ Å, $b = 3.31$ Å, $c = 4.09$ Å, and $\beta = 91.35°$. Similar results were reported by Kartavtseva *et al.*[10] Bai *et al.*[8] inferred that BFO films prepared by PLD have a rhombohedral structure, in contrast to Wang *et al.*[7] who reported the presence of a tetragonal structure in epitaxial $BiFeO_3$ thin films.

The dc magnetization of the films was measured as a function of temperature and magnetic field up to 1 T. Figure 4 shows the magnetic hysteresis loops M(H) of $Bi_{0.5}La_{0.5}FeO_3$ thin film. The observed M-H curves reveal weak ferromagnetism in BLFO thin films even at room temperature. As seen from Fig. 4(a), the value of the remanent magnetization M_r at room temperature for BLFO ($x = 0.5$) film is about 5 emu/g which is consistent with the value observed previously by Wang *et al.*[7] for the PLD deposited BFO films. The magnetization at corresponding temperatures is an order of magnitude higher than that of the bulk BLFO samples (see inset of Fig. 4(a)). Besides, the saturation magnetization at room temperature is ~7 emu/g at relatively low applied magnetic field. In BLFO thin films grown on glass substrate, the epitaxial strain induced by the substrate and film lattice mismatch cannot be responsible for the enhanced magnetism. Neutron diffraction measurements, performed by Béa *et al.*,[22] revealed that right monoclinically distorted BFO films show G-type antiferromagnetic ordering with no indication of any cycloidal modulation. Thus, the observed M(H) nonlinearity, finite coercitivity (Fig. 4) and the enhancement of M_r and M_s for BLFO thin films can be explained due to suppression of the cycloidal spin structure and the release of the locked magnetization.

Temperature dependences of the zero field cooled (ZFC) and field cooled (FC) magnetization curves measured at $H = 0.86$ T for BFO film are presented in Fig. 4(b). When decreasing the temperature below 200 K, the magnetization increases with respect to Curie's law for paramagnets, which is consistent with the unsaturated hysteresis loop up to 1 T at low temperatures. An inflexion point in the ZFC magnetization curve can be seen at temperature around 400 K, which could be related to the structural transition from the metastable monoclinically distorted perovskite phase to its more stable rhombohedral state. A small maximum at $T_2 = 670$ K, which happens to be around T_N of bulk BFO, can be attributed to the AFM-PM phase transition. At temperatures higher than 800 K, BFO thin film has a magnetization of ~0.6 emu/g which does not correspond to the value typical

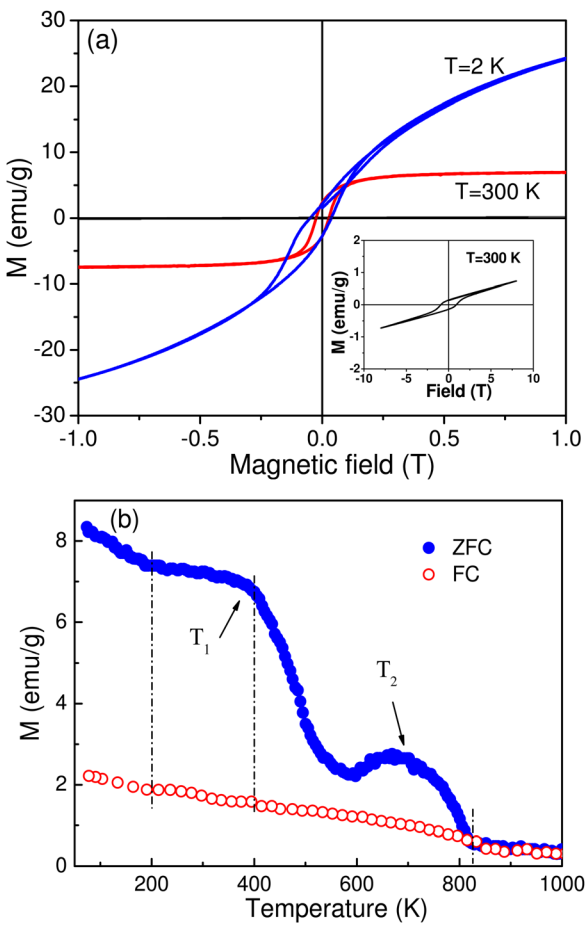

FIG. 4. (a) Field dependence of the magnetization obtained for the BLFO ($x = 0.5$) thin film. Inset shows the M-H curve of corresponding bulk sample at room temperature; (b) ZFC and FC curves of the BFO thin film.

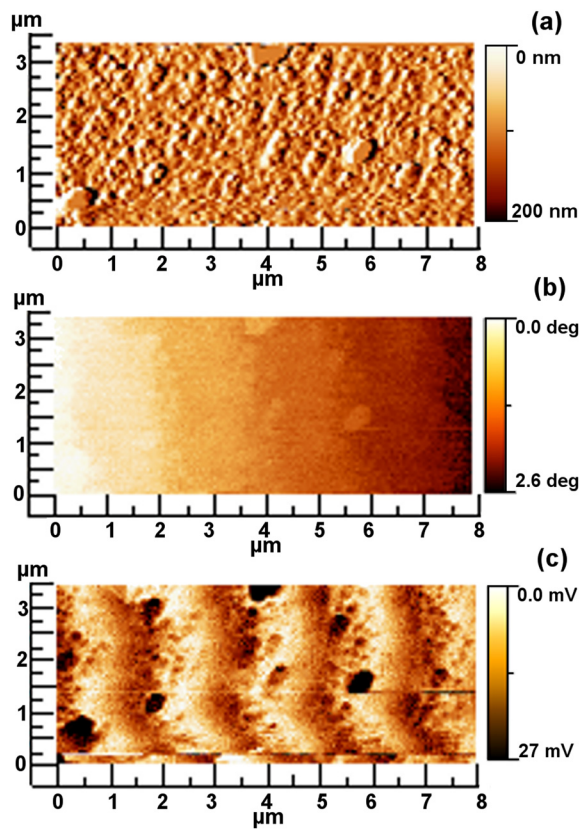

FIG. 5. MFM images of the BLFO ($x = 0.5$) film: (a) topography, (b) phase, and (c) amplitude.

for the ferromagnetic ordering. When field-cooled, the magnetization increases monotonically as the temperature decreases. The significant difference between the ZFC and FC curves confirms the irreversible structural phase transition in the thin films, occurred during heating up to 1000 K.

MFM scans were also performed on the BLFO films in order to study their magnetic domain structure. Figure 5 demonstrates the MFM images of the $Bi_{0.5}La_{0.5}FeO_3$ thin film obtained at room temperature. The periodic magnetic structure with a period of 1.5 μm is clearly seen in Fig. 5(c), which differs significantly from the topography structure (Fig. 5(a)). This periodicity reflects the presence of magnetic stripe domains in the BLFO thin films.

IV. CONCLUSIONS

The La-doped $BiFeO_3$ thin films ($x = 0.0, 0.3, 0.5$) were deposited onto glass substrate by thermal physical vapor deposition method. Structural and magnetic properties of thin films have been investigated. A significant enhancement of magnetization, compared to that of corresponding bulk ceramics, was observed in the monoclinically distorted BLFO thin films. The observed hysteresis loops and domain structure, the measured values of M_r and M_s indicate that the BLFO ($x = 0.0, 0.3, 0.5$) thin films are weakly ferromagnetic at room temperature in contrast to the corresponding bulk antiferromagnetic samples. Therefore, these films are good candidates for the observation of a linear magnetoelectric effect, prohibited in the bulk due to the spiral modulation of the G-type spin ordering.

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