# A Possible Origin of Ferromagnetism in Epitaxial BiFeO$_3$ thin Films

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We prepared (111) oriented BiFeO$_3$ (BFO) thin films with the different thicknesses of 30, 70, and 200 nm using pulsed laser deposition. We examined relations between the ferromagnetism and strain of these films from x-ray diffraction and superconducting quantum interference device data. The saturation magnetization values of the films are independent of strain and rather dependent upon the thickness only. From the results, we suggest that the ferromagnetism in the BFO thin films originate from extrinsic factors such as the coexistence of Fe$^{2+}$ and Fe$^{3+}$.

Key words : multiferroic, BiFeO$_3$ thin film, ferromagnetism, oxygen vacancies

## 1. Introduction

In recent years multiferroic materials, which exhibit ferroelectricity or antiferroelectricity, and simultaneously ferromagnetism or antiferromagnetism have attracted much attention due to their fundamental and practical interests [1]. With the simultaneous occurrence of the multi-order parameters, the magnetization can be induced by an electric field, or vice versa through magnetoelectric effects [2]. Magnetic phase controls by means other than an applied magnetic field enable us to overcome the difficulty in localizing a sufficient magnetic field and hence ultrahigh density in information storage could be realized using such materials [3]. Although the materials can offer a breakthrough for ultrahigh-density information-storage devices, the microscopic mechanism that underlies such multi-order parametric phenomena has yet to be known.

One of the first multiferroic materials found is BiFeO$_3$ (BFO). It exhibits a ferroelectric order below a Curie temperature $T_C$ of 1103 K [4, 5] and an antiferromagnetic order (G-type) below a Neel temperature $T_N$ of 643 K [6, 7]. It is a rhombohedrally distorted perovskite with the space group, R3c [8]. Recently, Wang *et al.* fabricated epitaxial BFO (001) thin films with a pseudo-tetragonal structure on SrTiO$_3$ (STO) substrates. Unlike its single crystalline form, it exhibits ferromagnetism, and the origin of which is attributed to a compressive strain that is imposed by the STO substrates [9]. However, there have been growing controversies over the origin of ferromagnetism in epitaxial BFO (001) films [10-12]. Eerenstein *et al.* reported that their stoichiometric BFO (001) films do not exhibit such enhanced ferromagnetism [9]. Ederer *et al.* revealed using first principle density functional theory calculations that the magnetization value is not influenced by strain [12]. In the work of Wang *et al.* the role of strain in enhancing the magnetism is likely to be uncertain because not only the strain but amount of Fe$^{2+}$ in their films exhibits thickness dependences [9, 11]. They still suggest that spin canting caused by a compressive stress be a possible mechanism of ferromagnetism in BFO thin films [11].

In the present work, we experimentally examine relations between the ferromagnetism and strain in epitaxial BFO (111) thin films with various thicknesses of 30, 70, and 200 nm on STO (111) substrates. Contrary to the (001) oriented films of Wang *et al.* the strain of the (111) oriented films exhibits little dependence on thickness. Hence we evidence that strain is not responsible for the enhanced magnetism in BFO thin films and suggest an alternative origin of the ferromagnetism in BFO thin films.

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## 2. Experiments

We fabricated epitaxial BFO (111) thin films of 30, 70, and 200 nm thicknesses on STO (111) substrates using pulsed laser deposition (PLD). The optimized deposition conditions used in the film growths are as follows: (i) laser source; KrF excimer with $\lambda = 248$ nm, (ii) energy density; 1.5 J/cm$^2$, (iii) oxygen partial pressure; 400 mTorr, (iv) repetition frequency; 3 Hz, (v) deposition rate; 0.05 nm/s; and (vi) deposition temperature; 625 °C. We employed a PANalytical high resolution x-ray diffracto-meter (HR-XRD) in order to perform 2Θ-Ω and Φ cans. For magnetic hysteresis loop measurements, we used a Quantum Design MPMS5 superconducting quantum interference device (SQUID) magnetometer.

## 3. Results and Discussion

Figure 1(A) shows HR-XRD 2Θ-Ω data of the (111)



reflections of the 30, 70, and 200 nm thick BFO films. The interplanar distances of the 70 and 200 nm thick BFO films along the (111) orientation are the same and slightly smaller than that of the 30 nm thick film, indicating the slight relaxation of stored elastic energy due to a lattice mismatch. The lattice constants along the (111) orientation $d_{III}$ of the 30, 70, and 200 nm thick films are 2.314, 2.311, and 2.311 Å, respectively. Figure 1(B) shows Φ scans of the (002) reflections of the STO (111) substrate and the 200 nm thick BFO film. Each peak is separated by 120°, indicating a threefold symmetry. Φ scans of the (002) reflections of the 30 and 70 nm thick films exhibit the same peak positions as those of the 200 nm thick film. As shown in Fig. 1, the XRD results clearly exhibit that the three different films are epitaxially grown on STO (111) substrates.

Figure 2 shows in-plane magnetic hysteresis loops measured by a SQUID magnetometer. As presented in Fig. 2, the individual films exhibit ferromagnetic hysteresis loops and their saturations at room temperature. Contrary to antiferromagnetism of bulk samples reported in Refs. [6, 7, 13], the BFO (111) films evidently exhibit ferro-magnetism. In addition, the magnetization value varies strongly with the film thickness and decreases with increasing thickness. The saturation magnetization values of the 30, 70, and 200 nm thick films are 3.2, 2.3 and 0.5 emu/cc, respectively, and are very small compared to magnetization values reported by Wang et al. [11].

Wang et al. proposed spin canting due to a compressive stress as a possible mechanism of the ferromagnetism in BFO thin films [9]. The magnetization values of their samples appear to increase with increasing strain. How-ever, their x-ray magnetic circular dichroism data clearly show the presence of $Fe^{2+}$ [11]. Thus strain is nothing but
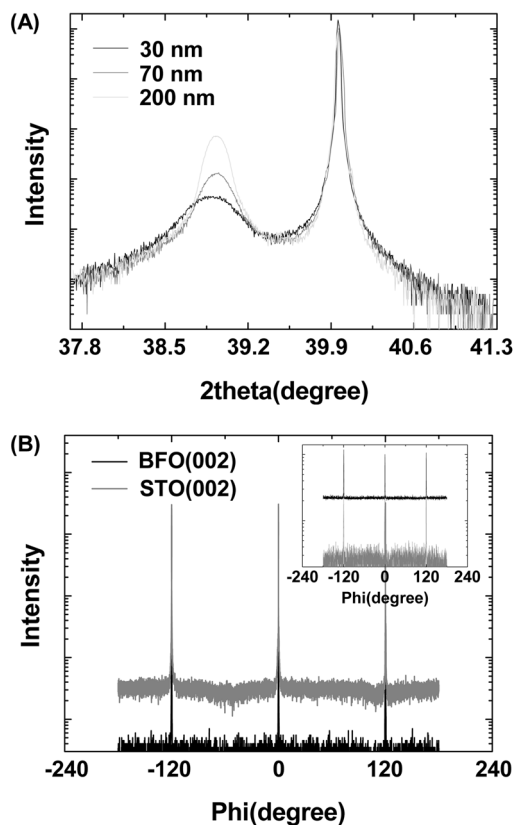
**Fig. 1.** (Color online) HR-XRD data of epitaxially grown BFO (111) films on STO (111) substrates. (A) 2Θ-Ω scans of the (111) reflections of the BFO films. (B) Φ scans of the (002) reflections of the STO (111) substrate and the BFO (111) film of 200 nm thickness. Inset: the black and red line represent Φ scans of the (002) reflections of 70 and 30 nm thick BFO (111) films, respectively.
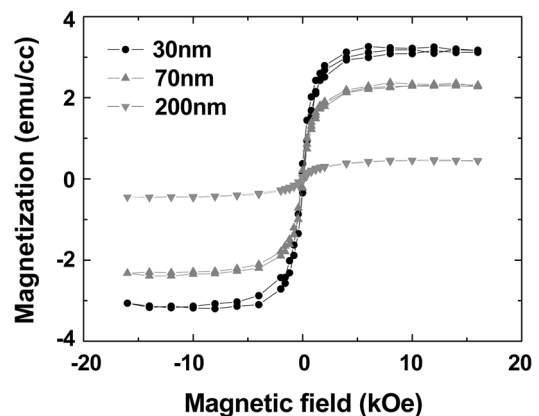


**Fig. 2.** (Color online) Room-temperature magnetic hysteresis loops measured by a SQUID magnetometer. The external mag-netic field is applied in-plane.
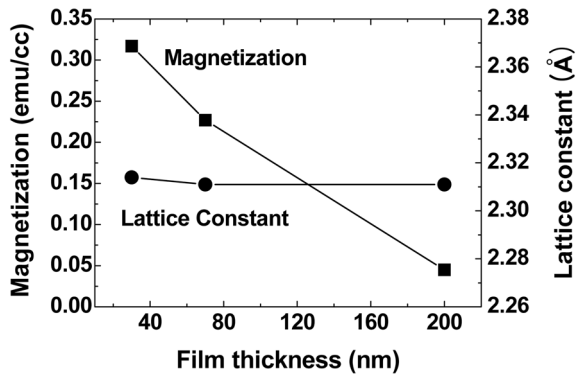
**Fig. 3.** Dependences of the saturation magnetizations and out-of-plane lattice constants ($d_{III}$) of the BFO (111) films on thickness. The solid lines are guide for eyes.

a possible origin of the ferromagnetism. As seen in Fig. 3, the magnetization values of the BFO (111) films studied here are independent of strain, and only show its dependence on thickness. Thus the spin-canting mechanism can not be the origin of the enhanced magnetizations. According to the x-ray photoelectron spectroscopy (XPS) data of Eerenstein *et al.*, there is no evidence of the presence of $Fe^{2+}$ ions in their BFO films [10]. The magnetization is reminiscent of those of bulk specimens and does not exhibit a strain dependence [10]. The question can be raised here is what the true origin of ferromagnetism in BFO thin films is. Ferrimagnetic alignment in which $Fe^{2+}$ magnetic moments are coupled antiparallel with those of $Fe^{3+}$ may give rise to a finite value of magnetization. The antiparallel coupling would be stabilized since 5 electrons in d-orbitals which are in high spin state at each site can hop to its neighboring site via oxygen and thus a more kinetic energy gain comes out. The resulting effect is known as superexchange interaction [14]. Theretore, the enhanced magnetization could result from a substantial $Fe^{2+}$ amount. We could not obtain a saturated polarization-electric field curve due to leakage current from our samples. We conjecture that the leakage current originates from the presence of $Fe^{2+}$ due to oxygen vacancies commonly occurring in the deposition processes of such perovskite thin films [11]. The larger amount of $Fe^{2+}$ in thinner films due to the higher fraction of oxygen vacancies is likely to be the mechanism of the larger magnetization value. Our films were fabricated in somewhat reducing condition. Thus, the thinner the films, the more the films are influenced by the reducing condition since oxygen ions in the thicker films have to travel along longer paths to come out of the film surface.

## 4. Conclusion

The magnetization in the PLD grown BFO (111) films exhibits little dependence on strain. We exclude strain effects from likely candidates for the origin of ferromagnetism found in BFO thin films. The ferromagnetism in BFO thin films may originate from extrinsic factors such as a substantial fraction of $Fe^{2+}$ which results from oxygen vacancies commonly produced during the deposition processes of oxide thin films.

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