Strain induced magnetoelectric coupling between magnetite and $BaTiO_3$

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(Received 21 December 2007; accepted 22 January 2008; published online 13 February 2008)

Magnetite (Fe_3O_4) thin films have been grown on ferroelectric $BaTiO_3$ (BTO) single crystal substrates by pulsed laser deposition. Transmission-electron microscope observations demonstrate the orientation relationship between Fe_3O_4 and BTO as $[400]_{Fe_3O_4}\|[200]_{BTO}$ and $[004]_{Fe_3O_4}\|[002]_{BTO}$. Experimental measurements of magnetization, coercivity and remanent magnetization of the films show abrupt jumps at around phase transition temperatures of BTO and opposite jump signs are observed for the in-plane and out-of-plane measurements. The magnetization jumps can be suppressed by a strong external magnetic field. These results were discussed in terms of the interface strain induced changes of magnetic domain structure in the Fe_3O_4 film. This work demonstrates the presence of strong magnetoelectric coupling between Fe_3O_4 and BTO. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2844858]

In recent years, multiferroic materials which exhibit simultaneous ferroelectric, (anti-)ferromagnetic ordering are particularly interesting because they offer the possibility for realizing mutual control of electric and magnetic properties known as the magnetoelectric effect.[1] This could be proved useful in spintronics and could lead to new types of transducers, actuators, and memory devices. However, the coexistence of strong coupling, stable ferromagnetism, and ferroelectrics is rarely satisfied in the single phase multiferroic materials, which has been a great challenge in this field.[2–6] It has been proposed that such a strong coupling can be realized by designing composites or composite thin films of piezoelectric and magnetostrictive phases which can be electromagnetically coupled via stress mediation.[7] Recently, there have been some reports on $BaTiO_3$–$CoFe_2O_4/SrTiO_3$ composite, $CoFe_2O_4/BaTiO_3$, $SrRuO_3/BaTiO_3$, $La_{0.67}Sr_{0.33}MnO_3/BaTiO_3$, and $Fe/BaTiO_3$ heterostructures,[8–13] which show the coupling effect manifested as a change in the magnetization and resistance at the structural phase transition temperatures of $BaTiO_3$. Eerenstein *et al.*[13] also demonstrated the electrically induced giant, sharp, and persistent magnetic changes at the interface of $La_{0.67}Sr_{0.33}MnO_3/BaTiO_3$.

Up to now, there have been no reports on the coupling composed of magnetite (Fe_3O_4) film and $BaTiO_3$ (BTO) substrate. Fe_3O_4 is a fascinating material that is still not well understood and has received an enormous attention due to its unique transport and magnetic properties.[14–17] BTO is a well-known room temperature ferroelectric that is tetragonal with $a=b=3.992$ Å and $c=4.036$ Å, which changes from tetragonal (T) to orthorhombic (O) at 290 K and rhombohedral (R) at 190 K, the symmetries of the T, O, and R states permit non-180 domains that render BTO ferroelastic.[18,19] The BTO substrate provides a surface lattice that can be dynamically changed with temperature. Considering the importance of Fe_3O_4, it is interesting to explore the possible magnetoelectric coupling effect between Fe_3O_4 and BTO. The detail picture of the magnetoelectric coupling effect between BTO and ferromagnetic materials is also an interesting topic, which is still not well established.

In this letter, we report the fabrication and characterization of Fe_3O_4 thin film grown on the ferroelectric BTO single crystal. Strong magnetoelectric coupling was observed in Fe_3O_4/BTO heterostructures as indicated by the remarkable changes of magnetization, coercivity, and remanent magnetizations of Fe_3O_4 film induced by the structural phase transitions of BTO. The mechanism of the coupling was also discussed.

Fe_3O_4 thin films were grown on (100) BTO substrates by pulsed laser deposition at 620 °C in vacuum (5×10^{-4} Pa) with a KrF excimer laser. The energy density of the laser pulse was about 1.5 J/cm^2 and the repetition rate was 2 Hz. The thickness of the film was about 80 nm. A Tecnai-F20 (200 kV) transmission electron microscope (TEM) was used for the microstructure analysis. The θ-2θ x-ray diffraction (XRD) patterns of the samples were obtained by using a Rigaku diffractometer with a Cu $K\alpha$ radiation. The magnetic property of Fe_3O_4 films was measured on a superconducting quantum interference device (Quantum Design MPMS XL7) magnetometer.

XRD pattern of a Fe_3O_4/BTO is displayed in Fig. 1(a) and it is recognizable that this single-phase film grows along the ⟨100⟩ direction. Moreover, the expected 90°domain structure in the BTO substrate (T phase) is also demonstrated by the presence of the (002) and (200) reflection peaks in Fig. 1(a). In order to directly reveal the microstructure features of Fe_3O_4/BTO, we performed an extensive TEM observation on a well-characterized sample. Figure 1(b) shows a high-resolution TEM image illustrating the cross-sectional structure of a Fe_3O_4/BTO specimen and the insets show the low-magnification bright-field TEM image and the corresponding selected-area diffraction pattern from the interface area. This as-grown film has a uniform thickness of about 80 nm. Two sets of electron diffraction spots in the shown diffraction pattern, arising, respectively, from film and substrate, can be well indexed on the Fe_3O_4 structure (a cubic inverse spinel cell with the lattice parameter of 0.840 nm) and the BTO

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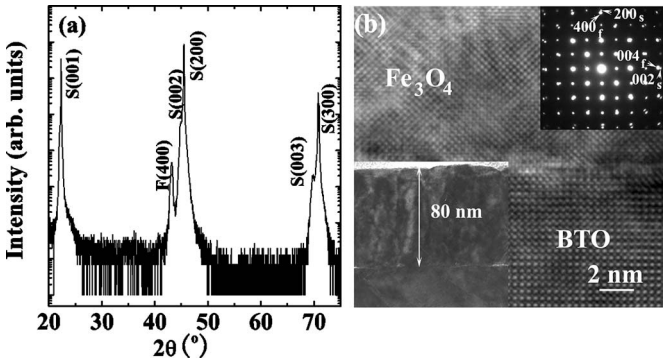

FIG. 1. (a) X-ray diffraction pattern of Fe_3O_4/BTO (100). *S* and *F* stand for BTO and Fe_3O_4, respectively. (b) High-resolution TEM image of the cross-sectional specimen of Fe_3O_4/BTO. The upper inset and the lower inset show the corresponding selected area diffraction pattern and the bright-field low magnification TEM image of the Fe_3O_4/BTO, respectively.

structure with the lattice constant of 0.399 and 0.4036 nm. This pattern clearly exhibits the orientation relationship of $[400]_{Fe_3O_4} \| [200]_{BTO}$ and $[004]_{Fe_3O_4} \| [002]_{BTO}$. A lattice mismatch of ~4.5% between Fe_3O_4 and BTO can be obtained from the splits of the diffraction spots.

Figure 2 shows the in-plane magnetic hysteresis loops of Fe_3O_4/BTO measured at various temperatures ($140\ K \leqslant T \leqslant 300\ K$), the temperature dependence of magnetization, coercivity (H_c), and the ratio of remanent to saturation magnetization (M_r/M_S). The *M-H* curves extend to ±1 T (not fully displayed) and only four loops near the *O-R* phase transition of BTO were indicated in Fig. 2(a). The loops were measured while sequentially decreasing the temperature. With decreasing temperature, the field cooling magnetization

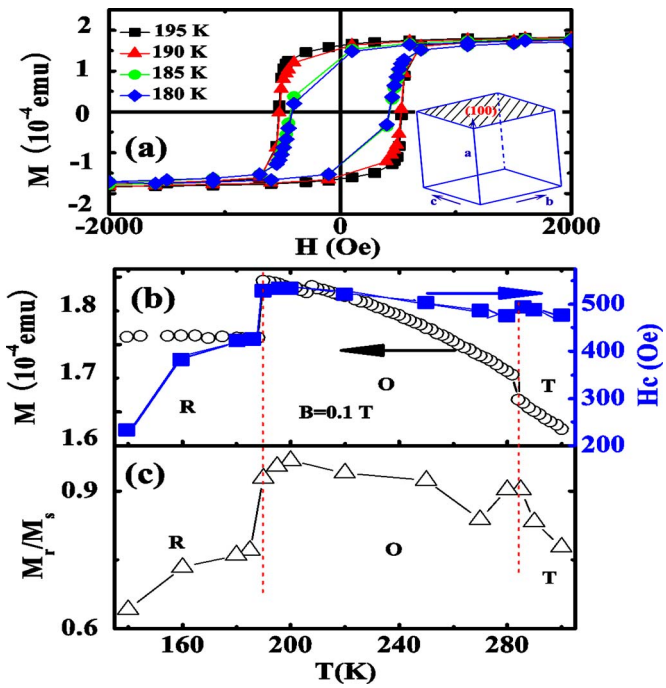

FIG. 2. (Color online) (a) The in-plane magnetic hysteresis loops measured at different temperatures. The inset depicts a representative BTO unit cell with reference axes. (b) Variation of the in-plane magnetization vs *T* under a magnetic field of 0.1 T and the corresponding change of the coercivity (H_c) vs *T*. (c) The in-plane M_r/M_s vs *T* obtained from the magnetization hysteresis loops. Letters *R*, *O*, and *T* denote the rhombohedral, orthorhombic, and tetragonal states of BTO substrate, respectively. The dotted lines are the boundaries of different phases of BTO.

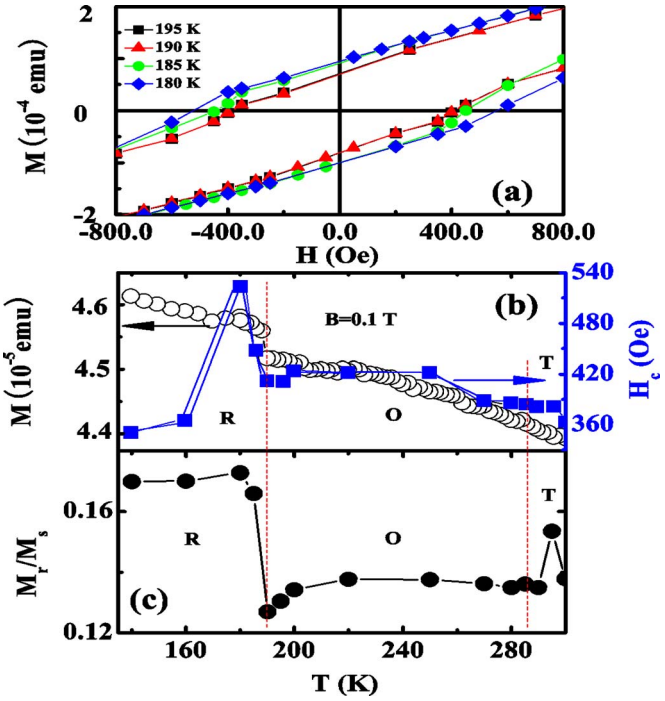

FIG. 3. (Color online) (a) The out-of-plane magnetic hysteresis loops measured at different temperatures. (b) Variation of the out-of-plane magnetization with decreasing temperature under a magnetic field of 0.1 T and the corresponding change of coercivity (H_c) vs *T*. (c) out-of-plane M_r/M_s vs *T* obtained from the magnetization hysteresis loops. The dotted lines are the boundaries of different phases of BTO.

shows an abrupt increase near the $T \rightarrow O$ transition and a dramatic decrease near the $O \rightarrow R$ transition. The observed magnetization jumps at the structural phase transitions (283 and 189 K) are consistent with the changes in the lattice parameters observed in BTO and the resultant changes of strain between Fe_3O_4 and BTO.[19,20] For the measurement with increasing temperature, the magnetization jumps change signs (not shown) with hysteresis. Hysteresis exists throughout the orthorhombic phase, which corresponds to the hysteretic behavior of the lattice parameters throughout the orthorhombic phase of the BTO,[20] which is attributed to the irreversible formation of domains in the orthorhombic phase of BTO. So the magnetic property of the top Fe_3O_4 film are strongly modified by the BTO lattice distortions during its structural phase transitions via magnetoelastic coupling at the interface.

As shown in Figs. 2(b) and 2(c), both H_c and M_r/M_s of Fe_3O_4 change as a function of temperature with cooling process. The obvious shift of the coercivity at the phase transition of BTO implies the dramatic sensitivity of the Fe_3O_4 film magnetic property to the in-plane lattice distortions in the underlying BTO. The obvious jumps in coercivity of $\Delta H_c/H_c \approx 3\%$ and $\approx 26\%$ occurs at the $T \rightarrow O$ and $O \rightarrow R$ transitions of the BTO substrate. Correspondingly, the remanent magnetization shown in Fig. 2(c) presents a jump with $M_r/M_s \approx 26\%$ at the $O \rightarrow R$ transition, which is consistent with the change of the coercivity.

Since the in-plane magnetic property shows dramatic changes around the structural phase transitions of BTO, it is interesting to see the behavior of the out-of-plane magnetic property. Figure 3 is the hysteresis loops of Fe_3O_4/BTO measured at various temperatures ($140\ K \leqslant T \leqslant 300\ K$), the temperature dependence of magnetization, coercivity (H_c),

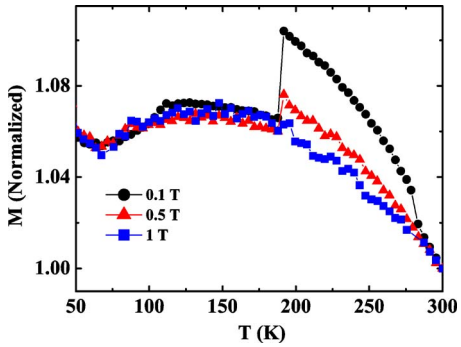

FIG. 4. (Color online) The normalized in-plane magnetization vs T for Fe_3O_4/BTO under different magnetic fields.

and the ratio of remanent to saturation magnetization (M_r/M_s). Compared with the in-plane magnetic hysteresis loops, the out-of-plane M-H curves measured perpendicular to the film plane exhibit a much slower approach to saturation, indicating the magnetic anisotropy of Fe_3O_4 film. With decreasing temperature, the jumps of the out-of-plane coercivity and remanent magnetization near the $T \rightarrow O$ transition is not obvious, while as shown in Figs. 3(b) and 3(c), the jumps near the $O \rightarrow R$ transition are dramatic with $\Delta H_c/H_c \approx 28\%$ and $M_r/M_s \approx 26\%$, respectively. The change in the coercivity and remanent magnetization correlates well with the changes of magnetization versus temperature shown in Fig. 3(b). It is noted that the signs of the jumps near the structural phase transition of BTO for the out-of-plane magnetic property are reverse to those of the in-plane magnetic property.

In order to get more insight into the origin of the magnetoelectric coupling between Fe_3O_4 and BTO, we also investigated the magnetic field dependence of the magnetization jumps and the results are shown in Fig. 4. It can be seen that the magnitudes of the magnetization jumps at the phase transitions of the BTO were suppressed by larger magnetic fields and almost no jumps were seen under a 1 T magnetic field. It is worth to note that we do not always produce sharp jump near the O-T transition, which could be caused by the different distributions of ferroelectric domains in different samples.

The temperature dependence of magnetization and the abrupt jumps at the phase transition temperatures of BTO observed in heterostructures composed of BTO and ferromagnetic are believed to be related to the strain effect.[8–13] We can consider the magnetoelastic energy induced uniaxial anisotropy, which has been used to explain the coupling effect between Fe and BTO,[12] to account for our results of Fe_3O_4/BTO heterostructures. The stress anisotropy energy can be expressed as $E=(-3/2)\,\lambda\sigma\cos^2\theta$, where λ and σ are the magnetostriction coefficient of the ferromagnetic material and the stress, respectively.[21] For Fe_3O_4, the in-plane direction is (100), which has a negative magnetostriction coefficient ($\lambda<0$).[21] In all temperature regimes, considering the difference of the in-plane lattice parameters between Fe_3O_4 and BTO, Fe_3O_4 film is under compressive stress ($\sigma<0$). Therefore, $\lambda\sigma \gg 0$, which means the energy is lower for the in-plane alignment of magnetization of Fe_3O_4. With decreasing temperature, the lattice mismatch between Fe_3O_4 and BTO increases abruptly at the $T \rightarrow O$ transition due to the dramatic decrease of the lattice parameter of BTO, resulting in the increase of the compressive stress and the resultant increase of strain anisotropy. This increase of strain anisotropy leads to the abrupt increase of the in-plane magnetization, coercivity, and remanent magnetization of Fe_3O_4 and the corresponding abrupt decrease of out-of-plane magnetization, coercivity, and remanent magnetization. While at the $O \rightarrow R$ transition, the lattice mismatch decreases abruptly due to the dramatic increase of the lattice parameter of BTO, resulting in a decrease of the compressive strain, which leads to the abrupt decrease of the in-plane magnetization, coercivity, and remanent magnetization of Fe_3O_4 and the corresponding abrupt increase of out-of-plane magnetization, coercivity, and remanent magnetization. For the suppression of the jumps of magnetization at the structural phase transition temperatures of BTO with strong magnetic field, it can be understood since all the magnetic domains are aligned by the magnetic field.

In summary, strong magnetoelectric coupling effect between Fe_3O_4 and BTO has been demonstrated. The magnetization, coercivity and remanent magnetization show dramatic jumps around the structural phase transition temperatures of BTO and these jumps can be suppressed by strong magnetic field. These results were explained by considering the interface strain induced anisotropy. This work indicates that ferroelectric substrates are useful for tuning the physical properties of oxide materials, which is significant for both research and device applications.

This work was supported by the National Science Foundation of China (Grant Nos. 50425205, 10674079, and 50272031), National 973 projects (Grant Nos. 2006CB921502 and 2002CB613505), and the Postdoctoral Foundation of China.

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