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Enhancement of ferroelectricity and ferromagnetism in rare earth element doped BiFeO3

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Abstract
Rare earth element doped BiFeO3 thin films were fabricated using the pulsed laser deposition method and various targets made from different starting Fe₂O₃ and Fe₃O₄ iron source materials. The films fabricated using the targets made from Fe₃O₄ exhibit great enhancement in their ferroelectricity, due to greatly reduced electrical leakage, as well as enhanced magnetization compared to those films deposited using targets from Fe₂O₃. It is suggested that the Fe³⁺ ion plays an important role in compensating for the charge imbalance and reducing current leakage, as well as enhancing the magnetic moment through the introduction of antiferromagnetic ordering at Fe²⁺ site.

Keywords
Enhancement, ferroelectricity, ferromagnetism, rare, earth, element, doped, BiFeO3

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Enhancement of ferroelectricity and ferromagnetism in rare earth element doped BiFeO$_3$

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Rare earth element doped BiFeO$_3$ thin films were fabricated using the pulsed laser deposition method and various targets made from different starting Fe$_2$O$_3$ and Fe$_3$O$_4$ iron source materials. The films fabricated using the targets made from Fe$_2$O$_4$ exhibit great enhancement in their ferroelectricity, due to greatly reduced electrical leakage, as well as enhanced magnetization compared to those films deposited using targets from Fe$_2$O$_3$. It is suggested that the Fe$^{2+}$ ion plays an important role in compensating for the charge imbalance and reducing current leakage, as well as enhancing the magnetic moment through the introduction of antiferromagnetic ordering at Fe$^{2+}$ site. © 2008 American Institute of Physics. [DOI: 10.1063/1.3035915]

BiFeO$_3$ (BF) is an excellent candidate for multifunctional applications at room temperature that are based on the magnetoelectric coupling effect in thin film samples since it has a high Curie temperature and a high Neel temperature ($T_C=1103$ K and $T_N=643$ K).$^1$ Since the renaissance of research into multiferroic phenomenon, significant improvements in both the ferroelectric and magnetic properties in BiFeO$_3$ have been achieved. For example, saturated ferroelectric hysteresis loops with large remnant polarization up to 60 $\mu$C/cm$^2$, as well as ferromagnetic hysteresis loops, have been observed in epitaxial BiFeO$_3$ thin films on single crystalline SrTiO$_3$ substrate.$^2,3$ Significant enhancement in both ferroelectric and ferromagnetic properties has also been achieved through sandwiching a barrier layer of insulating ferroelectric Bi$_4$Ti$_3$O$_12$ between the BiFeO$_3$ layer and the substrate or through codoping in both Bi and Fe sites in BiFeO$_3$ thin films.$^4,5$ Furthermore, improvements in the electrical polarization and the magnetic moment have been made through forming relaxor-type solid solution ferroelectrics and optimization of the preparation conditions.$^6-10$ However, it should be noted that much of the work reported so far only focus on the improvement in the ferromagnetic properties of BF films via chemical doping. There is a lack of study on whether or not both the ferroelectricity and the weak ferromagnetism can be significantly improved simultaneously. This issue is extremely important from the viewpoints of both fundamental and applied research.$^{11}$ Furthermore, the valence state of iron in BiFeO$_3$ is complicated due to the deficiency of Bi caused by the evaporation of Bi in the preparation process or oxygen vacancy. It has been believed that multiple valences of Fe$^{2+}$ and Fe$^{3+}$ can lead to different types of magnetism in BF, and the mixed valence of iron is also responsible for the electrical leakage in BiFeO$_3$. Therefore, it should be of crucial importance to investigate how the valence state of the iron source would affect the final ferroelectric and ferromagnetic performances in BiFeO$_3$. This is a very important issue that has not yet been noticed and studied before.

In this study, we report a significant effect of the iron source on both thin film and bulk BF samples. Both ferroelectricity and the weak ferromagnetism in doped BF can be significantly improved simultaneously by using Fe$_2$O$_4$ as the iron source rather than Fe$_2$O$_3$.

In this study, rare earth (RE) element doped bismuth ferrite ceramics with the general formula of Bi$_{0.5}$RE$_{0.1}$FeO$_3$ were fabricated by a traditional solid state reaction (RE=Gd, Nd, Sm). The starting materials included highly pure Bi$_2$O$_3$, La$_2$O$_3$, Gd$_2$O$_3$, Sm$_2$O$_3$, and Nd$_2$O$_5$. Two ceramic targets for each RE doped BiFeO$_3$ were fabricated using either Fe$_3$O$_4$ or Fe$_2$O$_3$ as the iron source material, respectively. These oxide materials were weighed out according to the molecular mole ratio with 5% extra bismuth, mixed and pressed into pellets, and then subsequently sintered at 1073 K for 3 h. The ceramics were crushed, ground, pressed into pellets, and sintered again at 1173 K for 1 h. The obtained ceramic pellets were used as targets for the thin film deposition. The thin film samples used in this work were deposited using a pulsed laser deposition system. Third harmonic generation of a neodymium-doped yttrium aluminum garnet laser with a wavelength of 355 nm and a repetition rate of 10 Hz was used as the laser source. The thick films were initially deposited on Pt/Ti/SiO$_2$/Si substrate at 550 °C, then cooled down to room temperature, following a rapid thermal process approach. During the deposition, the dynamic oxygen flow pressure was kept at 20 mTorr. All the films used in this study were made using exactly the same deposition conditions.

The phases and structures of the as-deposited films were determined by x-ray diffraction (XRD) using the Cu $K\alpha$ radiation of a JEOL 3500 XRD machine. Pt upper electrodes with an area of 0.0314 mm$^2$ were deposited by magnetron sputtering through a metal shadow mask. The thickness of the films was measured by an optical reflection method with a Filmtk™ 4000 system from Scientific Computing Interna-

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Results showed that all the thin films had a thickness of around 600 nm. The ferroelectric properties were measured at room temperature by an aixACCT EASY CHECK 300 ferroelectric tester. Magnetic properties of the thin film and ceramics samples were investigated using a Quantum Design magnetic properties measurement system.

Figure 1 shows the XRD patterns of the RE doped bismuth ferrite thin films. The XRD patterns of the doped BiFeO$_3$ thin films with the different iron sources, Fe$_2$O$_3$ and Fe$_3$O$_4$, are also shown for comparison. All the thin films doped with 10% RE elements, including Gd, Nd, and Sm, are single phase, with a structure that is the same as that of undoped BiFeO$_3$, regardless of the different starting iron source materials. What is important for our films is that we found no trace of any impurities in the deposited thin films.

Figure 2 shows the electrical polarization hysteresis loops ($P-E$ loops) of the RE doped bismuth ferrite thin films made from the targets with different iron source materials. The $P-E$ loops of the films fabricated from Fe$_2$O$_3$ targets are very rounded in shape, which means that these films are very leaky. However, the thin films deposited from targets with Fe$_3$O$_4$ as the starting iron source show much improved $P-E$ loops. The electrical leakage feature is greatly reduced. The remnant polarization of the 10% Nd and 10% Sm doped bismuth ferrite films made from the target with Fe$_3$O$_4$ as the iron source is around 80 $\mu$C/cm$^2$. This value is among the highest in all the BiFeO$_3$ reported so far and is very close to that of La and Nb codoped BiFeO$_3$ thin films. However, the 10% Gd doped BiFeO$_3$ thin film shows a remnant polarization of 40 $\mu$C/cm$^2$.

It should be noted that the $P-E$ loops for the BiFeO$_3$ thin films with starting materials including Fe$_3$O$_4$ are asymmetric. Asymmetry in a $P-E$ loop is usually seen if the top and bottom electrodes are asymmetric, but this is not the case for the thin films in the present study. Another possible reason for the observed asymmetry in $P-H$ loop is the existence of internal bias in the samples. For the ferroelectric materials, the internal bias usually is caused by pinning of oxygen vacancy at the domain wall. The samples fabricated using Fe$_3$O$_4$ iron source may contain more oxygen vacancy.

Figure 3 shows the magnetic properties of all the RE doped bismuth ferrite bulk samples with different starting iron source materials. The magnetization curves of the RE doped BiFeO$_3$ targets from different iron source materials (A) 10% Gd, (B) 10% Sm, and (C) 10% Nd doped BiFeO$_3$. 

FIG. 1. The XRD patterns of the RE doped BiFeO$_3$ thin films from targets with different iron source materials on Pt/Ti/SiO$_2$/Si substrate (a) 10% Gd, (b) 10% Nd doped, and (c) 10% Sm.

FIG. 2. Ferroelectrical polarization hysteresis loops ($P-E$ loop) of the RE doped BiFeO$_3$ thin films on Pt/Ti/SiO$_2$/Si made using different starting iron source targets. (A1) 10% Nd with Fe$_2$O$_3$, (A2) 10% Nd with Fe$_3$O$_4$, (B1) 10% Sm with Fe$_2$O$_3$, (B2) 10% Sm with Fe$_3$O$_4$, (C1) 10% Gd with Fe$_2$O$_3$, and (C2) 10% Gd with Fe$_3$O$_4$. All the loops were measured at a frequency of 100 Hz and room temperature.

FIG. 3. (Color online) The magnetization curves of the RE doped BiFeO$_3$ targets from different iron source materials (A) 10% Gd, (B) 10% Sm, and (C) 10% Nd doped BiFeO$_3$. 

iron source materials. RE element doped BiFeO₃ thin film samples are characterized by a net magnetic moment starting above room temperature (not shown here), while magnetization hysteresis (M-H) loops are not observed, due to the very strong diamagnetic signal from the substrate. Therefore, the target ceramics from different iron sources were measured in stead of thin films to check any difference in their magnetic properties caused by the iron sources. Results show that all the RE element doped bismuth ferrites, the values of the RE elements have strong magnetic moments. Therefore, in this study, which could be decreased bismuth deficiency in this case, the Fe²⁺ ions introduced into BiFeO₃ by Fe₃O₄ starting material under special treatment conditions, Fe²⁺ is the key to fabricating more insulating BiFeO₃ films. Both the ferroelectricity and the ferromagnetism in doped BF can be improved simultaneously by using Fe₃O₄ as the iron source.

We have shown that an Fe₃O₄ iron source is very critical for achieving better ferroelectric performance in the aspect of reduced electrical leakage in bismuth ferrite thin film, at least for the processing conditions presented in this work, although we cannot exclude the possibility that the electrical leakage problem in the BiFeO₃ may also be overcome using Fe₂O₃ as the starting material under special treatment conditions. Our work does indicate that under the normal processing conditions, Fe²⁺ is the key to fabricating more insulating BiFeO₃ films. Both the ferroelectricity and the ferromagnetism in doped BF can be improved simultaneously by using Fe₃O₄ as the iron source.

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