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Abstract

Rare earth element doped $BiFeO_3$ thin films were fabricated using the pulsed laser deposition method and various targets made from different starting Fe_2O_3 and Fe_3O_4 iron source materials. The films fabricated using the targets made from Fe_3O_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_2O_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 antiferrimagnetic ordering at Fe^{2+} 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_2O_3 and Fe_3O_4 iron source materials. The films fabricated using the targets made from Fe_3O_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_2O_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 antiferrimagnetic 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 $Bi_4Ti_3O_{12}$ 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_3O_4 as the iron source rather than Fe_2O_3.

In this study, rare earth (RE) element doped bismuth ferrite ceramics with the general formula of $Bi_{0.9}RE_{0.1}FeO_3$ were fabricated by a traditional solid state reaction (RE =Gd, Nd, Sm). The starting materials included highly pure Bi_2O_3, La_2O_3, Gd_2O_3, Sm_2O_3, and Nd_2O_5. Two ceramic targets for each RE doped $BiFeO_3$ were fabricated using either Fe_3O_4 or Fe_2O_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 thin 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 Filmtek™ 4000 system from Scientific Computing Interna-

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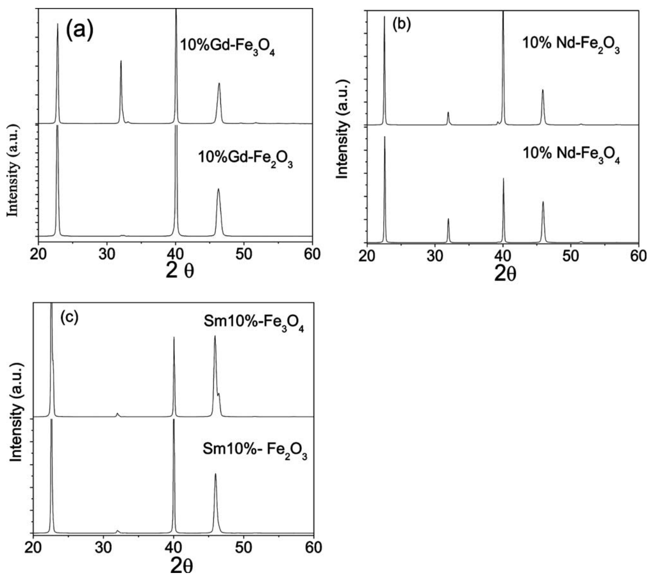

FIG. 1. The XRD patterns of the RE doped $BiFeO_3$ thin films from targets with different iron source materials on $Pt/Ti/SiO_2/Si$ substrate (a) 10% Gd, (b) 10% Nd doped, and (c) 10% Sm.

tional, USA. 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_2O_3 and Fe_3O_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 starting iron sources on plantized silicon substrates. It is obvious that for the same RE element doped $BiFeO_3$ thin film, the *P-E* loops are significantly different for different starting iron source targets. All the loops of the films fabricated from Fe_2O_3 targets are very rounded in shape, which means that these films are very leaky. However, the thin films deposited from targets with Fe_3O_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_3O_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.[11] 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_3O_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

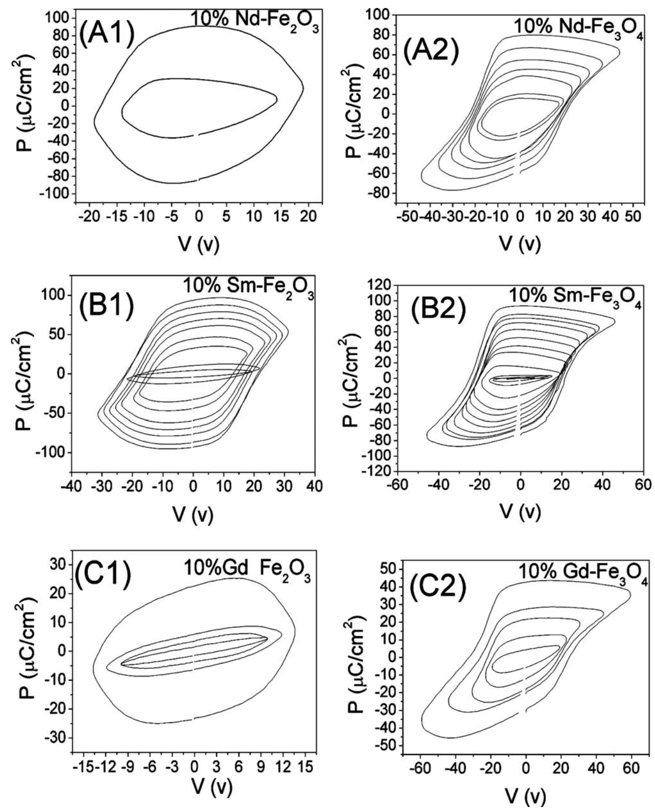

FIG. 2. Ferroelectrical polarization hysteresis loops (*P-E* loop) of the RE doped $BiFeO_3$ thin films on $Pt/Ti/SiO_2/Si$ made using different starting iron source targets. (A1) 10% Nd with Fe_2O_3, (A2) 10% Nd with Fe_3O_4, (B1) 10% Sm with Fe_2O_3, (B2) 10% Sm with Fe_3O_4, (C1) 10% Gd with Fe_2O_3, and (C2) 10% Gd with Fe_3O_4. All the loops were measured at a frequency of 100 Hz and room temperature.

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_3O_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

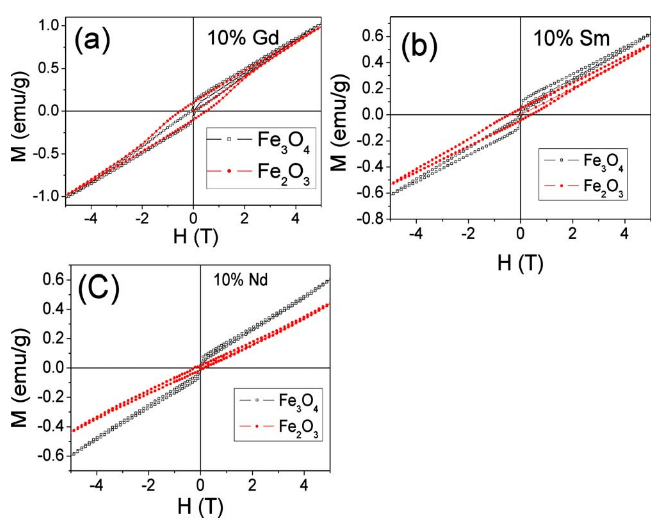

FIG. 3. (Color online) The magnetization curves of the RE doped $BiFeO_3$ targets from different iron source materials (A) 10% Gd, (B) 10% Sm, and (C) 10% Nd doped $BiFeO_3$.

iron source materials. RE element doped $BiFeO_3$ 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 doped $BiFeO_3$ targets show much enhanced magnetization with weak ferromagnetic hysteresis properties in comparison to the undoped $BiFeO_3$ sample.[4] Importantly, the differences in the *M-H* loops of the $BiFeO_3$ bulk samples made from different iron source materials are very obvious. The samples made using Fe_2O_3 show much larger coercive fields than those using Fe_3O_4 as the iron source. However, as shown in the *M-H* loops, the $BiFeO_3$ samples made from Fe_3O_4 exhibit superior ferromagnetic properties, with much enhanced magnetization at room temperature in both low and high fields compared to the Fe_2O_3 samples, except in the case of the Gd doped material for which the enhancement of magnetization is not as significant as the other two RE element doped samples. The magnetization values can reach 0.5 or 1 emu/g for RE=Nd and Sm or Gd, respectively. These are among the highest values for all the BF films reported so far.

Let us briefly discuss why the different iron oxides might lead to different performances in both the ferroelectric and magnetic states in RE element doped $BiFeO_3$. $BiFeO_3$ has a *G*-type antiferromagnetic ordered cycloid spin structure with a periodicity of about 62 nm. This unique spin arrangement cancels any macroscopic magnetic moment in single crystals, but in thin films or ceramics, this periodical structure could be broken due to the dimensional limitations of the grains. Also, the doping with RE elements can change the magnetic structure of bismuth ferrite, especially since some RE elements have strong magnetic moments. Therefore, in all the RE element doped bismuth ferrites, the values of the magnetic moment are improved. The differences in the *M-H* loops of the target ceramics from different iron source materials are to be expected, due to the variation in the iron valence states. It has been well accepted that bismuth deficiency is very common in bismuth ferrite due to the high volatility of the bismuth during the synthesizing process. However, 5% extra bismuth has been added into the target in this study, which could be decreased bismuth deficiency in thin films and targets in some extent. Another possibility is the existence of the oxygen vacancies in bismuth ferrite, which is very common for perovskite structured ferroelectric materials. The oxygen vacancy can cause a serious charge imbalance in the bismuth ferrite and thus can lead to a serious electrical leakage problem, which is the case in the ferroelectric loop measurements presented in this work. However, the Fe^{+2} ions introduced into $BiFeO_3$ by Fe_3O_4 starting material can compensate for the charge imbalance caused by the oxygen vacancy. This is clearly evidenced by the significant decrease in the electrical leakage in films deposited from the targets using Fe_3O_4 starting material, in which the Fe^{2+} content is as rich as the Fe^{3+}. Although the charge is more balanced in $BiFeO_3$ due to the existence of Fe^{2+}, the existence of Fe^{2+} will produce more oxygen vacancy. The pinning of oxygen vacancy at domain wall will be more serious due to the existence of more oxygen vacancy. As a result of pinning, internal bias will produce and cause asymmetry in the *P-E* loop. For the magnetic moment, the introduction of Fe^{2+} with an out shell electron configuration of $3d^6$ in $BiFeO_3$ to replace Fe^{3+} with an out shell electron configuration of $3d^5$ will modify the magnetic structure from antiferromagnetic to antiferrimagnetic at the Fe^{2+} site due to the different magnetic moments of Fe^{2+} and Fe^{3+}. The enhancement of magnetic moment in targets from a Fe_3O_4 iron source revealed that the valence state of the iron ions does not completely change during the sintering process. That is to say, not all of the Fe^{2+} ions can be oxidized into Fe^{3+} ions during the sintering process in ambient atmosphere. Therefore, Fe^{2+} ions can coexist with Fe^{3+} in the $BiFeO_3$ lattices and remain as Fe^{2+} if Fe_3O_4 is used as starting iron source. However, this speculation needs direct evidence, such as valence determination by x-ray photoluminescence spectra. Further experiment in checking valence state of iron in $BiFeO_3$ is undergoing.

We have shown that an Fe_3O_4 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 $BiFeO_3$ may also be overcome using Fe_2O_3 as the starting material under special treatment conditions. Our work does indicate that under the normal processing conditions, Fe^{2+} is the key to fabricating more insulating $BiFeO_3$ films. Both the ferroelectricity and the ferromagnetism in doped BF can be improved simultaneously by using Fe_3O_4 as the iron source.

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