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Magnetic properties of La doped Bi₂FeMnO₆ ceramic and film

Abstract

We present a comprehensive study of the magnetic properties for La doped Bi₂FeMnO₆ (LBFM) ceramic and film which was first deposited on (100) SrTiO₃ substrate by pulsed laser deposition method. The LBFM film is antiferromagnetic or weak ferrimagnetic at room temperature and it shows clear magnetic anisotropy. But it is not sure whether the spin-glass behavior is present in LBFM film because of the influence from substrate. Compared to the film, LBFM ceramic shows different magnetic properties. It has a lower T_N and all the observations indicate that LBFM ceramic shows spin-glass behavior.

Keywords

Magnetic, properties, doped, Bi₂FeMnO₆, ceramic, film

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Magnetic properties of La doped $\text{Bi}_2\text{FeMnO}_6$ ceramic and film

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We present a comprehensive study of the magnetic properties for La doped $\text{Bi}_2\text{FeMnO}_6$ (LBFM) ceramic and film which was first deposited on (100) SrTiO_3 substrate by pulsed laser deposition method. The LBFM film is antiferromagnetic or weak ferrimagnetic at room temperature and it shows clear magnetic anisotropy. But it is not sure whether the spin-glass behavior is present in LBFM film because of the influence from substrate. Compared to the film, LBFM ceramic shows different magnetic properties. It has a lower T_N and all the observations indicate that LBFM ceramic shows spin-glass behavior. © 2010 American Institute of Physics. [doi:10.1063/1.3503397]

I. INTRODUCTION

In recent years, double perovskites of $\text{A}_2\text{BB}'\text{O}_6$ ($\text{A}=\text{La}$, Bi , etc.; B or B' =transition metal such as Ni , Mn , Fe , and Co) have gained much interests.^{1–3} According to Goodenough–Kanamori’s rules, the superexchange magnetic interaction between B and B' , with and without e_g electrons, may lead to ferromagnetic oxides through $\text{B}-\text{O}-\text{B}'-\text{O}-\text{B}$ ordering.^{4–6} Increasing interests are focused on their attractive behaviors which are related to the coexistence of different competing factors of spin, charge, or orbital and lattice degrees of freedom, phase, mixed-valence and so on.^{7–9} In addition, they exhibit multifunctional behaviors, which make them promising candidates for spintronic applications. Recently, pulsed laser deposition (PLD) of epitaxial $\text{Bi}_2\text{FeMnO}_6$ films has also been reported.^{10,11} The stabilization of single-phase Bi-based perovskites are difficult because of their tendency of multiphase formation and the high volatility of bismuth.¹² Stabilization can be facilitated by a partial replacement of Bi^{3+} cations by La cations.^{13–16} In addition, $\text{LaMn}_{1-x}\text{Fe}_x\text{O}_3$ including $\text{La}_2\text{FeMnO}_6$ has been also reported to be an interesting mixed-valence manganites with perovskite structure.^{7,17,18} Therefore, La was chosen to substitute Bi in $\text{Bi}_2\text{FeMnO}_6$ to stabilization the phase.

Because the structure of films deposited at different conditions is still difficult to confirm, there will be always some difference in electric and magnetic properties between bulk and thin film samples.¹⁹ The structure and properties of the films were found to depend on the substrate type, film thickness, process condition during deposition, B/B' ordering and so on. In such a case, both La doped $\text{Bi}_2\text{FeMnO}_6$ (LBFM) ceramic and thin films were studied in the present paper.

II. EXPERIMENTAL DETAILS

Polycrystalline 20 mol % LBFM ceramics were synthesized by conventional solid state method as the target. LBFM

films were deposited on (100) SrTiO_3 substrate using a PLD system at 650 °C with 500–600 mTorr dynamic oxygen. The film was annealed at the same condition for 10 min and then cooled to room temperature rapidly. The phases of the target and film were determined by x-ray diffraction (XRD) using $\text{Cu } K\alpha$ radiation. Magnetic properties were measured using the commercial Quantum Design superconducting quantum interference device magnetometer (MPMS).

III. EXPERIMENTAL RESULTS AND DISCUSSION

As shown in Fig. 1, the LBFM diffraction peaks of (100), (200), and (300) were observed in the XRD pattern. It indicates the epitaxial growth of LBFM film on (100) SrTiO_3 (STO) substrate. There is no traceable impurity in the film which is believed to have a bulklike cubic structure. But there are unavoidable impurities of bismuth oxides in LBFM ceramics, which make the ceramic have worse crystalline quality than LBFM film.

As shown in Fig. 2(a), the magnetization hysteresis loops of LBFM film were measured at 5, 20, 50, 100, and 300 K. The inset is the magnification of hysteresis loops at 300 K. There is no change in the loop width below 20 K, but at higher temperature the loop width decreased rapidly as the increase in temperature. The M-H loops show small hysteresis.

FIG. 1. XRD pattern for LBFM film fabricated on (100) STO.

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FIG. 2. (Color online) Magnetization hysteresis loops of LBFM film (a) measured at various temperatures and the inset shows magnification of the hysteresis loops at 300 K; (b) measured with magnetic field applied parallel and perpendicular to the sample plane.

esis with small magnetization values which increases linearly with magnetic field and do not saturate at high magnetic field. This is a strong indication that our samples are antiferromagnetic or weak ferrimagnetic (ferromagnetic plus antiferromagnetic configuration) at room temperature. Figure 2(b) shows the in-plane and out-of-plane magnetic field dependence of magnetization measured at 5 K. The film shows anisotropy and out-of-plane is the easy magnetization direction.^{11,20} The out-of-plane zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves measured between 5 and 350 K were shown in Fig. 3. A spin-glasslike behavior was occurred at 18 K at 1 kOe applied field. This behavior is similar to $\text{Bi}_2\text{FeMnO}_6$ film.¹¹ It was not overwhelmed at 10 kOe as shown in Fig. 3 as an inset but the peak temperature shifts from 18 to 10 K. As we know, the ac magnetization measurement is very useful for the investigation of the spin

FIG. 3. (Color online) Temperature dependence of ZFC and FC magnetizations of LBFM film recorded at 1 kOe. The inset shows ZFC results at 10 kOe.

FIG. 4. (Color online) Magnetization hysteresis loops of LBFM ceramic measured at various temperatures. The inset shows the amplification of the loop at 160 K.

glass behavior. We have performed the frequency dependent measurement of the magnetization but there are many noises because of the influences of the substrate. The results are not shown because they are useless for the analysis of spin-glass. In such a case, whether the phenomena in the LBFM film can be classified as a classical spin-glass still remains open.

Figure 4 shows the magnetization hysteresis loops of LBFM ceramic measured at various temperatures. The sample shows unsaturated magnetization for an applied magnetic field up to 1 T. The magnetizations at 1 T for LBFM ceramic are 2.88, 1.94, 0.46, and 0.26 emu/g , corresponding to the temperature of 5 K, 50 K, 160 K, and 300 K, respectively. The inset shows the amplification of the loop at 160 K, a very small magnetic hysteresis was observed. While the hysteresis disappears at 300 K that is different from the LBFM film [shown in Fig. 2(a) inset]. Because the structure and properties of the LBFM films can vary depending on the substrate type, film thickness, and deposition conditions.

As shown in Fig. 5, ZFC and FC curves of LBFM ceramic were recorded at different applied field of 500 Oe, 1 kOe, 5 kOe, and 10 kOe. Similar to $\text{Bi}_2\text{FeMnO}_6$ film¹¹ and LBFM film, a spin-glasslike behavior was also observed. The ZFC-peak was not suppressed as the field reached 10 kOe and it shows field dependence. It is difficult to obtain the exact transition temperature. However, it is clear that the ZFC-peak temperature gradually decreases as the increase in the applied field. The high temperature (5–350 K) ZFC and

FIG. 5. (Color online) ZFC and FC magnetizations of LBFM ceramic recorded at different applied field of 500 Oe, 1 kOe, 5 kOe, and 10 kOe.

FIG. 6. (Color online) ZFC and FC magnetizations of LBFM ceramic recorded at 10 kOe, inset is the plot of $1/\chi$ vs temperature fitted to Curie-Weiss law.

FC magnetizations of LBFM ceramic were recorded at 10 kOe as shown in Fig. 6. The inset figure shows the reverse susceptibility ($1/\chi$) of LBFM ceramic. Above the spin-glass behavior, the antiferromagnetic transition at 250 K was observed. Bi *et al.*¹⁰ has calculated three structures of $\text{Bi}_2\text{FeMnO}_6$. For LBFM, we believe it exhibits phase transition although the uncertainties of the exact phases. The data from 350 to 250 K were fitted to the Curie-Weiss law. The parameters of Curie constant (C), effective paramagnetic moment (μ_{eff}), and Weiss constant (θ) were determined by the Curie-Weiss fitting to be $1.92 \text{ emu K mol}^{-1} \text{ f.u.}$, $3.91 \mu_B$, and -9 K , respectively.

As shown in Fig. 7(a), from the real part of ac susceptibility measured at different frequencies, we can see a peak

FIG. 7. (Color online) (a) Temperature dependence of the ac magnetization obtained with different frequencies, inset figure shows the shift in peak temperature (T_{peak}) with frequency; (b) the ac magnetization vs temperature under different applied static field and 10 Hz fixed frequency and $h_{\text{ac}} = 1 \text{ Oe}$.

which changes very little with different frequency (inset figure). The possible shift to high frequency is not clear, that is partially due to the less points measured around the peak. However, it can be found that all the curves on the left side shift clearly to high frequency, while, the curves on the right side of the peak remain the same as that of the lowest frequency. Figure 7(b) shows the real part of ac magnetization versus temperature at 10 Hz fixed frequency and $h_{\text{ac}} = 1 \text{ Oe}$. Different static fields of 200 Oe, 500 Oe, 700 Oe, 1 kOe, and 10 kOe were applied. It clearly shows that the values of m' decreased and the peak moved to low temperature when the field increases. This indicates that the possible spin glass state takes place at low temperature when increasing magnetic field. In another word, the magnetic field pushes the spin glass to occur at low temperature.

There are hysteresis loops below the spin glass transition temperature as show in Fig. 4 and a small negative θ value was obtained through the Curie-Weiss fitting in Fig. 6 inset. Therefore, similar to BiFeO_3 (Ref. 21) there are at least three clear evidences for spin-glass behavior in LBFM ceramic: first, there is a large difference between FC and ZFC at low temperature; second, the cusp was observed in ZFC curves; third, the peak temperature is dependent upon the frequency and applied field. Based on these data, we propose that the spin glass state probably arises from a weak ferromagnetic or ferrimagnetic transition around the T_g , or from the competition between ferromagnetic and antiferromagnetic transition.

IV. SUMMARY

LBFM ceramic and film which was deposited on (100) SrTiO_3 by PLD method are first studied. The LBFM film is antiferromagnetic or weak ferrimagnetic (ferromagnetic plus antiferromagnetic configuration) at room temperature. However, further studies should be carried out on the determination of antiferromagnetic spin configuration using neutron diffraction at temperatures above room temperature. Because of the substrate influence, whether the phenomena in the LBFM film can be classified as a classical spin-glass still remains open. For the LBFM ceramic, all the observations indicate that the spin glass state is present at low temperature. While compared to LBFM film, the ceramic shows a T_N below room temperature. The different properties between film and ceramic are due to the delicate effects like structure, strain, valence, spin, charge and so on.

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