Journal of Alloys and Compounds 669 (2016) 141–145

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Ferroelectric polarization induced nonvolatile modulation effect on magnetic properties in $Bi_{0.95}Ba_{0.05}FeO_3$ multiferroics

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ARTICLE INFO

Article history:
Received 13 October 2015
Received in revised form
25 January 2016
Accepted 29 January 2016
Available online 2 February 2016

Keywords:
Single phase multiferroics
Nonvolatile modulation
Magnetic properties
Raman spectrum
Electric field

ABSTRACT

In this paper, we demonstrate a nonvolatile modulation effect on the magnetic properties by electric (E)-field-induced ferroelectric (FE) polarizing in $Bi_{0.95}Ba_{0.05}FeO_3$ single-phase multiferroics. It is found that E-field has much effect on weak ferromagnetic order, but has little effect on strong antiferromagnetic order in the sample. The change of Raman scattering spectra with different FE polar states of the sample, as well as the magnetization change under different polarization times (t_p), indicates that the modulation effect on magnetism comes from E-field-induced the change of FE polarization, which couples with magnetic moments in $Bi_{0.95}Ba_{0.05}FeO_3$ sample.

1. Introduction

In the last decade or more, $BiFeO_3$ has been the most heavily investigated single-phase multiferroic due to the coexistence of its ferroelectric order and magnetic order at room temperature [1–6]. To date, three main aspects about $BiFeO_3$ have been well investigated. First, improving weak ferromagnetic properties in $BiFeO_3$ by elements substitution engineering [3,7–12]. Secondly, electric-field control of magnetism in ferromagnet/$BiFeO_3$ heterostructures [13–15], such as $Co_{0.90}Fe_{0.10}/BiFeO_3$ [16–19], $La_{0.7}Sr_{0.3}MnO_3/BiFeO_3$ [20,21], Permalloy/$BiFeO_3$ [22] and so on. In these heterostructures, $BiFeO_3$ served as an electrically controllable antiferromagnetic (AFM) pinning layer. And magnetic order in $BiFeO_3$ couples with ferromagnetic (FM) order in FM layer through interface exchange interaction, providing a pathway of modulating magnetism by an electric field. Thirdly, magnetoelectric (ME) coupling in $BiFeO_3$ bulk, thin films and nanowires [6,23–28]. In pure $BiFeO_3$, the intrinsic ME coupling between FE order and FM order has been confirmed [23–26] since it was first reported in $BiFeO_3$ thin film in 2003 [1]. Recently, electric-field controlling weak FM by a two-step sequential rotation of polarization vector in $BiFeO_3$ was predicted and was verified experimentally in $Co_{0.9}Fe_{0.1}/BiFeO_3$ heterostructure [26], which means that deterministic switching of the weak FM in $BiFeO_3$ is possible by the oxygen octahedral rotations following with E-field induced polarization rotation. However, this intrinsic ME coupling is also found to be relative weak [28–30]. The ME coefficient is much smaller than that in FM/FE composite [31,32]. One of the reasons may be the weak FM arisen from the canting of the antiferromagnetically aligned Fe^{3+} spins [33], which comes from the antisymmetric exchange (DM) interaction in $BiFeO_3$ [24,26]. It have been well reported that the enhanced ferromagnetism can be achieved in some A-site element substitution $BiFeO_3$ systems [7–12]. Therefore, enhanced ME coupling is desired in doped-$BiFeO_3$ single-phase multiferroics, in which relative few work about ME coupling had yet been done [6,16,28–30]. And the intrinsic coupling between FM and FE orders is deserved to be well further investigated for these single-phase multiferroics. In this paper, the magnetic properties of Ba-doped $BiFeO_3$ sample was investigated when the sample was in different ferroelectric polar states induced by E-field. Obvious nonvolatile modulation effect of E-field on magnetism was observed. Raman scattering spectra (*Rss*) was proposed to detect the E-field induced FE polarization, which couples with magnetic moments in the sample.

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http://dx.doi.org/10.1016/j.jallcom.2016.01.241
0925-8388/

2. Experiment

$Bi_{095}Ba_{0.05}FeO_3$ (named as BBFO) fine powders were prepared by sol–gel method. First, calculated amounts of high-purity bismuth nitrate ($Bi(NO_3)_3 \cdot 5H_2O$), ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) and barium nitrate ($Ba(NO_3)_2 \cdot 6H_2O$) were orderly dissolved in moderate deionized water (named as solution-1). Second, suitable amount of citric acid was dissolved in moderate ethylene glycol (solution-2). Third, solution-1 was slowly poured into solution-2 with continuously magnetic stirring to form transparent sol. The sol was then water-bath heated at 80 °C for 10 h, and then was dried in an oven maintained at 120 °C to get fluffy gel. Finally, the fluffy gel was calcined at 300 °C to get rid of organic matters. The obtained calcined-powders were then pressed into a bar and sintered at 800 °C for 450 s with a high heating rate of about 100 °C/s, then cooled rapidly to room temperature. The crystal structure of the sample was examined using X-ray diffraction (XRD). The chemical composition of the sample was checked by measuring the Energy Dispersion Spectrum (EDS). The bulk sample was cut into a 2 × 2 × 0.2 mm (L × W × H) slice. Capacitive structure with silver electrode was prepared for applying E-field on the slice, as shown in the inset of Fig. 1. Ferroelectric properties of the sample were measured by using a Ferroelectric test device (*Radiant MultiFerroic system*, Radiant Co., USA). Magnetic measurements were performed using a vibrating sample magnetometer (VersLab-VSM, Quantum Design Co., San Diego, CA, USA). Raman spectrometer (LabRAM HR Evolution, Jobin Yvon Co., Longjumeau, France) with laser wavelength of 532 nm was used to detect the *Rss* of the sample. In *Rss* measurements, the laser was accurately focused on the surface of the BBFO sample by tuning the objective lens in the Raman device. Then, *Rss* of the BBFO sample was measured. Continually, several *Rss* of BBFO sample were measured after the sample was polarized by different electric fields, respectively.

3. Results and discussion

The x-ray diffraction pattern of the BBFO sample is shown in Fig. 1. The peaks in XRD patterns consistent with a rhombohedral structure of space group (*R3c*) [6,23]. The sharpness features of the peaks indicate a high quality polycrystalline sample. No obvious trace of other impurity phases is indexed within the uncertainty of XRD, indicating the single phase formation of the BBFO sample, which is also confirmed by *Rss* of the sample shown later. Besides, the experimental results of the Energy Dispersion Spectrum (EDS) for the BBFO sample indicates the chemical uniformity and proper composition of the BBFO sample.

The ferroelectric properties of BBFO sample is presented in Fig. 2. It is obvious that distinct hysteresis characteristics can be observed in these BBFO sample. Besides, it can be obtained from the figure that, the values of remnant polarization (P_r) is 1.77 and 3.99 μC/cm^2 when the sample is polarized by E-fields of 10 and 20 kV/cm, respectively.

The tuning effect of E-field on magnetism of the BBFO sample was investigated by measuring magnetic hysteresis loops and thermomagnetic curves after BBFO slice was polarized by different E-fields. Here, we demonstrate that, before performing each magnetic measurement, an E-field is applied to the BBFO sample for some time (i.e., polarization time, t_P) and then is turned off. We name this E-field as the *ex situ* E-field (named as E_{ex}) to distinguish from *in situ* measurements, where the E-field is *in situ* applied to the sample during ongoing magnetic measurements. Fig. 3(a) presents typical M–H results with different E_{ex} at room temperature. It can be observed that the sample presents weak FM with an obvious AFM background that is weakened in thin film because of the suppression of the long-range AFM order [23,25]. The antisymmetric exchange interaction, which manifests from spin–orbit coupling, produces this weak FM through the canting of the Fe^{3+} spins [26,33]. This M–H behavior is similar to that reported in bulk $BiFeO_3$ [29]. In order to investigate E-field modulation effect on magnetism in BBFO sample, we performed the magnetic properties measurements when the BBFO sample was in different FE polar states produced by applying different E_{ex}. Fig. 3(a) presents the experimental results. We can see that M–H loop changes after BBFO sample suffered different E_{ex}, which means modulation effect of E-field on magnetism can be obtained directly in single-phase multiferroics. To further understand the relation between M and E_{ex}, we present the E_{ex} dependence of M for the BBFO sample with H = 5 kOe and T = 300 K, as shown in the inset of Fig. 3(a). It can be seen that M changes rapidly with E_{ex} increasing up to about 8–10 kV/cm, and then decreases with E_{ex} further increasing up to 20 kV/cm. It was reported that remnant magnetization (M_r) changes linearly with the change of E-field in $BiFeO_3$ thin film [30], where E-field is *in situ* applied to the film, and linear reverse piezoelectric (RPE) effect play a role in the linear ME effect in $BiFeO_3$ thin film. In our case, RPE effect should not play a role because E_{ex} is turned off (and RPE effect vanishes) when performing magnetic loop measurements. Here, the role of E_{ex} is to change the FE polar state of BBFO, as can be verified from the ferroelectric hysteresis loops shown in Fig. 2, where the remnant polar state (characterized by P_r) of BBFO is change by different E_{ex}. Besides, it is

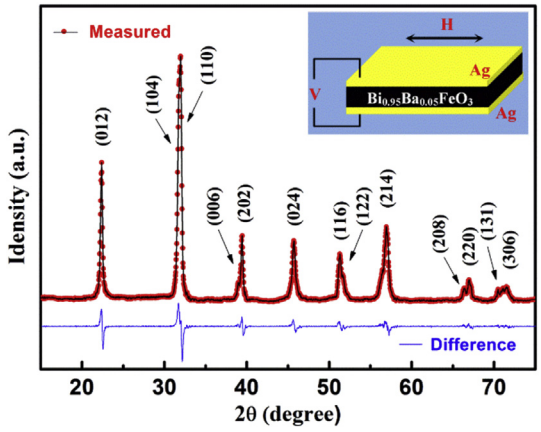

Fig. 1. The x-ray diffraction patterns of $Bi_{0.95}Ba_{0.05}FeO_3$ sample. The inset shows the schematic of the sample for magnetoelectric measurements.

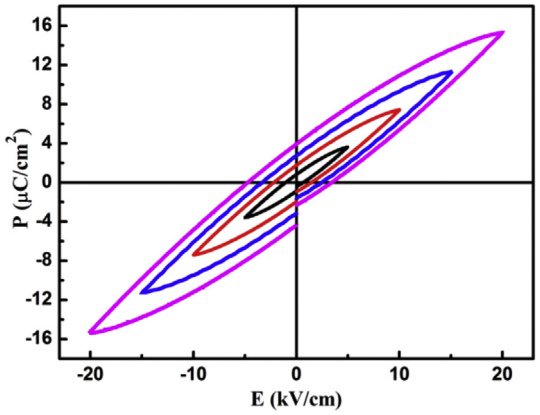

Fig. 2. Ferroelectric hysteresis loop of $Bi_{0.95}Ba_{0.05}FeO_3$ sample with different electric fields.

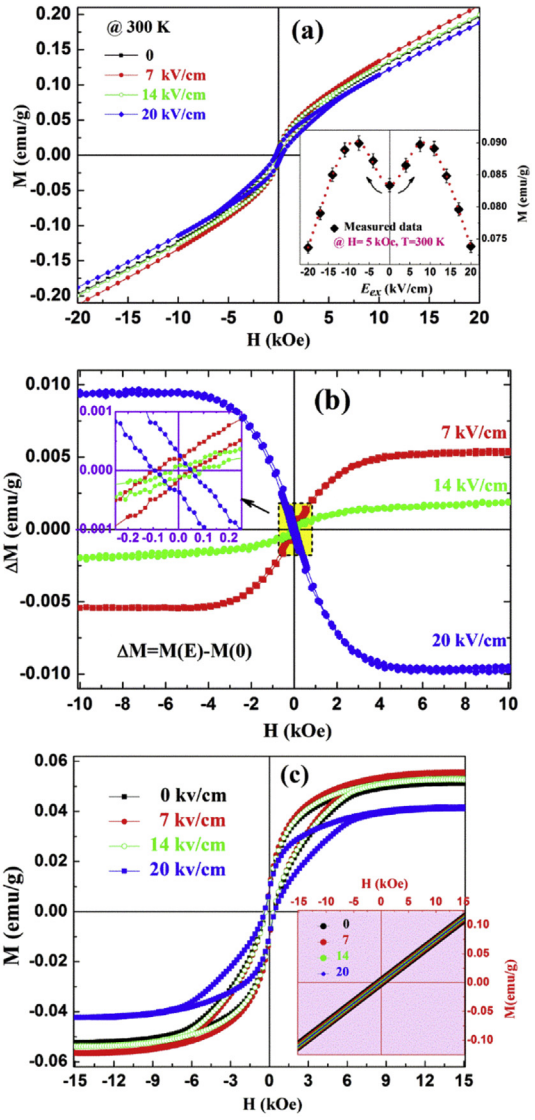

Fig. 3. (a) Typical M–H loops with different E_{ex} for $Bi_{0.95}Ba_{0.05}FeO_3$ sample at room temperature. The inset presents the dependence of M on E_{ex} with H = 5 kOe. (b) Magnetization shift (ΔM) as a function of H with different E_{ex}. (c) M–H loops of ferromagnetic hysteresis parts in $Bi_{0.95}Ba_{0.05}FeO_3$ sample with different E_{ex}. The inset presents the linear M–H parts, which corresponds to the antiferromagnetic parts. The above M–H results were calculated from Fig. 2(a) according to the linear relation between M and H in pure antiferromagnetic materials.

observed from the inset of Fig. 3(a) that, the behavior that M changes with E_{ex} is similar when E_{ex} was set as different directions, which induces different directions of FE polarization in BBFO slice. Therefore, the change behavior of M may correspond to the different FE polar states of the sample.

Different magnetic states, such as remnant magnetic (M_r) and saturated magnetic (M_s) state, may affect the tuning effect of E_{ex}, According to the M–H loops in Fig. 3(a), we calculated the values of magnetization shift (ΔM, defined as M(E)–M(0)) in different H and E_{ex}, where M(E) and M(0) are the magnetization at certain E_{ex} and zero, respectively. The results are shown in Fig. 3(b). It is observed that the absolute value of ΔM increases rapidly with H increasing from zero, and then reaches a saturation value in high H regions. Here, we define magnetization difference as ΔM/M(0). In high H regions, The values of ΔM/M(0) up to 8.4% and −20.0% were obtained when the sample was polarized by E_{ex} of up to 7 kV/cm and 20 kV/cm, respectively. This modulation effect of E_{ex} on magnetism is obvious in single-phase multiferroics [30]. Besides, as can be seen from the inset of Fig. 3(b), this modulation effect still remains when the sample is in M_r state (H = 0). Even though M_r difference (ΔM_r) is small, the value of $\Delta M_r/M_r(0)$ is still up to 2.5% when E_{ex} is 20 kV/cm.

It is reasonable to consider that the saturated value of ΔM corresponds to the saturated magnetization (M_s) state of the BBFO sample. But we can see from Fig. 3(a), the M of the BBFO seems hard to reach saturation even if H is larger than 20 kOe. As we know, pure $BiFeO_3$ mainly shows anti-ferromagnetism with weak ferromagnetism. In AFM materials, magnetization changes linearly with external magnetic field, which can also be confirmed from the high H regions in Fig. 3(a). Thus, FM parts and AFM parts in M–H loops can be separated by using linearly fitting method. Fig. 3(c) presents the results with different E_{ex}, the inset shows the linear M–H loops of AFM part. It can be seen that M presents obvious hysteresis behavior in FM part, and reaches saturation in high H regions, which corresponds to the saturation regions of ΔM presented in Fig. 3(b). Furthermore, E_{ex} makes no obvious change in AFM part (the inset of Fig. 3(c)). This may be attributed to the strong AFM coupling between nearest Fe^{3+} spins in bulk sample, which is hardly destroyed by external fields. However, E_{ex} makes M–H loops of FM part change remarkably. Especially, M_s obviously changes with E_{ex}, indicating a modulation effect on intrinsic magnetism in single-phase multiferroics. This result is different from the modulation effect of E-field on magnetism in FM/FE heterostructures [31,34], where M_s of FM phase generally does not change with E-field, suggesting the different modulation mechanisms between single-phase multiferroics and FM/FE heterostructures.

We notice that the tuning effect on magnetism in BBFO is non-volatile because the change of M still retains after E_{ex} is turned off. This non-volatile tuning effect of magnetism by E-field was rarely explored in single-phase multiferroics, in spite it has been well investigated in FM/FE heterostructures [35,36] where the tuning effect on magnetism by *in situ* E-field is obvious, and the strain effect and charge screen effect are considered as the main modulation mechanisms [35]. In BBFO sample, both the non-volatility of the modulation effect on magnetism and the change of M_s suggest that the modulation mechanism should be associated with the intrinsic coupling between FE polarizations (P) and magnetic moments [23]. ME coupling in multiferroic $BiFeO_3$ thin film had been theoretically observed [5,23,24,26], in which the Dzyaloshinskii–Moriya (DM) interaction and the possible ME switching scenarios in $BiFeO_3$ were well discussed. Recently, it was reported that FE P-switching in $BiFeO_3$ favors a two-step switching process [26], i.e., P rotates sequentially (in-plane 71° switch and then out-of-plane109° switch) when applied an E-field. This two-step P-switching are accompanied by oxygen octahedral rotations, which determine the DM interaction vector ($\vec{D}$) and weak ferromagnetism in $BiFeO_3$. In short, the $\vec{D}$ vector and $\vec{P}$ vector are coupled through P-switching driving the oxygen octahedral rotations, resulting in a possible rotation of magnetic moments in the sample, which is in agreement with the experimental observation [26]. In BBFO sample, once an E_{ex} is applied to the sample and then is removed, the sample should maintain in a remnant polarization (P_r) state, which drives the oxygen octahedral rotations, and consequently forces magnetic moments stay in a new state.

To confirm the relation between FE polarization and magnetism, we can change the polar state of the sample and detect the magnetization response. As we know, it takes time to complete the FE polarizing process in FE materials. At a certain E-field, different polarization times (t_P) should make the material be in different polar states until it is in saturation polarization. Therefore, when a certain E_{ex} is applied to BBFO for different time (t_P), different polar

states should be obtained. And we may obtain different magnetic states of the sample if there exists coupling between P and M. An experimental confirmation is carried out, i.e., M–H loops of BBFO were measured after the sample was suffered an E_{ex} of 7 kV/cm for different time t_P. Thus, we can obtain the relation between M and t_p. Fig. 4 presents the dependence of M on t_p (M-t_p curve) under H = 5 kOe. When t_p increases from zero to 10 min, no obvious change in M is observed. Further increasing in t_p induces a sharp increase in M (shadow region in the figure). This may correspond to an obvious FE polarizing in BBFO. M is relative stable when t_p is long enough, corresponding to the maximum remnant polarization (P_r) of BBFO. This change of M with t_p further indicates the relation between M and FE polarization.

In the above discussion, all results were obtained at room temperature. As we know, $BiFeO_3$ presents weak ferromagnetism and ferroelectricity over a broad range of temperature. To further investigate the ME coupling in different temperatures, we performed thermomagnetic measurements (M-T curve) for the BBFO sample with different polar states. Fig. 5 shows the experimental results. The dash line presents the M-T relation of the BBFO sample with non-polarized state. It can be seen that, once the polar state of the BBFO is changed by E_{ex} (7, 14 and 20 kV/cm, respectively), M jumps markedly to another value, and continues to decrease smoothly with T increasing. This result indicates the obvious coupling between P and M in a wide temperature region.

In $BiFeO_3$-based multiferroics, E-field induced FE polarization is realized through domain wall motion or domain rotation [16,37], which may change the crystal lattice vibration modes of the samples. Therefore, Raman scattering, which is very sensitive to the change of vibration mode, can be used to detect different FE polar states of the sample. Fig. 6 presents Raman scattering spectra (*Rss*) of BBFO slice after suffered different E_{ex}. For comparison, *Rss* of pure $BiFeO_3$ is also shown in the figure. According to the group theory, $BiFeO_3$ with rhombohedral *R3c* symmetry possesses thirteen Raman-active modes, which can be represented in irreducible notation as [38],

$$\Gamma_{Raman}(R3c) = 4A_1 \oplus 9E \quad (1)$$

where A_1 represents the symmetric transformation of a molecule under the rotation about the principle axis of symmetry. *E* represents two-fold degenerate vibration. It is reported that in $BiFeO_3$, Bi–O bands mainly contributes to A_1 modes and *E* modes with low wave numbers (less than 400 cm^{-1}) [38,39]. Therefore, the substitution of Ba at Bi-site in $BiFeO_3$ results to A-site disorder, which in turn broadens the Raman peaks and weakens the intensity of the peaks (i.e., tending to degenerate the vibration mode) since the life

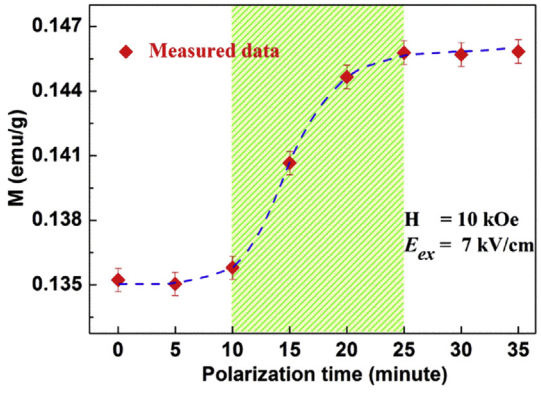

Fig. 4. The dependence of M on t_p for $Bi_{0.95}Ba_{0.05}FeO_3$ sample with H = 10 kOe and E_{ex} = 7 kV/cm. The dash line is for visual guide.

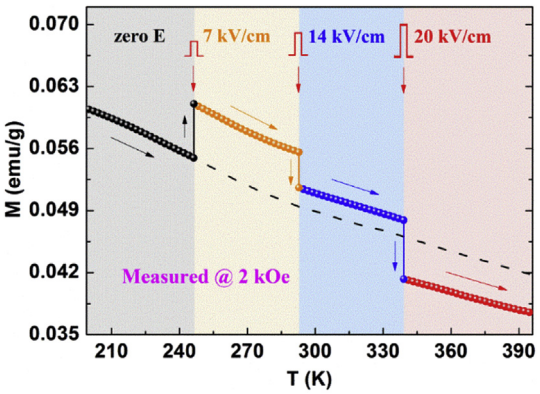

Fig. 5. M–T curve with different E_{ex} applied to $Bi_{0.95}Ba_{0.05}FeO_3$ sample during different temperature regions. The dash line present the M-T curve with E_{ex} = 0.

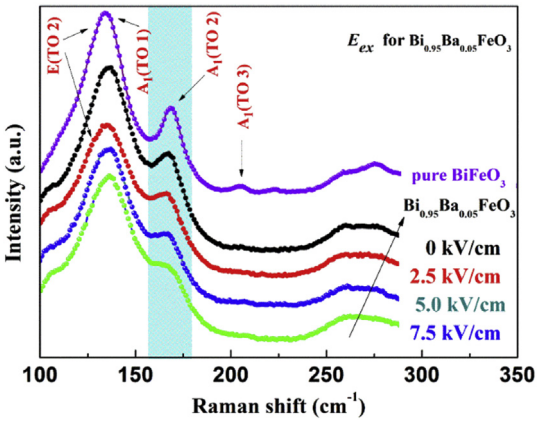

Fig. 6. Raman scattering spectra (Rss) of $Bi_{0.95}Ba_{0.05}FeO_3$ sample with different E_{ex}. Rss of the pure $BiFeO_3$ sample with zero E_{ex} is also presented.

time (τ) of phonon in real crystals can be reduced by the scatterings coming from defects, disorder, strain, etc. Here, τ is inversely proportional to the linewidth (WFHM) of the Raman peak. This changes can be observed from the A_1(TO2) and A_1(TO3) modes of pure $BiFeO_3$ and BBFO with zero E_{ex} in Fig. 6. More importantly, it is found from Fig. 6 that E_{ex} makes the *Rss* of BBFO sample change. Especially, with E_{ex} increasing, (1) the peak of A_1(TO2) mode is broadened and weakened obviously. (2) The two strongest A_1 modes (A_1(TO1) and A_1(TO2)) show blue shift (shift from 137 to 168 cm^{-1} to 143 and 176 cm^{-1}, respectively), presenting the deformation of BBFO sample after applied E_{ex}. This result indicates that the relative position of ions in BBFO sample is changed by E_{ex}, and reflects the change of FE polarization, which couples with magnetic moments in BBFO slice.

4. Conclusions

In summary, single-phase $Bi_{0.95}Ba_{0.05}FeO_3$ (BBFO) multiferroics was synthesized by sol–gel method with rapid thermal processing. E-field control magnetism was well investigated for the sample. The experimental results indicates that obvious modulation effect of E_{ex} on magnetic properties was obtained in this single-phase BBFO multiferroics over a broad range of temperatures, including room temperature. This modulation effect is comparable with that in some of FM/FE heterostructures. Raman scattering spectra and magnetic properties of the BBFO were measured when the sample was in different FE polar states, which were produced by changing

the polarization time (t_P) or the intensity of E_{ex}. The changes in *Rss* intensity, the shift of Raman vibration mode, and the change of M in BBFO slice, were obtained when applying E_{ex} with different t_P (or different intensity of E_{ex}) to the BBFO slice. The relevance of these changes indicates that the tuning effect of E-field on the magnetism should be attributed to the intrinsic coupling between magnetic and electric orders in BBFO multiferroics.

Acknowledgment

This work was supported by National Natural Science Foundation of China (Grant No. 11004031), Natural Science Foundation of Fujian Province (Grant No. 2010J01277), Program for New Century Excellent Talents of Fujian Province (Grant No. JA12054) and Key Project of Fujian Provincial Education Department (JA15100).

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