J Mater Sci (2011) 46:2649–2653
DOI 10.1007/s10853-010-5120-1

Electric-field-induced dielectric response and magnetization in nano–microscale lead-free multiferroic composite

Yun Zhou · Jincang Zhang · Zhenjie Feng · Beizhan Li · Li Li · Yuling Su · Chao Jing · Shixun Cao

Received: 2 August 2010 / Accepted: 27 November 2010 / Published online: 14 December 2010

Abstract A new kind of nano/microscale lead-free multiferroic composite with a formal of $0.4CoFe_2O_4$–$0.6[0.948(K_{0.5}Na_{0.5})NbO_3$–$0.052LiSbO_3]$ was prepared. The electric-field-induced dielectric (EID) and magnetization (EIM) behaviors were systemically investigated for this 0–3-type structured multiferroic ME composite. Significant electric-field-induced effects were obtained with a high tunability and a large EIM coefficient, which the former has a value of $K = 3.35\%$ under the low dc electric-field of 2 kV/cm and the later is in excess of 2.15×10^{-10} s/m at a low frequency of 1.0 kHz with a low magnetic bias field of 2000 Oe for this composite. It is also proved that its EIM behavior is strongly dependent on the bias magnetic field H_{Bias} and the frequency of driving electric-field. The measured EIM has an excellent linear relationship with the applied ac electric-field with amplitude varying from 7.1 to 73.6 V/cm. The electric-field-induced effects indicate that the 0–3-type particulate ME composites not only have physical interest but also have potential practical use.

A multiferroic material with two or more primary ferroic properties provides significant potentials for applications as the next-generation multifunctional devices [1, 2]. In general, multiferroic can be realized in single-phase or composite forms [3]. So far, multiferroic single-phase materials are rare, and their magnetoelectric responses are either relatively weak or occurs at temperatures too low for practical applications. Then in some composites by incorporating both ferroelectric and ferrimagnetic phases typically yield giant magnetoelectric coupling responses above room temperature, which makes them ready for technological applications. A two-phase composite can be described as 0–3-, 3–3-, 2–2-, and 1–3-type, in which each number denotes the connectivity of the respective phase [4]. The common connectivity schemes are 0–3-type particulate composites of piezoelectric and magnetic oxide grains, 2–2-type laminate ceramic composites consisting of piezoelectric and magnetic oxide layers [4]. In multiferroic system, the coupling between ferroelectric and ferromagnetic orders can produce some interesting effects, such as magnetoelectric (ME) and magnetodielectric (MD) effect [5]. The ME effect means that the electric polarization can be induced by a magnetic field H (MIE) or the magnetization can be induced by an electric-field E (EIM) [6]. The MIE and EIM effects can be expressed by an equal strength $\alpha = (\partial P/\partial H)_E = \mu_0(\partial M/\partial E)_H$ [7]. Usually, the MD effect is characterized by magnetic-field-induced dielectric response [8]. Up to now, the most studies on multiferroics focused on the magnetic-field-induced effects, while seldom report has been made on the electric-field-induced effects. For example, large MIE effects have been observed in two-phase composite, especially in some 2–2-type structured laminated composites. However, only a few reports have been made on the EIM effect in these 2–2-type structured laminated composites [5, 9, 10]. In fact, electric-field-induced effects have both physical interest and technological applications, such as coil-free electromagnet microwave applications and ME memory devices [9, 11, 12]. In this article, a new kind of nano/microscale lead-free $0.4CoFe_2O_4$–$0.6[0.948(K_{0.5}Na_{0.5})NbO_3$–$0.052LiSbO_3]$

Y. Zhou · J. Zhang (✉) · Z. Feng · B. Li · L. Li · Y. Su · C. Jing · S. Cao
Department of Physics, Shanghai University, Shanghai 200444, China
e-mail: jczhang@staff.shu.edu.cn

Y. Zhou
School of Science, China Jiliang University, Hangzhou 310018, China

(CFO/KNN–LS) multiferroic composite was prepared, and the electric-field-induced dielectric (EID) and magnetization (EIM) characteristics are systemically investigated for this particulate 0–3-type structured multiferroic ME composite. The EIM characteristics were detected using double coils [5, 12]. Significant electric-field-induced effects were observed with a high tunability and a large EIM coefficient. The results indicate that the particulate 0–3-type ME composites not only have physical interest but also have potential practical use in tunable microwave, coil-free electromagnet, and related magnetoelectric coupling devices.

Both precursor $0.948(K_{0.5}Na_{0.5})NbO_3$–$0.052LiSbO_3$ (KNN–LS) and $CoFe_2O_4$ (CFO) were adopted as the piezoelectric and magnetostrictive phases, respectively. KNN–LS was prepared by a solid-state reaction method, and CFO was synthesized using citrate gel method. The ME composites CFO/KNN–LS were prepared by mixing 40 mol% of CFO phase with 60 mol% of KNN–LS phase. The composites were examined by X-ray diffraction (XRD) as shown in Fig. 1. The patterns show that both CFO and KNN–LS phases are present in the ceramic. No impurity phases were detected. X-ray diffraction patterns show that CFO retains its cubic structure in the CFO/KNN composite and the lattice constant is $a = 8.370$ Å, whereas the KNN–LS shows mixed phases [13, 14]. The details of sample preparation and the confirmed multiferroicity can be found in Ref. 13. For EIM characterization, silver electrodes were deposited on 1 mm thick samples with a cubic shape of about $1 \times 4 \times 4$ mm^3 and then poled in silicone oil under a poling field of 2–14 kV/cm and at a poling temperature of 405 K to room temperature. The piezoelectric coefficient (d_{33}) of the composite is about 45 pC/N [13]. The EID properties were measured using LCR meter (ZM2353). For dielectric properties measurement, the sample was placed in a dc bias electric-field. The EIM measurement was performed with an induction method with a sine electric-field δE_{ac} (about 73.5 V/cm) on the sample by a signal generator [5, 12]. The piezoelectric strain is induced in KNN–LS phase due to the converse piezoelectric effect. Then the strain is acoustically transferred to CFO phase; as a result, an induced magnetization δM_{ac} in CFO phase is produced due to the magnetoelastic coupling. The EIM coefficient is defined as $\alpha_{EIM} = \mu_0(\delta M_{ac}/\delta E_{ac})$. For EIM measurement, the sample plane was perpendicular to the bias magnetic field. Double coils were placed in the bias magnetic field with its planes perpendicular to the magnetic field. The sine EIM along bias magnetic field in the sample induced voltage in the double coils due to the Faraday Effect [5]. All measurements were performed at room temperature.

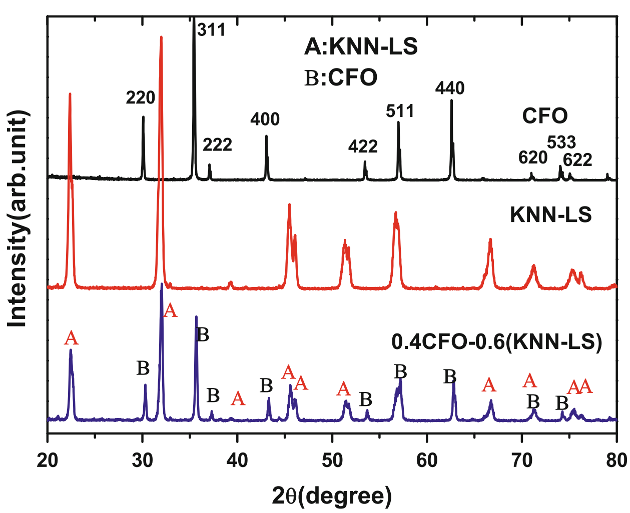

Fig. 1 (Color online) X-ray diffraction pattern of KNN–LS, CFO, and CFO/KNN–LS ceramic, where *A* denotes KNN–LS phase and *B* denotes CFO phase at room temperature

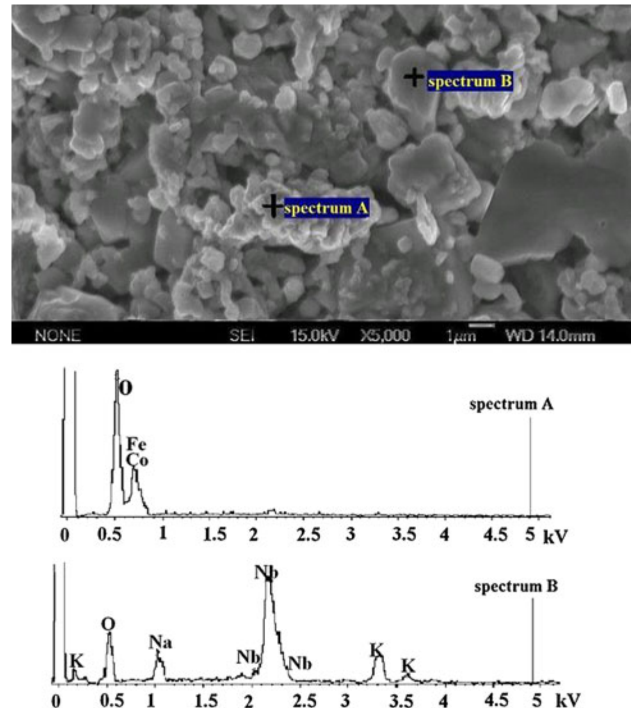

Fig. 2 EDS spectrum of CFO/KNN–LS ceramic at room temperature. The coexistence of CFO and KNN–LS phases in the ceramics is further evident by the bright CFO particle in spectrum *A* and the dark KNN–LS particle in spectrum *B*

Figure 2 shows two EDS spectra and their associated SEM fractograph of the composite. From the bright CFO particle in spectrum A and the dark KNN–LS particle in spectrum B, the coexistence of CFO and KNN–LS phases in the composite is further evident. The composite shows a homogeneous microstructure. It seems that the CFO particles are well distributed within KNN–LS matrix.

Figure 3 shows the results of dielectric constant variation as a function of frequency in the range of 0.5–200 kHz under different dc bias electric-field for the experimental CFO/KNN composite. The electric-field-induced variation $\Delta\varepsilon$ of dielectric constant is defined as $\Delta\varepsilon = \varepsilon(f,0) - \varepsilon(f,E)$ [15]. Here, $\varepsilon(f,0)$ and $\varepsilon(f,E)$ denote the zero-field and field-dependent dielectric constant at different frequencies. The results were measured on two kinds of measurement models for dc bias field related to the measuring silver electrode, i.e., the vertical model ($E_{\perp}$, longitudinal) and the parallel model ($E_{//}$, transverse), as shown in the insert of Fig. 3a and b. It can be seen that $\Delta\varepsilon$ increases with increasing dc bias electric-field (E_{Bias}), which means that ε decreases with increasing E_{Bias} for $\Delta\varepsilon = \varepsilon(f,0) - \varepsilon(f,E)$. This is one of the important properties for some materials to be used in tunable devices [15]. This behavior of the ceramic could be interpreted in terms of locking the moments of polar clusters due to application of external dc bias field. As the bias field increases, the moments parallel to the electric-field increase and reach the saturation. Therefore, very few dipoles are left to respond to the small signal oscillatory electric-field [16]. The value of $\Delta\varepsilon$ is larger under a higher dc bias field, and the transverse $\Delta\varepsilon$ is stronger than the longitudinal $\Delta\varepsilon$ as shown in Fig. 3. An interesting behavior observed from Fig. 3 is that the value of the $\Delta\varepsilon$ decreases with the increase in frequency, indicating the dielectric constant is correlative with both dc bias field and frequency. The decrease of $\Delta\varepsilon$ with the increase in frequency is mainly attributed to the dispersion of the dielectric constant (ε). The high value of $\Delta\varepsilon$ observed at lower frequencies is explained on the basis of space charge polarization due to inhomogeneous dielectric structure. The inhomogeneities present are grain structure, porosity, etc [17, 18].

Based on the strong field dependence of dielectric constant, it is worthwhile to investigate the dielectric tunability of the composite. In general, the tunability is expressed as

$$K = \frac{\varepsilon(f,0) - \varepsilon(f,E)}{\varepsilon(f,0)} \quad (1)$$

For this experiment, the frequency dependent of longitudinal and transverse tunability with a frequency range of 0.5–200 kHz is given in Fig. 4. The experimental studies

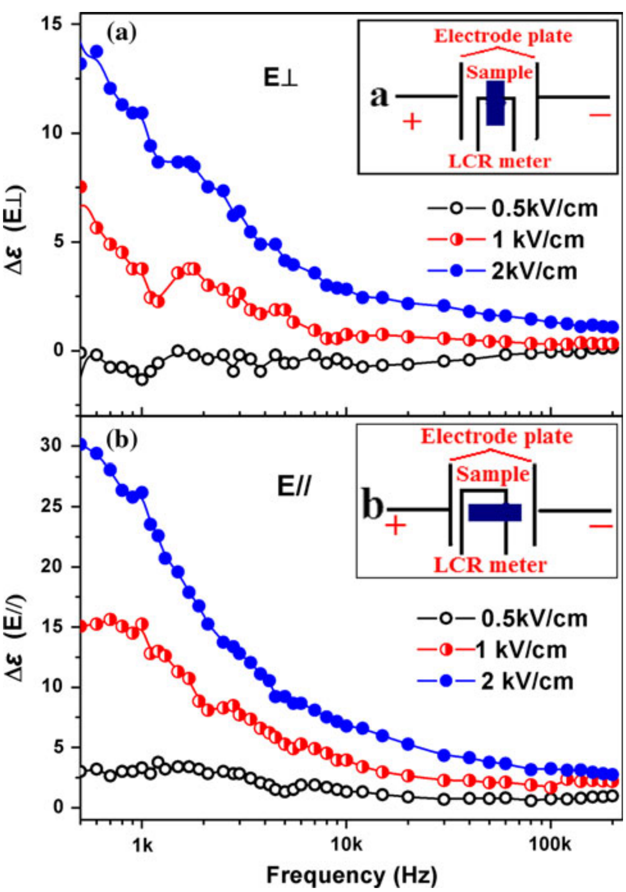

Fig. 3 (Color online) The electric-field-induced variation $\Delta\varepsilon$ of dielectric constant as a function of frequency for CFO/KNN–LS composite under different dc bias electric-fields. The *insets* show the measurement circuit

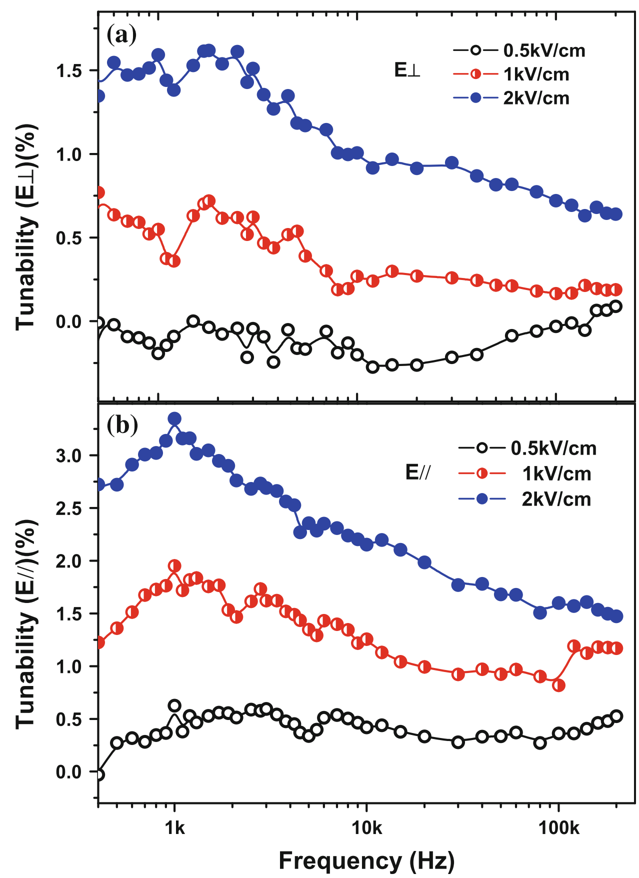

Fig. 4 (Color online) The frequency dependent of longitudinal and transverse tunability for CFO/KNN–LS composite under different dc electric-fields

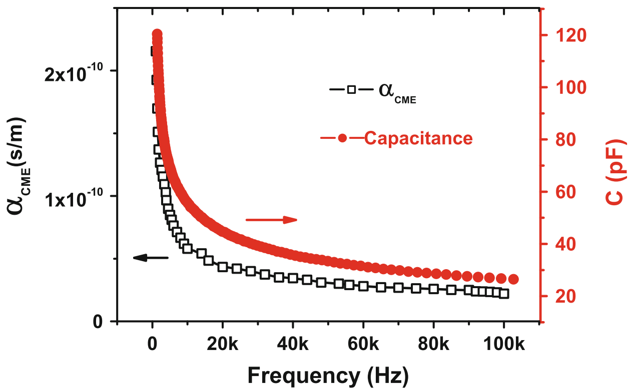

Fig. 5 (Color online) Frequency-dependent variations of the composite EIM coefficient and capacitance in a frequency region of 1.0–100 kHz for the composite. The EIM was measured under an electric-field of 73.6 V/cm and a bias magnetic field of 2000 Oe

carried out have revealed that the shape of both Figs. 3 and 4 are strongly dependent on how the electric-field is applied. It can be seen that the longitudinal $E_{\perp}$ tunability decreases with increasing frequency, while the transverse $E_{//}$ tunability increases initially with the increase in the frequency and reaches a maximum at $f = 1.0$ kHz, and then decreases with the further increase in the frequency. Higher tunability is achieved as the dc field increases. For example, at $f = 1.0$ kHz, the value of transverse tunability is 1.95% for $E = 1.0$ kV/cm, whereas the K value is as large as 3.35% under the dc electric-field of 2.0 kV/cm. It can also be seen that the transverse tunability is stronger than the longitudinal tunability. This is in agreement with the measured results shown in Fig. 3.

As expected, the changing capacitance in the materials would significantly affect the EIM behavior [5, 12]. Figure 5 shows the frequency dependent of the capacitance and EIM in a frequency region of 1.0–100 kHz for the composite. The EIM was measured under an electric-field of 73.6 V/cm and a bias magnetic field of 2000 Oe. It can be evidently seen that the capacitance and the EIM coefficient α_{EIM} output show the same change trend and decrease with the increase in frequency. The capacitance and the α_{EIM} decrease rapidly with a very high value at lower frequencies and decrease slowly with a very low value at higher frequencies. The high values of the capacitance and α_{EIM} at lower frequencies are attributed to different types of polarizations (electronic, atomic, interfacial, ionic etc.), and the low values at higher frequencies are only due to the electronic polarization.

In order to see the correlation of the induced saturation magnetization (δM_{ac}) with applied ac electric-field E_{ac} and frequencies, we measured the change of δM_{ac} with applied ac electric-field E_{ac} for various frequencies at the bias magnetic fields H_{Bias} of 2000 Oe, as shown in Fig. 6. The induced saturation magnetization (δM_{ac}) was obtained by

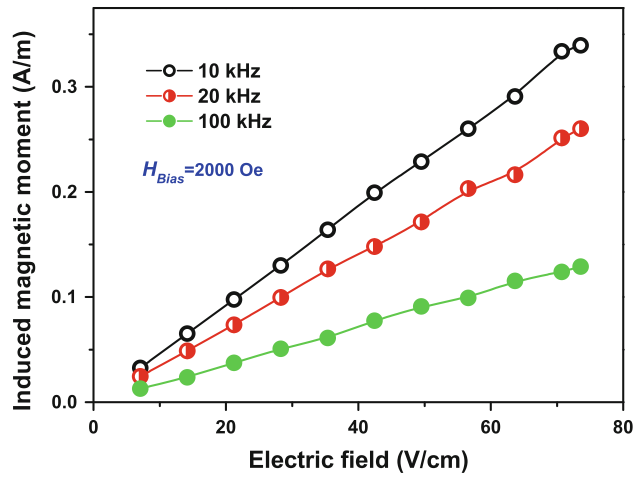

Fig. 6 (Color online) Induced saturation magnetization (δM_{ac}) as a function of applied ac electric-field for various frequencies at the magnetic bias fields H_{Bias} of 2000 Oe for CFO/KNN–LS composite

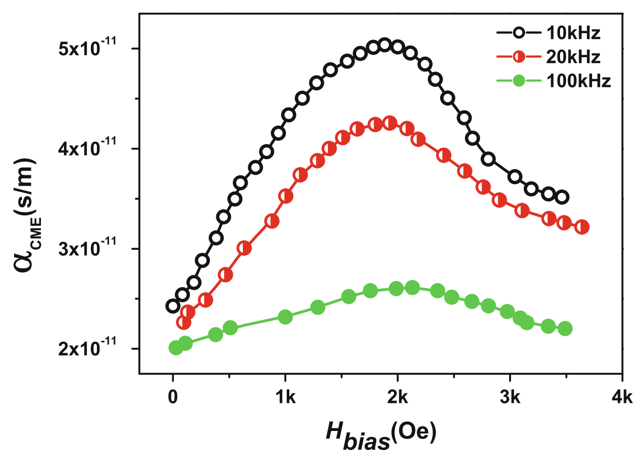

Fig. 7 (Color online) The dependence of EIM on magnetic bias field H_{Bias} with the frequency of 10.0, 20.0, and 100.0 kHz for CFO/KNN–LS composite

$\delta M_{ac} = m/V$, where m is the magnetic moment in the original and V is the composite volume. The detailed method for the calculated δM_{ac} can be found in Ref. 5. The results indicate that all the δM_{ac} respond almost linearly to applied ac electric-field E_{ac} in the entire field range of 7.1–73.6 V/cm, which is consistent with the results by Jia and Chen et al. [9, 10] in layer composites.

Figure 7 gives the dependence of EIM on magnetic bias field H_{Bias} below 4000 Oe at the frequency of 10.0, 20.0, and 100.0 kHz. It can be seen that all the EIM coefficient α_{EIM} increase initially with the increase in dc bias magnetic field and then decrease with the further increase in the field, agreeing with the experimental results of the layer composite [5, 9, 12]. This reason is that the magnetostrictive coefficient reaches saturation at a certain value of the magnetic field. Beyond saturation, the magnetostriction gets saturated, producing a nearly constant δM_{ac}, thereby decreasing $\alpha_{EIM}(\alpha_{EIM} = \mu_0(\delta M_{ac}/\delta E_{ac})$ with increasing magnetic field. The values of H_{Bias} corresponding to the maximum EIM coefficient α_{EIM}^{max} are about 1880 Oe for 10 kHz, 1930 Oe for 20 kHz, and 2130 Oe for 100 kHz, respectively. It seems that the value of H_{Bias} corresponding to α_{EIM}^{max} is dependent on the frequency and increases with the increase in the frequency. However, this behavior may be attributed to the magnetostrictive hysteresis, which causes the previous measurement impact on the subsequent [12].

Specifically, the greatest EIM response occurs at the frequency of 1 kHz. The maximum EIM coefficient α_{EIM} is determined to be 2.15×10^{-10} s/m with the H_{Bias} of 2000 Oe, suggesting that large α_{EIM} can be obtained in low frequency and low dc bias magnetic field. The maximum α_{EIM} is much bigger than that of single-phase materials. For example, α_{EIM} peaks at 4.1×10^{-12} s/m (Cr_2O_3) near the Neel temperature of 307 K [7, 19]. Importantly, the H_{Bias} of 2000 Oe is relatively low and easily obtained in practical applications using permanent magnets [9].

In summary, we successfully prepared a new kind of 0–3-type structured nano/microscale lead-free $0.4CoFe_2O_4$–$0.6[0.948(K_{0.5}Na_{0.5})NbO_3$–$0.052LiSbO_3]$ multiferroic composite and systemically studied the EID and magnetization properties. A significant electric-field-induced effect was observed with a high tunability and a large EIM coefficient. The former has a value of $K = 3.35\%$ under the low dc electric-field of 2 kV/cm, and the later is in excess of 2.15×10^{-8} s/m at a low frequency of 1.0 kHz with a low magnetic bias field of 2000 Oe for this 0–3-type structured multiferroic composite. The result proves that its EIM behavior is strongly dependent on the bias magnetic field H_{Bias} and the frequency of driving electric-field. The measured δM_{ac} has an excellent linear relationship with the applied ac electric-field with amplitude varying from 7.1 to 73.6 V/cm. The present experiment indicates that the 0–3-type ME composites not only have physical interest but also have potential practical use.

Acknowledgements This study is supported by the National Natural Science Foundation of China (NSFC, No. 10774097, 50932003), The Science and Technology Committee of Shanghai Municipality (No. 08dj1400202), and Special Research Foundation for the Doctoral Discipline of University (Grant no. 200802800003), and Foundation of the Zhejiang Education Committee (No. Y200909403).

References

1. Hill NA (2000) J Phys Chem B 104:6694
2. Nan C-W, Cai N, Shi Z, Zhai J, Liu G, Lin Y (2005) Phys Rev B 71:014102
3. Tan SY, Shannigrahi SR, Tan SH, Tay FEH (2008) J Appl Phys 103:094105
4. Nan C-W (2008) J Appl Phys 103:031101
5. Zhou J-P, Zhao W, Guo Y-Y, Liu P, Zhang H-W (2009) J Appl Phys 105:063913
6. Kida N, Ikebe Y, Takahashi Y, He JP, Kaneko Y, Yamasaki Y, Shimano R, Arima T, Nagaosa N, Tokura Y (2008) Phys Rev B 78:104414
7. EERENSTEIN W, Wiora M, Prieto JL, Scott JF, Mathur ND (2007) Nat Mater 6:348
8. Kimura T, Kawamoto S, Yamada I, Azuma M, Takano M, Tokura Y (2003) Phys Rev B 67:180401(R)
9. Jia Y, Wing S, Lai H, Chan W, Zhao X, Luo H (2006) Appl Phys Lett 88:242902
10. Chen SY, Wang DH, Han ZD, Zhang CL, Du YW, Huang ZG (2009) Appl Phys Lett 95:022501
11. Tokura Y (2007) J Mag Mag Mater 310:1145
12. Zhou J-P, Guo Y-Y, Zengzhe Xi, Liu P, Lin S, Liu G, Zhang H-W (2008) Appl Phys Lett 93:152501
13. Zhou Y, Zhang J, Li L, Su Y, Cheng J, Cao S (2009) J Alloys Compd 484:535
14. Zhang S-J, Xia R, Shrout TR (2006) J Appl Phys 100:104108
15. Tang XG, Chew K-H, Wang J, Chan HLW (2004) Appl Phys Lett 85:991
16. Laha A, Krupanidhi SB (2004) Mater Sci Eng B 113:190
17. Kamble YB, Chougule SS, Chougule BK (2009) J Alloys Compd 476:733
18. Devan RS, Kanamadi CM, Lokare SA, Chougule BK (2006) Smart Mater Struct 15:1877
19. Folen VJ, Rado GT, Stalder EW (1961) Phys Rev Lett 6:607