

# Electrical properties of $\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3\text{-Bi}_{3.4}\text{Nd}_{0.6}\text{Ti}_3\text{O}_{12}$ thin films derived by a sol-gel process

C. P. Cheng · M. H. Tang · Z. H. Tang ·  
Y. C. Zhou

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**Abstract** Magnetolectric (ME)  $x\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3\text{-(1-x)}\text{Bi}_{3.4}\text{Nd}_{0.6}\text{Ti}_3\text{O}_{12}$  (LCMO–BNT) composite thin films have been prepared by a sol-gel process and spin-coating technique. The effects of LCMO content on the microstructure, leakage current density, ferroelectric properties, fatigue endurance and ME voltage coefficient of LCMO–BNT thin films derived by sol-gel method were studied. It was found that the composite thin films have better fatigue endurance properties and lower leakage current densities compared with pure BNT thin films, as well as large ME voltage coefficients.

**Keywords** Multiferroic films · Electrical properties · Magnetolectric

## 1 Introduction

Multiferroic materials, which exhibit both ferroelectric and ferromagnetic properties in a single phase, have attracted increasing interest due to their potential application in multifunctional devices and their fascinating fundamental physics [1–3]. Examples of the potential applications include multistate memories and logical devices, tunable filters, sensors and new types of electromechanical devices

[4, 5]. However, the magnetolectric (ME) coupling coefficient in single-phase compounds at ambient conditions is typically too small to be useful in applications [6]. The primary requirement for the observation of the ME effect is the coexistence of magnetic and electric dipoles. Based on this outline, the ME effect could be realized in a composite consisting of both ferroelectric phase and ferromagnetic phase by using the product property, which is first proposed by Van Suchetelene [7]. Up to now, various ME composites have been developed [8, 9]. Most of them are bulk materials, e.g., the sintered composites of  $\text{BaTiO}_3\text{-NiCuZn}$  and  $\text{CuFe}_2\text{O}_4\text{-PbZr}_{0.53}\text{Ti}_{0.47}\text{O}_3$ , [10, 11] multilayer composites of  $\text{NiFe}_2\text{O}_4\text{-PZT}$  and Terfenol-D-PZT, [12, 13] etc. Recently, interest in multiferroic composite materials has gradually been focused on composite thin films [14–17]. Compared to bulk composites, ME composite thin films exhibit unique advantages. Their composition and connectivity could be modulated at the microscopic scale, and the artificial thin film heterostructures can thus be achieved, which have potential applications in all kinds of microdevices and integrated units [16]. ME coupling has been measured in thin films with ferromagnetic nanoparticles embedded in the ferroelectric matrix [16, 17]. Many studies have revealed that Nd-substituted  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  is the most promising candidate for use in Pb-free piezoelectrics because of its excellent piezoelectricity and polarization behaviors [18–20]. Nanoparticulate  $\text{Bi}_{3.15}\text{Nd}_{0.85}\text{Ti}_3\text{O}_{12}\text{-CoFe}_2\text{O}_4$  composite films with  $\text{CoFe}_2\text{O}_4$  nanoparticles embedded in  $\text{Bi}_{3.15}\text{Nd}_{0.85}\text{Ti}_3\text{O}_{12}$  matrix have been prepared by a chemical solution deposition method [21]. It was found that the conductivity has a great effect on the quality of the multiferroic composites and, [22, 23] doping with magnetic ions as acceptor dopants can reduce the conductivity of the ferroelectric thin film [24, 25]. Based on the above reasons, perovskite  $\text{Bi}_{3.4}\text{Nd}_{0.6}\text{Ti}_3\text{O}_{12}$  (BNT) and

C. P. Cheng · M. H. Tang (✉) · Z. H. Tang · Y. C. Zhou  
Laboratory of Low Dimensional Materials and Application  
Technology of Ministry of Education, Xiangtan University,  
Xiangtan 411105, People's Republic of China  
e-mail: mhtang@xtu.edu.cn

C. P. Cheng (✉)  
Faculty of Science, Hunan Institute of Engineering,  
Xiangtan 411104, People's Republic of China  
e-mail: chengchuanpin@163.com

perovskite  $\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$  (LCMO) are selected as the ferroelectric and ferromagnetic phases in the present composite thin films respectively and, the effects of LCMO content on the electrical properties and the ME coupling behaviors of the LCMO–BNT composite thin films are investigated in the present work.

## 2 Experimental details

The ME LCMO–BNT ( $x = 0.3, 0.4,$  and  $0.5$ ) composite thin films were fabricated on Pt/Ti/SiO<sub>2</sub>/Si(100) substrates by sol–gel method and spin-coating process. The detailed preparation procedure of precursor solution of BNT has been described elsewhere [26]. To obtain the precursor solution of LCMO, lanthanum acetate, calcium acetate and manganese acetate were dissolved in an aqueous solution of citric acid with the metal atomic ratio La/Ca/Mn of 0.4:0.6:1. After the chelating reaction, polyethylene glycol as a kind of surfactant and ethanol were added into LCMO solution. The final concentration of two kinds of precursor solutions was approximately 0.1 M. The preparation of the films consisted in spin coating the Pt(111)/Ti/SiO<sub>2</sub>/Si(100) substrates with the stock solution at 3,000 rpm for 30 s. The wet film samples were then fully dried in a rapid thermal processor (RTP-500) at 180 °C for 3 min followed by another 3 min at 400 °C to remove residual organic compounds. This coating process is referred to as one deposition. The coating and preheating process should be repeated several times to obtain the desired film thickness. Post annealing was performed at 750 °C for 15 min under an oxygen atmosphere by a rapid thermal annealing process. For comparison, pure BNT thin film ( $x = 0$ ) were fabricated simultaneously. The phase structure characterization of the LCMO–BNT thin films was carried out by a D/max-rA X-ray diffractometer with Cu K $\alpha$  radiation. For electrical measurements, Au top electrodes with a diameter of 200  $\mu\text{m}$  were coated on the composite thin films by DC sputtering using a shadow mask. The ferroelectric measurements were performed using a Radiant Technologies Precision Workstation ferroelectric tester. Both the AC magnetic field of  $H$  (10 Oe) generated by a pair of Helmholtz coils and the DC magnetic field generated by an electromagnet were parallel to the thin film plane. The Helmholtz coils were driven by a signal generator (Agilent 33120A) and a power amplifier (HAS 4014). The induced electrical field  $E$  was measured using a lock-in amplifier (SRS Inc., SR830).

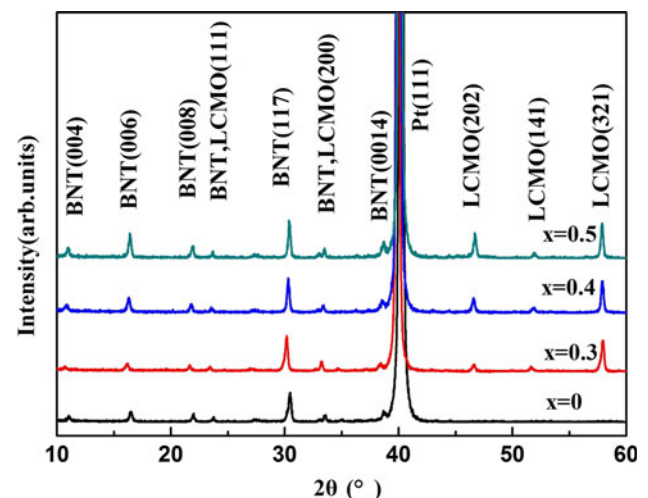
## 3 Results and discussion

Figure 1 shows the typical X-ray diffraction (XRD) patterns of the BNT–LCMO composite thin films with  $x = 0,$

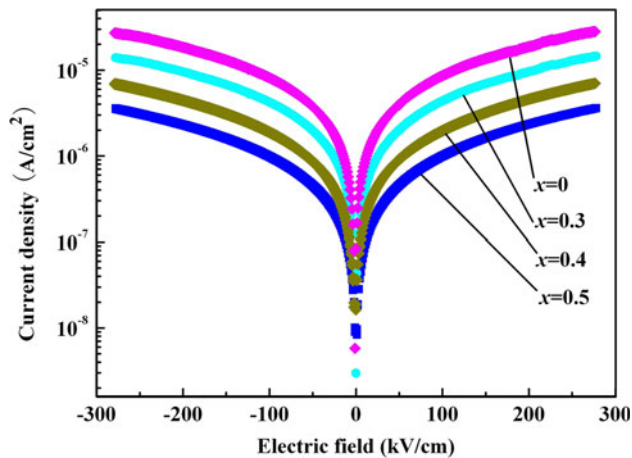
0.3, 0.4 and 0.5. The pure BNT thin film ( $x = 0$ ) is polycrystalline and has a single-phase of bismuth-layered perovskite structure. Two evident sets of well defined peaks are observed in the thin films with  $x = 0.3, 0.4$  and  $0.5,$  which belong to polycrystalline bismuth-layered perovskite structure BNT and perovskite LCMO. As expected, the intensity of LCMO diffraction peaks increases with the increase of LCMO content ( $x$ ) in composite films. There are no additional or intermediate phase peaks apart from LCMO and BNT, confirming the preparation of a material containing both ferromagnetic and ferroelectric phases.

The DC leakage current characteristics for LCMO–BNT thin films with different  $x$  values are shown in Fig. 2. The leakage current densities of LCMO–BNT thin films with  $x = 0, 0.3, 0.4,$  and  $0.5$  are  $1.3 \times 10^{-5}, 6.6 \times 10^{-6}, 3.2 \times 10^{-6},$  and  $1.6 \times 10^{-6}$  A/cm<sup>2</sup> at 250 kV/cm, respectively. From Fig. 2 one can see that the leakage current is determined by the LCMO content, which decreases with the increase of LCMO content. This is attributed to the fact that doping with acceptor dopants can reduce the conductivity of the ferroelectric thin films [24, 25].

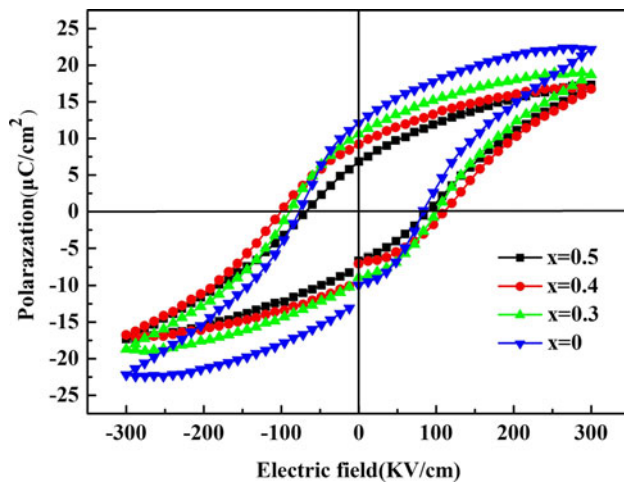
The polarization versus electric field ( $P$ - $E$ ) hysteresis loops of the composite films with  $x = 0, 0.3, 0.4$  and  $0.5,$  under the applied electric field of 300 kV/cm is shown in Fig. 3. The well-defined ferroelectric loops are observed. This indicates good ferroelectric properties of the composite films. As shown in Fig. 3, the remanent polarization ( $P_r$ ) decreases with the increase of  $x,$  that is, with the increase of the ferromagnetic phase. The  $P_r$  values are 12.4, 10.4, 9.1, and 7.1  $\mu\text{C}/\text{cm}^2$  under the condition of about 300 kV/cm electric field for the composite films with  $x = 0, 0.3, 0.4,$  and  $0.5.$



**Fig. 1** XRD patterns of the LCMO–BNT composite thin films with  $x = 0, 0.3, 0.4$  and  $0.5$



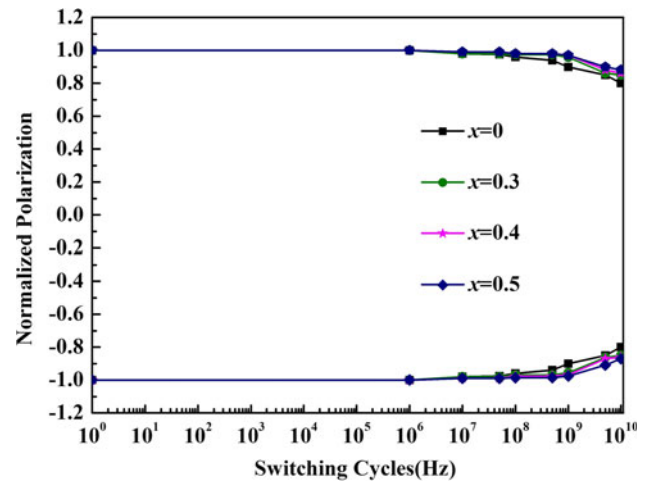
**Fig. 2** The DC leakage current characteristics of the LCMO–BNT films with  $x = 0, 0.3, 0.4,$  and  $0.5$



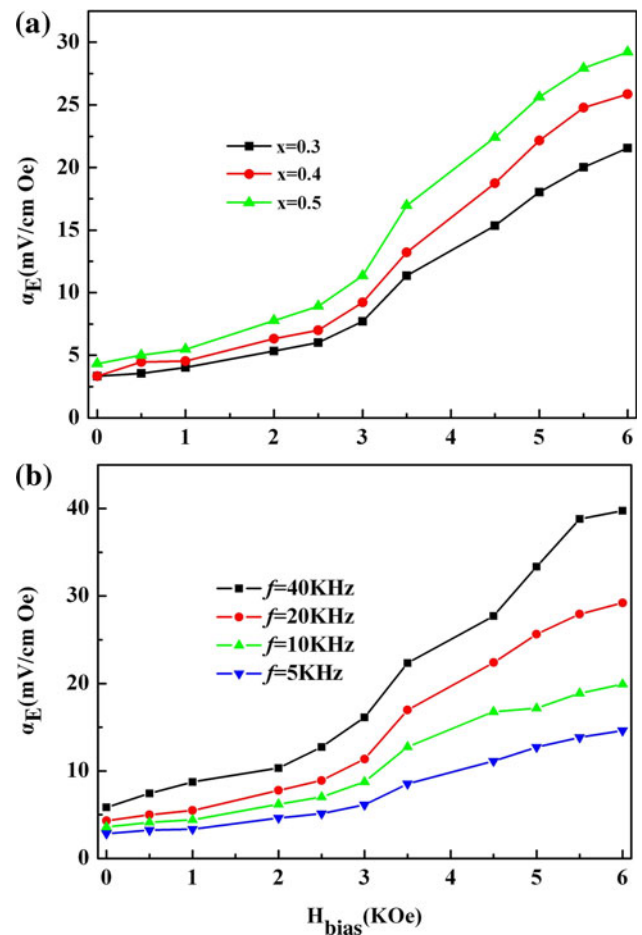
**Fig. 3**  $P$ - $E$  hysteresis loops

Considering the NvFeRAM application of magneto-electric thin films, fatigue characteristic is an important factor that should be considered. The fatigue characteristic of LCMO–BNT composite thin films with  $x = 0, 0.3, 0.4$  and  $0.5$  are displayed in Fig. 4. The test was performed at room temperature, using 100 kHz bipolar square pulses with a 240 kV/cm electric field. As shown in Fig. 4, all the samples possess good ferroelectric fatigue endurance. The fatigue endurance property is improved by adding LCMO phase, and a fatigueless performance up to  $10^9$  switching cycles is obtained for the LCMO–BNT composite thin film with  $x = 0.5$ , which is attributed to the fact that acceptor dopants can strongly improve the endurance characteristics of the thin film [27, 28].

The ME effect is determined by the ME voltage coefficient  $\alpha_E = dE/dH$  measured in terms of the induced electric field  $E$  under an applied AC magnetic field of



**Fig. 4** Fatigue characteristic of the LCMO–BNT composite films with  $x = 0, 0.3, 0.4,$  and  $0.5$



**Fig. 5** **a** Variations of  $\alpha_E$  with  $H_{\text{bias}}$  of LCMO–BNT composite films at 20 kHz and **b** variations of  $\alpha_E$  with  $H_{\text{bias}}$  at different frequencies  $f$  for the sample with  $x = 0.5$

$H$  superimposed onto a DC bias magnetic field  $H_{\text{bias}}$ . Figure 5a shows the variations of ME voltage coefficient  $\alpha_E$  as a function of applied magnetic bias  $H_{\text{bias}}$  at a fixed AC

magnetic frequency  $f = 20$  kHz for the LCMO–BNT composite films with  $x = 0.3, 0.4,$  and  $0.5$ , measured at room temperature. From Fig. 5a, one can see that the  $\alpha_E$  value increases by increasing LCMO content in LCMO–BNT composite thin films (from  $x = 0.3$  to  $0.5$ ) at any fixed  $H_{\text{bias}}$  in the range of 0–6 kOe. Figure 5b shows the variations of  $\alpha_E$  with  $H_{\text{bias}}$  at different frequencies  $f$  for the LCMO–BNT thin film with  $x = 0.5$ . An overall  $\alpha_E$  increase by increasing  $f$  from 5 to 40 kHz is observed. The variation of  $\alpha_E$  with  $f$  is most likely due to the frequency dependence of the dielectric constant for the individual phases, [19, 29] because a reduction in dielectric constant will increase the ME voltage coefficient [28]. One of the most important issues related to multiferroic thin films is the origin of the ME effects. In the multiferroic composite system, it is well-known that the ME coupling mainly arises from the magnetic–mechanical–electric interaction through the interface between the ferroelectric phase and the ferromagnetic phase. The composite thin films prepared with a lower content of ferromagnetic or ferroelectric phase result in the reduction of magnetostriction or piezoelectricity, respectively, leading to a decrease in the ME voltage coefficient as predicted theoretically [30]. The proper molar proportion of BNT and LCMO in the LCMO–BNT composite thin films causes the large ME voltage coefficient. A model aimed at studying the ME effect and its dependence on the conductivities of both inclusion and matrix phases of particulate composites predicts that the conductivity of either inclusion or matrix material is one of the possible key factors determining the magnetoelectric behavior of particulate composites [23]. From the model, one can deduce that the  $\alpha_E$  value of the composite with low ferromagnetic concentration will increase with increasing ferromagnetic concentration [23]. This prediction is consistent with the present experiments. In this work, the leakage current density decreases with increasing  $x$  value, and the LCMO–BNT thin film with  $x = 0.5$  has the lowest leakage current density, because the proper ferromagnetic concentration in the thin film reduces the leakage current. The LCMO–BNT thin film with  $x = 0.5$  has the maximum ME voltage coefficient of about 29.1 mV/(cm Oe) at a magnetic field frequency of 20 kHz. It was found that doping with acceptor dopants such as Co and other magnetic ions can reduce the conductivity of the ferroelectric films and then to improve its fatigue endurance performance [24, 25]. Our results show that LCMO–BNT composite thin films possess better fatigue endurance properties compared with pure BNT thin film, which may be primarily related to the effects of acceptor dopants such as Ca and Mn ions and fine grains in the thin films. The composite thin film with  $x = 0.5$  has the maximum ME voltage coefficient of about 40.1 mV/(cm Oe) at magnetic field frequencies below 40 kHz, which is ascribed to the proper LCMO concentration.

## 4 Conclusions

In conclusion, magnetoelectric LCMO–BNT composite thin films with  $x = 0.3, 0.4,$  and  $0.5$  were fabricated on Pt/Ti/SiO<sub>2</sub>/Si(100) substrates by a sol–gel process and spin-coating technique. The effects of LCMO content on the microstructure, leakage current density, ferroelectric properties, fatigue endurance and ME voltage coefficient of LCMO–BNT thin films derived by sol–gel method were studied. Our results show that the composite thin films have better fatigue endurance properties and lower leakage current densities compared with pure BNT thin films, and the composite thin films possess large ME voltage coefficients, which foreshow a new promising ME devices.

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