

Dielectric, ferroelectric, and ferromagnetic properties of $0.7\text{Bi}_{1-x}\text{La}_x(\text{Fe}_{0.9}\text{Cr}_{0.1})\text{O}_3-0.1\text{BaTiO}_3-0.2\text{PbTiO}_3$ solid solutions

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Solid solutions $0.7\text{Bi}_{1-x}\text{La}_x(\text{Fe}_{0.9}\text{Cr}_{0.1})\text{O}_3-0.1\text{BaTiO}_3-0.2\text{PbTiO}_3$ (BLxFOC-BT-PT, with $x = 0, 0.03, 0.05, 0.07$) solid solutions were prepared by the traditional ceramic process. X-ray diffraction results reveal that all samples show pure pseudocubic perovskites structure. The lattice parameter of the solid solutions increases linearly with the La content, indicating that La ions have entered crystal lattices to form a solid solution. The Curie temperature of the solid solutions decreases with the La content. Room-temperature polarization–electric field (P – E) curves indicate that the samples with $x = 0.03$ and 0.05 exhibit saturated P – E loops. Piezoelectric constant d_{33} of the solid solutions increases firstly and then decreases. Magnetizations of the solid solutions decrease with the La content. The evidence of weak ferromagnetism and saturated ferroelectric hysteresis loops in BLxFOC–BT–PT system at room temperature makes it a good candidate for multiferroic applications.

I. INTRODUCTION

In recent years, there has been increasing interest in multiferroic materials, which have two or more order parameters simultaneously such as ferromagnetic, ferroelectric, and/or ferroelastic ordering.¹ Coupling between ferromagnetic and ferroelectric ordering leads to magnetoelectric (ME) effect. The ME effect provides an additional degree of freedom in design of new functional sensor, current devices, transducers, and multistate memory devices.^{2,3} BiFeO_3 (BFO) is a well-known perovskite compound possessing ferroelectric ordering and canted spin aligned antiferromagnetic ordering simultaneously.¹ The Curie temperature and Néel temperature of BFO are of 1103 and 643 K, respectively, attracting high scientific attention to study coupling between antiferromagnetism and ferroelectricity. However, it is difficult to obtain pure BFO because of the easy formation of second phase during synthesis and because the valence fluctuation of $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$ ions and the formation of oxygen vacancies results in high leakage of BFO. Meanwhile, the overall magnetization of BFO is vanishing because of its spiral-modulated spin structure in the period of 62 nm.^{4,5} To overcome these deficiencies of single BFO, recent work mainly has focused on introducing perovskites (such as PbTiO_3 and BaTiO_3)^{6,7} to form binary or ternary solid solutions and doping on these solid solutions.^{8–11}

This study was based on our foregoing work.¹¹ Solid solution $0.7\text{Bi}(\text{Fe}_{0.9}\text{Cr}_{0.1})\text{O}_3-0.1\text{BaTiO}_3-0.2\text{PbTiO}_3$ was chosen to be doped La because of its lower dielectric loss in $0.7\text{Bi}(\text{Fe}_{1-x}\text{Cr}_x)\text{O}_3-0.1\text{BaTiO}_3-0.2\text{PbTiO}_3$ system. Jiang et al. reported La dopant in BFO ceramics could effectively restrain the second phase and leakage current.¹² Lanthanum doping is intended to improve ferroelectric and piezoelectric properties in our work. Dielectric, ferroelectric, piezoelectric, and ferromagnetic properties were investigated in this work.

II. EXPERIMENTAL PROCEDURE

Solid solutions $0.7\text{Bi}_{1-x}\text{La}_x(\text{Fe}_{0.9}\text{Cr}_{0.1})\text{O}_3-0.1\text{BaTiO}_3-0.2\text{PbTiO}_3$ ($x = 0, 0.03, 0.05, 0.07$) were fabricated by the conventional solid-state reaction method. Analytical-grade raw materials, Bi_2O_3 , Fe_2O_3 , Cr_2O_3 , La_2O_3 , BaCO_3 , and TiO_2 , were weighed and mixed in a ball mill for 12 h, using alcohol as media. After drying, the powders were calcined at 860–960 °C for 2 h in air and ball milled for another 12 h. The resultant powders were pressed into disks of 10 mm in diameter and 1 mm in thickness using a hardened stainless steel die at a pressure of 400 MPa, with polyvinyl alcohol (PVA) as binder. After burning off PVA, the pellets were sintered at 1060–1100 °C for 3 h in air. Silver paste was fired on both sides of the samples at 810 °C for 20 min as the electrodes for the dielectric and ferroelectric measurements.

Phase compositions of the specimens were characterized by an x-ray diffraction (XRD; Rigaku D/MAX-2400, Cu $K\alpha$ radiation). Microstructure of fresh fracture

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surfaces of sintered samples was examined by using a scanning electron microscopy (SEM; JSM-6360). The density of the samples was tested by Archimedes method. Temperature dependence of complex permittivity was measured by using an HP4284 impedance analyzer. Ferroelectric hysteresis loops were characterized using a ferroelectric test system (TF Analyzer 2000), and magnetic hysteresis loops were measured by Lake-Shore 7307 vibrating sample magnetometer (VSM).

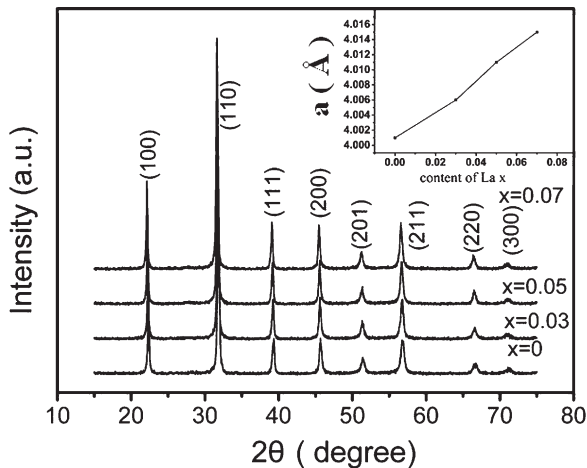


FIG. 1. X-ray diffraction patterns of the $\text{BL}_x\text{FOC-BT-PT}$ ceramics with different La contents.

III. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns for $\text{BL}_x\text{FOC-BT-PT}$ with $x = 0, 0.03, 0.05,$ and 0.07 . All samples possess single phase of pseudocubic perovskites structure. There was little change in phase structure by doping La. However, diffraction peaks of the samples shift toward lower angles with increasing La content. This result indicates that lattice constant of the samples increases with the La content. The lattice constant was calculated from XRD patterns by extrapolating functions, as shown in the inset in Fig. 1. The lattice parameter of the solid solutions increases linearly with the La content. That is because the radius of La^{3+} is larger than that of Bi^{3+} ,¹³ indicating that La ions have entered crystal lattices to form a solid solution.

Figures 2(a)–2(d) show SEM images of $\text{BL}_x\text{FOC-BT-PT}$ for $x = 0, 0.03, 0.05,$ and 0.07 , respectively. These images were taken from the fresh fracture surface. It can be seen that the samples with $x = 0.03$ and 0.05 are fully densified, containing no residual porosity and second phases, the relative density of samples for $x = 0, 0.03,$ and 0.05 is 92.5%, 94.3%, and 95.7%, respectively. The grain size is more homogeneous than that of the undoped sample. While with further increasing the La content, an inhomogeneous grain growth appears, as shown in Fig. 2(d). The relative density of the sample with $x = 0.07$ is 93.2%. The improvement of density for the samples with $x = 0.03$ and 0.05 can be attributed to

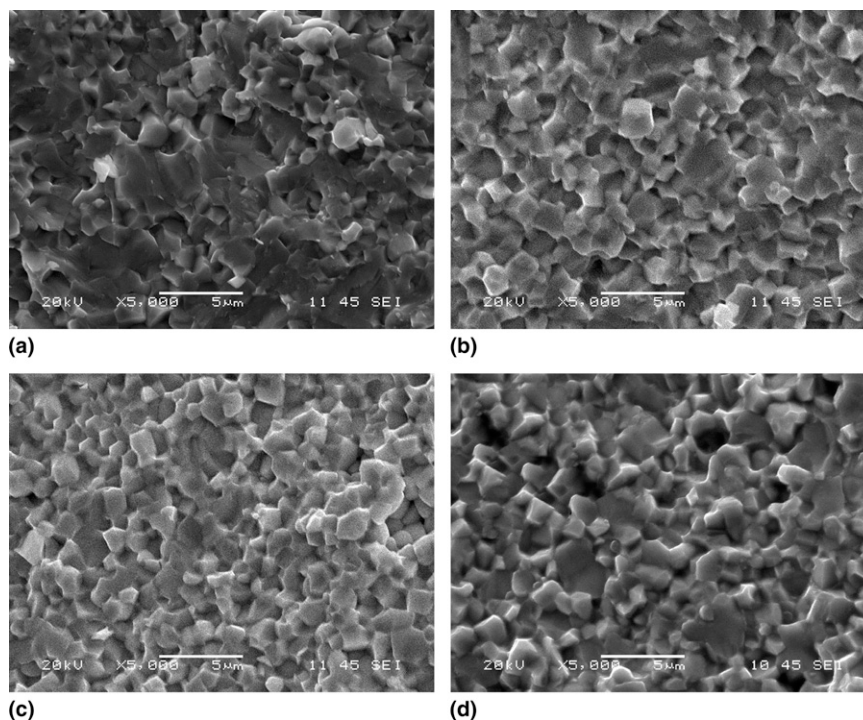


FIG. 2. Scanning electron microscopic images of fracture surfaces of the $\text{BL}_x\text{FOC-BT-PT}$ samples with different La contents. (a) $x = 0$, (b) $x = 0.03$, (c) $x = 0.05$, and (d) $x = 0.07$.

the A-site deficiency caused by the substitution of La^{3+} for Bi^{3+} , which favors the diffusion of the constituent ions during the sintering process. However, when $x = 0.07$, which may exceed the solubility limit of La ions in the solid solution, the sintering ability of the ceramic and the properties of the materials are deteriorated accordingly. It can also be found that the fracture surfaces of the undoped sample look more transgranular rather along grain boundary due to the intrinsic stress. The intrinsic stress was superimposed on the external stress, which prevented the fracture from beginning along grain boundaries. The transgranular fracture becomes more and more inconspicuous with the La content.

Figure 3 shows dielectric constant and loss of the samples as a function of temperature at 10^6 Hz. Dielectric constant maximum can be observed, revealing the ferroelectric–paraelectric phase transition of the BLxFOC–BT–PT ceramics. The dielectric peaks of the samples become broader with the La content, reflecting the diffuse characteristics of the phase transition.¹⁴ The peak dielectric constant decreases with the La content. The temperature at the peak determined the phase transition temperatures are about 621, 594, 573, and 548 °C for $x = 0, 0.03, 0.05,$ and 0.07 , respectively, decreasing with increasing in La content. The structure disorder and compositional fluctuation produced in the arrangement of cation at A-site with lattice vacancies lead to the microscopic heterogeneity in composition, resulting in the distribution of different local Curie regions.¹⁵ Therefore, the more La substitutions the higher degree of the structure and compositional disorder and thus more pronounced diffuse phase transition would be.

P – E curves of the BLxFOC–BT–PT samples with $x = 0, 0.03, 0.05,$ and 0.07 , respectively, are shown in Fig. 4. For the sample with $x = 0$, P – E loop has rounded corners and cannot reach saturation, indicating significant conductive losses. However, P – E loops of the samples with $x = 0.03$ and 0.05 reach saturation. We

considered that the electric resistivity of the doped samples increased because of the introduction of La, and the doped samples could endure higher electric field. Therefore, the P – E loops with $x = 0.03$ and 0.05 can attain saturation. The specimens will be completely poled, and hence the piezoelectric properties can be characterized. The conductive losses of the specimen with $x = 0.07$ is too significant to allow specimens to be completely poled. It is well known that most magnetic materials usually have high electrical conductivity. Thus, few multiferroic materials could exhibit the ferroelectric response properly. Magnetic materials with high insulating resistivity are very critical to possess the ferroelectric and ferromagnetic properties simultaneously. Otherwise, an applied electric field would cause an increase in current for conducting samples rather than inducing the electrical polarization. Therefore, the BLxFOC–BT–PT system possesses high insulating resistivity and good ferroelectric properties.

For piezoelectric measurement, we polarized the samples in the silicon oil under an electric field 25 kV/cm at 120 °C. The piezoelectric constant d_{33} was measured using a quasi-static d_{33} meter (Model ZJ-3, Institute of Acoustics Academic Sinica, Beijing, China). Figure 5 shows the dependence of the piezoelectric constant d_{33} on the La content. It can be seen that the piezoelectric constant d_{33} increases firstly and then decreases with the La content. The d_{33} of specimen with $x = 0.05$ is the largest. That is because La dopant can reduce leakage current to increase the electric resistivity of the samples when $x < 0.05$. Therefore, the samples can endure higher electric field and be poled completely. While with further increasing the La content, which may exceed the solubility limit of La ions in the solid solution, the sintering ability of the ceramic is deteriorated accordingly, leading to high conductivity in the sample with $x = 0.07$. Therefore, the sample cannot be poled completely, leading to a lower d_{33} value.

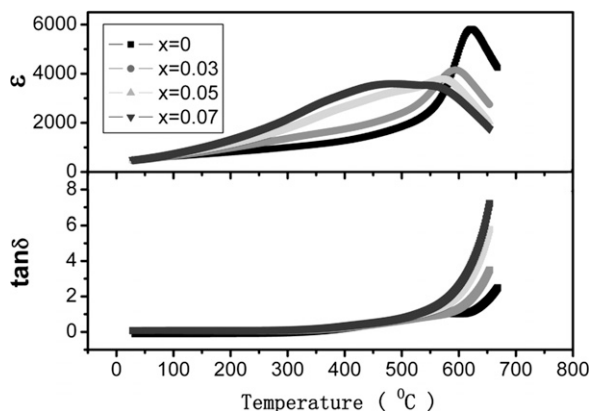


FIG. 3. Dielectric constant and loss of the BLxFOC–BT–PT ceramics as a function of temperature.

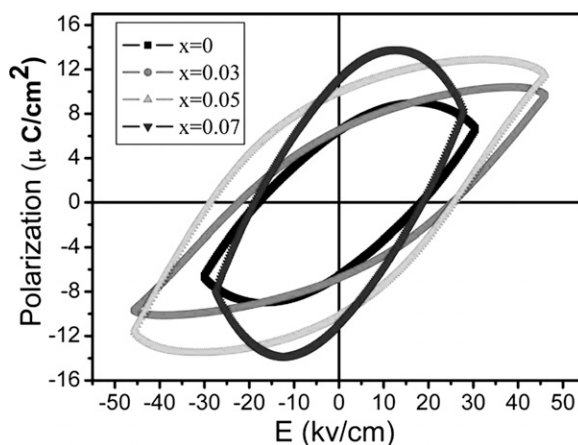


FIG. 4. Ferroelectric hysteresis loops of the BLxFOC–BT–PT samples with different La contents.

Figure 6 shows $M-H$ curves of the BL x FOC–BT–PT samples with $x = 0, 0.03, 0.05,$ and $0.07,$ respectively, measured at room temperature. The BL x FOC–BT–PT solid solutions exhibit symmetric magnetic hysteresis loops, indicating that they are magnetic ordered materials. The remanent magnetizations of BL x FOC–BT–PT for $x = 0, 0.03, 0.05,$ and 0.07 are about $0.11, 0.06, 0.05,$ and 0.04 emu/g, respectively, showing a slight fall with the increase of La content. The remanent magnetizations are relatively small compared with nominal ferromagnetic compounds. Small remanent magnetizations and unsaturated $M-H$ behavior of the solid solutions indicate that they

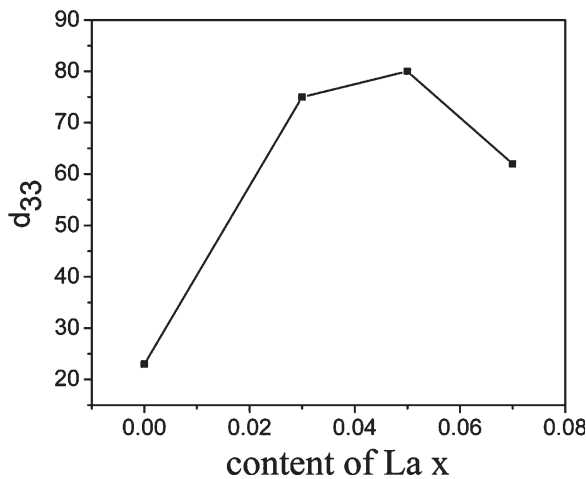


FIG. 5. Piezoelectric constant of the BL x FOC–BT–PT ceramics as a function of La content.

are basically antiferromagnetic with weak ferromagnetism.⁶ In such a case, spontaneous magnetization M_s could be obtained by extrapolating the linear portion of the $M-H$ curves to $H = 0$. The estimated values of M_s decreased with increasing x , were $0.15, 0.14, 0.1,$ and 0.09 emu/g, for $x = 0, 0.03, 0.05,$ and $0.07,$ respectively. Physical properties of BFO-based solid solutions with simultaneously occurring magnetic and electric orderings are not yet understood. Remanent magnetizations observed in this investigation reveal ferromagnetism, but weak compared with typical ferromagnetic compounds. The magnetic properties of $0.7\text{Bi}(\text{Fe}_{0.9}\text{Cr}_{0.1})\text{O}_3-0.1\text{BaTiO}_3-0.2\text{PbTiO}_3$ were discussed in our previous report.¹¹ We considered the possible reason for the slight fall in the magnetizations with the La content was the local ferromagnetic ordered structure ($\text{Fe}^{3+}-\text{Cr}^{3+}$) that might be formed between Fe^{3+} ions and Cr^{3+} ions was disturbed partly because of the introduction of La. Much more work is required to interpret the magnetization mechanism of the BiFeO₃-based materials.

IV. SUMMARY

Pure perovskite $0.7\text{Bi}_{1-x}\text{La}_x(\text{Fe}_{0.9}\text{Cr}_{0.1})\text{O}_3-0.1\text{BaTiO}_3-0.2\text{PbTiO}_3$ ($x = 0, 0.03, 0.05, 0.07$) solid solutions were prepared by the traditional ceramic process. The addition of La substitutions can increase the electric resistivity, the specimens can be completely poled, and the piezoelectric properties can be characterized. The BL x FOC–BT–PT ceramics are of weak ferromagnetism and saturated ferroelectric hysteresis loops simultaneously at room temperature. This will become a promising

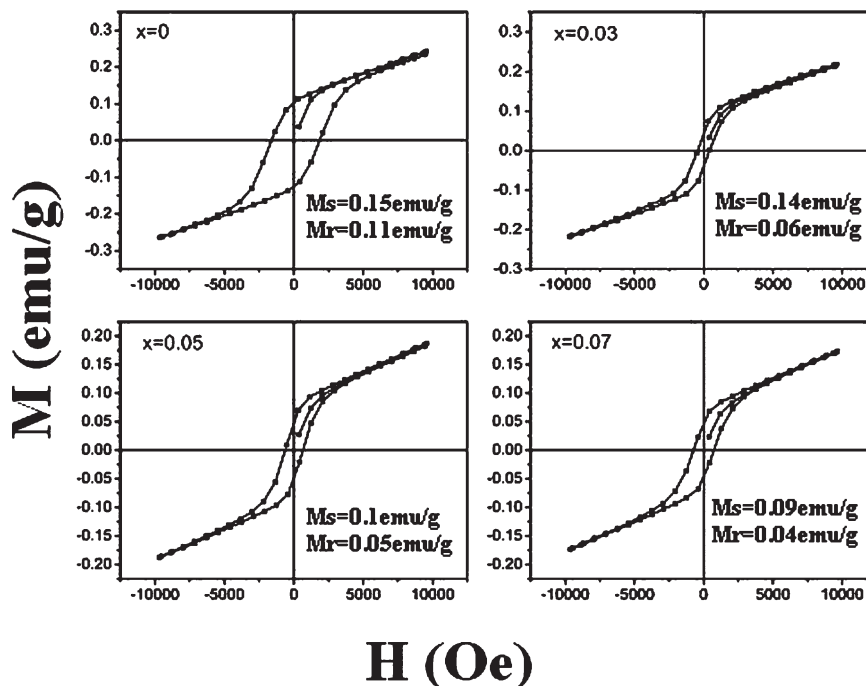


FIG. 6. Magnetic hysteresis loops of the BL x FOC–BT–PT samples with different La contents.

candidate as single-phase ferroelectromagnetic material for application of ferroelectricity, ferromagnetism, and magnetoelectricity.

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