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Dielectric, ferroelectric and piezoelectric properties of La-substituted $BiFeO_3$–$BaTiO_3$ ceramics

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Abstract

$(Bi_{1-x}La_x)FeO_3$–$BaTiO_3$ (BL_xF–BT) polycrystalline ceramics were prepared by the mixed oxide route and the effect of La substitution on the microstructure and electrical properties of the ceramics was investigated. The main crystal structure of the ceramics is a perovskite structure with weak secondary phase. The addition of small amount of La_2O_3 was quite effective to improve the remanent polarization P_r and low coercive field E_c. Because of the relative lower E_c, larger P_r and good densification, the piezoelectric properties of the ceramics are evidently enhanced at $x=0.02$: $d_{33}=168$ pC/N, $k_p=0.335$. An obvious relaxor characteristics was observed with increasing La_2O_3 content.

Keywords: C. Piezoelectric properties; D. Perovskite; Doping; Relaxor ferroelectrics

1. Introduction

The most widely used piezoelectric ceramics are lead oxide based ferroelectrics, especially Pb(Zr, Ti)O_3 (PZT) due to their high piezoelectric response close to a morphotropic phase boundary (MPB) between rhombohedral and tetragonal phases. However, conventional PZT ceramic materials have serious depoling and ageing problems at temperature above 200 °C that significantly limits their applications as high-temperature actuators and/or sensors, such as oil-flow control in automobile engines [1–3]. Therefore, researchers worldwide are looking for alternative new materials that may show higher working temperature.

New $BiMeO_3$–$PbTiO_3$(Me = Sc, In, Yb, etc) system with the higher Curie temperature at morphotropic phase boundary (MPB) than lead zirconium titanate Pb(Zr,Ti)O_3 (PZT) were developed [4–9]. The perovskite $BiScO_3$–$PbTiO_3$ (BS–PT) system has been reported as having piezoelectric properties comparable with PZT and high ferroelectric transition temperature (T_c, 450 °C) near the MPB [10,11].

Although BS–PT shows high temperature stability and improved properties compared to PZT, the high cost of Sc_2O_3 and currently restricts commercial exploitation. Further, because of the strong toxicity of lead oxide for the $BiMeO_3$–$PbTiO_3$ system, the use of the lead-based ceramics has caused serious lead pollution and environmental problems. Recently, much more attention has been paid to the research and development of lead-free high-temperature piezoelectric materials for replacing lead-based materials.

Following the development of $PbTiO_3$–Bi-based perovskite solid solutions with superior properties, lead-free piezoelectrics with a high Curie temperature and large piezoelectric responses, $BaTiO_3$ (BT) and Bi-based perovskites such as $BiScO_3$ [12], $BiFeO_3$ [13,14], $Bi(Zn_{1/2}Ti_{1/2})O_3$ [15], and $Bi(Mg_{1/2}Ti_{1/2})O_3$ [16] have been explored as candidates with superior properties.

Among them, the $BaTiO_3$–$BiFeO_3$(BT–BF) system exhibited a large small field piezoelectric constant d_{33} of 116 pC/N with a high Curie temperature of 619 °C [17].

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Meanwhile, a large number of multi-systems have been investigated [18,19]. Accordingly, in this study, BT–BF ceramics were fabricated with the amount of La_2O_3 to improve electrical properties.

2. Experimental procedure

The specimens were manufactured using conventional mixed oxide process. The used composition is as follows:

$0.71(Bi_{1-x}La_x)FeO_3$–$0.29BaTiO_3(x=0$–$0.05)+0.6$ wt% MnO_2 (BL_xF–BT)

High purity (with the purity of over 99%) oxide or carbonate powders of Bi_2O_3, TiO_2, Fe_2O_3, La_2O_3, MnO_2 and $BaCO_3$, were used as starting materials. The powders in the stoichiometric ratio of the compositions were mixed thoroughly in ethanol using zirconia balls for 24 h, and then dried and calcined at 850 °C for 2 h. After the calcination, the mixture was ball-milled again and mixed thoroughly with a PVA binder solution, and pressed into green disks with diameters of 13 mm under a pressure of 100 MPa. After the binder was burned out at 600 °C for 2 h, sintering was carried out in a closed Al_2O_3 crucible inside a furnace. A temperature of 1100 °C, a holding time of 1 h and heating rates of 3 °C min were used.

The crystalline structure of the sintered samples was examined using X-ray diffraction (XRD) analysis with Cu Ka radiation(D8 Advance, Bruker Inc., Germany) in the 2θ range of 20°–60°. The scanning electron microscopy (JSM-5610LV/Noran-Vantage) was employed to examine the microstructure of the ceramics. The sintered ceramics were coarsely polished and silver paste electrodes were formed at the two circular surfaces of the disk-shaped specimens after firing at 600 °C for 10 min. The samples were poled using electric fields of 4–6 kV/mm for 5 min while the sample was immersed in an 100 °C silicone oil bath. The relative permittivity ε_r at 1 kHz, 10 kHz and 100 kHz of the ceramics were measured as a function of temperature using an impedance analyzer (Agilent 4192 A). The electromechanical coupling factor kp was determined by the resonance method according to the IEEE Standard using an impedance analyzer (Agilent 4294 A). The piezoelectric coefficient d_{33} was measured using a piezo-d_{33} meter (ZJ-3A, China). The polarization–electric field (P–E) loops were observed at room temperature and 1 Hz using a ferroelectric tester (Premier II, Radiant Technologies).

3. Results and discussion

Fig. 1 shows the XRD patterns of the BL_xF–BT ceramic samples in the ranges of 2θ from 20° to 60°. All the compositions have the dominant perovskite structure with amount of impurities. It have been also reported that the second phases like $Bi_2Fe_4O_9$ and $Bi_{25}Fe_4O_{39}$ appear in $BiFeO_3$ ceramics [20]. The formation of these secondary phases in $BiFeO_3$ is well documented and has previously proven difficult to eliminate from bulk $BiFeO_3$ samples. The minor impurities in Fig. 1 may be identified to be close to $Bi_2Fe_4O_9$.

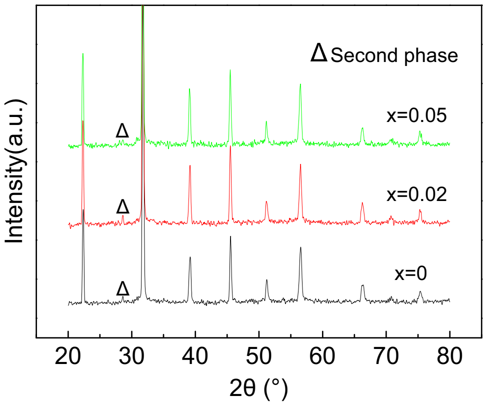

Fig. 1. XRD pattern of BL_xF–BT ceramics.

Fig. 2 shows the microstructure of the fabricated samples of BL_xF–BT ceramics. Grain size slightly increased with the amount of La_2O_3 addition and the grain growth inhibited with further increasing La_2O_3 content. As shown in Fig. 2, an obvious liquid phase is observed at grain boundaries for La_2O_3 modification ceramics and the samples with La_2O_3 addition show a most dense microstructure. This can be illustrated by the fact that La_2O_3 addition improves the sintering performance, and greatly assists in densification of the BL_xF–BT ceramics. According to Shannon ionic radii table [21], the radii of Bi^{3+} (0.117 nm, 12CN) is smaller than that of La^{3+} (0.136 nm, 12CN). Thus, the substitution of La^{3+} for Bi^{3+} leads to the lattice expansion of BL_xF–BT ceramics. Thus, the lattice distortion can improve the sintering, and also accelerate the densification of the ceramics.

Fig. 3 shows the P–E loops of the BL_xF–BT ceramics under an electric field of 5 kV/mm, while the variations of the remanent polarization P_r and coercive field E_c with x for the BL_xF–BT ceramics are shown in Fig. 4. All samples exhibit well developed P–E hysteresis loops. The remnant polarization P_r increases significantly from 1.6 $\mu C/cm^2$ for $x=0$ BL_xF–BT ceramics to 16 $\mu C/cm^2$ for $x=0.02$. For $x=0.03$, P_r reaches a maximum value of 17.2 $\mu C/cm^2$. On the other hand, the coercive field E_c decreases significantly from 26.4 kV/cm for $x=0$ BL_xF–BT ceramics to 22.0 kV/cm for $x=0.05$. The decrease in the E_c could possibly be explained by the appearance of random field near dipolar defects. The lower sintering temperature and liquid phase with La_2O_3 modification ceramics may lead to the formation of the dipolar defects, which are quenched above the ferroelectric transition temperature due to their extremely low mobility. The random field around dipolar defects can significantly lower the activation barrier required for the nucleation of domains, leading to a lower E_c [22].

As shown in Fig. 5, the BL_xF–BT ceramics also exhibit improved piezoelectric properties. It is observed that the electromechanical coupling factor k_p increases from 0.28 to 0.335 and the piezoelectric constant d_{33} increases from 130

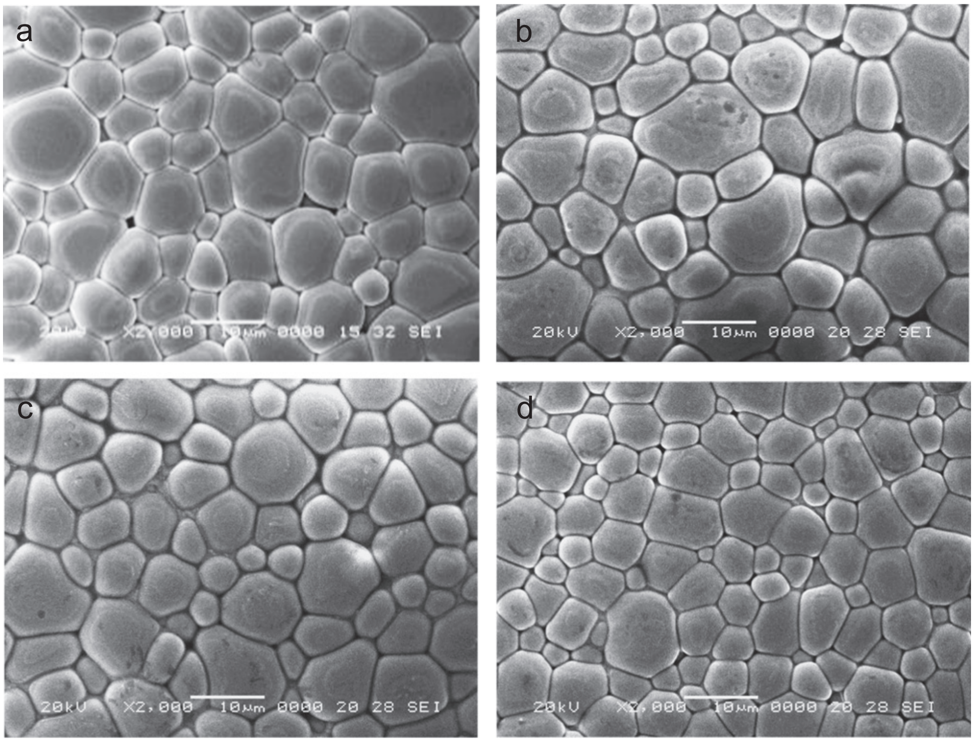

Fig. 2. SEM images of BL$_x$F–BT ceramics (a)$x=0$; (b)$x=0.01$; (c)$x=0.02$ and (d)$x=0.05$.

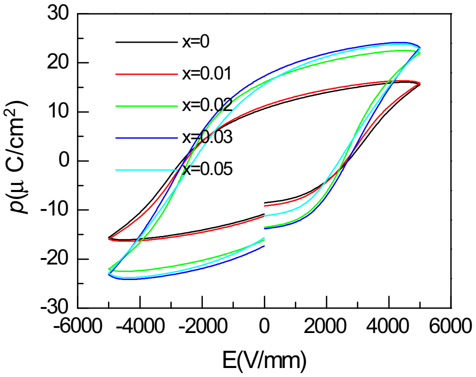

Fig.3. Room temperature P–E hysteresis loops of the BL$_x$F–BT ceramics.

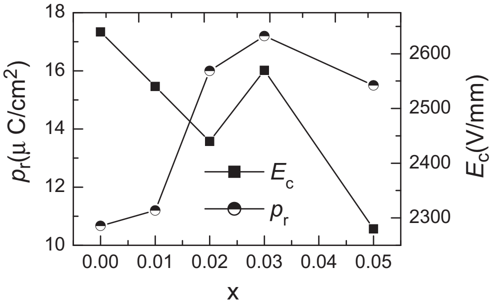

Fig. 4. Variation of P_r and E_c with x for BL$_x$F–BT ceramics.

to 168 pC/N as x increases from 0 to 0.02. And the piezoelectric properties were deteriorated with $x>0.03$ BL$_x$F–BT ceramics.

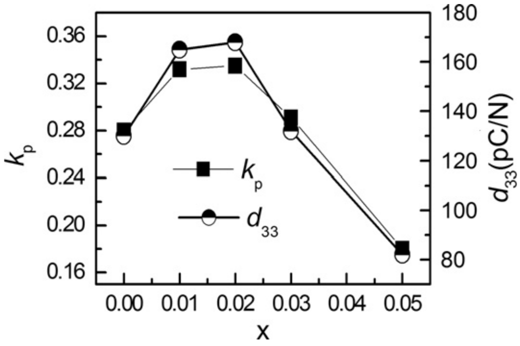

Fig. 5. Piezoelectric constant d_{33} and planar electromechanical coupling factor k_p for BL$_x$F–BT ceramics.

The references [18] reported that the $(0.9-x)$BaTiO$_3$–0.1Bi(Mg$_{1/2}$Ti$_{1/2}$)O$_3$–xBiFeO$_3$ ceramics shown maximum values of $d_{33}=94$ pC/N at $x=0.6$. Likewise, the $(1-y)$ BiFe$_{1-x}$(Mg$_{0.5}$Ti$_{0.5}$)$_x$O$_3$–yBaTiO$_3$ (BFMT–BT, $y=0.29$, $x=$ 0–0.12) ceramics, which were reported by Zhou et al., shown a maximum value of $d_{33}=155$ pC/N for $x=0.03$ BFMT–BT ceramics, but k_p shown a monotonic decrease with increasing Bi(Mg$_{1/2}$Ti$_{1/2}$)O$_3$ content [19]. Compared with Bi(Mg$_{1/2}$Ti$_{1/2}$) O$_3$ modified BT–BF system, the piezoelectric properties of La-substituted BT–BF ceramics are superior to those of BaTiO$_3$–Bi(Mg$_{1/2}$Ti$_{1/2}$)O$_3$–BiFeO$_3$ ceramics.

The improved piezoelectric properties can be attributed to the increased grain and densification, which makes it possible to apply a higher electric field during the poling process. Grain size greatly affects the extrinsic contributions to the piezoelectric performance. Fine-grained ceramics have limited domain variants and the domain reorientation is hindered by strong coupling between grain boundaries and domain walls, leading to lower polarization and piezoelectric response [23,24]. The improved piezoelectric properties may also be related to the decrease in the coercive field E_c and the increase in the remnant polarization P_r.

The temperature dependences of ε_r at 1, 10 and 100 kHz for the BL$_x$F–BT with $x=0$–0.05 are shown in Fig. 6. It can be seen that the ferroelectric–paraelectric phase transition peak for the ceramic with $x=0$ is relative sharp and the Curie temperature (T_c) is almost frequency-independent, suggesting that the ceramic is a normal ferroelectric. As x increases to 0.03, the peak becomes slightly broadened and frequency-dependent. However, when $x=0.05$, the transition peak becomes broadened significantly and more frequency-dependent. This suggests that a relaxor phase transition is induced after the high level doping of La_2O_3. The relaxor characteristics were observed in many ABO_3 perovskite, of which either A- or B-sites are occupied by at least two cations [25,26]. Ferroelectric relaxation is a thermally activated process. As several studies reported in the mixed A-site cation family, the addition of La^{3+} ions into BF–BT, different ions with a fluctuating composition, could lead to a local disorder at A-site and the disruption of long-range order, which could be a possible explanation for the relaxation in the high level doping of La_2O_3 ceramics.

From Fig. 6, it can be seen that the Curie temperatures (T_c) of BL$_x$F–BT ceramics are decreased with increasing La content. The correlation between T_c of perovskite ferroelectric materials and tolerance factor t was reported by Choi et al. [27]. The results indicated that a lower tolerance factor of the non-$PbTiO_3$ end member generally leads to a higher T_c for $PbTiO_3$–Bi-based perovskite solid solutions. The tolerance factor t is defined as

$$t=\frac{R_A+R_0}{\sqrt{2}(R_B+R_0)} \tag{1}$$

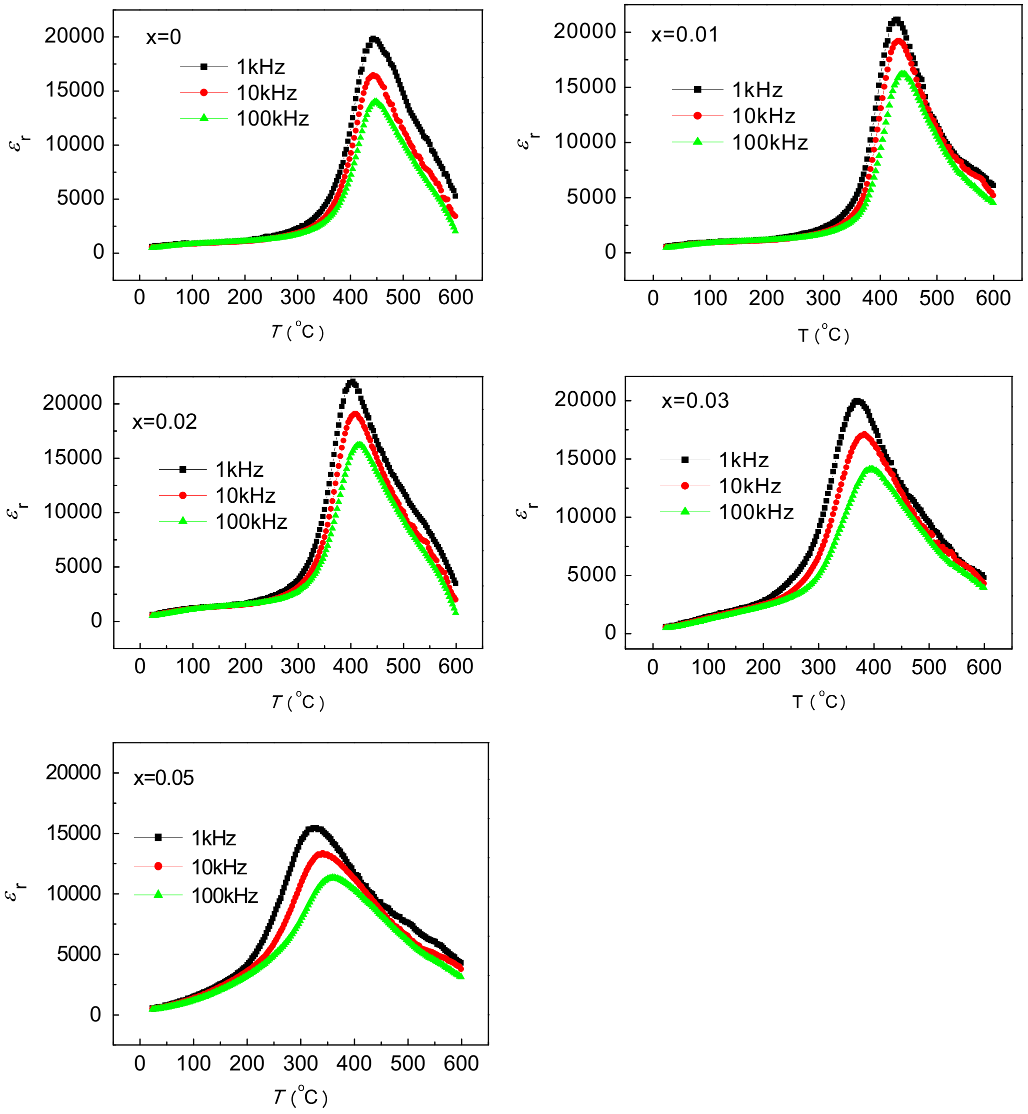

Fig. 6. Temperature dependences of dielectric constant ε_r at 1 k, 10 k and 100 kHz for BL$_x$F–BT ceramics.

with R_A, R_B, and R_O as the ionic radii from the A(XII), B(VI), and O sites, respectively. According to Shannon ionic radii table [21], the substitution of La^{3+} for Bi^{3+} leads to the increase of tolerance factor t for BL_xF–BT ceramics, which causes the decreasing $T_{c.}$

4. Conclusions

In this study, new La substitution piezoelectric ceramics BL_xF–BT were synthesized by conventional ceramic sintering technique, in which the crystalline structural, dielectric, ferroelectric and piezoelectric properties of the ceramics were also researched. The results of X-ray diffraction data show that the crystal symmetry remains virtually unaltered by the La_2O_3 substitution. The E_c shows a decrease with increasing La_2O_3 content and P_r first increases and then decreases. Piezoelectric properties show an increase with increasing La_2O_3 content and reach maximum of $d_{33}=168$ pC/N, $k_p=0.335$ for $x=0.02$ BL_x F–BT ceramics. The relaxor characteristics are more obvious with increasing La_2O_3 content.

Acknowledgments

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