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Ferroelectric properties of $Pb(Zr_{0.52}Ti_{0.48})O_3$–$Bi_{3.25}La_{0.75}Ti_3O_{12}$ ceramics

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Abstract

The ceramic samples of compound $(1-x)Pb(Zr_{0.52}Ti_{0.48})O_3$–$xBi_{3.25}La_{0.75}Ti_3O_{12}$ (when $x = 0$, 0.03, 0.05, 0.07, 0.10, 0.15 and 0.20) were prepared by a solid-state mixed oxide method. X-ray diffraction analysis showed that complete solid solutions occurred for all compositions. Perovskite phase with tetragonal crystal structure and corresponding lattice distortion was observed. Scanning electron micrographs of sample surfaces showed equiaxed grains for all compositions. Ferroelectric measurements revealed that the addition of small amount of BLT ($x = 0.03$) showed high remanent polarization ($\sim$33.5 $\mu C\ cm^{-2}$) and low coercive field ($\sim$2.74 $kV\ mm^{-1}$). Further increasing BLT content could maintain ferroelectric properties of PZT–BLT ceramics. Based on this study, ferroelectric properties of this PZT–BLT ceramic system can be improved for being further used in ferroelectric memory applications.

Keywords: A. Sintering; C. Ferroelectric properties; D. PZT; $Bi_{3.25}La_{0.75}Ti_3O_{12}$

1. Introduction

Ferroelectric materials are widely employed in device applications such as sensors, actuators and non-volatile random access memories [1]. Many of these applications require materials with superior dielectric and ferroelectric properties. Both PZT and BLT are important materials employed in these applications. PZT exhibits excellent ferroelectric properties such as high remanent polarization [1,2]. However, PZT still suffers from several problems, especially severe polarization fatigue after switching pulses [3–5]. BLT is known as an Aurivillius or bi-layered structured ferroelectric material [6]. BLT possesses a large spontaneous polarization and high fatigue endurance. However, the major problems of BLT are high leakage current, low remanent polarization and high processing temperature [7,8].

Modification of PZT with BLT is of considerable interest and has been widely explored, especially in the form of thin films. The product showed a combination of the fatigue-resistant characteristics of BLT and the superior dielectric and piezoelectric properties of PZT. In 2002, Bao et al. [9] studied the ferroelectric properties of a sandwich structured BLT/PZT/BLT thin films on $Pt/Ti/SiO_2/Si$ substrates. They reported that the sandwich structure exhibited a well-defined hysteresis loop with high remanent polarization values and dielectric constant which were comparable to those of some single epitaxial PZT thin films and much higher than those of single epitaxial BLT thin films. Recently, Thongmee et al. [10,11] studied a series of compounds with formula $(1-x)Pb(Zr_{0.52}Ti_{0.48})O_3$–$x(Bi_{3.25}La_{0.75})Ti_3O_{12}$ in ceramic form. The results revealed that an addition of 10 wt% BLT into PZT (0.9PZT–0.1BLT) could improve dielectric and ferroelectric properties of PZT ceramics. However, fundamental research on the combination of these two important ferroelectric materials in a form of bulk ceramic is quite scarce. Therefore, the aim of this present study is to determine the ferroelectric properties of $(1-x)$PZT–xBLT ceramics with BLT content (i.e. $x = 0$, 0.03, 0.05, 0.07, 0.10, 0.15 and 0.20). The samples were prepared by a solid state mixed-oxide method and characterized in terms of physical, phase formation and ferroelectric properties.

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The optimum composition for this ceramic system was reported and discussed.

2. Experimental

$Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) and $(Bi_{3.25}La_{0.75})Ti_3O_{12}$ (BLT) powders were prepared by a solid-state mixed oxide method. The starting chemicals used were PbO (99%, Fluka), ZrO_2 (99%, Riedel-de Haën), TiO_2 (99%, Riedel-de Haën), Bi_2O_3 (98%, Fluka) and La_2O_3 (99%, Cerac). The starting powders were weighed, ball-milled in distilled water for 24 h and dried using a freeze-drying method. The mixed powders were calcined at 750 °C for 4 h with a heating/cooling rate of 5 °C min^{-1} for BLT and at 800 °C for 2 h with a heating/cooling rate of 5 °C min^{-1} for PZT powder. The calcined PZT and BLT powders were then weighed, ball-milled and dried using the above procedure to produce a powder mixture of $(1-x)$PZT–xBLT, where x was the weight fractions and had the values of 0, 0.03, 0.05, 0.07, 0.10, 0.15 and 0.20. Each mixture was pressed to form disc-shape pellets with 3 wt% PVA (polyvinyl alcohol) added as a binder. The pellets were covered with their own powders and finally sintered at a temperature 1150 °C in air for 4 h with a heating/cooling rate 5 °C min^{-1}. The firing profile also included 1 h dwell time at 500 °C for binder burn-out.

Phase analysis of the ceramics was done using an X-ray diffraction (XRD, Phillip Model X-pert). The densities were measured using Archimedes' method. The theoretical densities of all ceramic samples were calculated based on theoretical densities of BLT (7.67 g cm^{-3}) and PZT (8.006 g cm^{-3}). The samples were polished and thermally etched at 1050 °C for 10 min with a heating/cooling rate of 5 °C min^{-1} prior to microstructural investigation using a scanning electron microscope (SEM, JEOL JSM-6335F). For ferroelectric properties characterizations, the sintered samples were lapped to obtain parallel faces which were pasted with silver paint as electrode. The samples were then placed inside the sample holder, submerged in a silicone oil bath and then mounted into a fixture connected to a high-voltage power supply. A ferroelectric hysteresis (*P–E*) loop was characterized using a commercial electrical fatigue testing device (TF Analyzer 2000, aixACCT systems).

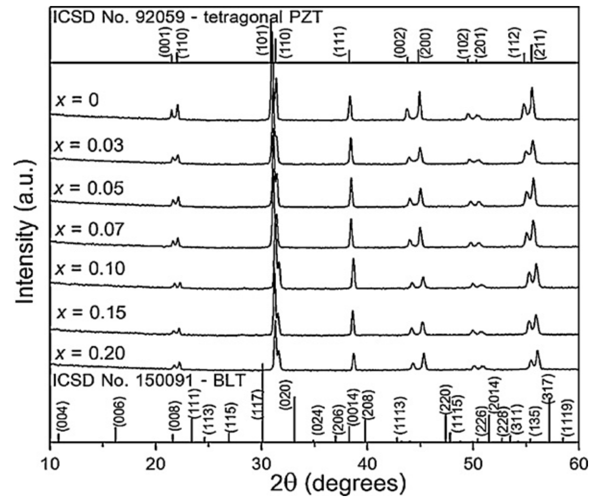

Fig. 1. X-ray diffraction patterns of $(1-x)$PZT–xBLT ceramics.

3. Results and discussion

X-ray diffraction (XRD) patterns of $(1-x)$PZT–xBLT ceramics with various x values are shown in Fig. 1. All patterns showed a complete crystalline solution of perovskite structure without the presence of pyrochlore or unwanted phases. The XRD pattern for PZT ceramic indicated mainly tetragonal phase which could be matched with ICSD file no. 92-059. All XRD peaks of the samples with BLT additions slightly shifted to the right while the tetragonal structure was maintained. The overall shift of the X-ray pattern suggested a slight decrease in the unit cell size of tetragonal PZT-based phase. The change in unit cell dimension seems to be in agreement with the fact that ionic sizes of Bi^{3+} and La^{3+} are slightly smaller that of Pb^{2+}. No BLT peaks were observed in all X-ray patterns. This indicated that the dissolution of BLT into PZT occurred during the sintering process.

Scanning electron micrographs in Fig. 2 reveal that all compositions had equiaxed grains. An addition of BLT up to 0.07BLT significantly reduced grain size while high density was maintained (see Table 1). A further increasing in the content of BLT up to $x = 0.15$ gradually increased grain size, while the density was lower as supported by a larger number of pores in their microstructures. It can also be noticed that the optimum composition that could produce ceramics with small

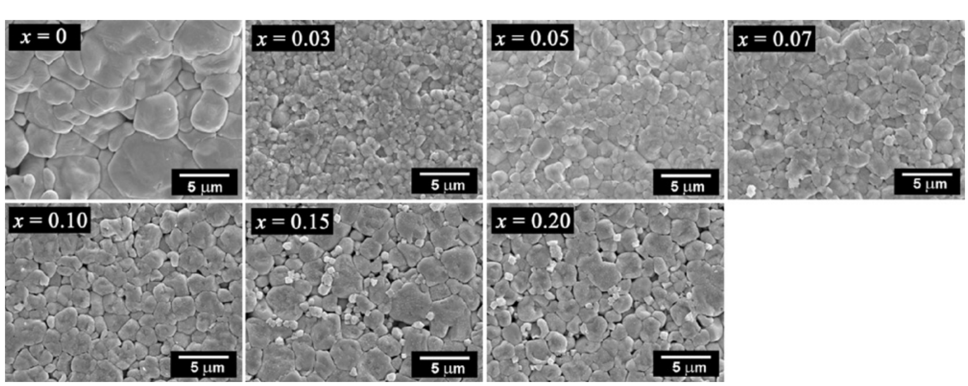

Fig. 2. SEM micrographs of $(1-x)$PZT–xBLT ceramics.

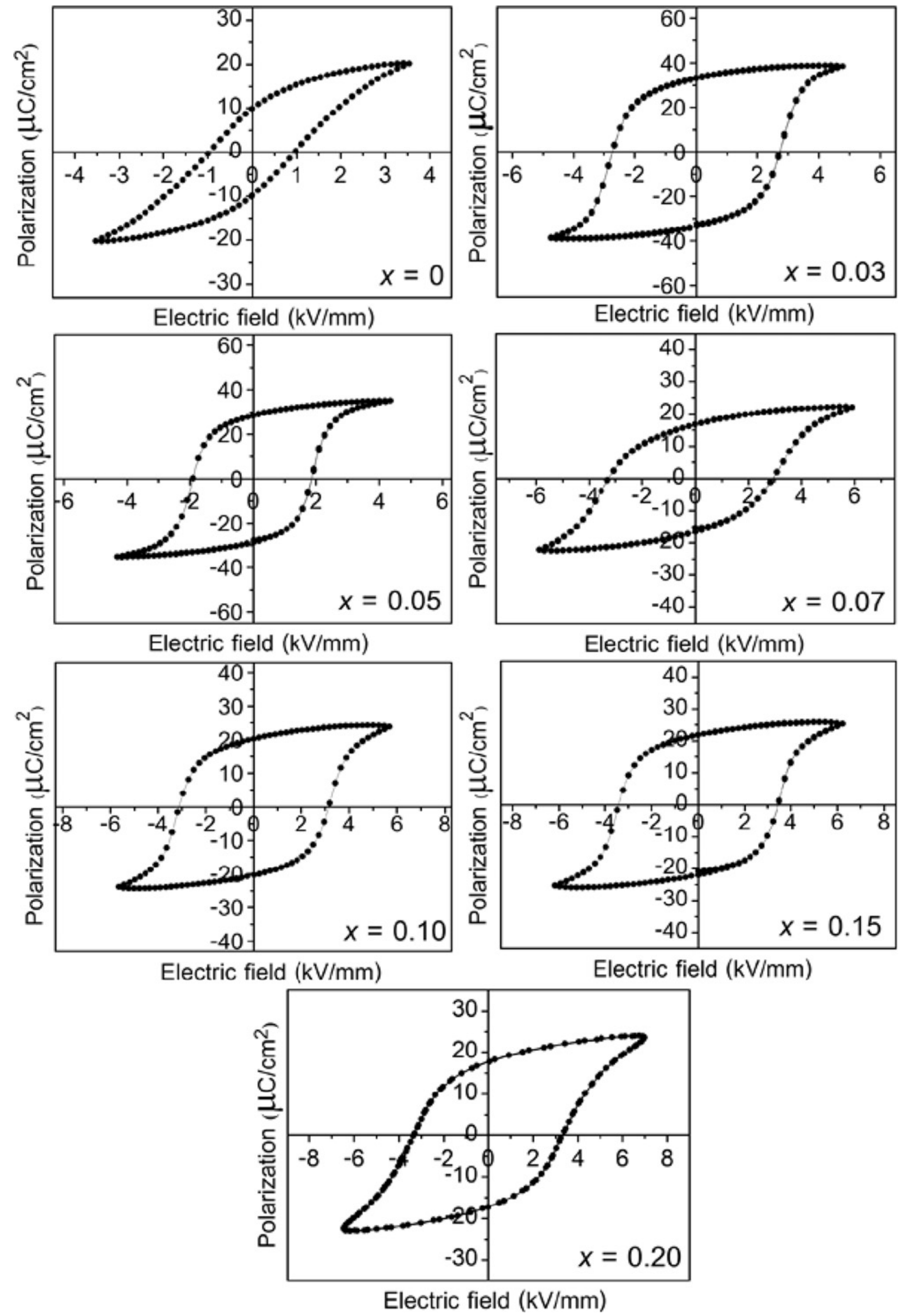

Fig. 3. *P–E* hysteresis loops of $(1 - x)$PZT–xBLT ceramics.

grain size (∼1.21 μm) and highest density (∼97.5%) was 0.97PZT–0.03BLT.

Polarization-field (*P–E*) hysteresis loops of $(1 - x)$PZT–xBLT ceramics are shown in Fig. 3. The well-developed and fairly symmetric hysteresis loops were observed for all compositions. From the polarization loop of the pure PZT sample, the remanent polarization (P_r) and the coercive field (E_c) are 11.12 μC cm^{-2} and 1.02 kV mm^{-1}, respectively. Starting from pure PZT, the addition of small amount of 0.03BLT (0.97PZT–0.03BLT) showed the remanent polarization and coercive field about 33.48 μC cm^{-2} and 2.74 kV mm^{-1}, respectively. Since the ferroelectric properties of the ceramics depend strongly on the poling and measuring fields [12,13], the ferroelectric parameters have thus been normalized in forms of P_r/P_{max} and E_c/E_{max}. Furthermore, the ferroelectric characteristics of the ceramics can be assessed with the hysteresis loop squareness (R_{sq}) which can be calculated from the empirical expression $R_{sq} = (P_r/P_{max}) + (-P_{1.1Ec}/P_r)$, where P_{max} is the maximum polarization obtained at some finite field strength below dielectric breakdown and $P_{1.1Ec}$

Table 1
Physical and ferroelectric characteristics of $(1-x)$PZT–xBLT ceramics.

Composition	Relative density (%)	Grain size (μm)	Ferroelectric properties				Loop squareness (R_{sq})
			P_r (μC cm^{-2})	E_c (kV mm^{-1})	P_r/P_{max}	E_c/E_{max}	
PZT	96.3	5.11 ± 1.66	11.1	1.00	0.50	0.26	0.63
0.97PZT–0.03BLT	97.2	1.21 ± 0.38	33.5	2.75	0.87	0.60	1.26
0.95PZT–0.05BLT	96.6	1.54 ± 0.54	28.7	1.86	0.82	0.45	1.21
0.93PZT–0.07BLT	96.4	1.55 ± 0.59	16.8	2.93	0.75	0.55	1.17
0.90PZT–0.10BLT	95.2	2.19 ± 0.62	20.2	3.17	0.85	0.54	1.24
0.85PZT–0.15BLT	93.9	1.81 ± 0.73	21.9	3.46	0.86	0.57	1.20
0.80PZT–0.20BLT	92.6	1.71 ± 0.79	17.6	3.29	0.76	0.48	0.99

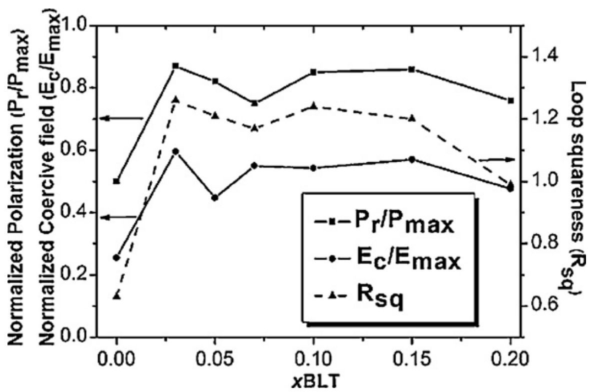

Fig. 4. The normalized polarization (P_r/P_{max}), normalized coercive field (E_c/E_{max}) and loop squareness (R_{sq}) of $(1-x)$PZT–xBLT ceramics.

is the polarization at the field equal to $1.1E_c$ [14]. For the ideal square loop, R_{sq} is equal to 2.00. These normalized values and hysteresis loop squareness are listed in Table 1 and plotted in Fig. 4 as a function of the BLT content (x value).

From Fig. 4, it could be seen clearly that all BLT-added samples showed higher values of normalized parameters and squareness when being compared to those of pure PZT. Their dependence on BLT concentration was also similar. Among the PZT–BLT samples investigated, the optimum composition seemed to be 0.97PZT–0.03BLT in which maximum density, microstructure homogeneity and ferroelectric properties were simultaneously obtained. The measured remanent polarization values of the PZT–BLT ceramics are higher than that of pure PZT (~11.12 μC cm^{-2}) and pure BLT (~10 μC cm^{-2}) [15]. On the other hand, the coercive field is lower than that of pure BLT ceramic (~4.04 kV mm^{-1}) [15]. These results suggested that BLT addition reduced the tendency of the sample to depolarized as well as induced higher endurance to switching field. This suggested that PZT–BLT ceramic might also possess better fatigue resistance. Based on this study, the ferroelectric properties of PZT–BLT ceramic system could be improved for being further particularly employed in ferroelectric memory applications.

4. Conclusions

Ceramics in the system $(1-x)Pb(Zr_{0.52}Ti_{0.48})O_3$–$x(Bi_{3.25}La_{0.75})Ti_3O_{12}$ (when $x = 0$, 0.03, 0.05, 0.07, 0.10, 0.15 and 0.20) were successfully prepared by a solid-state mixed oxide method. All PZT–BLT compositions in this study were identified by X-ray diffraction method as a single-phase material with a perovskite structure having mainly a tetragonal phase. BLT peaks were not observed in all samples which indicated complete dissolution of BLT into PZT lattice. SEM micrographs revealed that the PZT–BLT solid solutions had smaller grain sizes than that of pure PZT sample. In addition, ferroelectric properties of PZT–BLT ceramics were also found to enhance regardless of BLT content. In this study, 0.97PZT–0.03BLT showed maximum microstructural homogeneity and ferroelectric properties.

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