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Excellent electrostrictive properties of low temperature sintered PZT ceramics with high concentration $LiBiO_2$ sintering aid

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Abstract

The effect of $LiBiO_2$ (LBO) additive on the sintering of $Pb_{0.97}La_{0.03}(Zr_{0.53}Ti_{0.47})_{0.9925}O_3$ (PLZT) ceramics was carefully investigated. 6.0 wt% LBO added PLZT powders could be fully densified to 98% relative density at a temperature as low as 950 °C. It is worthy to notice that there are distinct enhancements in piezoelectric and electrostrictive properties by increasing the soaking time from 2 h to 7 h, which could mainly originate from the improvement of crystallinity and grain size of PLZT ceramics. By controlling the soaking time and concentration of LBO addition, PLZT ceramics sintered at 950 °C could exhibit high curie temperature of 240 °C and very high S_{11} of 0.22% under 3.0 kV/mm, which is even better than that of traditionally sintered PZT-5, PMN–PZT, and this is very promising for actuators designed in multilayer structure in high temperature environment.

Keywords: D. PZT; Low temperature sintering; High electrostrictive properties; High curie temperature

1. Introduction

For ferroelectric materials, one of the most important applications is piezoelectric actuator, which takes advantage of the piezoelectric coupling converting electrical into mechanical energy [1,2]. Piezoelectric actuator is usually classified into three categories: positioners, motors and vibration suppressors. Certain compounds are suited for particular application. PMN-PT relaxor ferroelectric is usually used for servo displacement transducers application (positioners) for its little strain hysteresis [3]. For ultrasonic motor application, hard piezoelectric ceramic (PZT based ceramics) is better suited because of its high mechanical quality Q and less heat generation during working [4]. Compared to PMN and PLZT ceramics, soft PZT ceramic is more preferred for pulse-driven motor application because it requires low dielectric permittivity aiming at a quick response. For this kind of application, the device is usually designed into multilayer structure in order to obtain high electric strain under small electric field [5]. Moreover, because piezoelectric actuators for high temperature environments are well under development, such as for aerospace applications and fuel injectors, Curie temperature consideration must be given to the selection of piezoelectric materials [6,7]. In previous literature reports, the compositions with high electrostrictive property (S_{11}) usually have relatively low Curie temperature (<150 °C), such as $(1-x)$PMN$-x$PT ($0<x<0.15$), PLZT(7∼9/65/35) etc. So the desired PZT material properties are low sintering temperature for cofiring with internal electrode, high electrostrictive properties, relatively high Curie temperature and low dielectric permittivity. As PZT is an age-old conventional piezoelectric material, low temperature sintering techniques of PZT ceramics have been extensively studied. In general, the ways to decrease the sintering temperature of PZT ceramics are adding low-melting-point sintering aids (ZnO, CuO, Li_2CO_3, B_2O_3, W_2O_3, PGO etc.) and/or synthesizing nanosized PZT powder [8–12]. How to retain the electrical properties of low temperature sintered PZT ceramics is always a challenge. Hayashi et al. reported that $LiBiO_2$ could be a useful sintering aid for the densification of PZT based ceramics (PZT, PMN–PZT, PNN–PZT etc.) [13–15]. Recently Sen

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et al. also reported that PZT could be sintered at "ultra"-low temperature 750 °C with the addition of LBO and the dielectric and piezoelectric properties are in some cases better than those of PZT samples by conventional sintering at high temperature [9]. However in their cases, the powder was prepared via a chemical syntheses method, and the process was complicated and sensitive, so it is difficult for industrial applications. Furthermore, from the results of published papers, most focused on the dielectric and piezoelectric properties, little attention has been paid to the electrostrictive properties of binary PZT ceramics.

In this present study, high concentration $LiBiO_2$ has been added to La modified PZT ceramic by traditional ceramic processing and we find by controlling the concentration of $LiBiO_2$ and soaking time, PZT ceramics could be well sintered at 950 °C, and their electrostrictive and piezoelectric properties are well kept. The electrostrictive properties of our 950 °C sintered samples are even better than those of the traditionally sintered PZT-5, PMN–PZT, larger than most results reported in other literatures as well [10,14,15]. The mechanism will be discussed in this paper.

2. Experimental

Undoped and different $LiBiO_2$ concentrations (1.0 wt%, 4.0 wt%, 6.0 wt% and 8.0 wt%) doped $Pb_{0.97}La_{0.03}(Zr_{0.53}Ti_{0.47})_{0.9925}O_3$ (PLZT) ceramics were prepared by traditional ceramic processing. During the first stage, $Pb_{0.97}La_{0.03}(Zr_{0.53}Ti_{0.47})_{0.9925}O_3$ was synthesized. Oxide powders of PbO, ZrO_2, TiO_2 and La_2O_3 were used as raw materials. The materials were weighed according to the stoichiometric proportions, milled with distilled water and agate balls for 8 h. The dried powders were then calcined in air at 850 °C for 2 h on recrystallized alumina crucibles. Then the calcined powders were ground and sieved through a 425 mm sieve. Next different $LiBiO_2$ concentrations (1.0 wt%, 4.0 wt%, 6.0 wt% and 8.0 wt%) were added to the PLZT oxide powder as a mixture of Li_2CO_3 and Bi_2O_3 powders. Sintering-aids-added PLZT oxide powders were mixed by ball-milling in distilled water for 24 h and then dried. The dry powders were mixed with polyvinyl alcohol (7 wt%). The powders were then pressed into pellets 13 mm in diameter and approximately 2 mm in thickness, then sintered between 800 and 1300 °C, depending on the amount of $LiBiO_2$. After that, the 2 mm disk samples were polished to 1.0 mm and electroded with silver paint for electrical measurements. The samples were poled at 120 °C for 15 min under an electric field of 40 kV/cm. The phase of the specimen was examined by X-ray diffraction with Cu Ka radiation (Rigaku RAX-10, Japan). The dielectric constant of each sample was calculated from the measured capacitance and the specimen geometry. The capacitance and dielectric loss tangent were measured with an inductance–capacitance–resistance (LCR) meter (Agilent 4294A). The microstructure and the chemical composition of the sintered ceramics were observed using a field-emission scanning electron microscope (FE-SEM, JSM-6700F, JEOL, Japan) and transmission electron microscope (TEM, 2011F, JEOL, Japan). The shrinkage was measured by thermal mechanical analysis (DIL402C, NETZSCH, German).

3. Results and discussion

Fig. 1(a) shows the bulk relative density and shrinkage of PLZT ceramics sintered at 950 °C with different $LiBiO_2$ concentrations. The result shows that the density and shrinkage of ceramics increase with increasing LBO concentration and PLZT ceramic with 6.0 wt% LBO addition shows a high density of about 7.63 g/cm^3, which corresponds to the relative density of approximately 98%. It confirms that the addition of sintering aids improved the sinterability of PLZT powders and 6.0 wt% LBO doped sintered body showed the highest density. Fig. 1(b) shows the relative density of without and with 6 wt% $LiBiO_2$ doped PLZT ceramic as a function of sintering temperature. The PLZT ceramics without LBO doping could not be fully densified below 1250 °C. However PLZT ceramic with 6.0 wt% LBO could be fully densified at 950 °C and reduced the sintering temperature by more than 300 °C. The density slowly decreases by further increasing the sintering temperature. Fig. 1(c) shows the shrinkage temperature dependence of PLZT green body with 6.0 wt% LBO. The green body began to shrink at 545 °C (approximately the melting point of LBO) and then the densification process began accelerating until the temperature is up to about 925 °C. After that, the shrinkage had no evident change and the shrinkage at 950 °C is about 15%.

Fig. 2 shows the micrographs of the surface of with and without sintering-aids-added PLZT ceramics. The results show that the addition of LBO can promote considerable grain growth at both sintering temperatures. Moreover, the grain size increases obviously by increasing the soaking time which is shown in Fig. 2(d) and (e). The PLZT ceramics with 6.0 wt% LBO sintered at 950 °C for 7 h show the uniform grain size distribution (1–2 μm) and no pores were observed on the surface. Based on all above results, it was determined that PLZT ceramics with 6.0 wt% LBO sintering aid were fully densified at 950 °C.

Fig. 3 shows the X-ray diffraction result of PLZT samples sintered at 950 °C. The result shows that there is a second phase in PLZT ceramics without and with 1.0 wt% LBO addition. The secondary phase has a TiO_2-rich composition, which is close to the composition of $PbTiO_3$. This means that there is still unreacted $PbTiO_3$ in our 950 °C sintered samples without and with 1.0 wt% LBO addition. When LBO concentration is more than 4.0 wt%, the samples show the typical perovskite structure and there is no second phase. This result confirms again that LBO sintering addition can promote the sintering of PLZT samples.

The temperature dependence of dielectric constant of LBO doped PLZT ceramics is shown in Fig. 4. The Curie temperature decreases notably with the increase of LBO

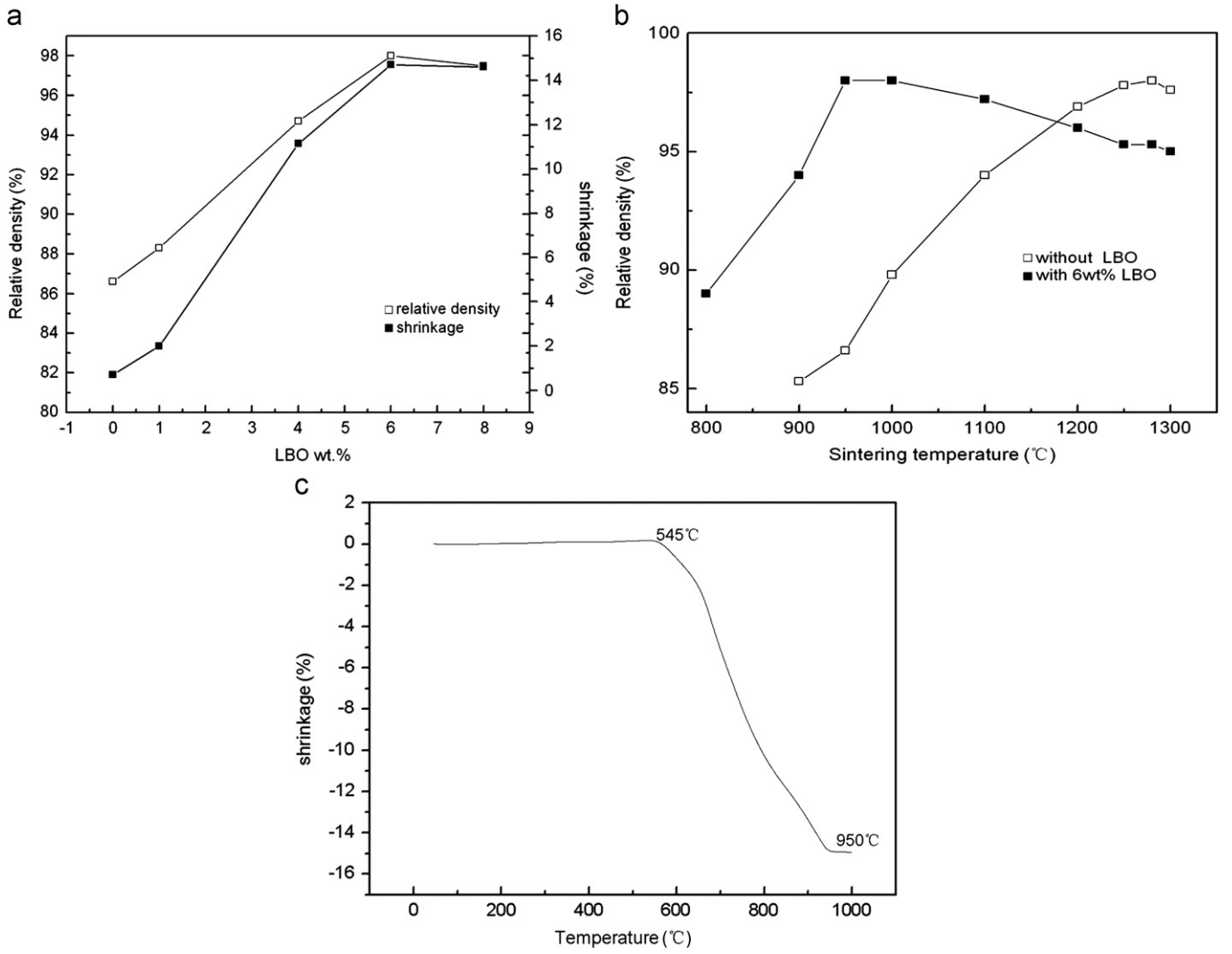

Fig. 1. Bulk relative density and shrinkage of PLZT ceramics sintered at 950 °C with different LBO concentrations (a), bulk relative density of PLZT ceramics without and with 6.0 wt% LBO as a function of sintering temperature (b), the shrinkage of PLZT green body with 6.0 wt% LBO as a function of temperature (c).

concentration. This may be attributed to the occupation of Bi^{3+} in A site of PLZT, which induces the distortion of the crystal structure and decreases the energy barrier between the tetragonal phase and the cubic phase. The Bi^{3+} doping can induce charge effects shown in the following equation:

$$Bi_2O_3 \rightarrow 2Bi^{\bullet}_{Pb} + 2V^{''}_{Pb} + 3O^{\times}_{O} \quad (1)$$

and the charged defects can be moved and trapped in new location as a function of electric field and this behavior induces a relaxed polarization which contributes to the dielectric loss tangent at low frequency [16], listed in Table 1. Due to the non-ferroelectric phase of LBO, d_{33} decreases with the increase of LBO doping concentration. However it is important to note that d_{33} and ε_{33} increases obviously if the soaking time increases from 2 h to 7 h. This phenomenon is similar with the result reported by Hayashi. He found that the piezoelectric properties could be increased obviously by post-annealing process [17]. Hayashi attributed the enhancement of piezoelectric properties to the removal of the second phase on the grain boundary by the post-annealing process. TEM microstructure of our PLZT ceramic sintered at 950 °C for 7 h is shown in Fig. 5(a). The composition of the grain boundary is analyzed by EDS, shown in Fig. 5(b). The result shows that Bi^{3+} is still present at the grain boundary and its concentration (about 3.0 wt%) is almost not changed compared to that of PLZT sintered for 2 h (not shown here). So in our case, this distinct enhancement of electrical properties could be mainly originated from the improvement of crystallinity and grain size of PLZT ceramics of 7 h soaking samples, which is shown in Fig. 2. If the soaking time is further increased higher than 7 h, the electrical properties are not be further increased and even decreased a little.

Fig. 6(a) shows unipolar field-induced longitudinal strain behavior of PLZT ceramics without and with 6.0 wt% LBO, and in order to make comparison, the longitudinal strain behavior of typical normal ferroelectric

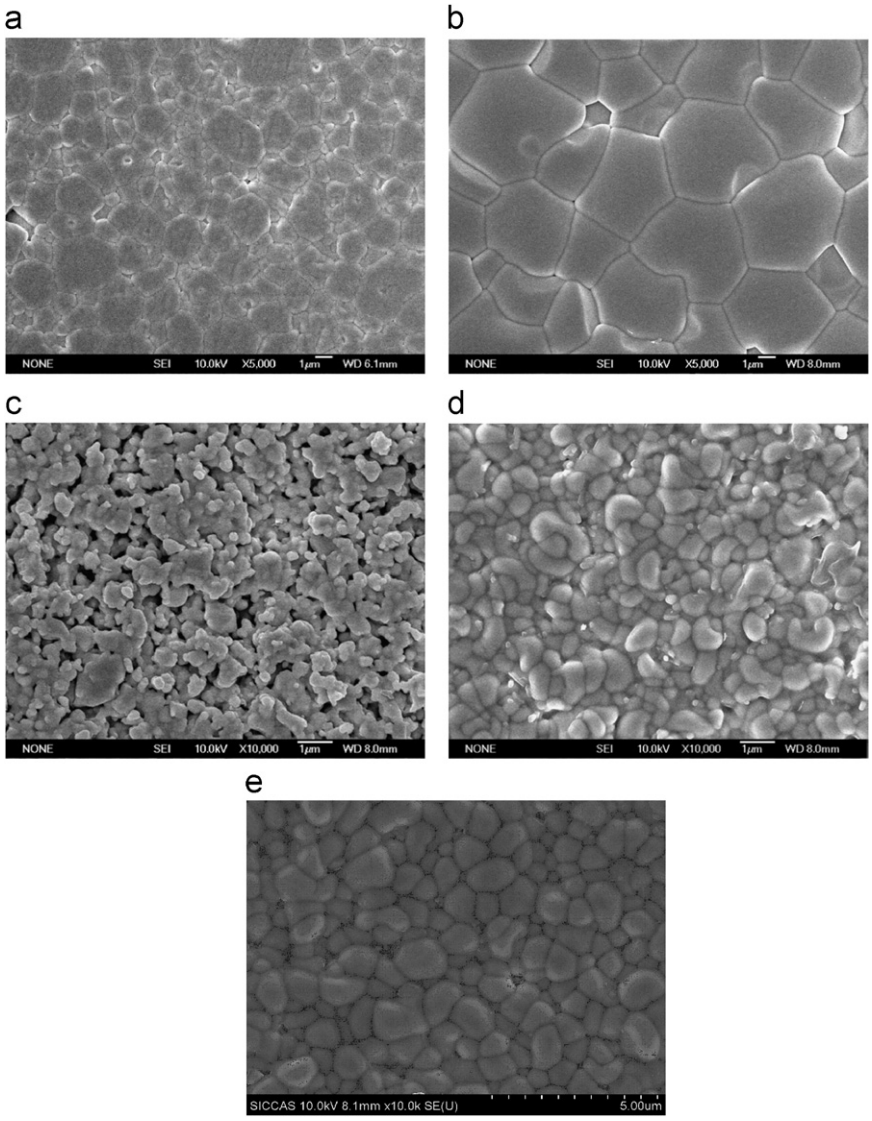

Fig. 2. Micrographs of surfaces of PLZT ceramic without LBO addition at (a) 1300 °C (c) 950 °C, with 6.0 wt% LBO addition at (b) 1300 °C (d) 950 °C for 2 h (e) 950 °C for 7 h.

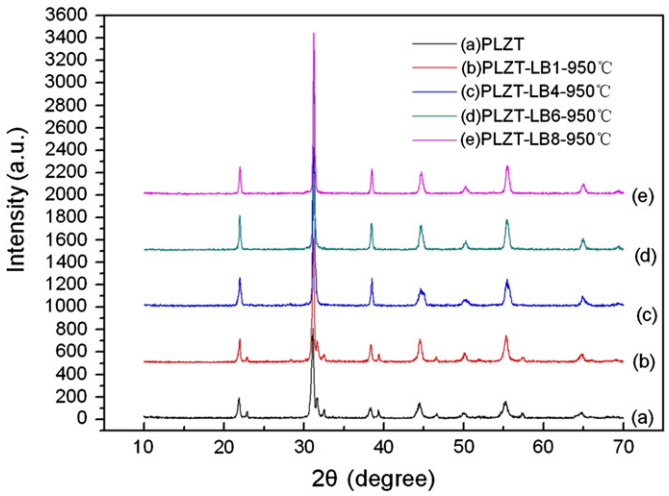

Fig. 3. XRD result of PLZT samples sintered at 950 °C.

ceramic PZT-5 ($d_{33}=550$, $T_c=348$ °C) and relaxor ferroelectric 0.25PMN–0.40PT–0.35PZ ($d_{33}=900$, $T_c=200$ °C) sintered at high temperature is also shown [18]. Compared to pure PLZT ceramics sintered at 1300 °C, there is a very little S_{11} decrease of LBO added PLZT ceramics sintered at 950 °C. Under 3.0 kV/mm electric field, its strain is as high as 0.22%, which is much larger than PZT-5 and 0.25PMN–0.40PT–0.35PZ, larger than most results reported in other literatures as well. Generally, the field-induced strain of ceramics includes two parts: piezoelectric response and electrostrictive response, shown in the following equation:

$$S(E) = dE + ME^2 + \cdots\cdots \quad (2)$$

where $S(E)$ is the electric-field-induced strain and E is the level of applied electric field. The coefficient "d" describes the reversible piezoelectric response. The latter one "M" is the electrostrictive coefficient. Usually in normal ferroelectric, its

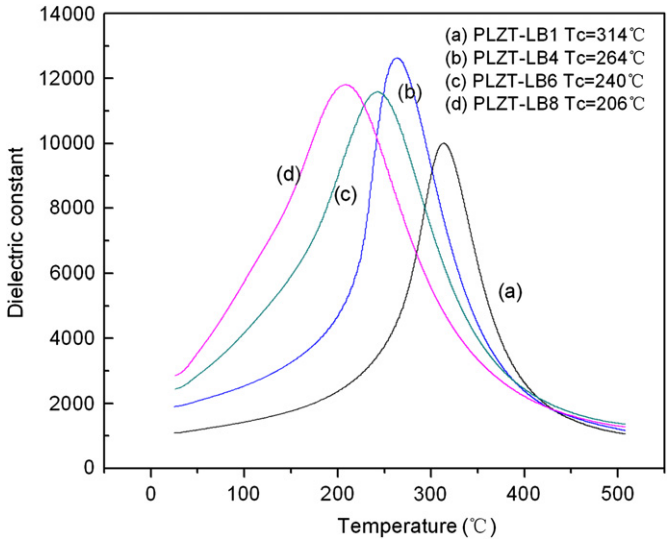

Fig. 4. Temperature dependence of dielectric constant of LBO doped PLZT ceramics.

Table 1
Electrical properties of PLZT ceramics.

	ε_{33}	T_c (°C)	$tg\delta$	d_{33} (pC/N)
Undoped (1300 °C)	1784	315	0.018	490
LB1 (1150 °C)	1617	314	0.02	440
LB4 (1150 °C)	1630	236	0.02	340
LB6 (950 °C, 2 h)	1900	240	0.028	308
LB6 (950 °C, 5 h)	1970	240	0.028	375
LB6 (950 °C, 7 h)	2040	240	0.025	435
LB8 (950 °C, 7 h)	2430	206	0.03	430

electrostrictive coefficient M is small and can be negligible compared to piezoelectric constant d, so piezoelectric response dominates. It is well known that 180° domain reversal does not contribute to the induced strain, but non 180° domain reversal does [19,20]. Since our sample is in the vicinity of morphotropic phase boundary (MPB), where tetragonal and rhombohedral phases coexist, there are two kinds of domain structures: 180° domains and non 180° (90°, 109°, 71°) domains [21]. When the electric field is large, the rotation of non 180° (90°, 109°, 71°) macrodomain may occur and induce large strain. For relaxor ferroelectrics, the electrostrictive coefficient M is large due to the existence of microdomain which has large response to electric field. La doped PZT ceramics have the characteristic of relaxor ferroelectric, diffused Curie peak and the frequency dependence of T_c, which is shown in Fig. 7. Its large field induced strain may be attributed to the coexistence of macrodomain and microdomain. Compared to pure PLZT ceramics, PLZT ceramic with 6.0 wt% LBO has more diffused Curie peak and lower Curie temperature, so microdomain contribution to field-induced strain is increased, which results in small change of S_{11} in spite of smaller d_{33} than pure PLZT ceramics. Fig. 6(b) displays the strong field-induced strain behavior of PLZT ceramic with 6.0 wt% LBO with different soaking times. The result shows

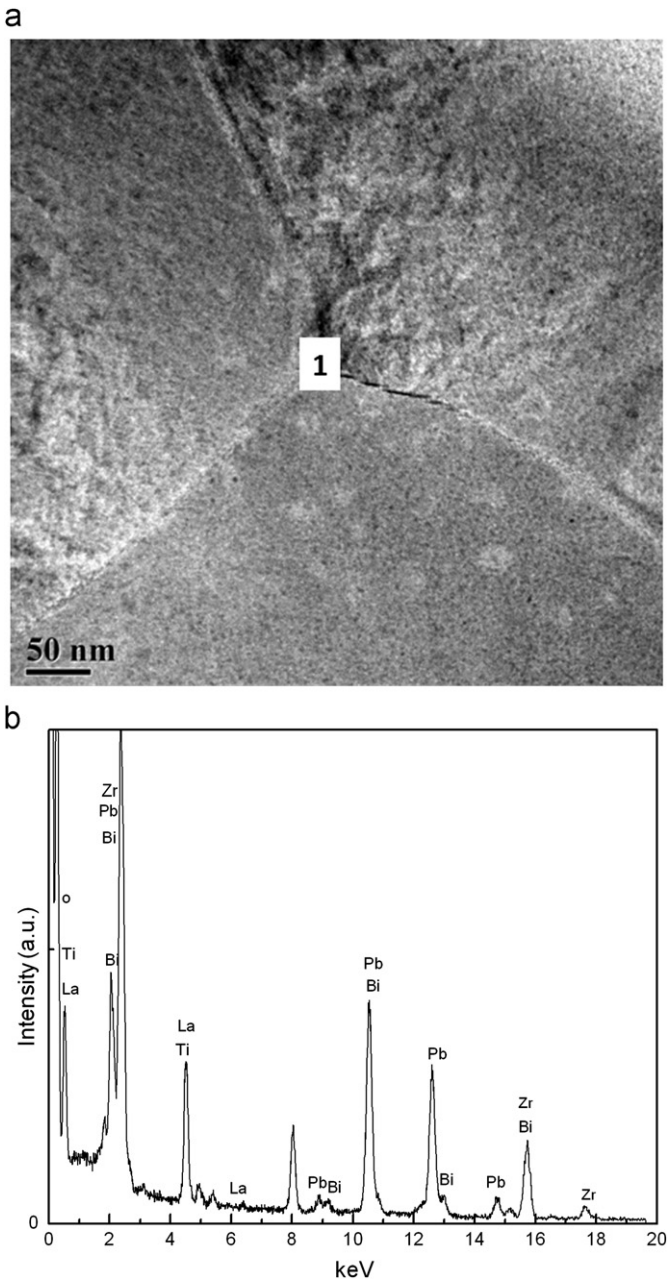

Fig. 5. TEM micrographs of surfaces of PLZT ceramic sintered at 950 °C for 7 h (a), EDS result of "1" site (b).

that the strain could be notably increased by increasing the soaking time.

4. Conclusions

Low temperature sintering of $Pb_{0.97}La_{0.03}(Zr_{0.53}Ti_{0.47})_{0.9925}O_3$ (PLZT) with $LiBiO_2$ sintering aid by traditional ceramic processing was carefully investigated and their electrical properties were examined. The results show that by controlling the concentration of $LiBiO_2$ and soaking time, PLZT ceramics could be well sintered at 950 °C, and their electrostrictive and piezoelectric

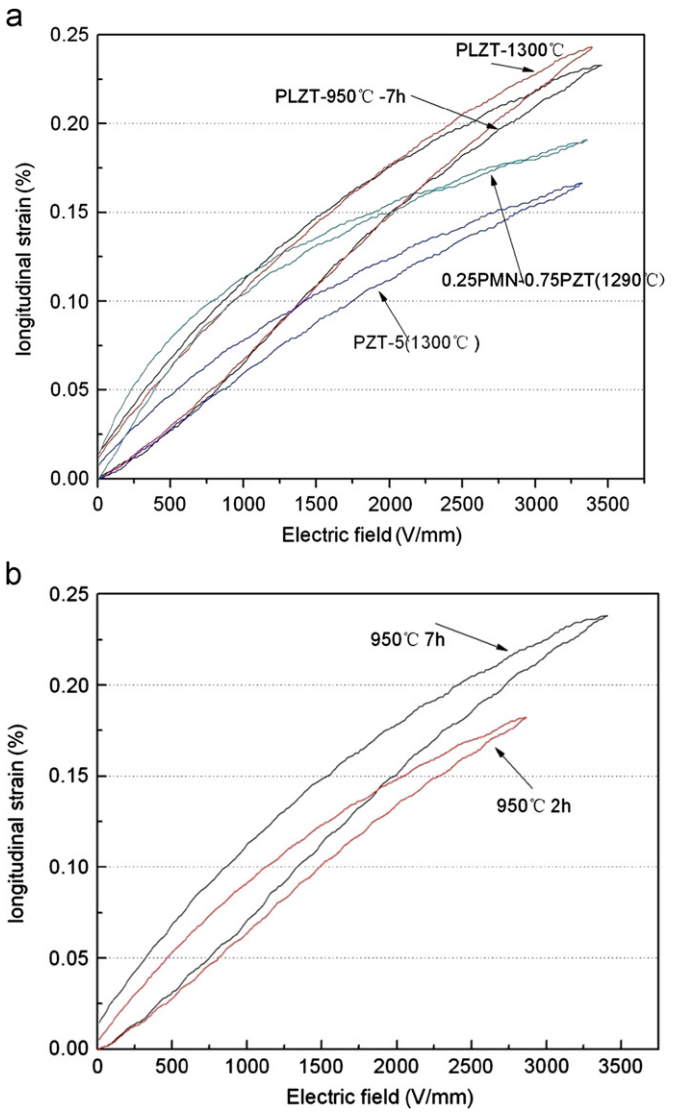

Fig. 6. The strong field induced longitudinal strain behavior of (a) pure, LBO added PLZT ceramics, PZT-5 and 0.25PMN–0.75PZT (b) LBO added PLZT ceramics for 2 h, 7 h.

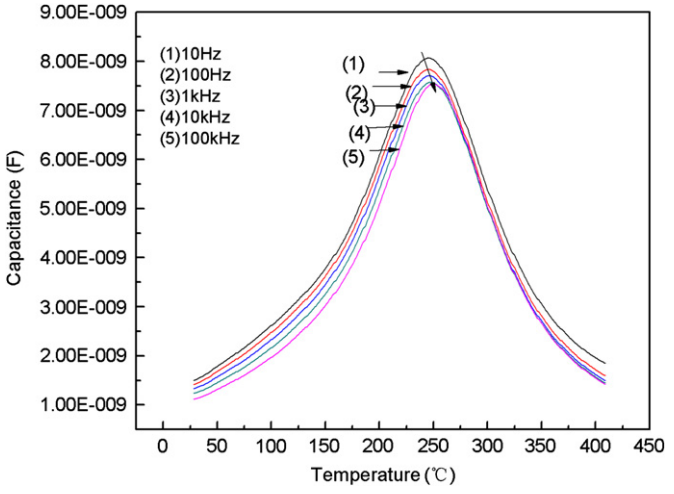

Fig. 7. Temperature dependence of capacitance of 6.0 wt% added PLZT ceramics at different frequencies.

properties are well kept. The electrostrictive properties of our 950 °C sintered samples are even better than those of the traditionally sintered PZT-5, PMN–PZT, larger than most results reported in other literatures as well. PLZT ceramics with 6.0 wt% LBO sintered at 950 °C for 7 h exhibited high Curie temperature of 240 °C, high piezoelectric d_{33} of 435, high S_{11} of 0.22% under 3.0 kV/mm, medium ε_{33} of 2040 and small $tg\delta$ of 0.025. These properties are very promising for actuators designed in multilayer structure, especially for pulse-driven motor application working in high temperature environment.

Acknowledgments

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