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Compositional effect on piezoelectric and anomalous photovoltaic properties of PLZT ceramics with fixed grain sizes

Jing-Feng Li · Daming Cheng

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Abstract Lanthanum-modified lead zirconate titanate (PLZT) ceramics possess the photostrictive effect applicable to photo-driven and wireless actuators. The piezoelectric and anomalous photovoltaic (APV) properties of PLZT ceramics with different compositions but the same grain size were evaluated to investigate the intrinsic compositional effects. After the adjustment of the sintering temperature and soaking time, the grain sizes of PLZT ceramics with different compositions were controlled in a narrow range of 0.7–0.8 μm. Both the maximum photocurrent and photo-EMF after grain size control were found at PLZT 4/52/48.

Keywords PLZT · Compositional effect · Grain size · Piezoelectric property · Photovoltaic effect

1 Introduction

Lead lanthanum zirconate titanate (PLZT) ceramics have been reported to have anomalous photovoltaic (APV) effect. PLZT is also a good piezoelectric material. Therefore, when PLZT is illuminated by light with certain wave length, there will be strain/stress generated in the material. This phenomenon is photostrictive effect [1]. With this property, PLZT has promising applications in photo-actuation, microsensing and MEMS [2, 3]. To boost the photostrictive performance, the piezoelectric property and the APV property should be enhanced. According to Poosanaasa and Uchino [4], the properties of PLZT ceramics, including ferroelectric, piezoelectric and APV properties, have strong dependence upon the compositions of the solid solution system. On the other hand, the photo electromotive force (photo-EMF) in APV effect has an inverse proportional relationship with the mean grain size of the PLZT ceramics [5–7]. To investigate the intrinsic compositional effect upon the performance of PLZT, the influence of the grain size should be eliminated.

In this study, by varying the sintering conditions according to the grain growth dynamic equation, we fabricated PLZT with 11 different compositions but the same grain size. The piezoelectric constants, the photo-EMFs and the photocurrents were systematically investigated.

J.-F. Li (✉) · D. Cheng
State Key Laboratory of New Ceramics and Fine Processing,
Department of Materials Science and Engineering,
Tsinghua University, Beijing 100084, People's Republic of China
e-mail: jingfeng@mail.tsinghua.edu.cn

2 Experimental

1. *Sample Preparation and Grain Size Control*

The composition of PLZT is expressed as $Pb_{1-x}La_x(Zr_yTi_{1-y})_{1-x/4}O_3$ (shortened as PLZT X/Y/Z, where $X=100x$; $Y=100y$ and $Z=100-Y$). In this study, 11 different compositions near the morphotropic phase boundary (MPB) were chosen to investigate piezoelectric and photo-induced properties. The PLZT ceramics with different compositions were all synthesized by oxide mixing method from commercially available oxide powders of β-PbO, La_2O_3, ZrO_2 and TiO_2. The prepared PLZT powders were compacted via die pressing and cold-isostatic pressing at 200 MPa. The green compacts were sintered in an Al_2O_3 crucible and buried with $PbZrO_3$ to prevent the evaporation of PbO.

To control the grain size, the following dynamic equation for grain growth was used to calculate the sintering times for different compositions.

Table 1 Sintering method for PLZT with different compositions.

	Composition	D_x (μm)	t_x^* (min)	Sintering	D_x^* (μm)
1	3/52/48	0.94	61	1,100 °C 9 min	0.72
2	3/54/46	0.92	65	1,100°C 120 min	0.79
3	3/56/44	0.88	74	1,050 °C 120 min	0.75
4	4/48/52	0.72	136	1,200 °C 120 min	0.72
5	4/50/50	0.78	107	1,200 °C 120 min	0.79
6	4/52/48	0.87	77	1,200 °C 89 min	0.79
7	4/54/46	0.75	120	1,200 °C 120 min	0.75
8	4/56/44	0.61	223	1,200 °C 132 min	0.79
9	5/50/50	0.41	735	1,400 °C 80 min	0.79
10	5/54/46	0.47	488	1,300 °C 120 min	0.79
11	5/56/44	0.42	683	1,300 °C 164 min	0.99

$$D^n = At \tag{1}$$

Where D is the mean grain size, t is the sintering time, n and A are constants. Here we assumed n=3. The grain size when sintered at 1,473 K for 120 min, D_x, was determined for each composition, as shown in Table 1.

According to equation (1),

$$t_x^* = \left(\frac{D_x^*}{D_x}\right) \times 120(\text{min}) \tag{2}$$

Where D_x^* is the grain size to be unified, t_x^* is the sintering time calculated for each composition, as shown in Table 1. However, the sintering time t_x^* from calculation has an extended range of value from 61 min to 683 min. Too short sintering time will result in incompletely developed microstructure, hence, undermine the properties of the ceramics. While a too long sintering time will result in the serious evaporation of the constituent oxide, especially the PbO, and result in the deviation of the composition. Accordingly, both sintering temperature and time were adjusted to produce PLZT ceramics with the same grain size and applicable density. After the experiments, the final sintering methods for different compositions were determined, as shown in Table 1.

2. *Microstructure Characterization and Property Testing*

For measurement of the grain size, the as-sintered specimens were polished to a mirror surface finish using diamond paste with 1 μm particle size. For the observation of the microstructure, the polished surface was subjected to thermal etching under 1,273 K for 30 min. The surface was observed with SEM (JSM-6460LV, JOEL). The grain size of each composition was determined by the line intercept method.

For measurement of piezoelectric constant d_{33}, the as-sintered specimens were mechanically processed into 1-mm-thick disk samples of 16 mm in diameter. Both sides of the disks were coated with silver paste to form electrodes. The disk samples were polarized perpendicular to each electrode surface under an electric field of 2 kV/mm for 10 min in a bath of silicone oil at 393 K. The piezoelectric constants, d_{33}, were measured using a d_{33} meter (ZJ-3A, Institute of Acoustic, Chinese Academy of Sciences).

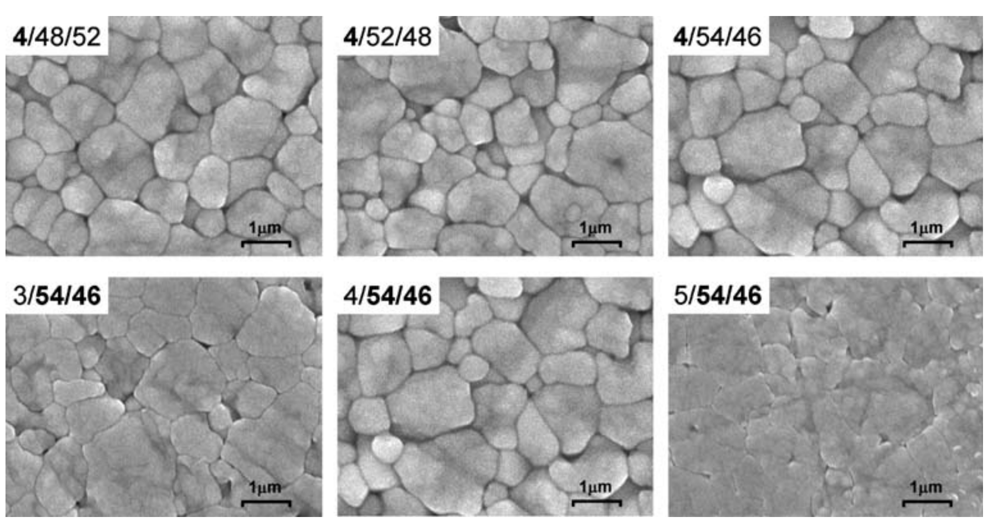

Fig. 1 Microstructures of six typical compositions: 4/48/52; 4/52/48; 4/54/46 and 3/54/46; 4/54/46; 5/54/46

For measurement of photo-EMF and photocurrent in APV effect of PLZT ceramics, the as-sintered specimens were cut into the dimensions 5×5×0.5 mm^3. Silver electrodes were added to the two ends of 5×0.5 mm^2 with the same method as described before. The sample was polarized under an electric field of 2 kV/mm for 10 min. One of the 5×5 mm^2 surfaces were polished as described above. The procedure for measuring photocurrents and photovoltages was proposed by K. Uchino et al. [8]. The photocurrents generated were measured with a high-impedance electrometer (Keithley 2410-C). By testing the photocurrents with different bias voltages on the sample, the photo-EMF and photocurrent were determined from the intercepts in the *I*–*E* relationship, as shown later.

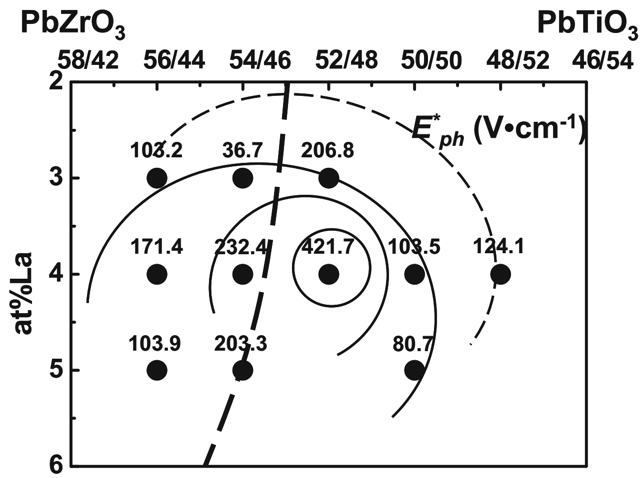

Fig. 3 Variation of photo-EMF after grain size control in the PLZT system

3 Results and discussions

After adjusting the sintering temperature and soaking time, the mean grain sizes of different compositions were in the range of 0.7–0.8 μm, as shown in Table 1. Microstructures of six typical compositions are shown in Fig. 1. All properties of PLZT ceramics were compared based on these grain sizes.

The piezoelectric constant, d_{33}, of different La/Pb ratios before and after grain size control demonstrated similar trends of variation of d_{33} with the composition: for each La substitution percentage, the maximum d_{33} have been found at MPB and decrease with decreasing Zr/Ti ratio. However, the difference between the d_{33} of the compositions after the grain size control is not as obvious as the results in a previous study [4]. This is because that the d_{33} usually has proportional relationship with the grain size, and after the grain size control, the influence of the grain size has diminished.

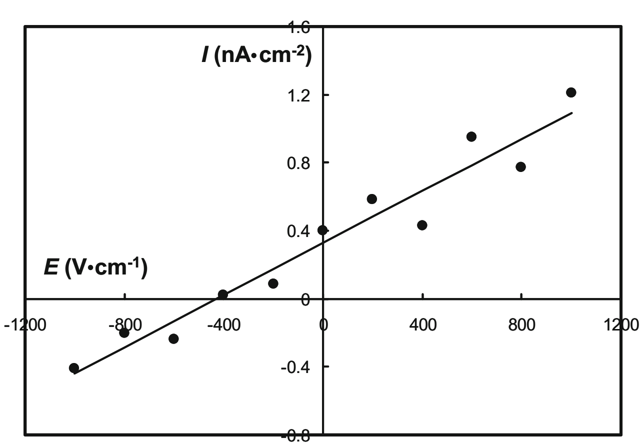

Fig. 2 *I*–*E* relationship of PLZT 4/52/48 in the APV property testing

Figure 2 shows a representative *I*–*E* relationship of the PLZT 4/52/48 ceramics. A straight line was fitted to the data, whose interceptions at *X*- and *Y*-axes correspond to photo-EMF and photocurrent values. Testing all the compositions with almost the same grain sizes gave the contour maps of photo-EMF and photocurrent, as shown in Figs. 3 and 4, respectively. Because of the photo-EMF has an inverse proportional relationship with the mean grain size, and when the grain size was fixed in a narrow range, its influence on APV properties has been eliminated. As a result, the trend of variation of photo-EMF with composition has been intensified, with the largest photo-EMF value at the composition of PLZT 4/52/48. After the grain size was fixed, both the maximum photocurrent and photo-EMF were found at PLZT 4/52/48. Uchino et al. [8] previously reported that PLZT 3/52/48 exhibited the maximum photocurrent and photovoltage, but in a recent paper [4] they found the maximum photovoltage at 5/54/46 and the maximum photocurrent at

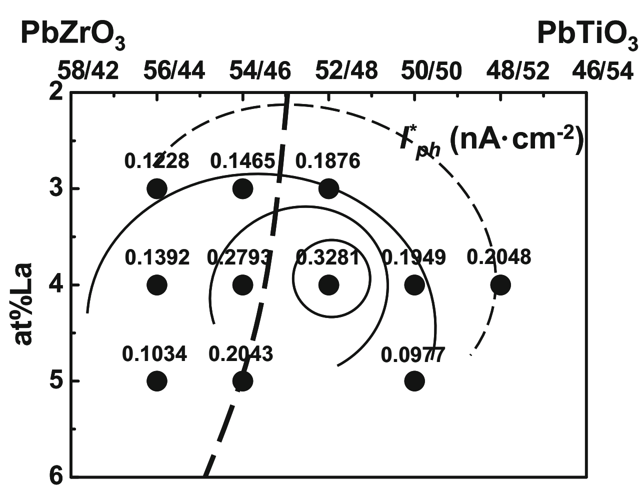

Fig. 4 Variation of photocurrent after grain size control in the PLZT system

4/48/52 after conducting a more-detailed investigation. However, their work did not consider the grain-size effect on the photovoltage, even though the grain sizes of the samples were different by three times within the composition range investigated by them. In the present study, the grain-size effect was greatly reduced, so the obtained results shown in Figs. 3 and 4 would be the intrinsic compositional dependences of photovoltage and photocurrent in the PLZT system.

4 Conclusion

The grain sizes of PLZT ceramics of different compositions near the MPB have been controlled in a narrow range by adjusting the sintering method for each composition according to the dynamic grain growth equation. The piezoelectric and APV properties of PLZT ceramics before and after grain size control have been tested. The trend of d_{33} variation with composition has been weakened, while for photo-EMF, it has been strengthened. Both the maximum photocurrent and photo-EMF after grain size control were found at PLZT 4/52/48.

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