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Characterization of Lead Lanthanum Zirconate Titanate (PLZT) Ceramics Sintered at Various Temperatures

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ABSTRACT

This article characterizes microstructure and electrical properties of lead zirconate titanate, PZT, ceramics doped with lanthanum oxide (La_2O_3). The $Pb_{1-x}La_x(Zr_{0.54}Ti_{0.46})O_3$ (x =0.01, 0.03 and 0.05) ceramics were prepared by a conventional mixed-oxide method, three sintering temperatures were performed: 1200°C, 1250°C and 1300°C. X-ray diffraction technique was employed to determine the lattice parameters of the ceramics, the tetragonal lattice parameters a and c were between 4.028 - 4.041 Å and 4.933 – 4.949 Å, respectively, the ratio of c/a = 1.22 was obtained. Dielectric, ferroelectric and piezoelectric properties of the ceramic system were largely controlled by the dopant content and sintering temperature.

Key words: PZT, La_2O_3, piezoelectric

INTRODUCTION

Perovskite lead zirconate titanate (PZT) system is most widely used in ceramic form, with composition close to the morphotropic phase boundary (MPB) of high piezoelectric coupling. Many researchers have studied the effect of additive oxides to PZT ceramics, in the vicinity of the MPB between rhombohedral and tetragonal phases, on the piezoelectric properties and microstructure (Garg and Agrawal, 2001; Ryu *et al*., 2001). The addition of lanthanum to PZT system, or simply PLZT, gave a high density transparency product with useful electro-optical properties, which was used as the basis of the optical memories (Santos *et al*., 2001). The effect of lead zirconate niobate (PZN) additive on the sintering behavior and piezoelectric properties of PZT ceramics was also reported to improve sinterability and maximum piezoelectric properties (Fan *et al*., 2002; Lee *et al*., 2004; Seo *et al*., 2004). In present work, effect of lanthanum additive at various sintering temperatures on the dielectric and piezoelectric properties of PZT (a Zr/Ti ratio of 54/46) ceramics was investigated.

MATERIALS AND METHODS

The studied ceramics of three nominal compositions were prepared by a conventional ceramic mixing method, the general formula: $Pb_{1-x}La_x(Zr_{0.54}Ti_{0.46})O_3$, where x = 0.01, 0.03 and 0.05. The commercially available oxide powders of high purity (all 99.9% purity) were used. PbO, ZrO_2, TiO_2 and La_2O_3 (Fluka chemika) of the required amounts were carefully weighed and mixed by wet ball milling for 24 hours using zirconia balls and acetone as media. The mixture

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powder was dried at 100°C for 12 hours. After drying, the mixture powder was calcined in a closed alumina cup at 800°C for 4 hours at a constant heating rate of 300°C/h. The calcined powder was then ground in a mortar and pestle to crush agglomerates to pass through a 100 mesh sieve and was cold isostatically pressed in a 13 mm die at a pressure of 150 MPa into pellets using deionization water as a binder. The pellets were placed into the covered alumina crucible, a $Pb(Zr_{0.54}Ti_{0.46})O_3$ atmosphere powder were placed on the top, bottom and in the vicinity of the pellets in order to maintain stoichiometries as closely to the nominal compositions as possible. Moisture contents and binder were removed by heating the sealed alumina crucible at 500°C for 1 hour at the constant heating rate of 300°C/h. Then, the pellets in the sealed alumina crucible were sintered for 1 hour. Three sintering temperatures were carried out: 1200°C, 1250°C and 1300°C, yielding three pellet samples for each composition. Hence, there were totally 9 samples. The samples were characterized for weight loss, sintered density by using density determination (AG 204, Mettler Toledo). X-ray powder diffraction (XRD) analysis was carried out at room temperature to determine phase structure and lattice parameters. The JEOL model JDX-3530, Ni filtered Cuk_α radiation at 30 kV, 40 mA, were used. Data collection was performed in the 2θ ranging from 20°-60° of a step scan with a step size of 0.02° and counting time of 0.5 s per step.

Polished surface microstructure was examined by scanning electron microscope (SEM, JSM-5410, JEOL). Samples were polished to a 1 mm finish and thermally etched at 100°C lower than their sintering temperature. For the piezoelectric property measurements, the sintered pellets were lapped and silver pastes was applied on the lapped surfaces and were fired at 100°C for 12 hours for electrode formation. The electrode specimens were poled in a silicone oil bath at 120°C for 20 min by applying a DC field, according to coercive field of each specimen. The specimens were aged for 24 hours prior to testing. The ferroelectric polarization versus electric field (P-E hysteresis) were measured by using an RT66 standard ferroelectric test system. The piezoelectric constant (d_{33}) was measured by using a piezometer (PM 25, Piezometer system; UK). The electromechanical coupling coefficient (k_p) was determined by the resonant and antiresonant technique. The dielectric properties were measured at a frequency of 1 kHz by using an impedance analyzer (HP 4194A, Impedance/Gain Phase Analyzer, Hewlett Packard, UK).

RESULTS AND DISCUSSION

Weight loss and bulk density

Three nominal ceramic compositions prepared by the conventional solid-state method are listed in Table 1, presenting the percent weight loss, shrunk diameter, shrunk thickness on sintering, and sintering density. The discrepancy in weight loss was relatively small. It was less than 5%, which was mostly due to the PbO loss during sintering (Zai *et al*., 2001). The shrunk diameter and thickness on sintering were about 11-15%. The sintering density was varied with the sintering temperature and the amount of lanthanum content. When more lanthanum was doped, the density was increased from 7.5 g/cm^3 to 7.8 g/cm^3.

Phases and microstructures

The phase formation behavior of the sintered ceramics was revealed by an XRD method. The XRD patterns of PLZT ceramics shown in Figure 1 were identified as a material with perovskite structure having rhombohedral and tetragonal symmetry according to JCPDS card no.33-784 and 73-2022, respectively. The tetragonal lattice parameters were determined from the evolution of the (001) and (110) tetragonal peaks by using least square method. The results given in Table 2 revealed that the tetragonal cell

parameters and cell volume of PLZT ceramics were not varied with the sintering temperature and the amount of La_2O_3, tetragonal lattice constant a = 4.03-4.04 Å, c = 4.93-4.95 Å, and cell volume V = 80.03-80.83(Å)^3 were obtained.

There is a small pyrochlore phase in each sample. The amount of lanthanum content does not affect the pyrochlore phase of the sample.

SEM micrographs of PLZT caramics are shown in Figure 2. The influence of sintering behavior and the amount of La_2O_3 doped on the microstructure of PLZT system were observed. The grain was bigger at higher sintering temperature and less La^{3+} dopant. The large grain size revealed hexagon shape indicated that surface grains grew extensively during sintering. Extensive grain of PLZT ceramics belonged to the 0.01 mol% La_2O_3 doped sample sintered at 1300°C. The average grain size reported in Table 2 were determined from line intercept method.

Ferroelectric, dielectric and piezoelectric characterizations

The typical shapes of measured ferroelectric polarization versus electric field (P-E hysteresis) of PLZT ceramics sintered at different temperatures are shown in Figure 3. When more La_2O_3 was added, normal ferroelectric behavior with rectangular loop was formed, and the remanent polarization (Pr) was increased. The effect of sintering temperature on ferroelectric properties assessed from polarization–field (P–E)

Table 1 Some physical properties of the sintered $Pb_{1-x}La_x(Zr_{0.54}Ti_{0.46})O_3$ ceramics.

Sample	Lanthanum composition (x)	Sintered temperature (°C)	Weight loss (%)	Shrunk diameter (%)	Shrunk thickness (%)	Density (g/cm^3)
$PL_{0.01}ZT$	0.01	1200	0.6	13.3	12.4	7.47
		1250	0.9	15.2	11.8	7.50
		1300	1.0	12.8	12.0	7.47
$PL_{0.03}ZT$	0.03	1200	1.0	14.0	12.9	7.68
		1250	1.1	14.3	12.8	7.68
		1300	1.0	14.4	11.7	7.62
$PL_{0.05}ZT$	0.05	1200	1.8	14.1	13.0	7.75
		1250	1.6	14.1	13.8	7.73
		1300	1.2	13.7	13.2	7.82

Table 2 Effect of La_2O_3 doped on tetragonal structure and average grain size of PLZT ceramics.

Sample	a(Å)	c(Å)	V = a^{2}c(Å^3)	grain size(μm)
$PL_{0.01}ZT$ (1200 °C)	4.033	4.939	80.317	7.1
$PL_{0.01}ZT$ (1250 °C)	4.029	4.934	80.092	7.9
$PL_{0.01}ZT$ (1300 °C)	4.028	4.933	80.030	8.5
$PL_{0.03}ZT$ (1200 °C)	4.031	4.937	80.227	5.7
$PL_{0.03}ZT$ (1250 °C)	4.041	4.949	80.829	6.8
$PL_{0.03}ZT$ (1300 °C)	4.036	4.944	80.546	8.3
$PL_{0.05}ZT$ (1200 °C)	4.030	4.936	80.166	3.5
$PL_{0.05}ZT$ (1250 °C)	4.032	4.938	80.254	5.7
$PL_{0.05}ZT$ (1300 °C)	4.030	4.936	80.162	8.1

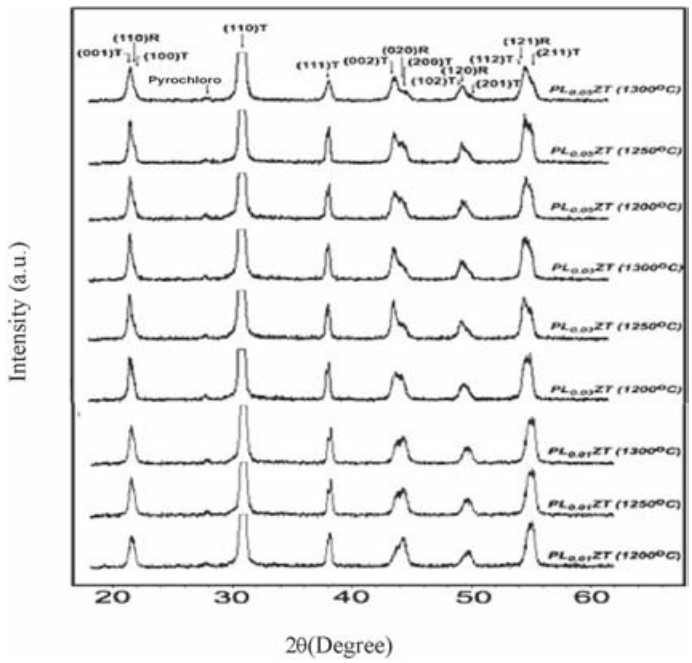

Figure 1 X-ray diffractogram of $Pb_{1-x}La_x(Zr_{0.54}Ti_{0.46})O_3$ ceramics.

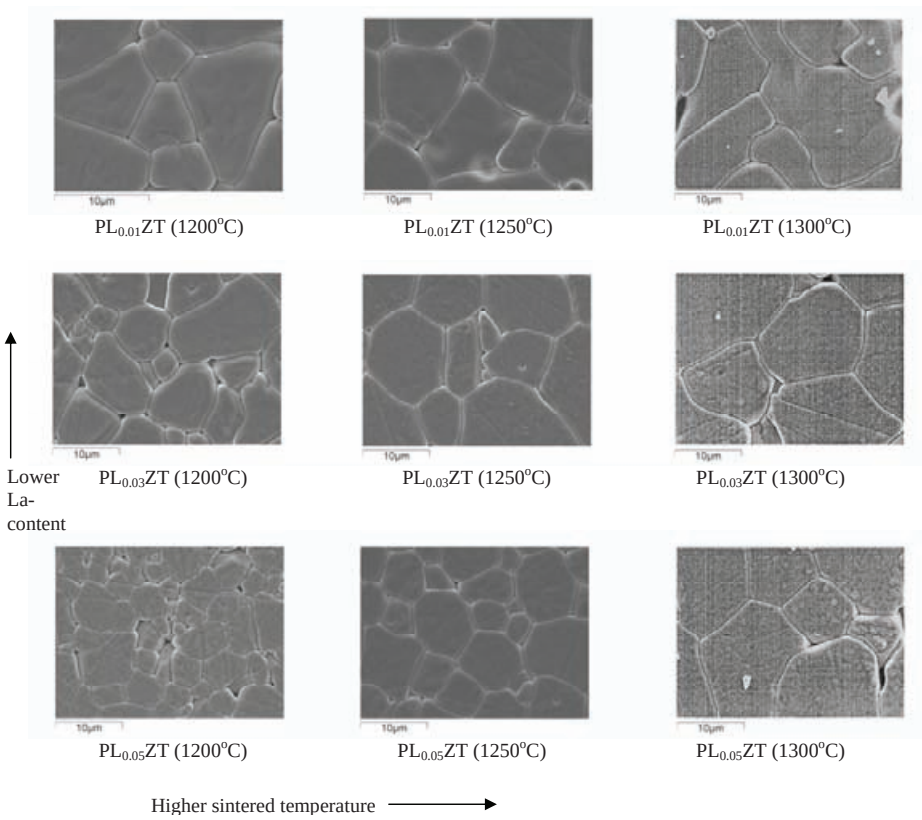

Figure 2 SEM micrographs of thermally etched polished surface of PLZT ceramics.

measurements are listed in Table 3. Remanent polarization (Pr) and coercive field (E) of the $PL_{0.05}ZT$ sample was observed to decrease with the increasing sintering temperature. This is probably due to smaller grain size at lower sintering temperature, and polarization switching is thus suppressed.

Dielectric and piezoelectric properties for PLZT ceramics measured at room temperature are given in Table 3. Both dielectric constant (ε) and

Table 3 Summarize of ferroelectric, dielectric and piezoelectric properties for PLZT system.

Sample	Pr (μC/cm^2)	E(kV/cm)	ε	tan δ	k_P%	d_{33} (pC/N)
$PL_{0.01}ZT$ (1200 °C)	70.3	1.045	448	0.2895	0.49	221
$PL_{0.01}ZT$ (1250 °C)	116.6	1.216	531	0.3943	0.48	235
$PL_{0.01}ZT$ (1300 °C)	69.6	0.777	640	0.2396	0.39	198
$PL_{0.03}ZT$ (1200 °C)	191.4	0.841	630	0.5590	0.53	265
$PL_{0.03}ZT$ (1250 °C)	107.1	0.658	678	0.3731	0.53	279
$PL_{0.03}ZT$ (1300 °C)	149.5	0.755	678	0.2538	0.43	178
$PL_{0.05}ZT$ (1200 °C)	289.0	1.075	765	0.7440	0.60	331
$PL_{0.05}ZT$ (1250 °C)	271.6	0.866	740	0.3578	0.60	307
$PL_{0.05}ZT$ (1300 °C)	199.2	0.793	686	0.2608	0.59	293

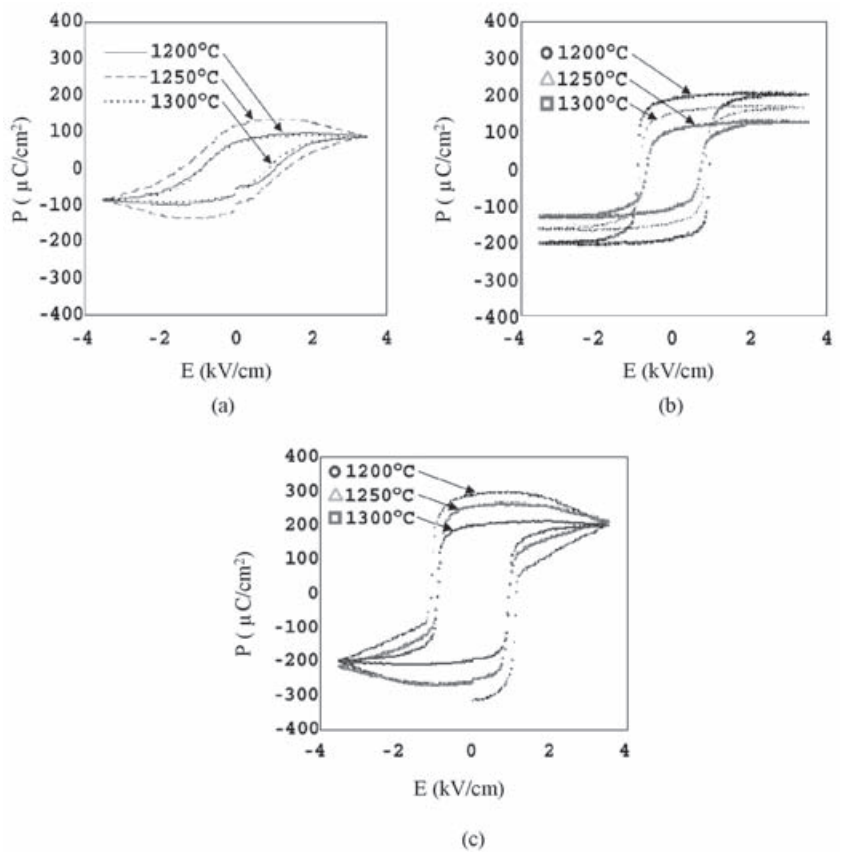

Figure 3 P–E hysteresis as a function of sintering temperature for (a) $PL_{0.01}ZT$ (b) $PL_{0.03}ZT$ and (c) $PL_{0.05}ZT$ ceramics.

dielectric loss (tan δ) were increased with the increasing amount of La_2O_3. Piezoelectric properties for PLZT system are also revealed in Table 3 Both piezoelectric coefficient (d_{33}) and planar electromechanical coupling factor (k_p) for PLZT system were increased with the increasing La_2O_3 dopant, but both d_{33} and k_p were fluctuated with the sintering temperature.

CONCLUSION

Lead zirconate titanate doped with lanthanum La^{3+} ceramics were obtained by employing mixed-oxide method sintered at 1200, 1250, and 1300°C. Under the observation of SEM micrograph, the grain size was found to increase with increasing the sintering temperature and less La^{3+} dopant. XRD analysis indicated a small amount of pyrochlore phase in each ceramics. The amount of lanthanum did not affect the tetragonal parameters. Ferroelectric, dielectric and piezoelectric measurements showed a dependence of those properties on the amount of lanthanum and sintering temperature. The $Pb_{0.95}La_{0.05}(Zr_{0.54}Ti_{0.46})O_3$ ceramics sintered at 1200°C showed the optimum condition to obtain better ferroelectric, dielectric and piezoelectric properties.

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