

Structural and dielectric properties of phosphorous-doped PLZT ceramics

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Abstract. In the present work we have reported the unique effects of P₂O₅-doped PLZT ceramics with composition (Pb_{0.92}La_{0.08})(Zr_{0.65}Ti_{0.35})O₃ + *x* wt% of P₂O₅ (where *x* = 1, 3 and 5) prepared chemically by co-precipitation method. X-ray diffraction studies suggest that the prepared compound was very fine (10–25 nm), homogeneous and of rhombohedral symmetry. The apparent density of samples decreased with the P⁵⁺ additions. Studies of dielectric constant and dielectric loss as a function of frequency (10–1000 kHz) and temperature suggest that the compound undergoes diffuse type of phase transition without any sign of relaxor behaviour. With increasing *x*, dielectric constant was found to decrease appreciably, whereas Curie temperature (*T*_C) was found to increase.

Keywords. Ceramics; X-ray diffraction; pyrochlore phase; PLZT; dielectric properties.

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1. Introduction

Lanthanum modified lead zirconium titanate (PLZT) ceramics, a solid solution of PbTiO₃ (ferroelectric) and PbZrO₃ (antiferroelectric), are considered to be quite attractive for many device applications such as non-volatile memories, transducers and phonographic pick-up. The formation of PLZT solid solution depends to a large extent on the physiochemical characteristics of the starting raw materials [1]. It is well-known [2] that conventional (high-temperature solid state reaction) method of preparing PLZT powders causes compositional fluctuation and chemical inhomogeneity, which impair the electromechanical properties of the finished products. However, the sintering of PZT at high temperature gives rise to lead loss, which drastically degrades the device performance. Generally, atmosphere-controlled sintering of PZT can prevent lead loss at high temperature. Another alternative is the use of low-temperature sintering aids where, so far, a lot of work has been done

[3–17] in which, the researchers have found bulk density varying from 90 to 98% of the theoretical value after sintering in the temperature range 900–1300°C. A recent observation [18] reported that PZT could be sintered at low temperature by adding P₂O₅ without compromising the dielectric property. But no systematic study on dielectric property was reported by the authors in the paper. As no systematic work on the effect of P₂O₅ doping on structural and dielectric properties has been done, we present here our study on the (Pb_{0.92}La_{0.08})(Zr_{0.65}Ti_{0.35})O₃ + *x* wt% of P₂O₅ (where *x* = 1, 3 and 5) prepared chemically by co-precipitation method.

2. Experimental

The starting materials were Pb(NO₃)₂ (lead nitrate), La(NO₃)₃·6H₂O (lanthanum nitrate), ZrO(NO₃)₂·2H₂O (zirconyl nitrate) and C₁₂H₂₈O₄Ti (titanium isopropoxide). The powder composition Pb_{0.92}La_{0.08}(Zr_{0.65}Ti_{0.35})O₃, i.e. PLZT (8/65/35) was prepared by dissolving lead, lanthanum and zirconyl nitrates in double distilled water in the desired ratio. Liquid tetraisopropyl titanate was, then added directly to the nitrate solution while stirring. The details of the preparation method are given elsewhere [19]. Ammonia solution was added to the aqueous nitrate solution to obtain the precipitate, which was then vacuum filtered after repeated washing with distilled water. The filtrate was then dried at 200°C. The dried cake was crushed and thoroughly ground in an agate mortar and calcined at 600°C for 2 h in an alumina crucible. The calcined powder was then pulverized and mixed with pentavalent cation (P⁵⁺) in the oxide form, i.e. P₂O₅ in 1, 3 and 5 wt%. Homogeneously mixed powder was compacted into disc-shaped samples of about 1–2 mm thickness and 13 mm diameter by cold pressing the calcined powder at a pressure of (5.3×10⁷ kg/m²) using a hydraulic press. Sintering of these disc-type samples was conducted at 1000°C for 3 h. During sintering, PbZrO₃ powder (sample weight: PbZrO₃::2:1) was used as lead source in the crucible to minimize volatilization of lead. The formation and quality of the desired composition were checked by the X-ray diffraction (XRD) analysis of the sintered pellets with X-ray diffractometer (PW-1140/90) using CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$) in a wide range of Bragg angles (20°–60°) at room temperature.

For dielectric measurement sintered disc were ground and lapped to make the surface flat and parallel and subsequently electroded by applying silver paste on both the flat faces. Measurement of dielectric constant (ϵ) and dissipation factor ($\tan \delta$) were carried out by HP-4192A capacitance measuring assembly as a function of frequency (10 kHz–1 MHz) at room temperature and as a function of temperature (32–575°C). The microstructures of the samples were analyzed by scanning electron microscope (LEO 435VP).

3. Results and discussion

3.1 XRD analysis

XRD pattern of the specimens (PLZT doped with different wt% P₂O₅) sintered at 1000°C have been compared in figures 1a–d. The diffraction peaks in the powder

(PLZT) pattern (figure 1a) are found to be very sharp and single, which indicates the formation of a single-phase compound with better homogeneity and crystallization of the material.

The PLZT thus obtained is stoichiometric and very pure. In figures 1b–d some pyrochlore phase was observed in the compound doped with P_2O_5 . Relative amount of pyrochlore phase to the perovskite phase was estimated (given in table 1) using eq. (1).

$$\% \text{Pyrochlore} = I_{\text{PYRO}} / (I_{\text{PYRO}} + I_{110}), \quad (1)$$

where I_{PYRO} and I_{110} are the intensity of the corresponding peaks.

The presence of pyrochlore phase due to the P_2O_5 addition was also reported in [18]. The change in the intensity of some reflections of doped PLZT may be due to variation of particle size and presence of P_2O_5 in different amounts. The linear particle size (P) was calculated using Scherrer's equation (eq. (2)) from the strong reflection (110) (table 1)

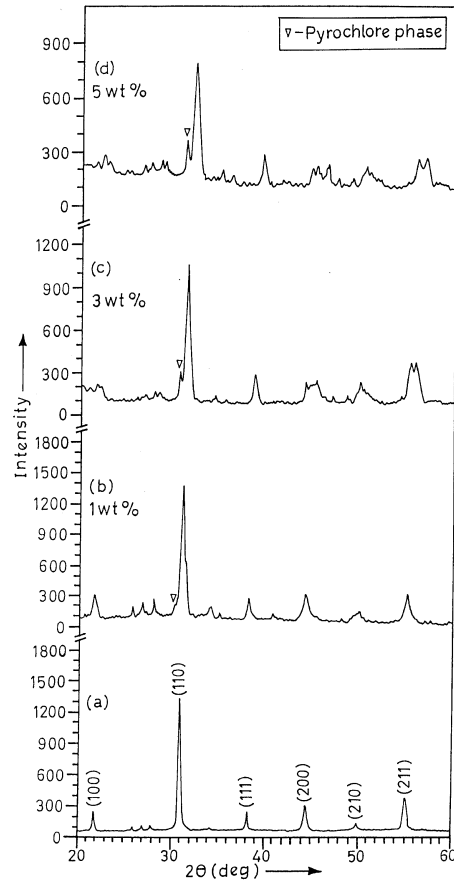


Figure 1. X-ray diffraction pattern of (a) PLZT, (b) PLZT + 1 wt%, (c) PLZT + 3 wt% and (d) PLZT + 5 wt% added P_2O_5 at room temperature.

Table 1. Some properties of $(\text{Pb}_{0.92}\text{La}_{0.08})(\text{Zr}_{0.65}\text{Ti}_{0.35})\text{O}_3 + x \text{ wt}\% \text{ of } \text{P}_2\text{O}_5$, where $x = 1, 3$ and 5 .

	PLZT	PLZT +1 wt% P_2O_5	PLZT +3 wt% P_2O_5	PLZT +5 wt% P_2O_5
Lattice Parameter (Rhombohedral)	4.705(4)	4.071(1)	4.076(0)	4.109(0)
a (Å) and α (deg)	89.8(2)	90.1(2)	91.5(0)	92.2(6)
% Pyrochlore	–	13	21	30
Density (g/cc)	6.71	5.87	4.63	4.34
Particle size (nm)	25	16	15	10
ϵ_{max} (100 kHz)	2400	1140	335	175
T_C ($^\circ\text{C}$)	230	318	391	458
γ	1.90	1.90	1.91	1.60

$$P = K\lambda/\beta_{1/2} \cos \theta \quad (K = 0.89, \beta_{1/2} = \text{half-width of peak}). \quad (2)$$

The apparent density of the samples measured by Archimedes method was observed to be decreasing by adding 1, 3, 5 wt% of P_2O_5 . We had added P_2O_5 (fusion temperature $\sim 580^\circ\text{C}$) to promote liquid phase sintering so that PZT can be formed at a low temperature. Our results are in confirmation with [18] where it is reported that addition of P_2O_5 above 2 wt% leads to decrease in density. This is because addition of P_2O_5 above the optimum limit inhibits densification due to the formation of a thick coating of the liquid around the grains [20].

3.2 Dielectric studies

We have done the detailed dielectric analysis of the P_2O_5 -doped PLZT which has not been reported so far. Dielectric constant and $\tan \delta$ variation with temperature as a function of frequency was measured at 10, 50, 100, 500 kHz and 1 MHz. We did not find any change of T_C with different frequency, which is the characteristic of normal ferroelectrics.

Figure 2 shows the variation of the dielectric constant (ϵ) at 100 kHz with increment of temperature for all four different compositions. Similar to normal ferroelectrics, the dielectric constant increases gradually with increasing temperature up to the transition temperature (T_C), then it decreases. Here the region around the peak (ϵ_{max}) is broadened, which is one of the most important characteristics of a disordered perovskite structure with diffuse phase transition having compositional fluctuations. Compositional fluctuation may be developed at the A site which is occupied by Pb^{2+} , La^{3+} or at the B-site occupied by Zr^{4+} , Ti^{4+} and P^{5+} . Hence structural disorder arises due to the presence of voids and to the type and size of impurities added. This leads to microscopic or nanoscopic heterogeneity in the compounds with different local Curie points. We have noticed that as doping concentration of phosphorus is increased, the dielectric constant decreased considerably. In general, the reduction in dielectric constant is attributed to the reduced

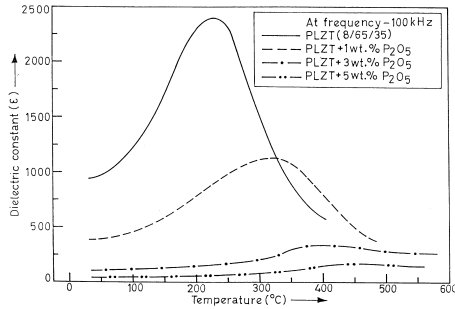


Figure 2. Dielectric constant variation as a function of temperature at 100 kHz.

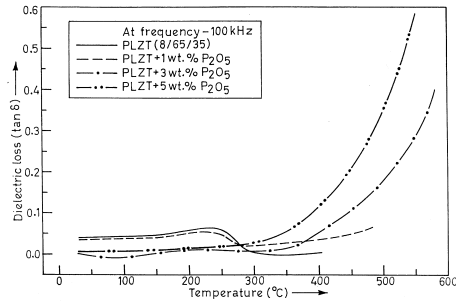


Figure 3. Temperature dependence of dissipation factor ($\tan \delta$) at 100 kHz.

dipole moment of the lattice due to the presence of dopant. In our case, as the amount of P^{5+} doping is very small, the large decrease in dielectric constant may be due to the decrease in density and the increase in the amount of pyrochlore phase in the ceramics.

Further examination of the degree of diffuseness in the dielectric peaks of the compounds was estimated using the relationship [21]

$$(1/\varepsilon - 1/\varepsilon_{\max}) \propto (T - T_C)^\gamma, \quad (3)$$

where ε_{\max} is the maximum value of ε at T_C and γ is a measure of diffuseness. The value of γ was found to lie between 1 and 2, which was extracted from the plot of $\ln(1/\varepsilon - 1/\varepsilon_{\max})$ vs. $\ln(T - T_C)$ by fitting a straight line equation. This confirms that diffuse phase transitions occur in the materials with high degree of disorder and there is a deviation from the Curie–Weiss type of phase transition.

Figure 3 shows the variation of loss factor ($\tan \delta$) with temperature. Dielectric loss was found to be almost constant up to 250°C, then it increases with rise in temperature, which may be caused by the losses due to electrical conduction. In general, the dielectric losses [22] and dielectric constant follow the similar temperature behaviour. In the case of sharp ferroelectric–paraelectric phase transition, both dielectric constant and dielectric losses peak at the same temperature and both follow the Curie–Weiss behaviour as expected from Kramer–Krönig relations. In P^{5+} -doped samples, as the ferro–paraelectric transition become diffuse, the dielectric constant and losses peak at different temperatures and their separation of maxima depends upon the degree of broadening of the transition in dielectric vs. temperature variation which itself deviate from the Curie–Weiss law of phase transition.

4. Conclusions

In the present work we have reported the unique effects of P_2O_5 -doped PLZT ceramics with composition $(Pb_{0.92}La_{0.08})(Zr_{0.65}Ti_{0.35})O_3 + x$ wt% of P_2O_5 (where $x = 1, 3$ and 5) prepared chemically by co-precipitation method. The prepared compound was found to be very fine (10–25 nm) and homogeneous. X-ray diffraction studies confirmed rhombohedral symmetry for the synthesized compound.

P⁵⁺-doped samples, which have some pyrochlore phase, show low dielectric constant. The apparent density of the samples decreased with the addition of P⁵⁺. A study of dielectric constant suggests diffuse type of phase transition without any sign of relaxor behaviour in the material. With increasing x , dielectric constant was found to decrease appreciably, whereas Curie temperature (T_C) as determined from dielectric constant vs. temperature plots was found to increase. The prepared ceramics have very low dielectric loss, high transition temperature and low temperature coefficient of capacitance, which may be useful for device applications.

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