RESEARCH ARTICLE

Effect of Lanthanum Substitution on the Structural, Dielectric, Ferroelectric and Piezoelectric Properties of Mechanically Activated PZT Electroceramics

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ABSTRACT

Different compositions of $(Pb_{1-x}La_x)(Zr_{0.60}Ti_{0.40})O_3$ (abbreviated as PLZT x/60/40; x=0, 0.07, 0.08 and 0.10) ceramics were prepared by a combinatorial approach of high energy mechano-chemical ball milling and cold isostatic pressing (CIP). X-ray diffraction patterns and transmission as well as scanning electron microscopy images were used for the micro-structural and morphological studies. The average particle size of PLZT milled powders was measured from the TEM images and was found to be in the nm range. XRD patterns of the sintered PLZT x/60/40 ceramics confirm the perovskite phase formation after heat treatment. SEM images of sintered PLZT x/60/40 ceramics show a close packed dense structure. PLZT 8/60/40 ceramics show the fine grains (~1.3 μm) with density ~97 per cent. Dielectric constant and loss were measured as a function of temperature. PLZT 8/60/40 ceramics shows the highest of room temperature dielectric constant ~2480 measured at 1 kHz. Ferroelectric studies were done with the help of polarisation (P-E) and strain (S-E) *vs.* electric field measurements. PLZT 8/60/40 ceramics shows the maximum value of remnant polarisation (~35.5 μC/cm²) and strain (~0.25 per cent), respectively. PLZT x/60/40 ceramic samples were poled at optimised poling conditions. The measured values of piezoelectric charge coefficient (d_{33}) and electromechanical coupling factor (k_p) of PLZT 8/60/40 ceramics were found to be, ~690 pC/N and ~71 per cent, respectively.

Keywords: Mechanical activation, ferro electricity, piezoelectricity, PLZT, Electroceramics

1. INTRODUCTION

Lead based and lanthanum substituted PZT (PLZT) ceramic systems show all the aspects of the dielectric, piezoelectric, pyroelectric, ferroelectric and electro-optic properties desired in such materials. These best properties make them used widely in numerous devices such as different types of sensors, actuators, nano-positioners and transducers[1-3].

The amount of lanthanum substitution in the basic PZT system was selected on the basis of morphotropic phase boundary (MPB, a region of maximum piezoelectric and dielectric response)[3-5], that depends on the Pb/La ratio[6-7]. At the vicinity of the MPB, PLZT ceramics show outstanding piezoelectric properties, which can be attributed to the unique structural feature of the coexistence of tetragonal and rhombohedral phases. In the vicinity of the MPB region, the six domain states of the tetragonal structure along the (100) direction (90° and 180° domains) coexist with the eight domain states of the rhombohedral along (111) directions (71°, 90°, and 180° domains). This results in 14 possible available directions for spontaneous polarisation[8]. Off-valent donors and La^{3+} replacing Pb^{2+}, counteract the natural p-type conductivity of the PZT and thus, increase the electrical resistivity. The donors are usually compensated by A-site vacancies, which enhance domain reorientation and as a result ceramics show square hysteresis loops, low coercive fields, high remnant polarisation, high dielectric constants, maximum coupling factors, higher dielectric loss, high mechanical compliance, and reduced aging[2].

Due to high volatility of lead, to ensure good electrical properties, ceramics should be prepared at low calcination and sintering temperatures. This condition was achieved by the synthesis of nano sized fine powders by using the mechanical activation method[9-11] with optimised high energy mechano-chemical (HEM) ball milling parameters because the properties of ferroelectric ceramics are greatly affected by the milling parameters[12-13]. The main advantage of this HEM ball milling method is that no excess PbO was added in the starting composition because of lower calcination and sintering temperatures, without compromising the electrical properties of electro-ceramics. Usually, to carry out dielectric and electrical measurements, ceramic powders are first mixed with binder and then uniaxially pressed in to the shape of ceramic disks but in this study no binder was added. Instead, ceramic powders were cold isostatically pressed (CIP). This eliminated the binder addition and binder burnout steps that help to increase the density, electrical properties and reduced the contamination risk.

The present study deals with the optimisation of the lanthanum substitutionat the A-site of PZT ceramics by studying a range of compositions. For this purpose microstructural properties such as particle size, grain size, density and electrical properties such as dielectric constant, loss, ferroelectric hysteresis (P-E) and electric field induced strain (S-E) hysteresis loops, remnant polarisation, coercive field, strain, d_{33}, k_p of the PLZT x/60/40 ceramics were measured and studied. Substitution of 8 at% of La^{+3} in the $(Pb_{1-x}La_x)(Zr_{0.60}Ti_{0.40})O_3$ (PLZT 8/60/40) system which is close to the MPB, shows the optimum properties.

2. EXPERIMENTAL WORK

For synthesis of PLZT electro-ceramics PbO, La_2O_3, ZrO_2, TiO_2 (99.9 per cent pure, Sigma–Aldrich, USA) were used as raw materials. Stoichiometric quantities of raw powders were weighed and placed in agate vials along with zirconia balls (Tosoh, Japan). Distilled water was added to the powders and these were subjected to ball milling operation using a high energy ball mill of M/s Fritsch GmbH (Pulverisette[5]) at room temperature. Milled powders were calcined at 800 ℃ for 4 h and again ball milled for 10 min to get rid of agglomeration. Calcined powders were cold isostatically pressed (CIP) at 300 MPa. CIPed cylindrical green rods of PLZT ceramics were densified by sintering at 1200 ℃ for 4 h.

For more details, readers are suggested to look into our previous publications[7,14-17]. The salient features of the processing technique is that :

(i) No excess PbO was added to the starting material because of lower calcination and sintering temperatures that may be attributed to the very fine scale particle sizes after HEM ball milling[10,14], and

(ii) No binder was added in this process.

This process has removed the binder addition and burnout step and avoided the contamination risk involved.

X-ray diffraction (XRD) patterns of the sintered ceramics were recorded at room temperature using Philips X'pert PW-3020 X-ray diffractometer with monochromatic CuKα radiation (λ = 1.5406 Å) over a wide range of Bragg angles; 2θ from 20º to 80º (step size = 0.02º). The XRD patterns were used for the calculation of an average crystallite size 'P' by using the Scherrer formula[18].

A FEI Tecnai 20G2 transmission electron microscope (TEM) was used to examine the particle size for the milled powders. SEM (LEO-440i) was used to examine the milled powder and grain morphology of fractured surface of sintered compacts. The density of the PLZT 8/60/40 was calculated using the Sartorius density measurement system (using Archimedes principle).

Sintered samples were sliced into thin disks, about 1mm in thickness, in conformity with the IEEE standards[19]. PLZT samples were electrically poled with carefully optimised poling conditions[15-16]. A piezoelectric Berlincourt meter, SENSOR SS-01 Piezo-d Meter, Canada was used for piezoelectric charge coefficient (d_{33}) measurement. Dielectric properties and planar coupling factors (k_p) were determined by the resonance and anti-resonance method using an LCR meter (Agilent E-4980A). The P-E and S-E hysteresis loops were traced using an advanced ferroelectric evaluation system (M/s aixACCT system, Germany). The SIOS laser interferometer of class 2M was used for S-E studies.

Strain hysteresis value is calculated from the S-E curves by using the equation.

$$\text{Strain hysteresis (\%)} = \frac{\Delta x}{x_{max}} \times 100 \tag{1}$$

where x_{max} is the maximum strain in the specimen subjected to maximum applied field, Δx is the difference between the strain values in both directions at ½ E_{max} field.

3. RESULTS AND DISCUSSION

3.1 Micro-structural Characterisation

Figure 1 shows the XRD patterns for the sintered PLZT x/60/40 ceramics. After the sintering of ceramics, XRD patterns of the all PLZT compositions show the disappearance of the extra peaks of unreacted PbO and other raw oxides that were present in the case of XRD pattern of as milled ceramics[14], confirms complete perovskite phase formation matched by JCPDS 53-0698 file. During the heat treatment of compact PLZT ceramics, reaction of the oxides takes place and a complete phase transformation into the desired PLZT phase is formed. No other phases were detected in sintered PLZT, indicating that the remaining oxides in the ceramics already reacted leading to the formation of the perovskite phase.
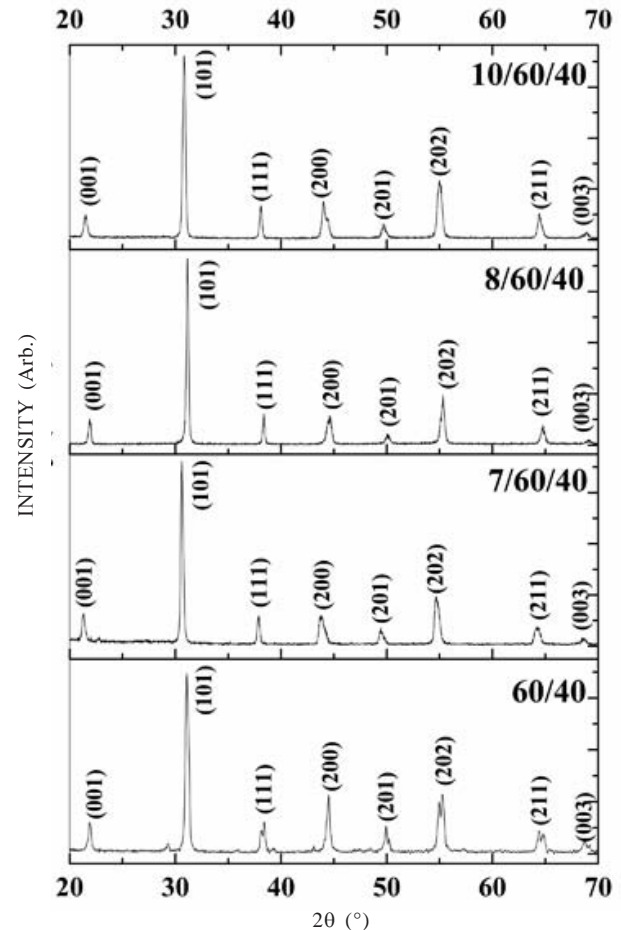

Figure 1. XRD patterns for the sintered PLZT x/60/40 ceramics.

Both SEM and TEM techniques were employed to determine the particle size and for the purpose of a correlative comparison. Figure 2 shows the SEM images for milled powders of different compositions of PLZT ceramics. The pressure generated from the high energy mechano-chemical milling is high enough to break down the particles of the PLZT powders into nanometer range. Reduction in particle size makes the particles highly reactive and causes an agglomeration between the particles. From Fig. 2 it is clear that particle size of milled powder is very fine and due to the reduction in their surface to volume ratio, their reactivity also increased. At room temperature, partial perovskite phase formation for the milled powders shows, the energy supplied by the HEM ball milling process can trigger the partial chemical reaction[14]. Since SEM images of PLZT ceramics show only the agglomerated powders, TEM images were also taken for the milled powders of PLZT 8/60/40 ceramics (a composition which is close to the MPB).

TEM was also used for examining the microstructure of the material. The TEM image of the milled powder shows that the particle size of PLZT 8/60/40 milled for 5 h has deviated from the spherical shape, has non-uniform broadly distributed particle size range (Fig. 3). The size of high energy ball milled powders is in the nanometer range. The reduction in particle size results in an increase in the surface to volume ratio making the particles highly reactive and causing an agglomeration between the particles as seen in Fig. 3. The sol-gel process results in spherical particles whereas mechano-chemical processing results in elongated/flaky particles on account of the high mechanical impaction forces that result in mechanical deformation[6,20]. The average particle size calculated from the TEM image was found to be ~ 25 nm. During the high energy ball milling process, mechanical energy is applied to PLZT powders by high strength collision and high pressure impact between the milling media and the milled powder. All of these results in the particles of the PLZT powders to be in nanometer size.

High density and uniform microstructure are among the most desirable features for PLZT based electro-ceramics in obtaining many of its optimal electrical and mechanical properties. Since the properties of the electro-ceramics are also highly density dependent, ceramics should have minimum porosity to carry out electrical measurements. The density of the sintered PLZT ceramics was calculated using the Archimedes principle. PLZT 8/60/40 ceramics showed the maximum density of 7.73 gm/cm^3 (which is ~ 96.61 per cent of the theoretical density).
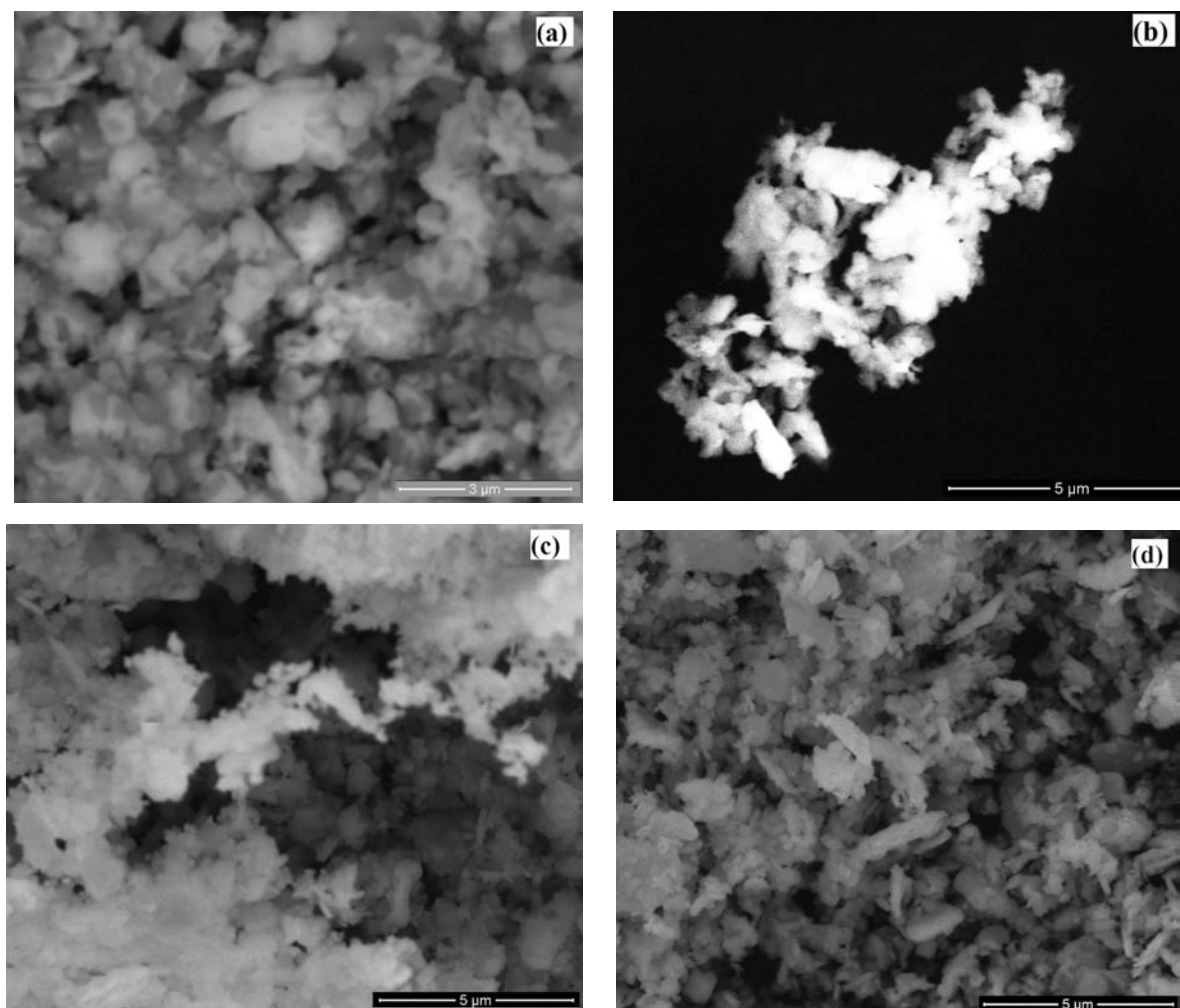

Figure 2. SEM images of the PLZT (a) 0/60/40, (b) 7/60/40, (c) 8/60/40, and (d) 10/60/40 as milled powders.
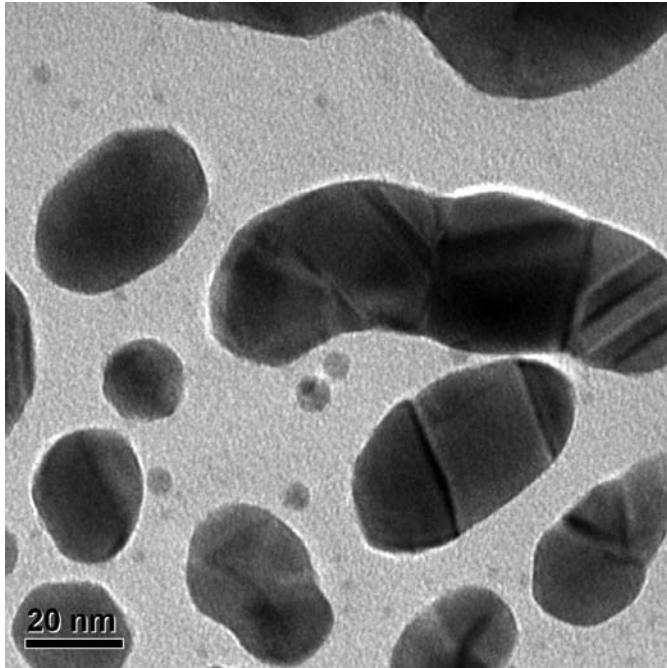
Figure 3. TEM image of as milled powders of PLZT 8/60/40 ceramics.

Figures 4(a) to 4(d) shows the SEM images of fractured surfaces of the PLZT x/60/40 sintered pellet. The base composition (PZT) shows bigger grains compared to La substituted ones with less dense microstructure. Grain shape of the PZT system is also not uniform and that also has an effect on the electrical properties. With increase in lanthanum substitution in the PZT system, the grain size decreases and ceramics show better microstructure and uniform grain size. The fractured surface of the PLZT ceramics after sintering shows a dense microstructure, uniform grain size with clearly visible grain shapes. The grain size has significant influence on electrical properties such as ferroelectric, dielectric and piezoelectric properties of electro-ceramics. The addition of lanthanum has affected the microstructure of the ceramic material. Scanning electron microscopy images of the fractured surface of La modified PZT shows that the grain size decreased when compared to unmodified PZT ceramics[21]. It was presumed that minute chemical in-homogeneities on the A and B sites of the perovskite prevented the growth of grains. Another possibility would be the formation of second phases on a very small scale at the grain boundaries.

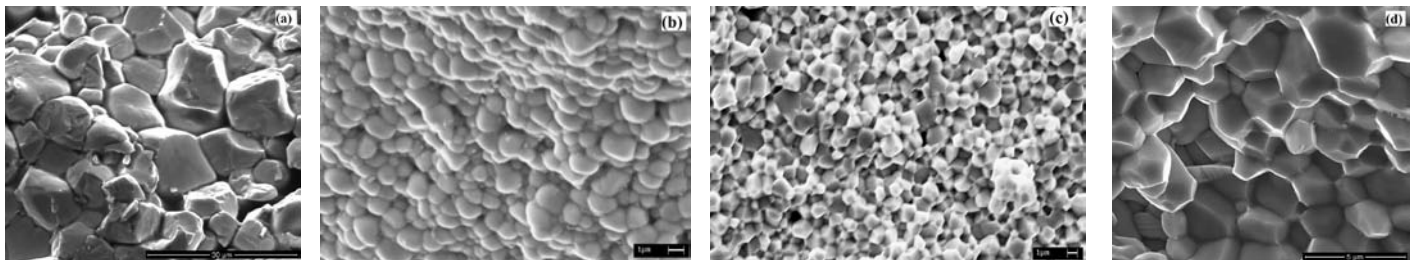Figure 4 (c) shows the SEM micrograph for the sintered pellet of PLZT 8/60/40 ceramics indicating a very dense structure with a uniform grain size. Grain shapes are clearly visible, indicating the existence of a polycrystalline microstructure. The average grain size was found to be ~ 1.3 μm. Ferroelectric and piezoelectric properties directly depend on the grain size of the ceramics and the properties of the fine grained ceramics were found to be better compared to conventional ceramics[22].

Since the grain size is an important factor that affects the dielectric constant, tetragonality (c/a ratio), phase transition temperature (T_c), polarisation, piezoelectric and pyroelectric properties of ferroelectric ceramics, the grain distribution for the PLZT 8/60/40 ceramics was also studied. Figure 5 shows the grain size distribution for the PLZT 8/60/40 ceramics. Grain sizes of sintered compacts have a broad variation from 0.5 μm to 3.5 μm but the maximum number of grains fall in the range of 1.5 μm - 2.0 μm.

3.2 Dielectric Properties

The temperature dependent dielectric constant (K) and loss study helps to determine the nature of the ferroelectric phase transition. Figures 6 (a) and 6 (b) show the dielectric constant and dielectric loss vs. temperature graphs, respectively for the PLZT x/60/40 ceramics at a frequency of 1 kHz.

It is apparent from Fig. 6 (a) that the variation of dielectric constant with temperature shows sharp peaks (as in normal ferroelectrics) around Tc for PZT ceramics when compared to La substituted PLZT ceramics. PLZT 7, 8, and 10/60/40 ceramics show the broadened dielectric constant vs. temperature curves. This broadening is believed to be due to
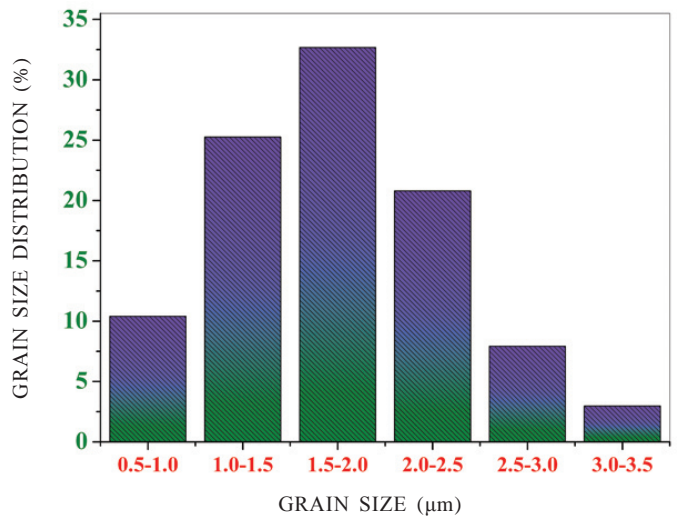

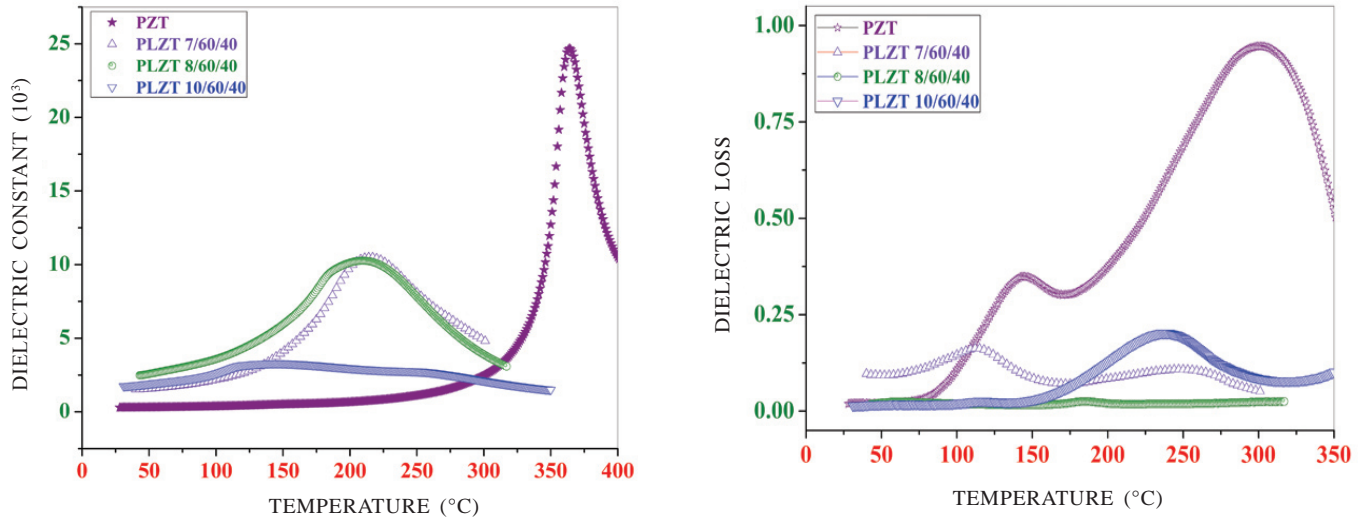**Figure 5. Grain size distribution of PLZT 8/60/40 sintered ceramics.**

Figure 4. SEM images of fractured surface of sintered PLZT (a) 0/60/40, (b) 7/60/40, (c) 8/60/40, and (d) 10/60/40 ceramics.

Figure 6. (a) Dielectric constant and (b) dielectric loss *vs*. temperature curves of PLZT x/60/40 ceramics measured at 1 kHz.

compositional fluctuations, and/or substitutional disordering in the arrangement of cations in one or more crystallographic sites of the structure, which leads to microscopic or nanoscopic heterogeneity in the compounds, with different local Curie points[23-25]. The broadening increases as a function of lanthanum substitution. The detailed explanation of the diffuse phase transition for PLZT 8/60/40 ceramics is already discussed in a previous publication[26].

Substitution of La[+3] to the PZT system not only enhances the domain reorientation but also is maintained in the form of an extensive solid solution throughout the system and decreases the stability of the ferroelectric phases in favor of the paraelectric and anti-ferroelectric phases resulting in reduction of the T_c with increasing lanthanum[2]. Decrease in transition temperature is also notice in the present study. Dielectric properties of PLZT 8/60 /40 ceramics are given in Table 1.

Table 1.   Micro-structural, dielectric, ferroelectricand piezoelectric properties of PLZT ceramics

	PZT 60/40	PLZT 7/60/40	PLZT 8/60/40	PLZT 10/60/40
Crystallite size (nm)	22	29	35	26
Grain size (μm)	9.5	1.5	1.3	1.8
d_{33} (pC/N)	156	465	690	250
k_p	0.31	0.54	0.71	0.33
P_r (μC/cm²)	8.4	28.3	35.5	4.9
E_c (kV/cm)	9.5	9.4	7.6	9.4
Strain (%)	0.13	0.23	0.25	0.18
Strain hysteresis (%)	10.5	5.3	2.2	34.1
K (RT)	291	1524	2480	1740
T_c (ºC)	364	214	209	144
K (T_c)	24688	10504	10266	3298

3.3 Ferroelectric Properties

Ferroelectrics ceramics are categorised based on the value of remnant polarisation (P_r) and coercive field (E_c). P_r is related with non-zero polarisation in ceramics after removal of the external electric field and the necessary electric field required to bring the P_r to zero is called E_c. Both the parameters can be evaluated from the saturated P-E hysteresis loops. Figure 7 show the P-E hysteresis loops for different compositions of PLZT electro-ceramics. The PZT system shows very low P_r and high E_c when compared with lanthanum substituted PLZT.

The PLZT 8/60/40 composition showed a P_r of 35.5 μC/cm² and a coercive field E_c of 7.6 kV/cm, which are far better than other compositions. The coercive field, remnant polarisation and shape of the loop are affected by many factors like charged defects, mechanical stresses, preparation conditions and thermal treatment. The shape of hysteresis loop for PLZT 8/60/40 shows a high squareness and saturation. The loops also indicate good homogeneity and uniformity of the grain size. P-E loops for all compositions were measured at same electric field.

When an electric field is applied to the ceramic sample, in addition to the polarisation, strain is also developed due to the converse piezoelectric effect of the lattice as well as switching and movements of domain walls. An application of electric field results in the creation of a large strain linked to the piezoelectric effect[1,15].

$$\partial d_{kij} = \frac{\partial \eta_{ij}}{\partial E_k} \qquad (2)$$

where d_{kij} is the piezoelectric coefficient, η_{ij} is the strain and E_k is the applied electric field

Figure 8 shows electric field induced unipolar strain hysteresis curves for different compositions of PLZT electro-ceramics recorded at room temperature. PZT system shows less strain, but as the amount of lanthanum substitution increases, the unipolar strain also increases. At high electric field, the alignment of domains saturates and the loss (represented by the area of the loop) decreases. The PLZT 8/60/40 electro-ceramic exhibited a 0.25 per cent strain with minimum hysteresis loss of ~2 per cent at ~60 kV/cm, due to increase in the alignment of domains.

High remnant polarisation, low coercive field, well saturated loops, high strain and low hysteresis loss possibly
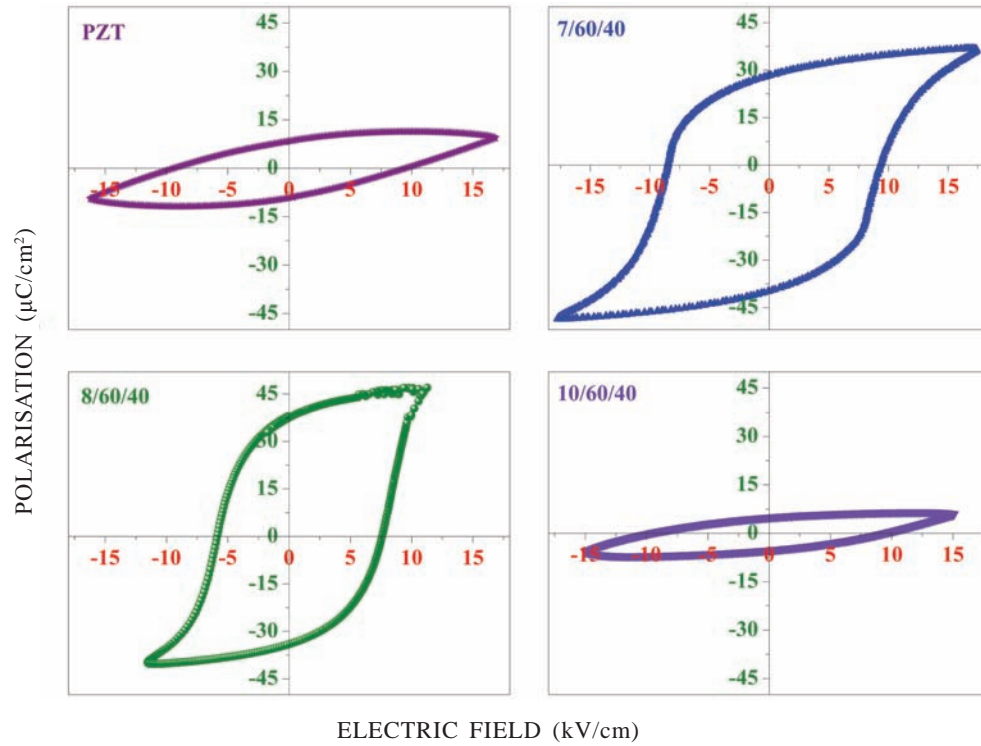
Figure 7. Polarisation *vs.* electric field hysteresis curves for PLZT x/60/40 ceramics measured at 1 Hz and 25 °C.
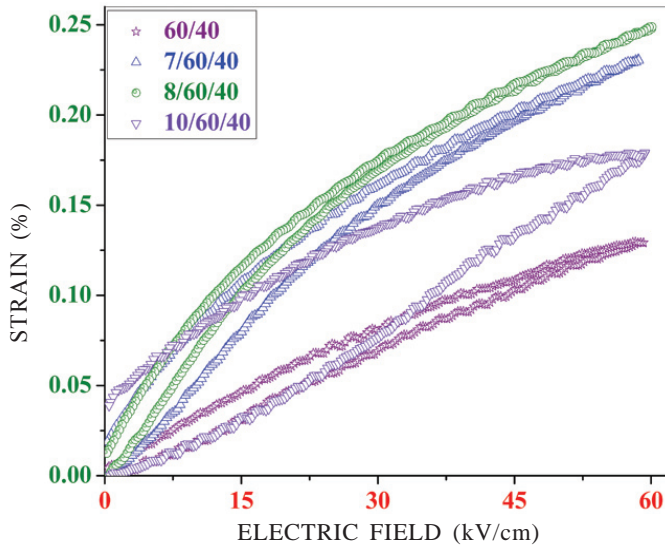

Figure 8. Strain *vs.* electric field hysteresis curves of PLZT x/60/40 ceramics measured at 1 Hz and 25 °C.

be attributed to uniform distribution of grain sizes, uniform distribution of composition, fewer defects and imperfections in the crystallites[8,27]. All the parameters that are related to ferroelectric properties are given in Table 1.

3.4 Piezoelectric Properties

Piezoelectric properties of the PLZT x/60/40 ceramics depend on many factors, such as compositions, processing techniques, morphotropic phase boundary conditions (MPB), grain size, poling conditions etc. PLZT ceramics prepared by the mechano-chemical route followed by cold isostatic pressing

improve the materials density and retain their fine grain size, which in turn influences the domain wall motion and switching phenomena. The composition PLZT 8/60/40 is located near the MPB region. On account of this, it is expected that the increased number of directions of spontaneous polarisation will help to improve the piezoelectric properties. The values for piezoelectric properties such as charge coefficient (d_{33}) and coupling factors (k_p) for the PLZT electro-ceramics were found to be very good and are listed in Table 1. The value of d_{33} for PLZT 8/60/40 ceramics was found to be 690 pC/N. The value of planar coupling factor (k_p) was determined using the resonance and anti-resonance method[14] and was found to be ~0.71.

4. CONCLUSIONS

PLZT x/60/40 compositions were successfully prepared by using high energy milling, ciping and solid state sintering. PLZT 8/60/40 composition shows the best properties. HEM ball milling helps to prepare this ceramics without excess PbO, with reduced calcination and sintering temperatures. Ciping helps to remove the binder adding and burnout step which reduced the contamination and improved electrical properties. An improvement was seen in the dielectric properties with composition variations. Improvement was also found in the micro-structural properties of the ceramics like particle size, grain size and density as well as ferroelectric properties such as shape of the hysteresis loop, remnant polarisation, coercive field and strain for PLZT 8/60/40 ceramics. PLZT 8/60/40 ceramics possess fine grains ~1.3 μm, maximum P_r and strain of ~35.5 μC/cm² and 0.25 per cent, respectively. The d_{33} and k_p values were found to be 690 pC/N and 71 per cent, respectively.

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CONTRIBUTORS

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