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Synthesis, Structural and Electrical Properties of Lanthanum-modified Lead-zirconate-titanate System

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ABSTRACT

Lead-zirconate-titanate (PZT) ceramics with zirconate-titanate (65:35) have been synthesised with the substitution of lanthanum (6, 7 and 8 mol %). Samples were prepared by solid-state reaction route.The x-ray diffraction study shows the formation of a single phase with rhombohedral structure. There is a transformation in crystal structure from tetragonal to co-existence of tetragonal, and rhombohedral to a single rhombohedral phase with the increase in the lanthanum concentration in the basic PZT composition. Results of a detailed dielectric study indicate the diffuse-phase transition at higher values of lanthanum concentration, which may be attributed to the microscopic heterogeneity in the composition. Dielectric properties of the poled and unpoled samples have also been compared and found that the values decreased after poling. Ferroelectric hysteresis behaviour was also studied as a function of temperature for all the three compositions, which showed typical variation of ferroelectric nature. Piezoelectric charge coefficient (d_{33}) decreases with increase in the lanthanum and with the increase of frequency as well, up to the measured limit.

Keywords: Lead-zirconate-titanate ceramics, PZT, ferroelecrtric behaviour, piezoelectric charge coefficient, rhombohedral structure, lanthanum-substituted PZT ceramics, PLZT

1. INTRODUCTION

Ceramics-based lead-zirconate-titanate (PZT) systems are widely used in various memory elements[1] and in pyroelectric devices[2,3]. Depending upon the specific requirement for different applications of piezoelectric ceramics, various compositions of the PZT system may be chosen[4]. Various impurities have been added to improve the piezoelectric and pyroelectric properties[5,6]. The distinctive features of PZT are high sensitivity, non-hygroscopicity, mechanical strength, simplicity of preparation, and ease in poling in a given direction. The main advantage of $Pb(Zr,Ti)O_3$ series is the possibility of controlling their electrophysical properties and Curie temperature with the aid of modifying additions, lanthanum being the most effective one[7-9]. The unique characteristic of lanthanum-substituted PZT (PLZT) $[Pb_{1-x}La_x(Zr_yTi_{1-y})_{1-x/4}O_3]$ ceramics have led to their wide use in smart sensors and optical processing devices for military applications. All the samples under study were characterised by the 65:35 (zirconate-titanate) ratio with lanthanum concentration at 6, 7, and 8 mol per cent. As has been shown earlier[7-9] that 65:35 composition corresponds to the morphotropic boundary phase region, thus providing high sensitivity of the ceramic structure and properties to external influences. Substitution of La^{3+} for Pb^{2+} is designed to be compensated by the introduction of B-site vacancies.

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2. EXPERIMENTAL DETAILS

The PbO, La_2O_3, ZrO_2 and TiO_2 powders were used in the present study to prepare the PLZT ceramics. The raw materials were weighed according to the formula $Pb_{1-x}La_x(Zr_{0.65}Ti_{0.35})_{1-x/4}O_3$ with x = 0.06, 0.07 and 0.08, where the charge neutrality due to the aliovalent replacement was maintained by the presence of the negatively charged B-site vacancies[10]. Excess PbO (2 Wt %) was taken to compensate for the loss of lead during sintering.

The starting powders were ball-milled for 6 h in planetary ball mill using high-purity zirconia balls and distilled water as media. After drying, these were calcined in alumina crucibles at 800 °C for 4 h in the air. The calcined powders were again ball-milled for 6 h followed by drying and re-calcined at 850 °C for 4 h. The recalcined powders were again ball-milled for about 4 h and then dried and sieved. Pellets of 10 mm dia were made using hydraulic press and were sintered at 1250 °C for 4 h in closed alumina crucible in a lead-rich atmosphere.

The experimental density of all the sintered samples was measured by Archimedes principle. The x-ray diffraction analysis of the samples was carried out using Philips diffractometer model PW-3020. The samples for dielectric measurements were polished and then electroded with gold by sputter coater (Desk II TSC Cold Sputter/Etch Unit). The dielectric properties (dielectric constant, ε', and loss tangent, tan δ) were measured using an automated setup as a function of temperature and frequency. The setup consists of an LCR meter HP 4284A and a programmable temperature chamber (AR imagetronics) interfaced to a PC. The ferroelectric hysteresis behaviour was studied at different temperatures and at 50 Hz operating frequency using modified sawyer-tower circuit. The samples were poled in silicon oil at 150 °C under 30 kV/cm electric field for half-an-hour.

3. RESULTS & DISCUSSION

All the samples exhibited densification better than 95 per cent of the theoretical density. The experimental density increased with the lanthanum concentration in the present system. The x-ray diffraction patterns of all the three compositions are shown in Fig. 1. All the diffraction peaks were indexed in different crystal systems (tetragonal and rhombohedral) using observed interplanar spacing d in a standard computer program *xlat*.

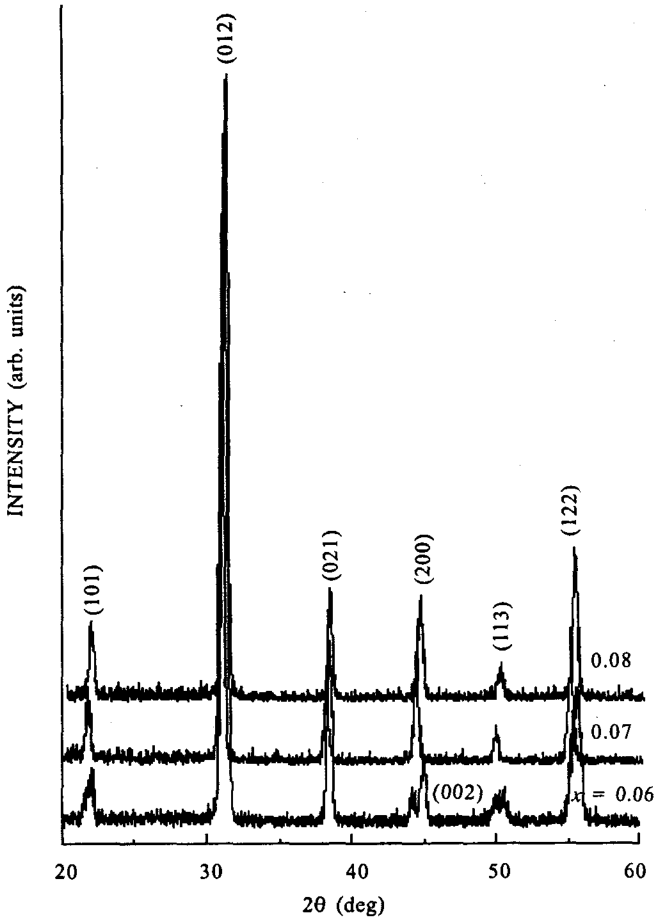

Figure 1. X-ray diffraction patterns for the samples with compositions $Pb_{1-x}La_x(Zr_{0.65}Ti_{0.35})_{1-x/4}O_3$.

A rhombohedral unit cell was finally selected on the basis of the best agreement between the calculated and the observed interplanar spacing d of all the diffraction lines of PLZT, and minimum $\Sigma\Delta d = S(d_{obs} - d_{cal})$, which shows a single-phase formation with rhombohedral structure. For composition; x = 0.06, (200) peak splits into two peaks completely, which corresponds to the tetragonal phase. For x = 0.07 and 0.08, the unsplit shape of (200) reflection line clearly indicates that rhombohedral phase is being favoured for higher content of lanthanum. Incorporation of lanthanum ions thermodynamically into the lattice of perovskite structure stabilises the rhombohedral phase against the tetragonal phase[11]. Temperature variation of dielectric constant (ε′) and loss tangent (tan δ) was studied for all the samples at different frequencies. Figure 2 shows the result for $x = 0.07$. All the samples showed an increase in the dielectric constant with temperature reaching maximum, and then a decrease with further increase in the temperature. Figure 3 shows the temperature dependence of dielectric constant (ε′) and loss tangent (tan δ) at a fixed frequency of 1 kHz for all the three compositions. Evidently, addition of lanthanum moves the diffused-phase transition region towards a lower temperature as well as significantly decreases the value of dielectric constant at maxima. As a consequence, the value of dielectric constant at room temperature becomes relatively low.

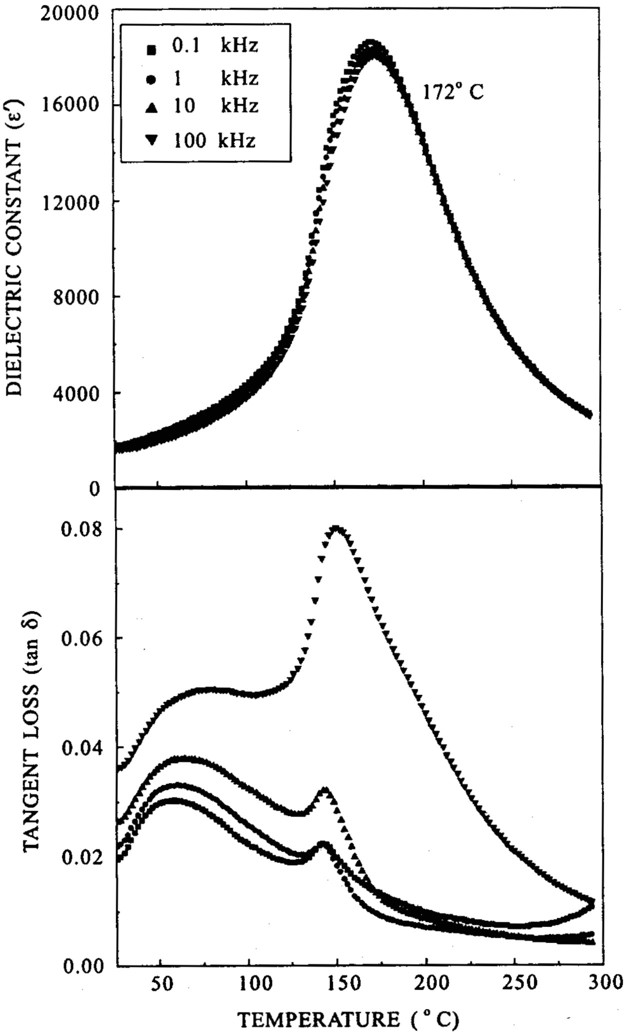

Figure 2. Variation of dielectric constant (ε′) and loss tangent (tan δ) with temperature for $x = 0.07$.

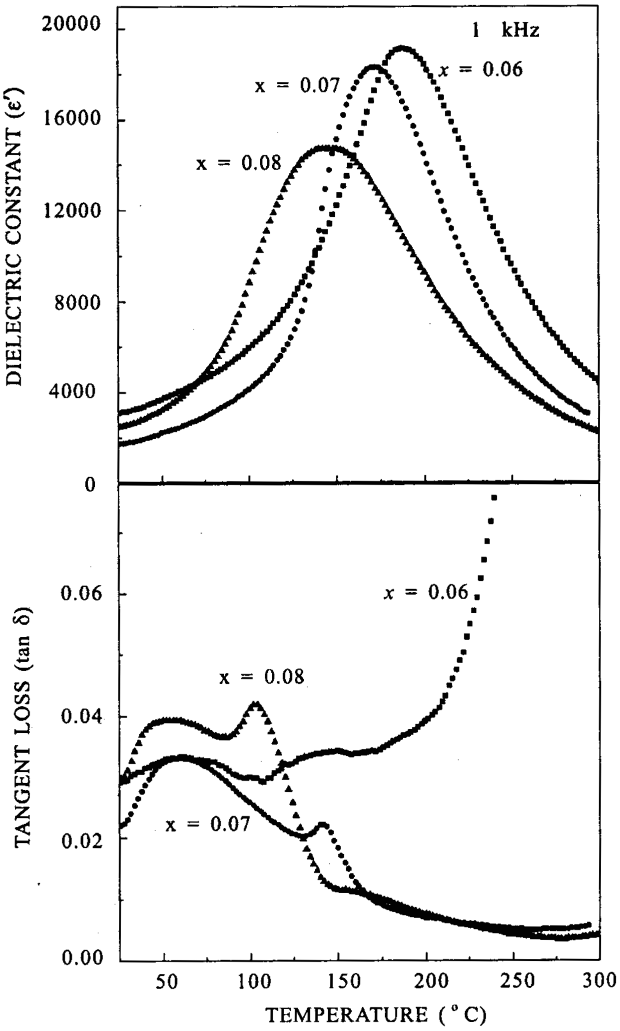

Figure 3. Temperature dependence of dielectric constant (ε′) and loss tangent (tan δ) for different concentrations of x measured at 1 kHz.

For $x = 0.06$ and 0.07, the difference in the peak value of dielectric constant at 1 kHz is modest, where the specimen contains both the tetragonal and rhombohedral phases. This can obviously be attributed to the enhanced ability for the polar nanodomains to follow the ac drive due to the maximisation of polarisation directions inherent to two phases. On further increment of the lanthanum content ($x = 0.08$), the dielectric constant at maxima decreases significantly, which can be interpreted by the reduced directions of domain reorientation due to the appearance of the single phase (rhombohedral). Additionally, the poor polarisability of lanthanum ions compared with that of lead ions is also responsible for the low dielectric maximum. Curie temperature decreases with the increase in the amount of lanthanum in the PZT system. The peak in dielectric plots becomes broader with higher lanthanum concentration. The broadening of the dielectric peak may be considered due to the disorder in the arrangements of rare earth and other atoms, leading to a microscopic heterogeneity in the composition, and thus, a distribution of different local Curie points[12,13]. The structural disorder in the compounds arises due to the presence of number of voids and size of impurities. The degree of disorder or diffusivity (γ), in all the three compositions was calculated using the following expression[14]:

$$\ln(1/\varepsilon - 1/\varepsilon_{max}) = \gamma \ln(T - T_C) + a$$

where ε_{max} is the maximum value of ε at T_C. The values of γ calculated from the slope of graphs (Fig. 4) were found to be 1.98, 1.96, and 2.40, respectively (for 6, 7 and 8 mol %) lanthanum, which confirms the diffuse phase transition in the materials. The degree of relaxor behaviour in the PLZT is known to increase with the increase in lanthanum content. It is believed that the coupling of ferroelectrically active oxygen octahedral is gradually weakened by the aliovalent lanthanum ions, and the resultant A-site vacancy. For high lanthanum content compositions, sufficiently strong decoupling results in the stabilisation of nanometer-sized local polar regions (polar nanodomains). Correspondingly, the macroscopic properties change from normal ferroelectric to relaxor ferroelectric types with increase in lanthanum content[15].

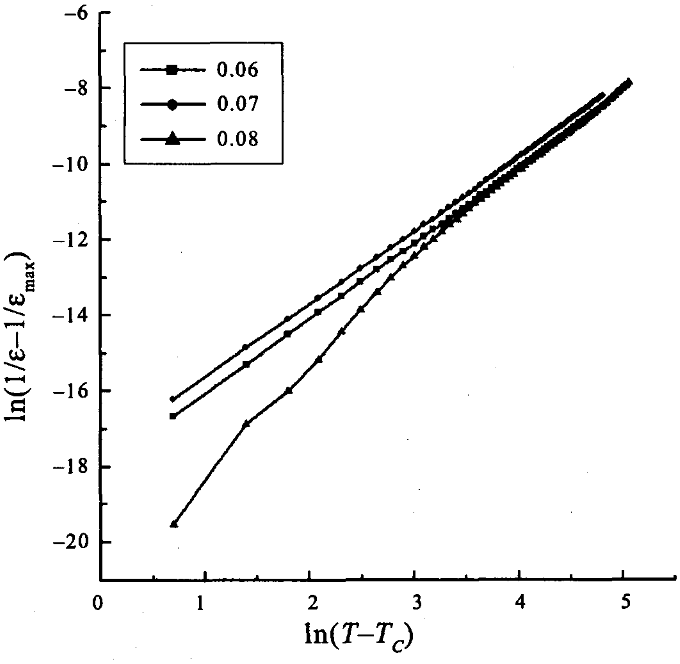

Figure 4. Variation of $(1/\varepsilon - 1/\varepsilon_{max})$ with $T - T_C$

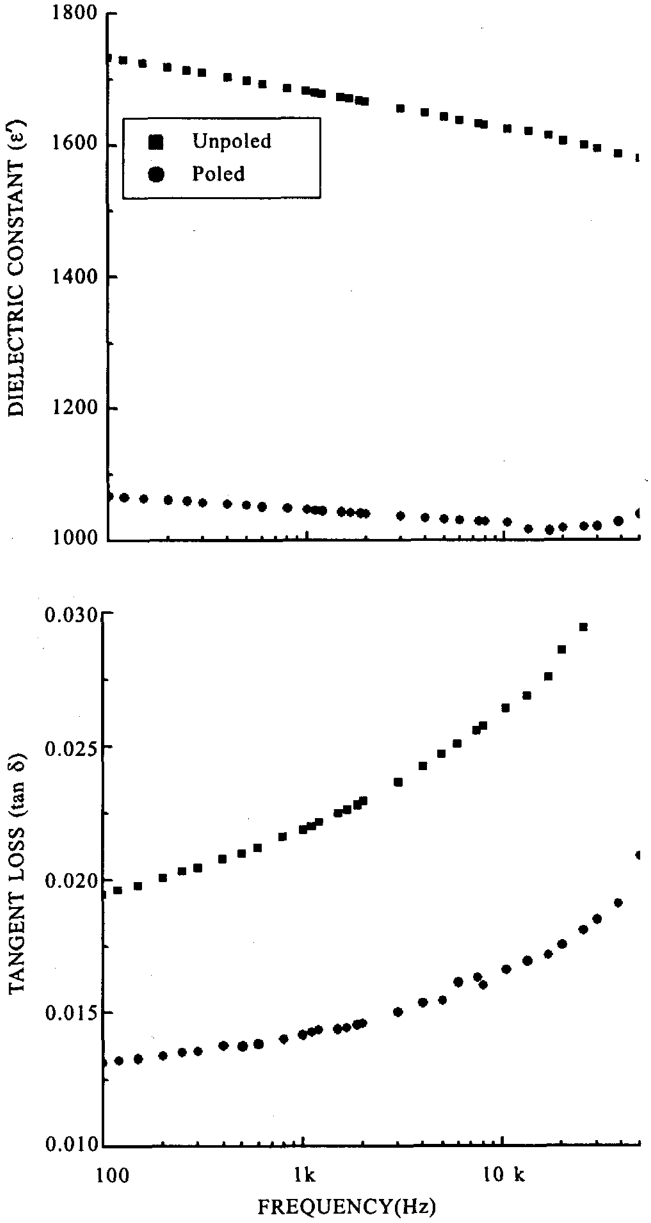

Figure 5. Room temperature behaviour of dielectric constant and tangent loss for poled and unpoled samples for $x = 0.07$.

Room temperature behaviour of dielectric constant (ε') and loss tangent ($\tan \delta$) was observed before and after poling for all the samples. Figure 5 shows the typical result for the composition with x = 0.07. All the samples show decrease in dielectric constant (ε') and loss tangent ($\tan \delta$) after poling. After poling, dielectric constant (ε') and $\tan \delta$ show less dependency on frequency. The decrease in dielectric parameters may be due to the dominance of 90° domains contribution to the dielectric properties after poling[16,17]. These aligned 90° rotated domains after poling cause more mechanical stress and enhance the anisotropy, that results in decrease in dielectric constant.

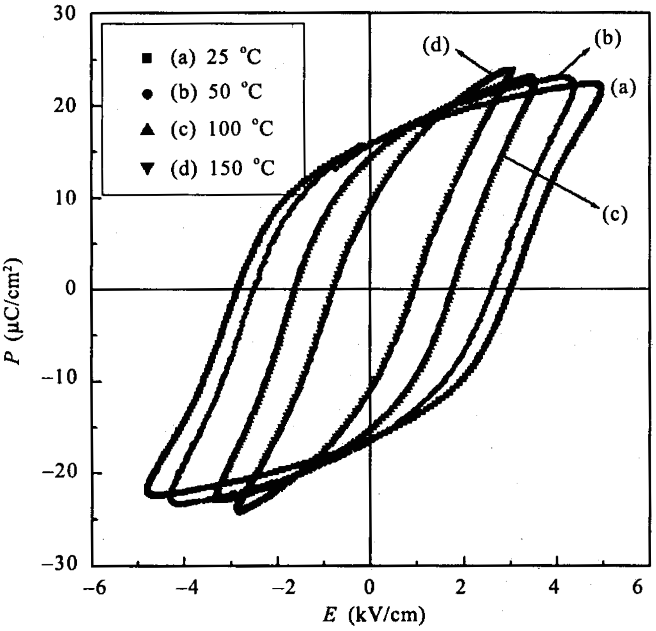

Figure 6. Typical ferroelectric hysteresis behaviour for the sample with $x = 0.06$ at different temperatures.

Ferroelectric hysteresis behaviour was studied for all the compositions at different temperatures. Figure 6 shows the typical behaviour for the sample with x = 0.06. With increase in temperature, there is a decrease in the area of the loop, which is a normal characteristic of ferroelectric materials. The variation in the values of coercive field (E_c) and remnant polarisation (P_r) with temperature has been plotted in Fig. 7 for all the three compositions. With increase in temperature, both E_c and P_r show a decreasing trend.

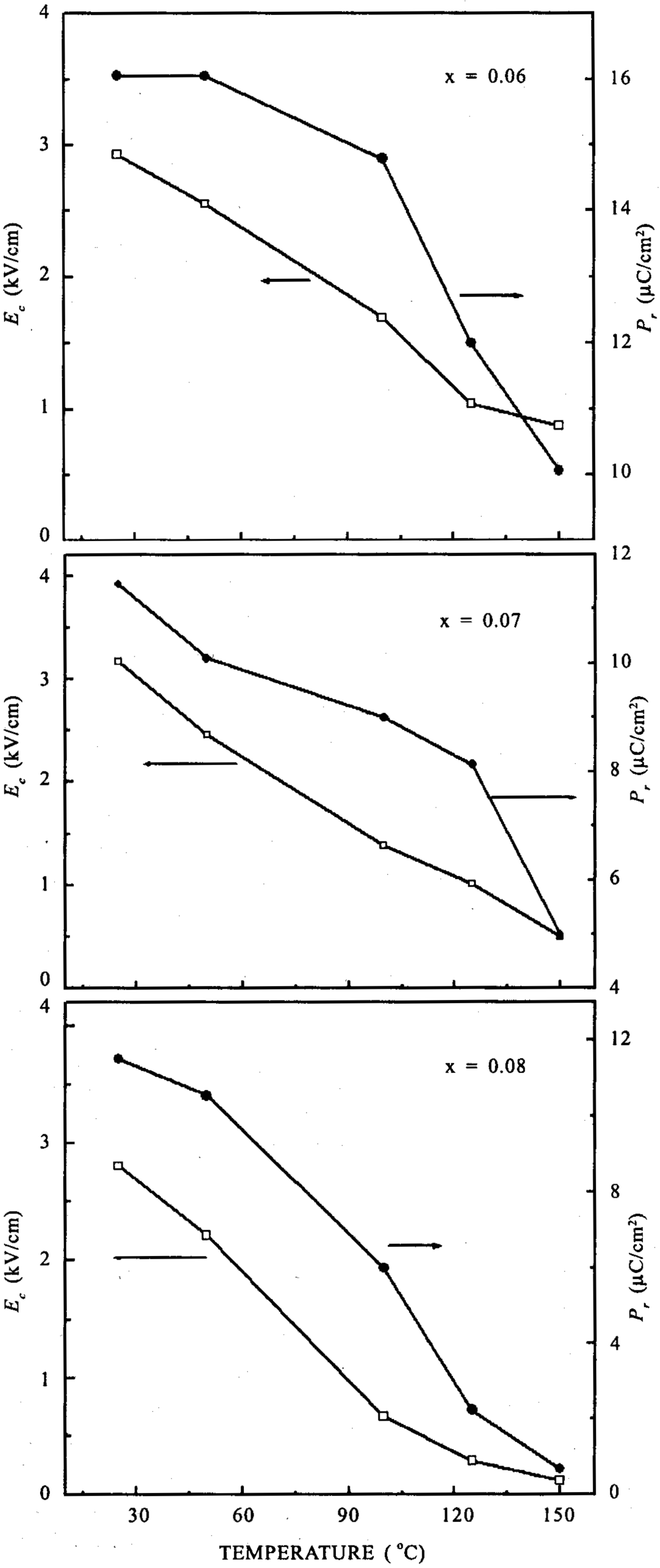

Figure 7. Temperature dependence of E_c and P_r for $x = 0.06$, 0.07 and 0.08.

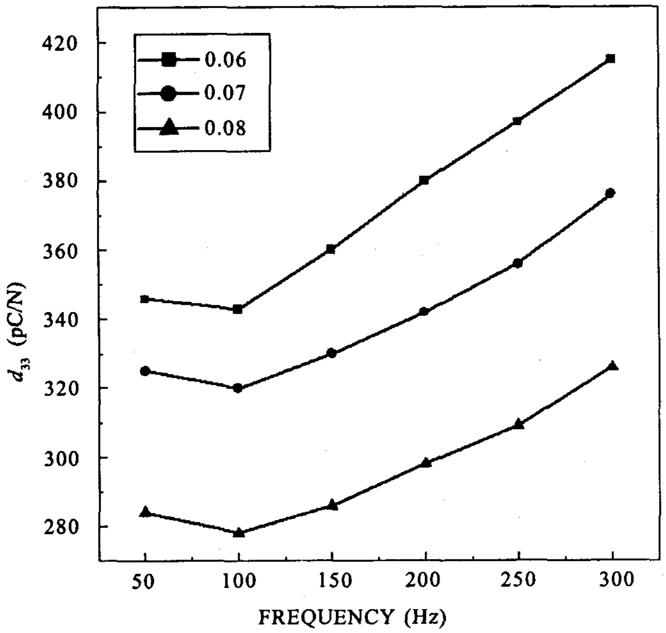

Figure 8. Variation of d_{33} with frequency

The variation of piezoelectric coefficient, d_{33} with frequency has been shown in Fig. 8. The value of d_{33} decreases with higher lanthanum content which can be attributed to the minimisation of number of polar directions as the structure traverse from coexistence of mixed phases to a single phase. The variation in d_{33} wrt frequency was measured from 50 Hz to 300 Hz. In this measured frequency range, it is observed that the value of d_{33} increases with increase in frequency, which may be due to the domain wall response to the applied frequency. There may be a possibility that after certain frequency range, the d_{33} value would decrease, as domain wall would not respond to the higher frequency.

4. CONCLUSIONS

The lanthanum-modified PLZT system was readily prepared by the solid-state reaction method. The substitution of lanthanum creates more structural disorder in the PZT. Room temperature values of dielectric constant and tangent loss decrease after poling, which may be due to the dominance of 90° domains. There is a decrease in coercive field (E_c) and remnant polarisation (P_r) with increase in temperature. Also with increase in lanthanum substitution, broadening in the dielectric peak is observed leading to diffuse-phase transition.

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