

EFFECT OF Ca ON DIELECTRIC PROPERTIES OF LEAD LANTHANUM ZIRCONATE TITANATE PEROVSKITE CERAMICS

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ABSTRACT

The objective of the present work is to investigate the effect of Ca^{+2} ions on dielectric properties of PLZT. The investigation reported here was aimed at developing a system with enhanced ferroelectric properties and studying the effect of calcium doping on the behaviour of PLZT ceramics. Calcium doped PLZT with general formulae $\text{Pb}_{0.9}(\text{La}_{1-z}\text{Ca}_z)_{0.1}(\text{Zr}_{0.65}\text{Ti}_{0.35})_{0.975}\text{O}_3$ where $z=0, 0.02, 0.04, 0.06$ were synthesized by solid state reaction method. X-ray diffraction analysis indicates the formation of single phase rhombohedral structure. Crystallite size, as calculated from Scherrer's equation, was found to be 25 nm. Measurement of dielectric constant as a function of temperature (35 - 450°C) indicates that the compound undergo diffuse type of phase transition. Hysteresis loop parameters (E_c and P_r) are found to decrease with calcium doping. The remnant polarization is observed to be maximum for $z=0.0$ having value of order of $7.34 \mu\text{C}/\text{cm}^2$.

Keywords: PLZT, Dielectric constant, ferroelectricity, polarization

INTRODUCTION

Ferroelectricity and related phenomena in ceramics have been exciting research areas in technologies and material sciences for a few decades. From the point of view of applications in electronics and optics, the applications of ferroelectricity have been attractive and an extremely active research area resulting in a huge leap of literature on ferroelectric materials. The biggest use have been in the areas such as dielectric ceramics for capacitor applications, ferroelectric thin films for non volatile memories, piezoelectric materials for medical ultrasound imaging and actuators, and electro-optic materials for data storage and displays. Lead zirconate titanate (PZT), a solid solution of PbTiO_3 ($T_c=490^\circ\text{C}$) and PbZrO_3 ($T_c=230^\circ\text{C}$) crystallizes in ABO_3 type

perovskite structure where Pb^{+2} occupies the A sites and Zr^{+4} and Ti^{+4} ions are accommodated at the B sites. It occupies an important place in the field of ferroelectricity as its properties can be easily modified with addition of appropriate substituents for specific applications. The most common substituent is La^{+3} on Pb^{+2} site, leading to well known high performance PLZT having lower curie temperature, high dielectric constant and high optical transparency as compared to PZT. The double doped PZT with common formulae of $\text{Pb}_{0.9}(\text{La}_{1-z}\text{R}_z)_{0.1}(\text{Zr}_{0.65}\text{Ti}_{0.35})_{0.975}\text{O}_3$, where $R = \text{Bi}, \text{Cs}, \text{Fe}, \text{Na}$ were investigated for their dielectric, structural, optical, ferroelectric and piezoelectric properties. The purpose of investigation reported here was to partially substitute Pb^{+2} by Ca^{+2} and La^{+3} . The investigation reported here was aimed at developing

a system with enhanced ferroelectric properties and studying the effect of calcium doping on the behaviour of PLZT ceramics.

EXPERIMENTAL PROCEDURE

The objective of the present work is to investigate the effect of Ca^{+2} ions on dielectric properties of PLZT. The compounds used in the investigation were synthesized by using conventional solid state reaction method. The polycrystalline sample with formulae $\text{Pb}_{0.9}(\text{La}_{1-z}\text{Ca}_z)_{0.1}(\text{Zr}_{0.65}\text{Ti}_{0.35})_{0.975}\text{O}_3$ where $z=0.00, 0.04, 0.06, 0.20$ were prepared using required amount of analytical grade reagents PbO , ZrO_2 , La_2O_3 , CaCO_3 , TiO_2 as starting materials. The weighed reagents were thoroughly mixed in acetone media. The well mixed powders were dried and calcined at 1000°C for 3 hours. The process of grinding and calcination was repeated till homogenous powders of PLCZT were obtained. The homogenous fine powders of PLCZT were then used to make cylindrical pellets of thickness 1-2 mm and diameter about 8 mm under isostatic pressure of 31.2×10^6 Pascal, using a uniaxial hydraulic press. These pellets were then sintered at 1200°C for 2 hours. To prevent the PbO loss, lead zirconate (PZ) powder was used as a setter during sintering. The quality and formation of desired compounds were checked by XRD diffractometer (Bruker D8 advance) using CuK_α radiation ($\lambda=1.5418 \text{ \AA}$) taken on calcined powder at room temperature. Using Scherer's equation: $P_{\text{hkl}}=(0.89 \lambda)/(\beta_{1/2}\text{Cos}\theta)$ the calculation of average crystallite size (P) was done from the broadening of XRD peaks, here $\beta_{1/2}$ represents the half peak width and θ is bragg angle. The distribution of grains on the surface of ceramic was analyzed by scanning electron microscope (SEM). The sintered pellets were cleaned and then gold deposited to analyse the microstructure. Grain sizes were calculated using linear intercept technique from the micrographs of SEM. The pellet surfaces were painted with high purity silver paste and cured at 600°C for 1h to form perfect electrodes on the sample surface. Dielectric measurements of sample were conducted using LCR meter connected with a desktop computer. The room temperature

dielectric constant (ϵ) and dissipation factor ($\tan\delta$) were acquired for sample in frequency range 100 Hz – 1 MHz and temperature range 40°C – 250°C as a function of temperature, where it undergoes ferroelectric to paraelectric phase transition. At various applied field and frequencies the Polarization-electric field (P-E) hysteresis loops were carried out at room temperature by modified Sawyer-tower circuit (Automatic PE loop tracer system, Maine India Electr. Pvt. Ltd).

RESULTS AND DISCUSSION

The variation of dielectric constant (ϵ) and $\tan\delta$ (dielectric loss) with frequency of all the samples at room temperature were measured in the frequency range of 10^2 Hz to 10^5 Hz as shown in Fig. 1 (a) and (b) respectively. Dielectric constant (ϵ) and $\tan\delta$ was found to decrease with increase in frequency. Generally both of these parameters decrease with increase in frequency and hence show a typical characteristic of a dielectrics (ferroelectric). In this audible range of frequencies all the polarization is present, but the space charge polarization is prominent as per the theory of dielectric polarization. The mechanism of variation in dielectric constant of the ceramic with frequency can be explained in terms of four types of polarization's which contribute to the dielectric constants of materials. These are: electronic, ionic, orientation and space charge polarization. At very low frequency (less than 10 kHz), all the contributions may be active. From the nature of the variation of ϵ with frequency, it is possible to find out which contributions are predominately present in the compound in a particular frequency range. In the region of frequency under investigation only the contribution of Polar Regions to the total dielectric constant undergo dispersion. All these spontaneously polarizable regions make a contribution to the dielectric constant only at temperature below the transition point.

The space charge contributions depend upon the purity and perfection of the material and exhibit itself prominently at low frequencies and is purely

surface effect phenomenon. Increase in the space charge polarization of a solid increases the value of ϵ and $\tan\delta$. This polarization arises due to defects and impurities present either in the bulk or at the surface of the crystal or both. Due to large polarization of defects in the crystals, the space charge polarization increases and thereby ϵ and $\tan\delta$ of the crystal

become high. The dipolar orientation effect can sometimes are exhibited some materials even up to 10^{10} Hz. The ionic and electronic polarizations always exist above 10^{13} Hz. Only pure electronic polarization exist above 10^{15} Hz as a result of which the dielectric constant of the material falls down to a very low value.

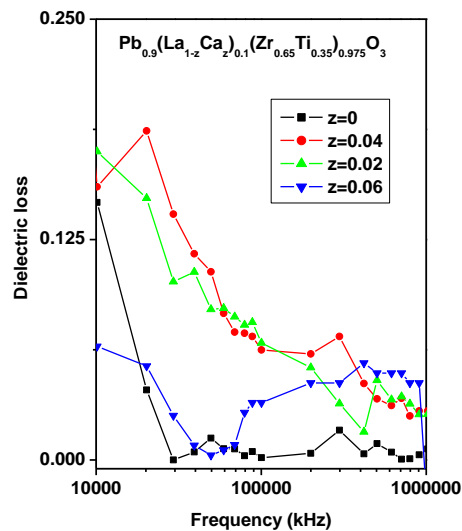
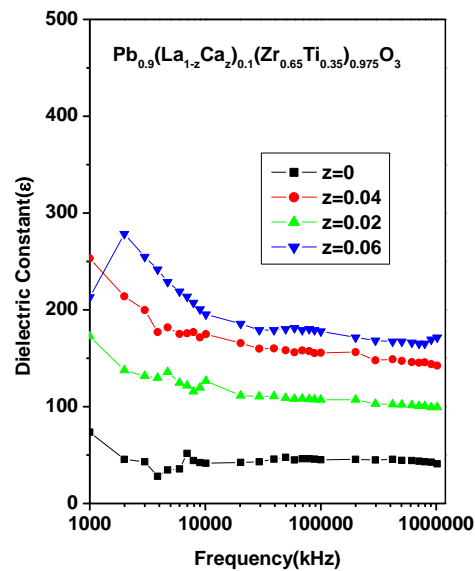


Fig. 1 a). shows the frequency dependence of dielectric constant
b). dielectric loss of various composition of calcium doped PLZT.

Pressed ceramic samples generally contain voids, grain boundaries and other defects. However, if the density of the sample approaches the single crystal value, then this effect is practically eliminated. The number of polarizable entities will be enhanced due to increase in density or packing fraction and they exhibit larger ϵ values. The dielectric loss in pellet samples is mostly due to the scattering mechanism. The scattering cross section depends upon grain size, intergrain space and grain boundaries. Therefore, the loss factor decreases smoothly with increase of frequency because of high packing fraction of pellet. The smaller grain size also affects the scattering and increases the scattering amplitude. Furthermore, the space charge may arise from the charges present at the surface of the crystallites.

Figure 2 and 3 show that the variation of ϵ and $\tan\delta$ with temperature (35 °C - 250 °C) at 100

kHz frequency for different calcium modified PLZT compositions respectively. The dielectric curve is a broadened peak rather than a sharp peak (as in normal ferroelectrics) around T_c which is one of most significant characteristics of a disordered perovskite structure with a diffuse phase transition. The broadening is due to compositional fluctuations, and/or substitutional disordering in the arrangement of cation in one or more crystallographic sites of the structure. The position of transition temperature does not shift much with increase in calcium concentration up to 6 mol% and but it shifts slightly towards higher temperature at 20 mol%. In general the dielectric property shows grain size dependence where a decrease in grain size corresponds to decrease in ϵ_{\max} with a lowering in T_c

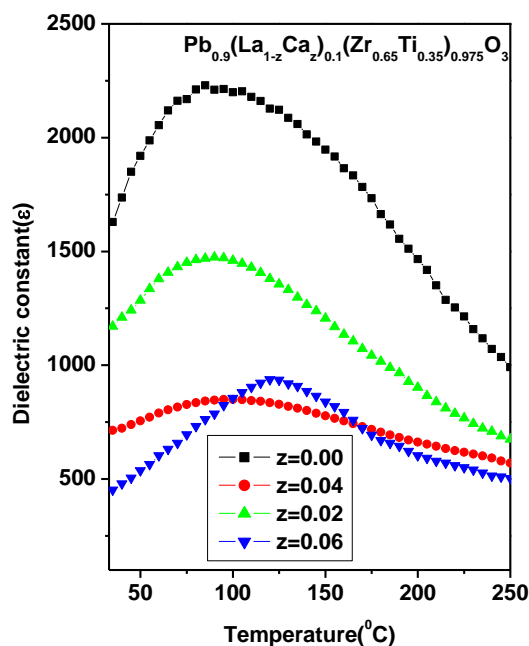


Fig. 2. Variation of dielectric constant as a function of temperature of PLCZT compositions.

The cyclic Born-Von-Karman condition has to be replaced by boundary conditions on the surface for the grains of smaller size according to lattice dynamical view point, which gives rise to lowering of dielectric constant for grains of smaller size.

As consequence of this, wave vector shows discrete behaviour and there is no longer involvement of lattice vibrations with wave vector $|K| < \pi/D$, D is the grain size.

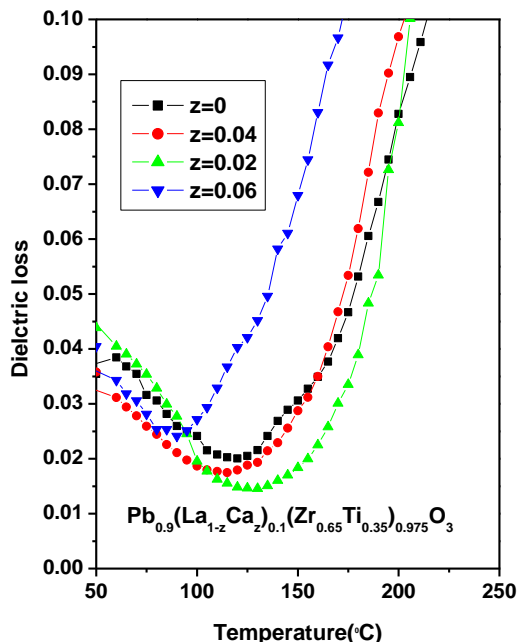


Fig. 3. Shows the loss tangent of PLCZT compositions as function of temperature

According to type and size of the impurities added, structural disorder arises in the compound. The disorder is consequence of compositional fluctuation which may be developed at A site occupied by Pb^{+2} , La^{+3} , Ca^{+2} or at the B site occupied by Zr^{+4} , Ti^{+4} . It has been noticed that as the doping concentration of calcium is increased the value of dielectric constant decreases significantly. The declining dielectric constant is result of reduced dipole moment due to presence of the dopant. As the size of calcium is smaller the decrease is due to reduction of density and increase of pyrochlore phase.

The modified Curie-Weiss law describes the permittivity versus temperature dependence, which is followed by normal ferroelectrics:

$$\frac{1}{\epsilon} = \frac{1}{\epsilon_{max}} + \frac{(T - T_c)^\gamma}{2\delta^2}$$

The diffusion exponent γ and diffusion coefficient δ gives information about the diffuseness of phase transition. These parameters can be determined through the logarithmic plot of type $\log(1/\epsilon - 1/\epsilon_{max})$ versus $\log(T - T_c)$ (Fig. 4). The graph should give the linear behaviour where the value of slope of graph (γ) is expected to be 2. But the value of γ in our work comes out to be in the range 1 to 2 ($1 \leq \gamma \leq 2$). So we may consider in this case that the phase transition is not purely diffuse type. The value of γ decreases as the concentration of dopant is increased from 0 to 6 mol% and at 20 mol % it suddenly increases.

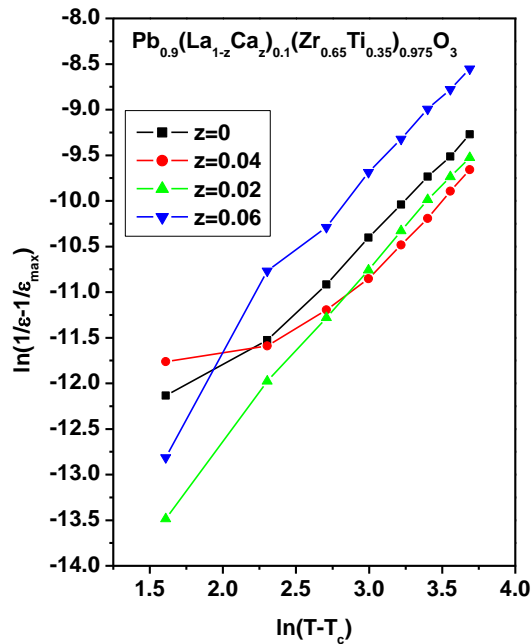


Fig. 4. Variation of $\ln(1/\epsilon - 1/\epsilon_{max})$ vs $\ln(T - T_c)$ at 100 KHz

The results for the hysteresis loops obtained at room temperature with applied field upto 25 Kv/cm are shown in Figure 5. The saturation polarization was obtained using a high electric field. The value of remnant polarization (P_r) and coercive field (E_c) were measured at room temperature from their hysteresis loops. As it is already known that when

electric field is applied to a ferroelectric material polarization would firstly increase with applied field until saturation state is reached which corresponds to initial state of polarization of ferroelectric material and beyond it there would be formation of P-E loop.

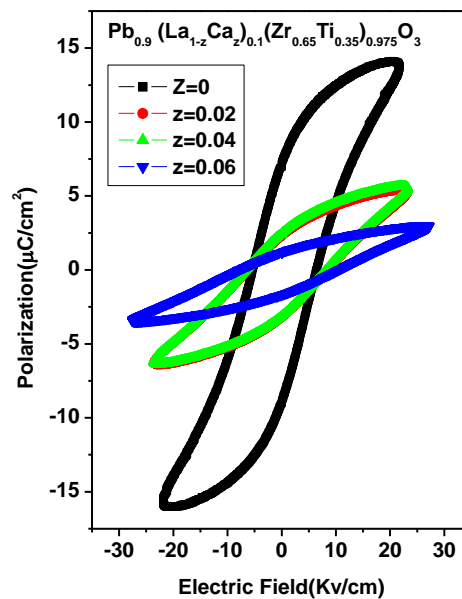


Fig. 5. Shows the hysteresis loops of calcium doped PLZT at various compositions

The value of Pr is found to decrease with increasing concentration of calcium.

CONCLUSION

I have studied the effect of calcium doping on the properties of PLZT. Calcium doped PLZT with general formulae $Pb_{0.9}(La_{1-z}Ca_z)_{0.1}(Zr_{0.65}Ti_{0.35})_{0.975}O_3$ where $z=0, 0.02, 0.04, 0.06$ were synthesized by solid state reaction method. Measurement of dielectric constant as a function of temperature (35 - 450°C) indicates that the compound undergo diffuse type of phase transition. Hysteresis loop parameters (E_c and P_r) are found to decrease with calcium doping. The remnant polarization is observed to be maximum for $z=0.0$ having value of order of $7.34 \mu C/cm^2$. This composition provides useful information for new material development.

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