Effect of Nd on Structural and Dielectric Properties of Lead Lanthanum Zirconate Titanate Perovskite Ceramics

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***Abstract*— In this paper I have reported the double doped La and Nd modified PZT (54/46) with different doping concentration x= 0, 0.02, 0.04, 0.06 near the morphotropic phase boundary (MPB) prepared by solid state reaction method. $Pb_{1-3x/2}La_x(Zr_{0.54}Ti_{0.46})_{1-5x/4}Nd_xO_3$ where x=0, 0.02, 0.04, 0.06) which were prepared by conventional mixed oxide (solid state reaction) method. Detailed studies of the structural and electrical properties of the samples have been carried out to investigate the effect of paired doping on PZT ceramics. The dielectric constant, loss of $Pb_{1-3x/2}La_x(Zr_{0.54}Ti_{0.46})_{1-5x/4}Nd_xO_3$ strongly suggest that these compounds are suitable for the preparation of high value capacitors and may be good candidates for device applications.**

***Keywords*— Nd ion, PZT ceramics, dielectric constant, dielectric loss**

I. INTRODUCTION

Lead zirconate titanate (PZT; $Pb(Zr_{1-x}Ti_x)O_3$) has been a widely studied ceramic system due to its ferroelectric and electromechanical features. Particularly, the near morphotropic phase boundary (MPB)[1] region (x = 0.46) has received special attention because of the high dielectric and piezoelectric responses that can be exploited, among others, in sensors, actuators and memory applications[2-4]. The decrease in Curie temperature with the addition of lanthanum suggests that these ceramics could have large room temperature pyroelectric coefficient and may be potentially useful for pyroelectric infrared detector application. In order to enhance ferroelectric and pyroelectric properties of PLZT, several researchers have studied double doped PZT ceramics. In this paper we have reported the systematic work on Nd doped PLZT. Further the particle/crystallite size (nanometer) shows a significant effect on physical properties of materials. Substitution of some ions at different atomic sites also plays an important role in reducing the particle size [5]. For this reasons double doped PZT has become a most attractive topic now a days. In the present work, we have synthesized double doped (La, Nd)PZT compound with a general formula $Pb_{1-3x/2}La_x(Zr_{0.54}Ti_{0.46})_{1-5x/4}Nd_xO_3$ for different La and Nd concentrations (x=0, 0.02, 0.04, 0.06) using solid state reaction method. Detailed studies of the structural and electrical properties of the samples have been carried out to investigate the effect of paired doping on PZT ceramics.

II. EXPERIMENTAL PROCEDURE

The composition $Pb_{1-3x/2}La_x(Zr_{0.54}Ti_{0.46})_{1-5x/4}Nd_xO_3$ where x=0, 0.02, 0.04, 0.06 were prepared by conventional mixed oxide (solid state reaction) method, using required amount of analytical grade reagents PbO, La_2O_3, ZrO_2, TiO_2, Nb_2O_5 and Nd_2O_3 as starting materials. The weighed individual reagents were homogeneously mixed in acetone media for 3h. The well mixed powder were calcined at 1000°C for 3 hour in alumina crucible. Now the pellet was being formed by calcined powder having thickness 0.8-1 mm and diameter 8-9 mm at a pressure of ~ 31.2 x 10^6 Pa, using by hydraulic press. These pellet were then sintered at 1100 ^{0}C for 2 h). After sintering the pellet flat surface of the pellet were polished by high purity silver paste and then dried at 260 ^{0}C for 30 min. In order to prevent PbO loss and to maintain the stoichiometric of the compounds, the pellets were placed in a covered alumina crucible with lead zirconate titanate powder during sintering. The densities of sintered pellets were calculated by Archimedes's method.

The formation and quality of the $Pb_{1-3x/2}La_x(Zr_{0.54}Ti_{0.46})_{1-5x/4}Nd_xO_3$ compound in calcined powder as well as in sintered pellets were studied using an x-ray diffractometer (PW 1140/90), using Cu Kα (λ=0.15418 nm) in a wide range of Bragg angles ($20^\circ \leq 2\theta \leq 60^\circ$) at room temperature.

III. RESULTS AND DISCUSSION

X-ray diffraction pattern of the $Pb_{1-3x/2}La_x(Zr_{0.54}Ti_{0.46})_{1-5x/4}Nd_xO_3$ where x=0, 0.02, 0.04, 0.06 is shown in Fig.1 respectively, which confirms the mixed rhombohedral (F_R) and tetragonal (F_T) phases in all samples. The percentages of both the phases were estimated by the following ratios:

$$\%F_R = 100 \times A_{(020)}/A_{Total}$$

$$\%F_T = 100 \times A_{(200)} + A_{(002)}/A_{Total}$$

Where $A_{(hkl)}$ stands for the area under the each indexed (hkl) peak and A_{Total} refers to the total area under the curve in the chosen interval. The $Pb_{1-3x/2}La_x(Zr_{0.54}Ti_{0.46})_{1-5x/4}Nd_xO_3$ thus obtained is stoichiometric and very pure. From XRD graph we have seen that pyrocholore phase was observed in the compound at higher value of Nd composition. The relative amount of pyrocholore phase to perovskite phase was estimated by

$$\% \text{ pyrocholore} = \{A_{pyrocholore}/A_{pyrocholore} + A_{(110)}\} \times 100$$

Where $A_{pyrocholore}$ and $A_{(110)}$ are the areas under the pyrocholoro peak and the (110) perovskite phase [7]. The value of pyrocholore is very small 3~4%. It is observed that La and Nd doping decreases the unit cell volume. The crystallite size (p) and lattice strain (η) were calculated using following Williamson-Hall equation [8-9].

$$\beta_{1/2} \cos\theta = K\lambda/p + \eta \sin\theta$$

Where K=0.89, $\beta_{1/2}$ is full width at half maxima, θ is Bragg angle. The crystallite size and lattice strain were calculated by

intercept and slope of sinθ versus β½ cosθ graph respectively. The values of crystallite size were found between 19 nm to 40 nm. It was observed that increases the doping content decrease the crystallite size up to 4% and then slightly increased at 6 % doping content.

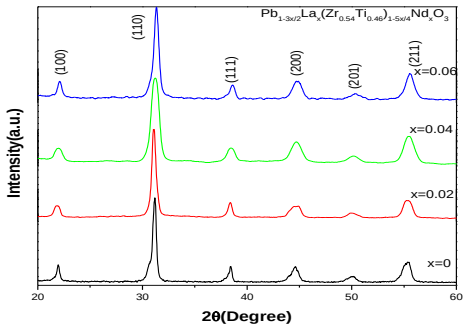

Fig. 1 X-ray diffraction pattern of $Pb_{1-3x/2}La_x(Zr_{0.54}Ti_{0.46})_{1-5x/4}Nd_xO_3$; where x=0, 0.02, 0.04, 0.06

Fig. 2(a)-(d) shows scanning electron micrograph of the surface of sintered pellets of $Pb_{1-3x/2}La_x(Zr_{0.54}Ti_{0.46})_{1-5x/4}Nd_xO_3$ where x=0, 0.02, 0.04, 0.06. These micrographs suggested that the sintered pellets were relatively dense and with minor porosity in the material.

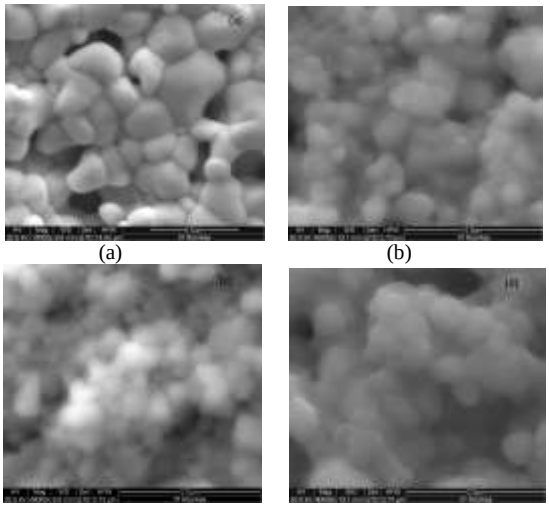

Fig. 2(a)-(d) SEM Micrograph of $Pb_{1-3x/2}La_x(Zr_{0.54}Ti_{0.46})_{1-5x/4}Nd_xO_3$ ceramics with (a) x=0, (b) x=0.02, (c) x=0.04 and (d) x=0.06

The average grain size was determined by linear interception method. The average grain size of the materials was found to lie between 2000 to 4000 nm. We have observed that average grain size decreases up to 4% doping content and then increases. Nd is an effective grain growth inhibitor, the doping ion concentrate near the grain boundaries which is responsible for the mobility of grains resulting the grain size is decreases with doping concentration. But beyond the 4% doping content new biphasic structure, fluorite and perovskite phases, responsible for the grain growth [10].

Fig. 3(a) shows the variation of dielectric constant versus temperature at 1 kHz frequency for all different compositions. Dielectric constant were found to increase gradually to its maximum value (ε_{max}) with increase of temperature up to the transition temperature (T_c) and then it decreases smoothly for all compositions, indicating the phase transition in $Pb_{1-3x/2}La_x(Zr_{0.54}Ti_{0.46})_{1-5x/4}Nd_xO_3$ ceramics. Qualitatively, the broadened peak around Curie temperature indicates that the phase transitions are of a diffuse type. The maximum value of dielectric constant decreases up to 4% Nd doping and then increases. The decrease in ε_{max} were expected to be due to decrease of grain size of the sample [11, 12].

Fig. 3(b) shows the variation of dielectric loss with temperature at 1 kHz frequency $Pb_{1-3x/2}La_x(Zr_{0.54}Ti_{0.46})_{1-5x/4}Nd_xO_3$ ceramics respectively. Initially dielectric loss is small but beyond the transition temperature its increases sharply. This is possible due to the high concentration of charge carriers present in the samples at higher temperature [13, 14].

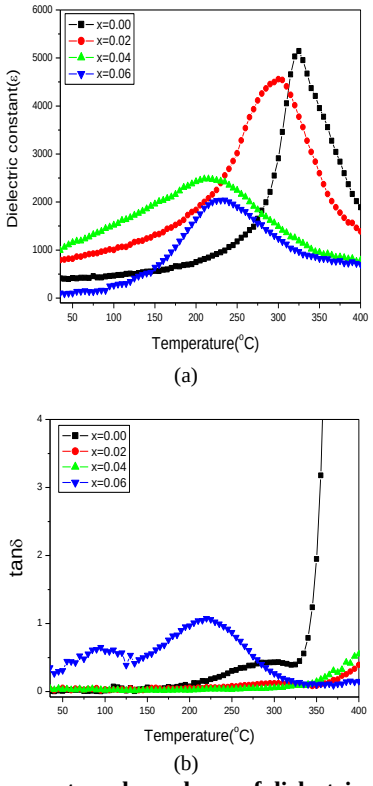

Fig. 3(a) Temperature dependence of dielectric constant (b) dielectric loss for the $Pb_{1-3x/2}La_x(Zr_{0.54}Ti_{0.46})_{1-5x/4}Nd_xO_3$ ceramics for various compositions at 1 kHz frequency

The variation of grain size and ε_{max} with compositions are shown in Fig. 4. Besides, it is also observed that the transition temperature (Curie temperature) of $Pb_{1-3x/2}La_x(Zr_{0.54}Ti_{0.46})_{1-5x/4}Nd_xO_3$ ceramics decreases with increasing Nd concentration upto 4% and then slightly increases. Curie temperature is decreased from 324°C for La free sample to 210°C for La and Nd (x =0.04) doped sample and then increases with doping content. A decreased structural strain in

PLNZT samples is attributed to be the cause for the decrease in Curie temperature [13].

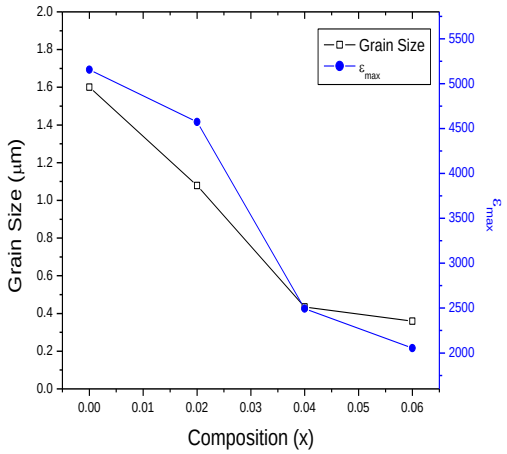

Fig. 4. Variation of grain size and ε_{max} with contents of $Pb_{1-3x/2}La_x(Zr_{0.54}Ti_{0.46})_{1-5x/4}Nd_xO_3$ ceramics

Fig. 5 shows the P–E loops of different Nd modified PLZT compositions. Well saturated loops are observed for the compositions. However, the nature of loops are found to change with doping concentration, the remnant polarisation (P_r) increases up to 2% doping concentration of La and Nd, beyond that P_r decreases with increasing doping, which is affected by the porosity of the material which is also confirmed by the SEM micrograph and E_c is increased due to the decrease in grain size for all different compositions [16].

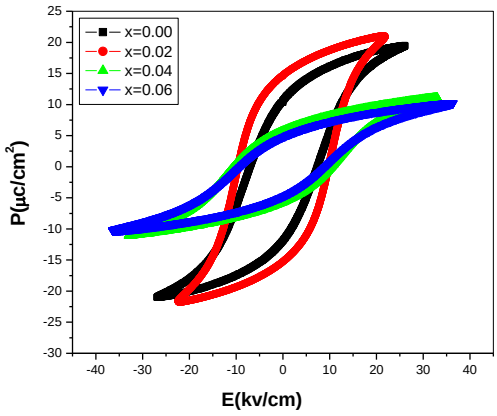

Fig. 5 Room temperature polarization behaviour of $Pb_{1-3x/2}La_x(Zr_{0.54}Ti_{0.46})_{1-5x/4}Nd_xO_3$

Variation of dielectric constant and dielectric loss with frequency of $Pb_{1-3x/2}La_x(Zr_{0.54}Ti_{0.46})_{1-5x/4}Nd_xO_3$ ceramics is shown in Fig. 6. It is observed that dielectric dispersion is higher at lower frequency range which is attributed to space charge accumulation. At higher frequency we have got the constant value of dielectric constant which is due to the dipole relaxation phenomena i.e. dipoles are unable to move with frequency [15]. Dielectric dispersion also depends upon the grain size of the material. It decreases with the increasing of the grain size of material. From Fig. 7, it is observed that dielectric losses firstly decreases with frequency and then attain a constant value. At very low frequency dipoles follow the field, as the direction of the field is switch so the direction of the polarization will also switch in order to align with new field, this cannot occur instantaneously but some time is needed for the rotation of dipoles, is known as characteristic time. If the field is switched, there is a characteristic time that the space charge, hopping, orientation, ionic and electronic polarisation takes to adjust, called the relaxation time are ~10^{-5}, 1, 10^{-11}, 10^{-13}, and 10^{-15}s respectively. Therefore, if the electric field switches direction at a frequency higher than ~10^5 Hz, the space charge polarization cannot 'keep up' with the alternating field, the polarisation direction is unable to remain aligned with the field. Corresponding to each polarization we find dispersion region.

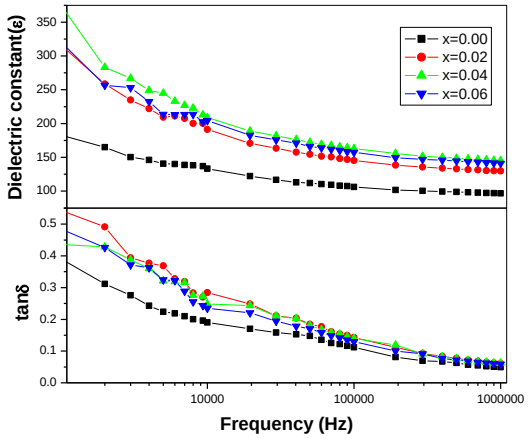

Fig. 6 Frequency dependence of dielectric constant and loss of $Pb_{1-3x/2}La_x(Zr_{0.54}Ti_{0.46})_{1-5x/4}Nd_xO_3$ ceramics

IV. CONCLUSION

In the present work, X-ray diffraction analysis shows the formation of single pure phase. Lanthanum and Niobium doping did not show any structural change in PZT. Crystallite size and grain size were simultaneously decreases with doping concentration and increases after 4% doping. When equal to or more than 4% La was added, a pyrochlore phase was formed, and the dielectric properties were reduced. SEM micrographs show that our samples are homogeneous. It is also confirmed from the SEM micrographs that the grain size increases with increasing sintering temperature. Analyzing a SEM micrograph it can be concluded that the particle size follows the Gaussian distribution. A study of dielectric constant suggests diffuses type of phase transition. With increasing *x*, dielectric constant at transition temperature was found to decreases appreciably. Curie temperature was found to shift to lower temperature with increasing doping concentration but at higher composition Curie temperature shift towards higher temperature. Dielectric dispersion study confirmed that the low frequency dispersion in compounds.

Maximum dielectric constant was found to be strongly dependent on grain size of the sample. The P-E loop measurement of PLNZT sample shown saturated single loops, we have got better value of remnant polarisation for 2% doping concentration of La and Nd with PZT. We have got the well saturated PE-Loop having higher value of remnant polarisation for 2% doping concentration. It is finally concluded that the dielectric constant, loss of $Pb_{1-3x/2}La_x(Zr_{0.54}Ti_{0.46})_{1-5x/4}Nd_xO_3$ strongly suggest that these compounds are suitable for the preparation of high value capacitors and may be good candidates for device applications.

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