Structural and Dielectric Properties of Lanthanum Substituted Lead ZirconateTitanateFerroelctrics

P. Geetha[1], P. Easwaraji[2], M. Srikanth[3]

(Physics Department, G.M.R.I.T, India)

Abstract:*Lanthanum substituted Lead ZirconateTitanateFerroelectric materials were prepared using solid state reaction method.The basic composition chosen for the present study is $PbZr_{0.65}Ti_{0.35}O_3$. The constituent raw materials (mostly oxides and carbonate) were weighed in proportions required to give the following selected compositions. (a) $PbZr_{0.65}Ti_{0.35}O_3$ (b) $Pb_{1-x}La_x(Zr_{0.65}Ti_{0.35})_{1-x/4}O_3$, where x varies from 0.06 to 0.08 insteps of 0.01.The values of experimental density (measured by Archimedes Principle), theoretical (XRD) density and relative density of isostatically sintered pellets are measured with respect to La as substituent.As La substitution increases the experimental density with the large continuous reduction in the theoretical density. Structural information of the samples was investigated using X-ray diffractometer. Microstructural information of the samples wereinvestigated usingScanning Electron Microscopy (Philips XL 30 ESEM). Temperature variation of dielectric constant (ε) and loss tangent (tanδ) was studied for all the samples at different frequencies.It is clear that, the increase in the dielectric constant with temperature reaching maximum, and then a decrease with further increase in the temperature for the Lanthanum substituted materials. The value of dielectric constant decreases with higher lanthanum content which can be attributed to the minimization of number of polar directions as the structure traverse from coexistence of mixed phases to a single phase.*

Keywords:*Ferroelectrics, microstructure, PZT Ceramics, XRD, dielectric constant, grain size,*

I. Introduction

The importance of ferroelectrics in electric, electronic devices and in various other fields is influenced by its physical and chemical properties of ferroelectrics, which in turn are dependent on the mode of preparation. The desired properties can be obtained only by virtue of the presence of certain combinations of the chemical constituents, firing schedule that influences not only the chemical composition such as valence state of the constituent cations and the oxygen content but also controls the microstructures.The ceramic process of synthesizing materials depends to a great extent on the particle size, shape and particle size distribution of the starting materials. Impurities either inherent or as additives and /or dopants in the starting materials also play an important role in modifying the properties of synthesized ceramic materials. Thus, the characterization of the processed materials becomes all the more necessary when one has to study the effect of additives and or dopants on various properties of host material. Therefore, the material preparation and characterization are important aspects of a study concerned with the development of any ceramic material [1].In this connection, the technique & process of material preparation various experimental techniques that are adopted to characterize and study the electrical properties of the present materials for investigations are described.From the examinations of XRD patterns which revealed that the crystal structures of all the samples with various compositions were composed of rhombohedral and tetragonal phases.

II. Materials Preparation

The starting materials are highly pure analytical reagent grade (99.9% Pure) chemicals are used. The required quantities of the reagents for each composition are calculated. Using these chemicals the samples of ferroelectrics to be formed are prepared by following the procedure discussed below. The basic composition chosen for the present study is $PbZr_{0.65}Ti_{0.35}O_3$. The constituent raw materials (mostly oxides and carbonate) were weighed in proportions required to give the following selected compositions.(a) $PbZr_{0.65}Ti_{0.35}O_3$ (b) $Pb_{1-x}La_x(Zr_{0.65}Ti_{0.35})_{1-x/4}O_3$, where x varies from 0.06 to 0.08 insteps of 0.01. The raw materials are taken in correct proportions of the oxides of rare earth lanthanum and titanium ions along with lead zirconium according to the solid state reaction were mixed by grinding into fine powder in an agate mortar with pestle for 6 hours and thus mixed thoroughly in the presence of ethyl alcohol. The Powder ferroelectric samples are calcinated in alumina crucibles for 4 hours at 800 C in the air and then it is allowed to cool in the muffle furnace. The pre-sintered samples were again grinded for 6 hours followed by drying and re-calcined at 850 C for 4 hours. The pre-sintered powders were again grinded and 10% of polyvinyl alcohol is added as a binder. The granulated powder is pressed in to pellets of 10mm diameter at a pressure of 4 tons per square inch using hydraulic press, which were placed in aluminum crucibles and sintered in air for 4 hours at 1250 $^{\circ}$C and later the furnace is switched off and allowed to cool naturally in air atmosphere.

III. Experimental Setup

X-ray diffraction technique is used for the structural/phase analysis of the material. The structural information of the samples were investigated using X-ray diffractometer (INEL, Co K_α radiation. $\lambda = 1.788A^0$). Maximum voltage and current used in this characterization is 30KV and 15mA. The basic principle is that for a fixed wavelength (λ), the constructive interference occurs for a fixed set of an interplanar spacing (d) and incidence angle (θ). According to Bragg's condition of diffraction $\lambda = 2d \sin\theta$.

The scanning electron microscope was used to determine the average crystallite size and the surface morphology. It gives information about the grain evolution and grain size. It also gives the information about the inter-granular and the intra-granular pores and the distribution of grains in the bulk samples. Microstructural information of the samples were investigated using Scanning Electron Microscopy (Philips XL 30 ESEM), voltage applied to the electron gun is 20KV.

For the dielectric measurement silver paint was applied on both sides of the pressed pellets and the samples were fixed in the spring loaded sample holder attached to a heating and cooling chamber. The parallel capacitance(C) and the dissipation factor (D) for all the samples were measured using an Agilent 429A impedance analyzer in the frequency range 100Hz-1MHz in a temperature range of 300 to 600K with a Lab-Equip temperature control unit. The temperature and measurement process were controlled electronically by a homemade program using lab view software.

IV. Results And Discussions

The values of experimental density (measured by Archimedes Principle), theoretical (XRD) density and relative density of isostatically sintered pellets are measured with respect to La as substituent. 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. As La substitution increases the experimental density with the large continuous reduction in the theoretical density. The computed values of the density are presented in the table I with the error $\pm$ 0.05.

Table I : Variation of experimental density (dex, g/cc) and theoretical density (dth, g/cc) procedures as a function of substitution

x	d_{ex}	d_{th}
0.00	6.24	6.33
0.06	6.39	6.53
0.07	6.52	6.65
0.08	6.54	6.65
0.10	6.56	6.65

The obtained theoretical density is decreasing with concentration 0.08 to 0.10 is due to the replacement of Pb with La (A-site substitution) because the atomic weight of lead is more than that of lanthanum so the molecular weight decreases as La is added. La doping reduced tetragonality of the PLZT crystal lattice, which leads to a reduction in internal stresses, thus allowing crystallites in grains to accommodate more closely to form a denser micro-structure. Thus it can be concluded that the La doping increase densification of PLZT ceramics. The relative density d_{rel}, x=0 = 98.57% also computed from equation (3.3) and we noted that d_{rel} La = 98.06 %.

Structural information of the samples were investigated using X-ray diffractometer (INEL Co K_α radiation, λ=1.788A$^\circ$), Maximum voltage and current used in this characterization is 30 KV and 15 mA. The XRD patterns of the samples with various compositions are as shown in the figures. The XRD peaks are found to be sharp, which indicates good homogeneity and crystallization of the ceramic samples. There is no unwanted secondary peak in XRD pattern. From the examinations of XRD patterns which revealed that the crystal structures of all the samples with various compositions were composed of rhombohedral and tetragonal phases. Lattice planes belong to rhombohedral ($\blacktriangle$) and tetragonal ($\blacktriangledown$) phases are indexed using JCPDS file numbers 52-1411 and 46-0504 respectively. For the composition x = 0.06, the lattice planes belongs to both rhombohedral and tetragonal crystal structure. The intensity of the lattice planes (101), (012), (003), (202), (113), (104) and (024) belongs to rhombohedral phase is retains the same as increase the La(x) content in the samples. Incorporation of lanthanum ions thermodynamically into the lattice of perovskite structure stabilizes the rhombohedral phase against the tetragonal phase[2].But the lattice plane (113) belongs to rhombohedral phase is disappeared at the composition x=0.10. From the structural analysis, it is observed that the decrease in intensity of lattice planes belongs to tetragonal and retains the same for the planes belongs to rhombohedral[3]. Therefore, the crystal structure of the samples transform from multi phaserhombohedral and tetragonal phase to single phase rhombohedral phase as the composition changed from x = 0.06 to x = 0.10. The lattice parameters (a,c) for tetragonal crystal structure are 3.98 A$^\circ$, 4.052 A$^\circ$ and for rhombohedral phase are 5.74 A$^\circ$, 7.14 A$^\circ$.
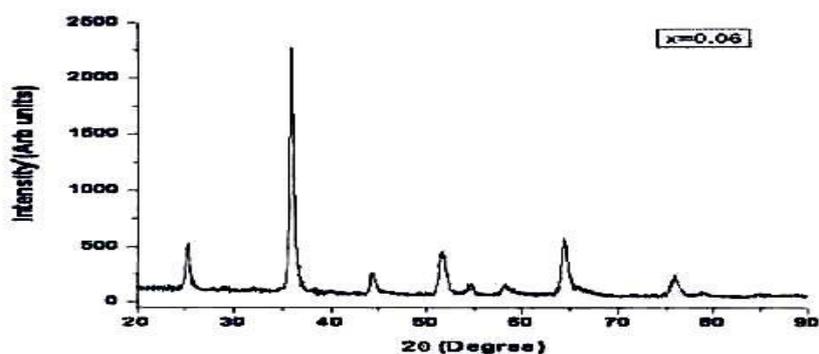
Fig.1(a): XRD pattern of Pb$_{1-x}$ La$_x$ (Zr$_{0.65}$Ti$_{0.35}$)$_{1-x/4}$ O$_3$at Composition X = 0.06
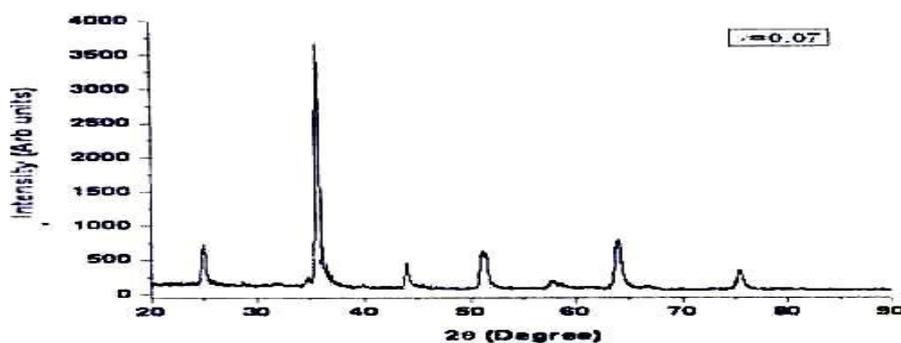

Fig.1(b): XRD pattern of Pb$_{1-x}$ La$_x$ (Zr$_{0.65}$Ti$_{0.35}$)$_{1-x/4}$ O$_3$at Composition X = 0.07
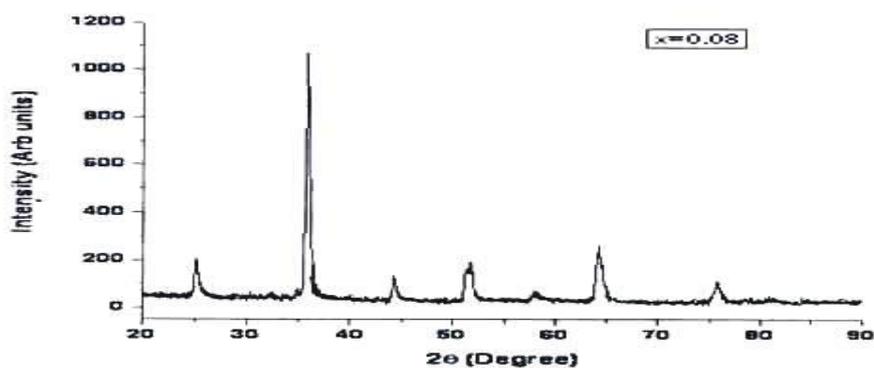

Fig.1(c): XRD pattern of Pb$_{1-x}$ La$_x$ (Zr$_{0.65}$Ti$_{0.35}$)$_{1-x/4}$O$_3$at Composition X = 0.08
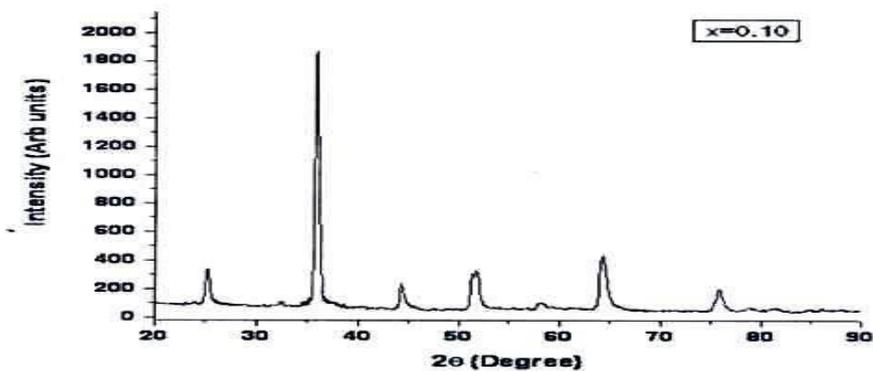

Fig.1(d): XRD pattern of Pb$_{1-x}$ La$_x$ (Zr$_{0.65}$Ti$_{0.35}$)$_{1-x/4}$ O$_3$at Composition X = 0.10
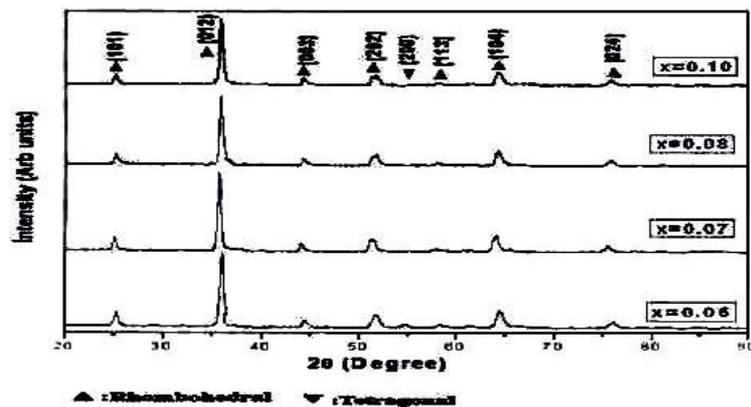
Fig.1(e): XRD pattern of $Pb_{1-x} La_x (Zr_{0.65}Ti_{0.35})_{1-x/4} O_3$ at Composition   x = 0.06., 0.07., 0.08. & 0.10
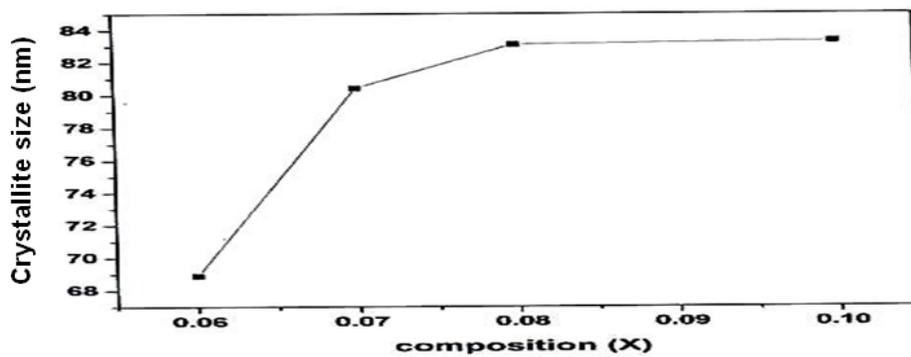

Fig.1(f) Variation of Crystallite size with composition of $Pb_{1-x} La_x (Zr_{0.65}Ti_{0.35})_{1-x/4} O_3$.

The syntheses of the samples are involved, in which the powder is grinded several times as a result the grain size of all the samples comes down. The crystallite sizes of all the samples are estimated from XRD line broadening analysis using Scherer formula. Fig.1(f) shows the variation of crystallite size with composition(x) of the samples. The crystallite size is increased from 68nm to 83nm as increase the lanthanum concentration from x=0.06 to 0.07, thereafter a slow increment of crystalline size is observed. This results revealed that at lower concentration of La(x=0.06 to 0.07), the crystal structure of the samples is combination of tetragonal and rhombohedralphase. As increase the La content (x=0.08 to 0.10), the tetragonal phase is disappeared and single phase rhombohedral crystal structure is likely to form.

Microstructural information of the samples were investigated using Scanning Electron Microscopy (Philips XL 30 ESEM), voltage applied to the electron gun is 20KV.The SEM microstructure of all samples is given in figure below:
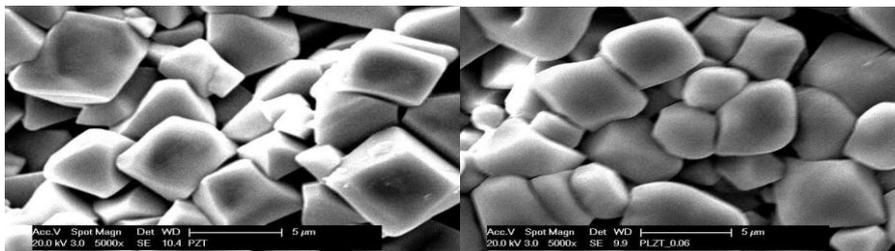

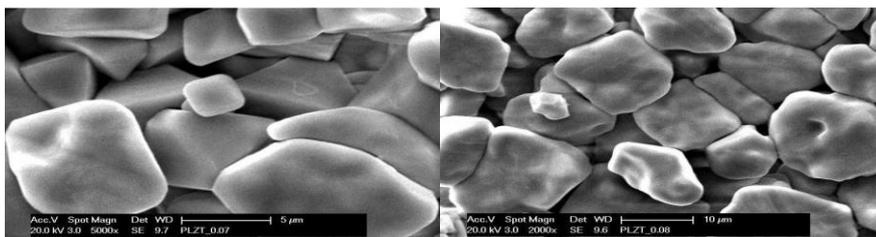**Fig.2(a): SEM micrograph of PZT   Fig.2(b): SEM micrograph of PLZT at x=0.06**

Fig.2(c): SEM micrograph of PLZT at x=0.07   Fig.2(d): SEM micrograph of PLZT at x=0.08
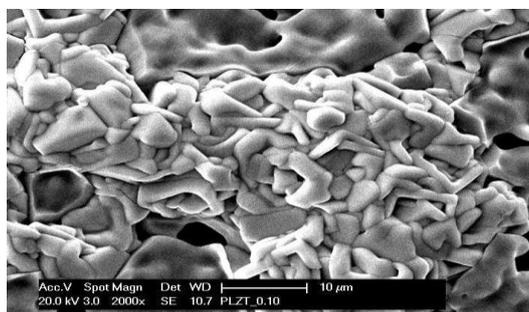

Fig.2(e): SEM micrograph of PLZT at x=0. 10

Fig.2(a), (b), (c), (d) & (e) illustrate the SEM micrographs of PZT and PLZT ceramic samples respectively. Fig.2(a) shows the microstructure of the pure PZT sintered at 1250 ^{0}C for 4 hours. From the microstructure it can be inferred that the grains of PZT are square in shape with an average grain size ranging from 4-7 μm. From fig.2(b), (c), (d), the average grain size is increasing as it is shown in the fig.2 (f). A general trend can be observed that with increasing amount of B-site substitution the grain growth increases.
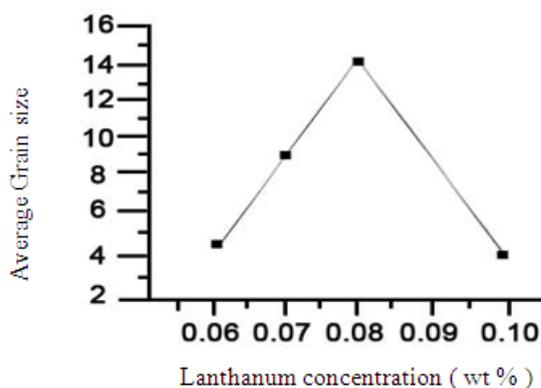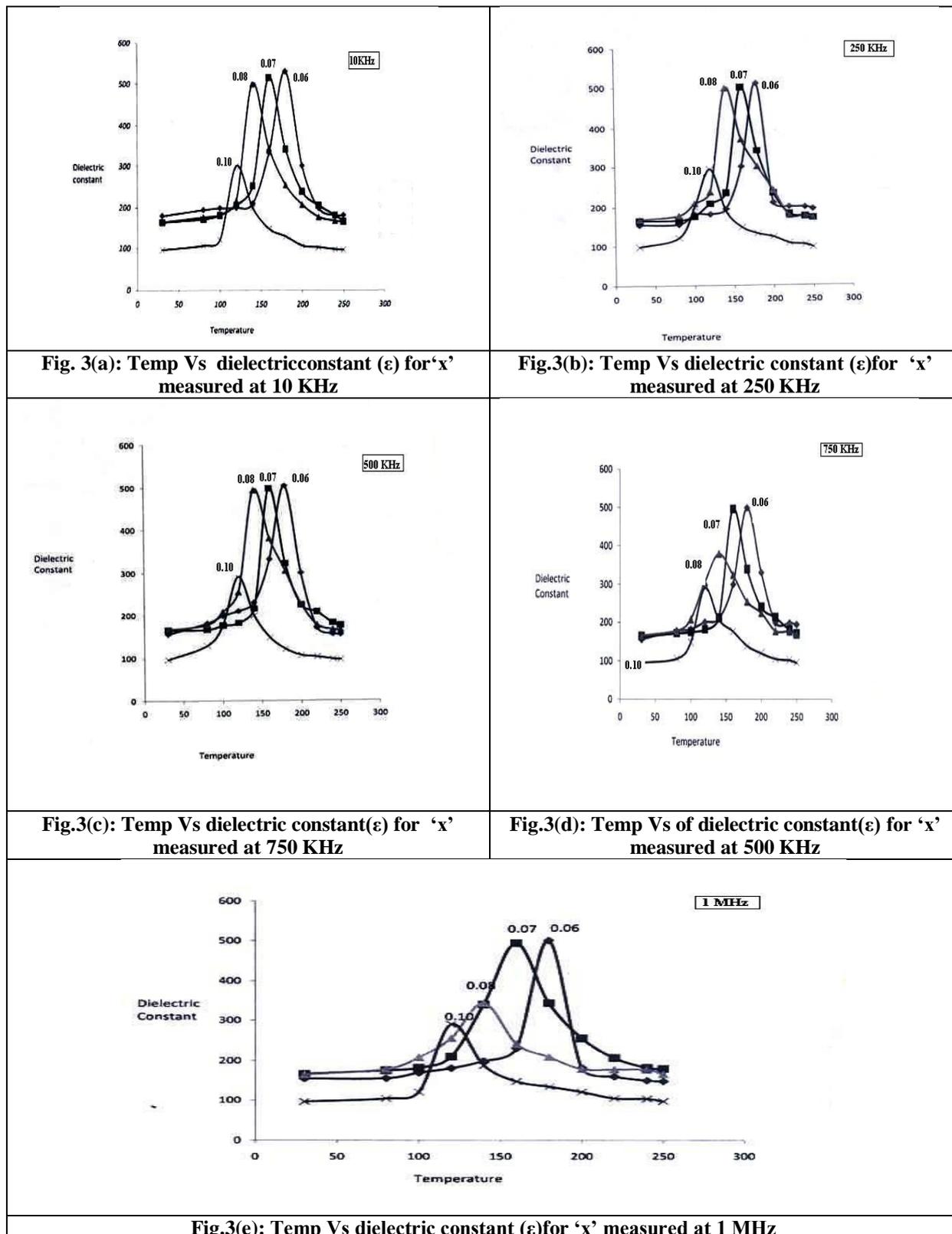

Fig.2(f): Variation of average grain size with composition of
Pb$_{1-x}$La$_x$ (Zr$_{0.65}$Ti$_{0.35}$)$_{1-x/4}$O$_3$

Temperature variation of dielectric constant (ε) and loss tangent (tanδ) was studied for all the samples at different frequencies.Fig.3 (a), (b), (c), (d), (e) shows the variation of dielectric constant against temperature at different frequencies for the prepared samples. It is clear that, the increase in the dielectric constant with temperature reaching maximum, and then a decrease with further increase in the temperature. Fig.4(a,b,c,d) shows the temperature dependence of dielectric constant (ε) and loss tangent (tanδ) for various frequencies for all the compositions. Evidently, addition of lanthanum moves the diffused – phase transition [4] region towards a lower temperature as well as significantly decreases the value of dielectric constant at maxima.

Fig. 3(a): Temp Vs dielectricconstant (ε) for'x' measured at 10 KHz	Fig.3(b): Temp Vs dielectric constant (ε)for 'x' measured at 250 KHz

Fig.3(c): Temp Vs dielectric constant(ε) for 'x' measured at 750 KHz	Fig.3(d): Temp Vs of dielectric constant(ε) for 'x' measured at 500 KHz

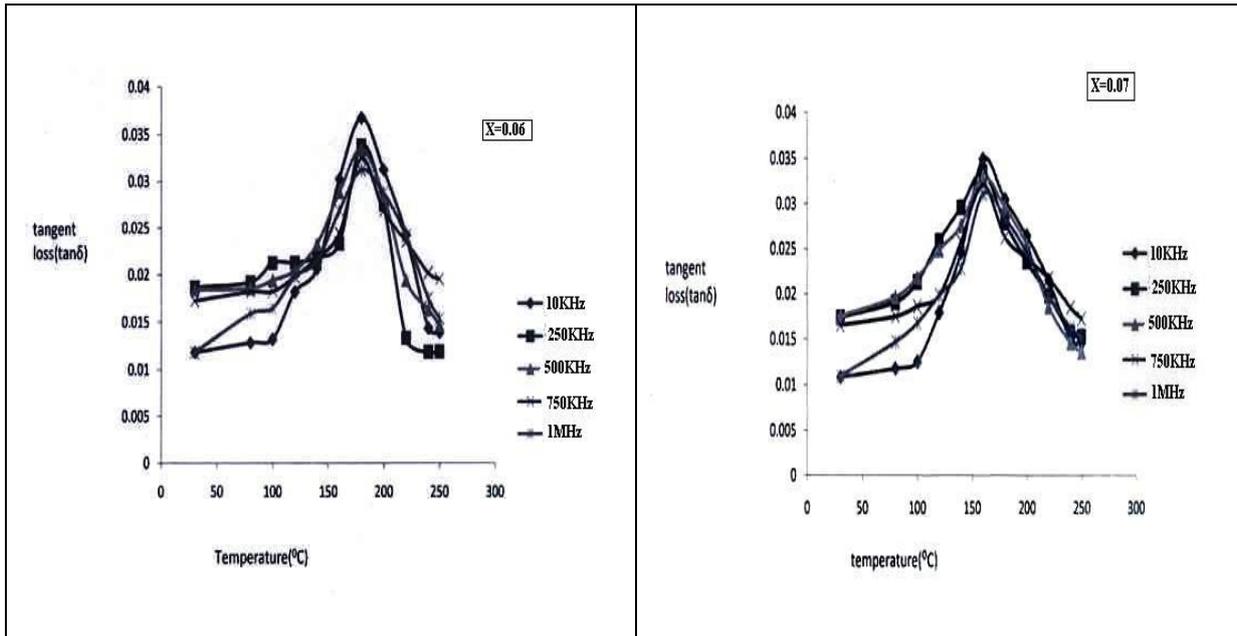Fig.3(e): Temp Vs dielectric constant (ε)for 'x' measured at 1 MHz

Fig.4(a): Temperature Vs Tan (δ) for x = 0.06

Fig 4.(b): Temperature Vs Tan (δ) for x = 0.07
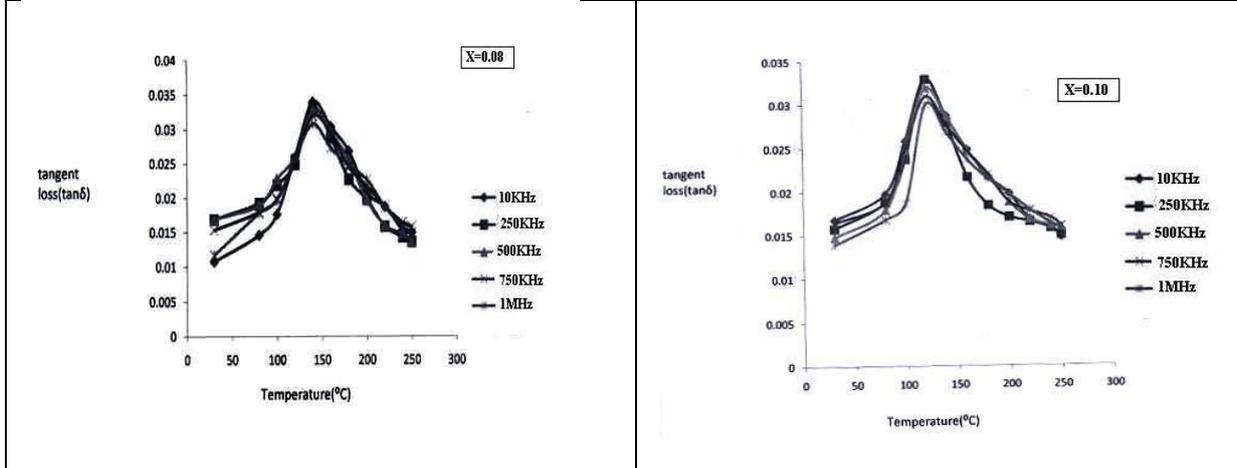

Fig.4(c): Temperature Vs Tan (δ) for x = 0.08

Fig.4(d): Temperature Vs Tan (δ) for x = 0.10

Fig.5(a): variation of dielectric constant with Temperaturefor x = 0.06 composition at different frequencies

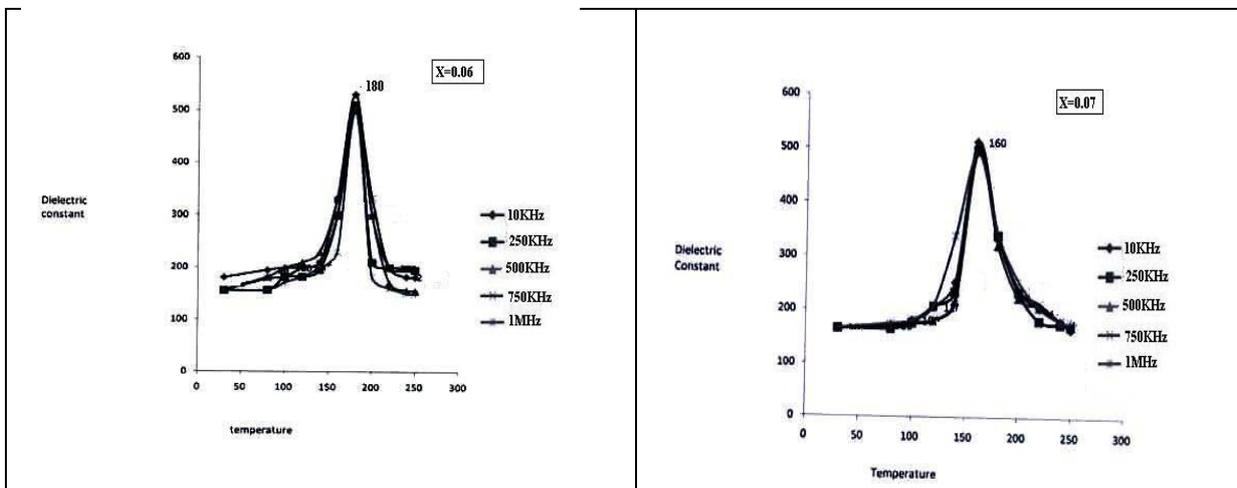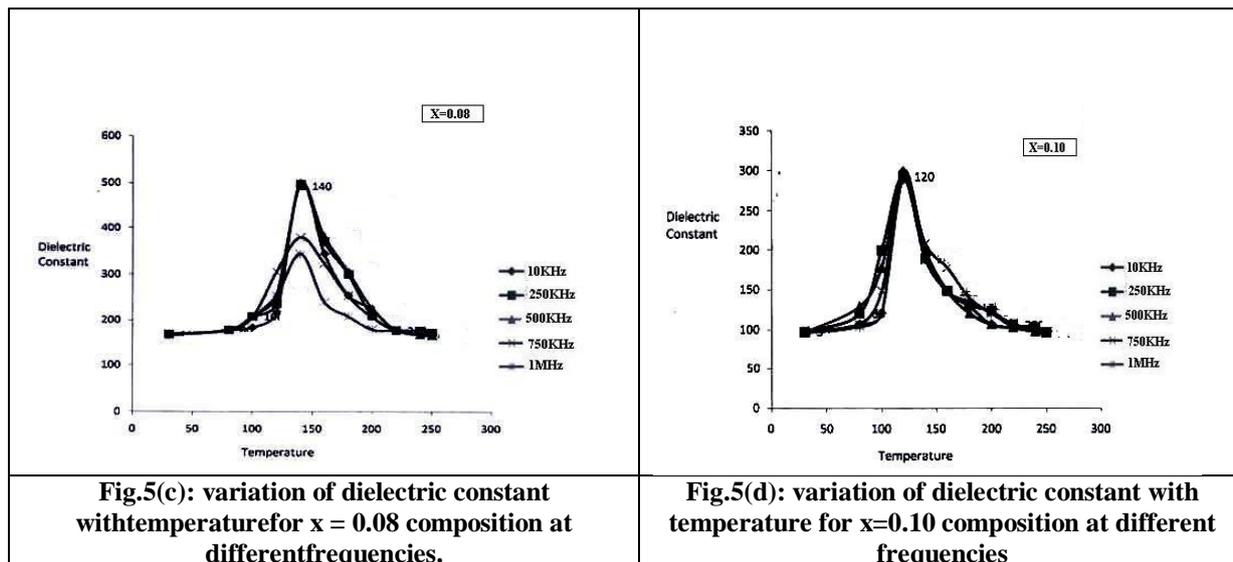**Fig.5(b): variation of dielectric constant with temperaturefor x = 0.07 composition at different frequencies**

Fig.5(c): variation of dielectric constant withtemperaturefor x = 0.08 composition at differentfrequencies.	Fig.5(d): variation of dielectric constant with temperature for x=0.10 composition at different frequencies

For x = 0.06 and 0.07compositions, the difference in the peak value of dielectric constant at various frequencies is modest, where the specimen contains both the tetragonal and rhombohedral phases. This can obviously be attributed to the enhanced ability for the polar nano domains to follow the ac drive due to the maximization of polarization 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 decrease with the increase in the amount of lanthanum in the PZT system. The peak in dielectric peak may be considered due to the disorder in the arrangement of rare earth and other atoms, leading to a microscopic heterogeneity in the composition, and thus, a distribution of different local curie points [5, 6].

Fig.5 (a, b, c, d) shows temperature variation of PZT & PLZT ceramics at various frequencies. Dielectric constant (ε) of any material, in general, is influenced by bipolar, electronic, ionic and interfacial polarizations .Interfacial polarization increases due to the creation of crystal defects and dipolar polarization decreases due to the increase in randomness of the dipoles with temperature. However, the temperature effect on ionic and electronic polarizations is very small. The increase in 'ε' with temperature suggests the increase in interfacial polarization.

Initially, both ε and tanδ decreases with the increase in frequency. The fall in arises from the fact that polarization does not occur instantaneously with the application of the electric field, which is further due to the inertia of the dipoles and the delay in response towards the impressed alternating electric field leads to dielectric loss and decline in ε. At low frequencies, all types of polarization contribute and as the frequency is increased, polarizations with large relaxation times cease to respond and hence the decrease in 'ε'.

At lower frequencies 'ε' is maximum because the contributions from the space charge polarization are large. The space charge polarization arises by the accumulation of charges mainly due to vacancies of lead and oxygen at the grain boundaries and at the electrode interface. At higher frequencies, contributions from the polarizations having high relaxation time cease resulting in the decrease in 'ε'. The same type of frequency-dependent dielectric behavior is found in many other ferroelectric ceramic systems [4]. The value of dielectric constant decreases with higher lanthanum content which can be attributed to the minimization of number of polar directions as the structure traverse from coexistence of mixed phases to a single phase.

V.   Conclusions

1. La substitution on PZT Ceramics was used to enhance and modify its properties. La substitution contribute to increase in dielectric properties of PZT Ceramics

2. With the substitution of La on Lead Zirconium Titanate following structural and dielectric parameters obtained that makes them ideal as futuristic materials.

3. La doping increases the experimental density with the reduction in tetragonality of the PZT crystal lattice, which leads to the formation of denser micro-structure.

4. XRD studies showed the incorporation of lanthanum ions thermodynamically into the lattice of perovskite structure stabilizes the rhombohedral phase against the tetragonal phase

5. Microstructure study reveals that almost uniform grain growth and grain compaction with well-defined grain boundaries is observed with the increase in substitution of La in PZT ceramics. Dielectric constant increases gradually with increment in the temperature and passes through a maximum (Curie temperature, T_c) and then decreases due to the phase transition from ferroelectric to the paraelectric phase in La PZT ceramics. This work also helps us to get familiarized with several instruments used in the present study.

References

[1]. G. Goodman, 'Ceramic Capacitor Materials', in Ceramic Materials for Electronics. Ed. by R. C. Buchanan. Marcel Dekker, New York, pp. 79–138 (1986).
[2]. Gupta,S.M;Li,J.F.&Vichland,D.Co-existence of relaxor and normal ferroelectric phases for La modified PZT at morphotropic phase boundary J.Amer.Ceram.Soc.,1998,81, 447-64.
[3]. Prakash,C. & Thakur, 0.P.Effects of Samarium modification on the structural and dielectric properties of PLZT ceramics. Material Lettice, 2003, 57, 2310.
[4]. Sarabjit Singh, O. P., Synthesis, Structural and Electrical Properties of Lanthanum-modified Lead-zirconate-titanate System. Def. Sci. J, Vol. 55, No. 3, July 2005, pp. 349-356
[5]. Lines,m.e.&Glass,A.M.Principles and applications of ferroelectrics and related materials.Claredon,Oxford,1977.
[6]. Chen, et.al. Structural origin of relaxorperovskites. J.Phys. Chem. Solids, 1966, 57, 1525-536.