# Structural and Electrical Properties of Lead Zirconate Titanate [$Pb(Zr_xTi_{1-x})O_3$] Ceramics

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***Abstract*- Lead Zirconate Titanate [PZT: $Pb(Zr_xTi_{1-x})O_3$; x = 0.40, 0.45, 0.55 and 0.60] ceramics were prepared by mixed oxide method at high temperature. Preliminary structural analysis through X-ray diffraction technique suggests about the formation of compounds at room temperature in tetragonal crystal system. Their tetragonality exhibits a decreasing trend with the increase in $Zr^{4+}$ concentration. Micro structural analysis using SEM-microphotographs suggests that the grains are uniformly distributed on the surfaces of the samples with small porosity. Study of dielectric properties at different temperatures and frequencies exhibits high dielectric constant and low loss tangent along with the transition temperature well above the room temperature. The ferroelectric to paraelectric transition temperature in PZT samples exhibits a decreasing trend with the increase in $Zr^{4+}$ concentration. Study of ac-conductivity at different temperatures and the value of activation energy in different regions suggest that the conduction process in the materials is of mixed type; singly ionized in ferroelectric region and doubly ionized in paraelectric region.**

***Keywords: PZT; XRD; SEM; Dielectric constant; Tangent loss; AC-conductivity.***

## I. INTRODUCTION

Lead Zirconate Titanate (PZT) ceramics [1-3] is an excellent dielectric, piezoelectric and ferroelectric material that has wide applications in electronic and electro-optic devices such as actuators, transducers, pressure sensors, electro-optical modulators, etc [4-8]. It is the solid-state solution of ferroelectric $PbTiO_3$ and antiferroelectric $PbZrO_3$ forming a perovskite $ABO_3$ structure (A = mono or divalent and B = tri-hexavalent ions) in which A-site is occupied by $Pb^{2+}$ ions and B-site by $Zr^{4+}$ or/and $Ti^{4+}$ ions. At room temperature, it exhibits two ferroelectric phases: tetragonal in titanium rich composition and rhombohedral in zirconium rich composition [9-10]. At morphotropic phase boundary (MPB) between these two phases electrical and electromechanical properties of the materials increase to a great extent [11].

The material properties of PZT based ceramics can be considerably modified in accordance with the requirements through variations in Zr/Ti ratio, suitable substitutions, synthesis technique, calcination and sintering temperatures and other physical conditions [12-13]. The dopants for PZT are mainly of two types: donor dopants and acceptor dopants. The donor or soft dopants modify the material properties by creating Pb-vacancies when higher valence ions substitute at A and/or B-sites. On the other hand, the acceptor or hard dopants cause O-vacancies by substituting lower valence ions at A and/or B-sites [14-15]. It has been well established that La-modified PZT has tremendous electrical and electromechanical applications in research as well as industries [16-17].

From the literature survey of PZT based materials, it is observed that most of the works reported in this field are concerning to the effect of different processing, dopants and other physical conditions on structural and electrical properties of PZT ceramics [18-23]. Though, a systematic analysis of structural and electrical properties of PZT compounds with different Zr/Ti ratio is yet to be required. In this paper, we report the detailed study of the effect of change in Zr/Ti ratio (from 40/60 to 60/40) on structural, microstructural, dielectric and ac conductivity behaviors of Lead Zirconate Titanate (PZT) ceramics.

## II. EXPERIMENTAL DETAILS

Polycrystalline samples of $Pb(Zr_xTi_{1-x})O_3$ [x = 0.40, 0.45, 0.55 and 0.60] were prepared through Solid-State Reaction technique at high-temperature using the ingredient oxides; PbO, $ZrO_2$ and $TiO_2$ (99.9% purity, M/S Loba Chemie, Inc. Bombay, India) in suitable stoichiometry. Extra 3% lead oxide was added to the mixture to compensate lead loss during the high temperature calcination and sintering. The well mixed ingredient oxides in an alcohol medium were calcined at an optimized temperature 1100°C for 10 hours. Using polyvinyl alcohol (PVA) as binder, the calcined powders were converted into pellets at $4\times10^6$ N/m$^2$ pressure. These pellets were, then, sintered at an optimized temperature 1200°C for 10 hours so as to get maximum density (97% of theoretical density).

Structural analysis of the calcined powders were carried out using the data obtained through X-ray diffractometer (Rigaku Miniflex, Japan) at room temperature with Cu $k_\alpha$ radiation ($\lambda$ = 1.5405 Å) in a wide range of Bragg's angles 2θ ($20° \leq 2\theta \leq 80°$) at the scanning rate of 3°/min. The microstructural analysis of the surfaces of sintered pellets was done using microphotographs obtained by Scanning

Electron Microscope (SEM, JEOL JSM-5800). To analyze electrical properties of materials, the smooth flat surfaces of pellets were painted with high quality air-drying silver paint so that they act like electrodes. The pellets were dried at 150°C for 4 hours and then cooled to room temperature. Now, using Phase Sensitive Multimeter (PSM-1735) along with its accessories (computer based arrangement, variac and sample holder, furnace & thermocouple} various data were recorded in a wide range of temperature (room temp. to 500°C) and frequency (100 Hz to 1 MHz) and using these data, different electrical parameters were analyzed.

## III. RESULTS AND DISCUSSION

### *a) Structural analysis*

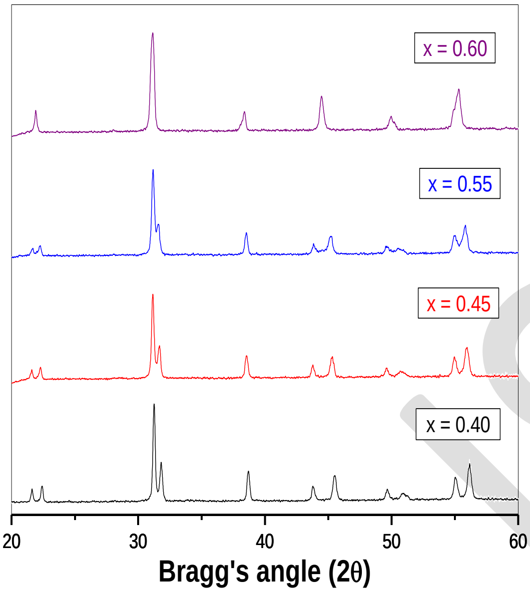

Fig-1 Comparison of XRD patterns of $Pb(Zr_xTi_{1-x})O_3$ with x = 0.40, 0.45, 0.55 and 0.60.

Comparative XRD patterns of $Pb(Zr_xTi_{1-x})O_3$ {x = 0.40, 0.45, 0.55 & 0.60} at room temperature are shown in Fig-1. Using the computer program, POWDMULT [24], most of the reflection peaks were indexed in different crystal system and unit cell configurations. With the best agreement between observed (obs.) and calculated (cal.) d-spacing (ie., $\sum\Delta d = d_{obs} - d_{cal}$ = minimum), it is found that all the samples are in single phase tetragonal crystal structure. Lattice parameters of the PZT compounds are compared in table-1 which clearly shows that the tetragonal behavior of materials decreases with the increase in $Zr^{4+}$ concentration. It is due to the fact that lead titanate ($PbTiO_3$) has tetragonal symmetry with high tetragonal ratio (c/a = 1.06) whereas lead zirconate (PbZrO3) has rhombohedral symmetry. As the ionic radius of Zr4+ (rZr4+ = 0.84 Å) is higher than that of Ti4+ (rTi4+ = 0.61 Å), increase in zirconium ions in the system replaces more titanium ions and thus distorts the structure and tetragonal ratio. The decrease in c/a ratio may be attributed to the pressure generated under the action of zirconium substitution at the position of titanium [25-26]. Crystallite size of PZT samples was roughly estimated by broadening of few XRD peaks (in a wide 2θ range) using Scherrer's equation [27]; D = Kλ/ (β1/2cosθhkl), where K = 0.89, λ = 1.5405 Å and β1/2 = peak width of the reflection at half intensity. The average crystallite size of PZT samples was found to be in the range of 21-32 nm [28].

| Structural parameters | Zr concentration in PZT | | | |
|---|---|---|---|---|
| | x = 0.40 | x = 0.45 | x = 0.55 | x = 0.60 |
| a (Å) | 3.9807(43) | 4.0400(21) | 4.0043(29) | 4.0560(16) |
| c (Å) | 4.1343(43) | 4.1324(21) | 4.1128(29) | 4.0730(16) |
| c/a | 1.0386(43) | 1.0321(21) | 1.0271(29) | 1.0042(16) |
| $T_C$ (°C) | 438 | 405 | 365 | 388 |
| Grain size (in µm) | 5.6 | 3.6 | 2.3 | 2 |

Table-1 Comparison of lattice parameters, crystallite size and grain size of $Pb(Zr_xTi_{1-x})O_3$ with x = 0.40, 0.45, 0.55 and 0.60.
(The number in parenthesis is the estimated standard deviation).

### *b) Microstructural analysis*

The comparative microphotographs of surfaces of sintered PZT pellets at room temperature with different Zr-concentration (40%, 45%, 55% & 60%) are shown in Fig-2. Their microstructures, clearly, show that all the ceramic samples are fabricated through almost uniform, densely packed and uniformly distributed grains separated by grain boundaries. The average grain size estimated by linear intercept method is as given in Table-1. It decreases with the increase in Zr-concentration in material. Their grains size is found to be larger than the average crystallite size.

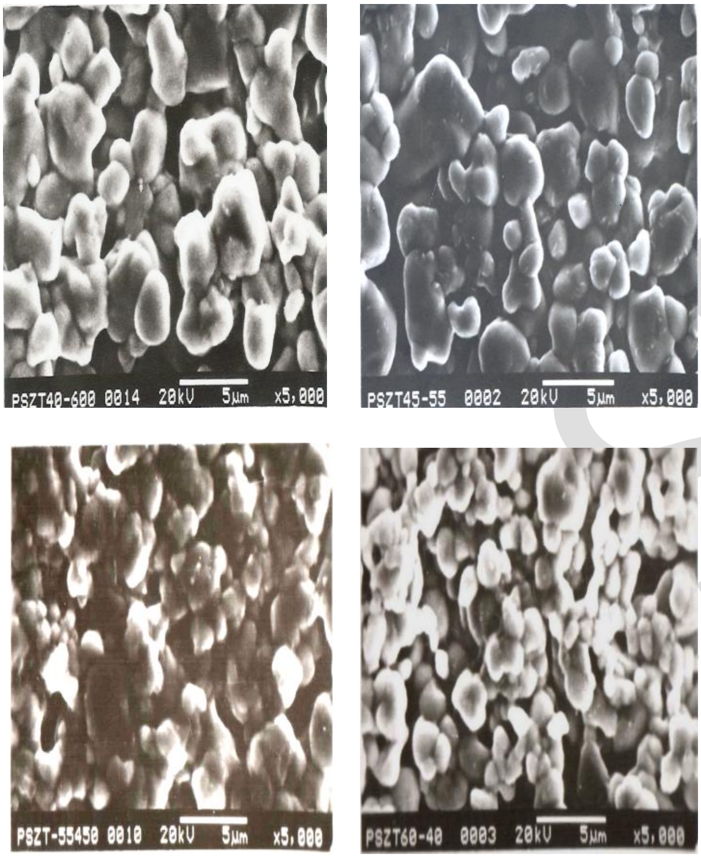

Fig-2 Comparison of SEM- microphotographs of Pb($Zr_xTi_{1-x}$)$O_3$ with x = 0.40, 0.45, 0.55 and 0.60.

### *c) Dielectric analysis*

The temperature dependence of dielectric constant ($\varepsilon_r$) of PZT samples {Zr/Ti = 40/60, 45/55, 55/45 & 60/40} at 10 kHz and 100 kHz is shown in Fig-3

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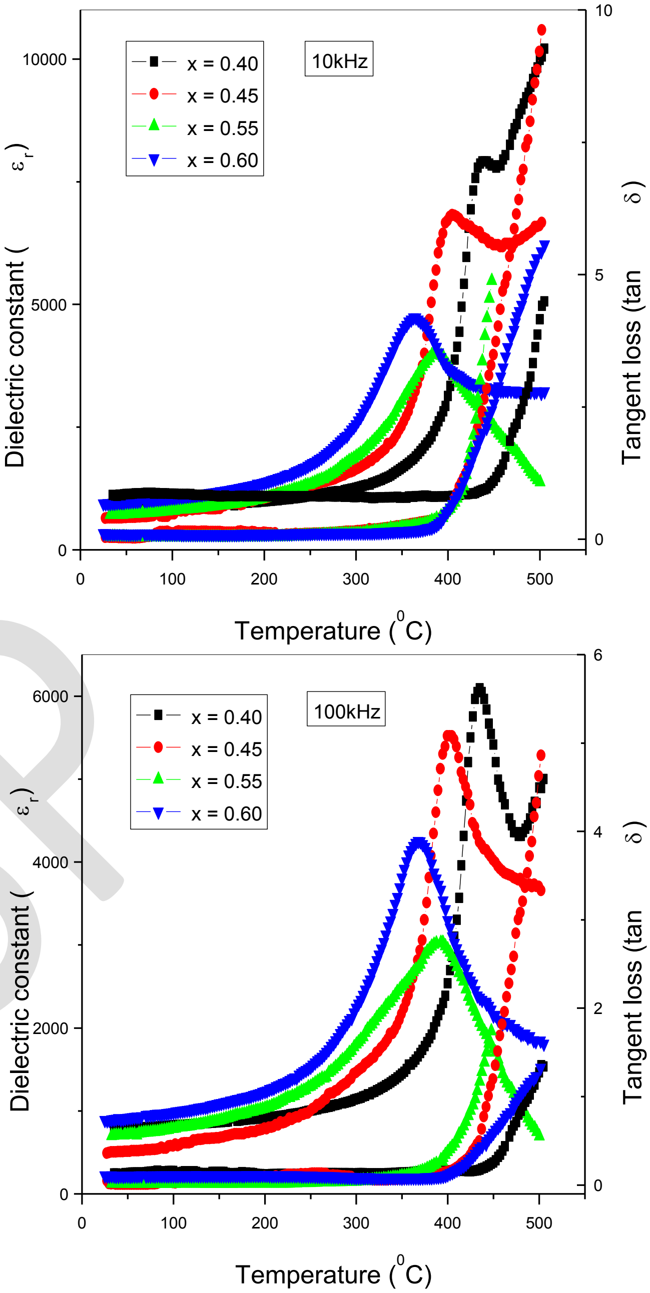

Fig-3 Temperature-frequency dependence of $\varepsilon_r$ and tanδ of Pb($Zr_xTi_{1-x}$)$O_3$ with x = 0.40, 0.45, 0.55 and 0.60.

Dielectric constant ($\varepsilon_r$) of the samples is found to decrease with the increase in frequency which suggests about the normal ferroelectric dielectric behavior of the materials. High $\varepsilon_r$ at low frequencies suggests simultaneous presence of all the types of polarizations, i.e., space charge, dipolar, ionic and electronic polarizations. They get ceased, in order, with the increase in frequency and at very high frequencies (≥ $10^{15}$ Hz) only electronic polarization remains in existence [12, 29]. Though, due to experimental limitations we could not proceed above 1 MHz. With the gradual increase in temperature, $\varepsilon_r$ increases first slowly upto nearly 150°C and then rapidly upto a maximum value $\varepsilon_{max}$. Temperature corresponding to $\varepsilon_{max}$ is called Curie or transition temperature ($T_c$) at which transition of phase takes place between ferroelectric-paraelectric states. The higher value of $\varepsilon_r$ at higher temperatures is due to space charge polarization originating from mobility of ions and imperfections in the materials. If the temperature of the samples is further increased above $T_c$, $\varepsilon_r$ decreases rapidly [30-31]. The $T_c$ of PZT samples is found to decrease with the increase in Zr-concentration. It may occur since transition temperature is high in case of higher concentration of titanium [or tetragonal ratio] and decreases with the increase in Zr-concentration. This $T_c$ is found to be almost insensitive to the change in frequency which supports the non-relaxor behavior of the materials. With the variation in Zr-concentration in PZT compounds, the value of $\varepsilon_{max}$ exhibits a decreasing trend from x = 0.40 to 0.55 but then shows an increased value for the Zr-content x = 0.60.

The temperature dependence of tangent loss (tanδ) of PZT samples with varying Zr/Ti ratio at 10 kHz and 100 kHz is shown in Fig-3. It is observed that the values of tanδ are very low at room temperature and remains almost low until a very high temperature near by the transition temperature ($T_c$). Beyond this temperature, tanδ exhibits a considerable increase which may be due to oxygen vacancies. Since at higher temperatures, oxygen vacancy increases, gets activated and becomes more mobile which increases the polarization. It is also observed that tanδ decreases with the increase in frequency which suggests about the decrease in polarization with increase in frequency [12, 21, 32].

### *d) AC conductivity analysis*

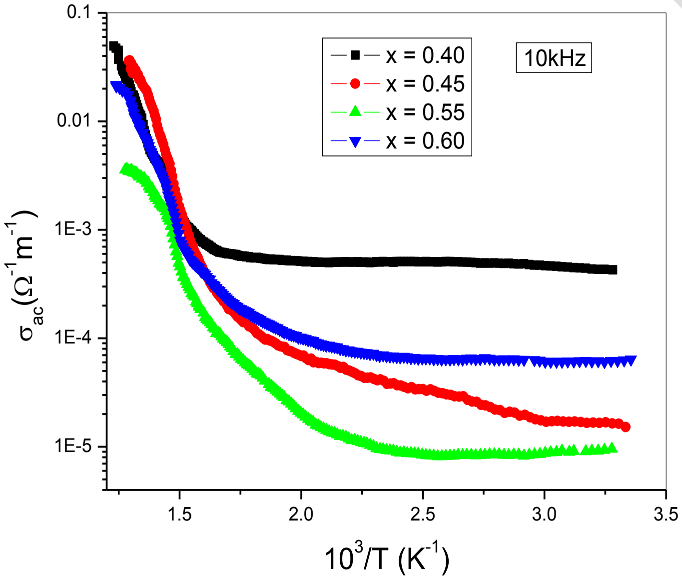

Fig- 4 Temperature-frequency dependence of ac conductivity of $Pb(Zr_xTi_{1-x})O_3$ with x = 0.40, 0.45, 0.55 and 0.60 at 10 kHz.

AC conductivity ($\sigma_{ac}$) of PZT samples were calculated at different temperatures using formula; $\sigma_{ac} = \omega\varepsilon_o\varepsilon_r \tan\delta$, where ω is the angular frequency and $\varepsilon_o$ is the permittivity of free space. Its temperature dependence at 10 kHz is shown in Fig-4. In the higher temperature region, $\sigma_{ac}$ exhibits an increasing trend with the increase in temperature mainly due to the increase in polarizability. Their values almost fall on a straight line at very high temperatures above $T_c$ which indicates a typical behavior of the dc component [12]. This linear variation of $\sigma_{ac}$ over a wide temperature region supports the existence of thermally activated transport properties in the materials obeying the Arrhenius equation; $\sigma_{ac} = \sigma_0 \exp(-E_a/K_BT)$, where $\sigma_o$ is the pre-exponential term, $K_B$ the Boltzmann's constant and $E_a$ the activation energy. The estimated values of activation energy ($E_a$) of the materials at 10 kHz indicate its dependence on ionization level of oxygen vacancies [33-34]. The activation energy of PZT samples with Zr-content x = 0.40, 0.45, 0.55 & 0.60 below $T_c$ are estimated as 0.88, 1.65, 0.54 & 0.34 and above $T_c$ as 1.15, 0.93, 0.32 & 1.12 respectively. The value of $\sigma_{ac}$ less than 1 eV indicates the ferroelectric region which may be caused due to the presence of singly ionized oxygen vacancies in the conduction process. But the activation energy greater than 1 eV may be due to double ionized oxygen vacancies in paraelectric region.

## IV. CONCLUSION

Polycrystalline ceramic samples of $Pb(Zr_xTi_{1-x})O_3$ {where, x = 0.40, 0.45, 0.55 and 0.60} were prepared using high temperature solid-state reaction technique. The structural analysis through XRD-technique confirms their formation in single phase tetragonal crystal system whose tetragonality almost decreases with the increase in Zr-concentration. Crystallite size of PZT-compounds is found to be in nanometer range. Microstructural analysis through SEM-microphotographs shows that the samples are almost made up by uniform, densely packed and uniformly distributed grains separated by grain boundaries. Their grain size decreases with the increase in Zr-concentration. The dielectric analysis reveals that dielectric constant of PZT compounds is very high for the Zr-content x = 0.40 and decreases with the increase in Zr-concentration until x = 0.55. With the further increase in Zr-content, it exhibits an increasing trend until x = 0.60. The ferroelectric-paraelectric phase transition temperature ($T_c$) of the materials exhibits a decreasing trend with the increase in Zr-concentration. The dielectric/tangent loss of PZT compounds is found to be very low and almost remains very low until a high temperature close to $T_c$. Thus, with the high dielectric constant and low tangent loss, the PZT compounds are highly suitable as capacitive material even at high temperatures. The conduction process in these compounds is almost due to singly ionized in ferroelectric region and doubly in paraelectric region mainly due to ionized oxygen vacancies.

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