4. ELECTRICAL AND OPTICAL CHARACTERIZATIONS OF LEAD ZIRCONATE TITANATE (PZT) CERAMICS

4.1 INTRODUCTION

Though a lot of work has been carried out on the synthesis and characterization of PZT powders, the electrical and optical properties of PZT powder have rarely been studied. A detailed literature survey revealed that the electrical properties of PZT ceramics were rarely investigated [13, 14]. The electrical properties of PZT having Zr/Ti ratio of 52/48 have been studied very rarely [15]. The perovskite lead zirconate titanate ferroelectric system is one of the most interesting materials to be studied from the fundamental and application point of view, especially for compositions near the MPB region. They exhibit a great variety of physical behavior and excellent electromechanical properties, thus making the material suitable for various sensors and actuators applications [3, 18].

In the present study, the temperature dependent band gap variation of the PZT material has been discussed and such optical study is rarely reported for this material. In the present work, the Pb(ZrxTi1-x)O3 powders were synthesized by sol-gel method as described in Chapter 3. The structural and phase formation were confirmed by XRD and FTIR studies. The thermo gravimetric analysis of the sample was studied. The surface morphology and particle size of the samples were imaged using scanning electron microscopy (SEM). The crystallite size was calculated using Scherrer's formula. The variation of crystallite size with calcined temperature has also been reported. In this work, the temperature dependence of dielectric constant, loss tangent and dc conductivity (range from 25 °C to 500 °C) were carried out at different frequencies in the range 100 Hz - 1MHz. The P-E loop of PZT (52/48) pellet was obtained to find out the remnant polarization (P_r) and coercive electric field (E_c) for various applied voltages. The results were analyzed and discussed in detail.

4.2 RESULTS AND DISCUSSION

4.2.1 Structural and morphological studies
The powder XRD patterns were obtained for the powders calcined at 600 °C, 700 °C, 800 °C, 850 °C, 900 °C and 1000 °C using PANalytical X’pert diffractometer in the range of Bragg’s angle (2θ) 10°- 90° with the Cu Kα line (λ=1.54 Å) and these patterns are shown in Figure. 4.1. It is clear from the figure that, in the case of the sample calcined at 600 °C, crystallization is almost complete and the perovskite PZT phase along with a small impurity phase is formed. The impurity phase was identified as pyrochlore phase. The XRD patterns for the samples calcined at temperatures 700 °C and 800 °C also show that the perovskite phase is observed along with the pyrochlore phase. However, this impurity phase is found to gradually decrease from 700 °C to that calcined at 800 °C.

For the sample calcined at a temperature of 900 °C, pyrochlore phase disappears and the peaks of the perovskite phase are observed clearly confirming the formation of PZT. Thus, it is observed that the pyrochlore phase gradually decreases with the increase of calcination temperature from 600 °C and it disappears at 900 °C. A sharp intensity peak (2θ = 31.20°) indicates the formation of perovskite PZT phase which can be matched with the JCPDS file no. 33-0784. The XRD pattern clearly shows no unwanted phase formation like pyrochlore, indicating that the sol-gel process used in the present study is a suitable technique. The XRD pattern at 1000 °C shows the presence of pyrochlore phase and this may be due to the melting of PbO at high temperature. The broad XRD peaks clearly indicate the presence of nano crystalline particles. From the XRD patterns, the crystallite size was calculated with the help of Scherrer’s formula (t = 0.9λ/βcosθ) (where λ – wavelength used, β – Full Width at Half Maximum (FWHM) and θ - diffraction angle) and it is given in Table 4.1. Figure 4.2 shows the XRD pattern of the PZT (52/48) powder calcined at 850 °C for 3 hrs. For electrical characterizations, this powder was calcined at 850 °C for 3 hrs and pelletized and then sintered at 875 °C for 4 hrs and the pellet thus prepared was used for the electrical study.
Figure. 4.1: XRD patterns of PZT powders calcined at different temperatures.

Figure. 4.2: XRD pattern of the PZT (powder) calcined at 850 °C for 3 hrs.
Figure. 4.3: TGA/DTA curve for the PZT powders synthesized by sol-gel route.

Figure. 4.3 shows the thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of the PZT (52/48) powders carried out in Helium atmosphere with the heating rate of 20 °C/min. TG curves exhibit three major losses; the first one located between 180 °C and 246 °C (of about 9%) may be due to the elimination of water content from the prepared sample; the second occurring between 290 °C and 392 °C (of about 22%) due to the major decomposition reaction of citric acid and other organic compounds and the third one located between 546 °C and 730 °C is due to removal of nitrates and the combustion of residual carbon contents. The DTA curves are in conformity with these observations. There are two exothermic peaks in DTA curve at 334 °C and 540 °C. The first one may be corresponding to the combustion of most of the organic species entrapped in PZT polymerized gel such as citric acid and titanium (IV) isopropoxide. The second with a temperature range of 430 °C – 656 °C is due to the decomposition of organic compounds and it indicates the beginning of crystallization of the perovskite phase.
Figure 4.4: SEM image of the PZT (a) powder and (b) pellet.

Figure 4.4 (a) and (b) show the typical SEM image of the PZT powder and pellet calcined at 900 °C and sintered 875 °C respectively. From SEM analysis, the primary particle size of the powder has been determined. The primary particle size of the PZT powder has been found to be approximately in the range of 200–300 nm. The surface morphology of the PZT (52/48) pellet was imaged using scanning electron microscope. Figure 4.4 (b) shows SEM image of the PZT (52/48) pellet. From the SEM image, it is observed that the average size of the particle is around 300-500 nm and distribution of particle size of the pellet is not uniform. It may be due to agglomeration of particles that resulted during the preparation of pellet (with addition of PVA and sintered at 875 °C for 4 hrs).

4.2.2 Optical study

The UV-vis Diffused Reflectance Spectra (DRS) of PZT powders calcined for 3 hrs at 850 °C and 900 °C are presented along with the energy band gap values in Figure 4.5. The band gap of PZT powder was calculated from the absorption of visible wavelength. The band gap is 3.64 eV at 850 °C and 3.51 eV at 900 °C. From this study, it has been observed that the band gap decreases with increase in the calcined temperature and this is confirmed by the results reported earlier on such optical studies [7, 9, 69]. The variation of the crystallite size and band
The energy gap of PZT powders with temperature is given in Table 4.1. The results show that the crystallite size increases with increase in calcined temperature which is in agreement with the experimental results of Smitha et al. [9] and Ghasemifard et al. [7].

![UV-vis DRS spectra of PZT powders calcined at 850 °C and 900 °C for 3 hrs.](image)

When the relation between the crystallite size and the energy gap is considered (Table 4.1), it is observed that the band gap decreases with increase in the crystallite size. This is in agreement with the experimental results of Schuppler et al. [70] and also with the theoretical calculations of Chang et al. [69]. Schuppler et al. showed that with increase in crystallite size, the photoluminescence of SiOₓ decreases i.e., band gap decreases. The theoretical calculations of Chang et al. through the surface bond contraction model showed that the width of the band gap grows as the dimensions of the crystallite size decreases. The "quantum confinement" theory [71, 72] also showed the similar size induced band gap expansion.
Table 4.1: Crystallite size, lattice parameter and band gap of PZT (52/48) powders for different calcined powders

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Average Crystallite Size (nm)</th>
<th>Lattice Parameter (Å)</th>
<th>Bandgap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>a</td>
<td>c</td>
</tr>
<tr>
<td>600</td>
<td>21.2</td>
<td>3.9</td>
<td>4.1</td>
</tr>
<tr>
<td>700</td>
<td>25.6</td>
<td>3.8</td>
<td>4.0</td>
</tr>
<tr>
<td>800</td>
<td>28.2</td>
<td>3.8</td>
<td>4.0</td>
</tr>
<tr>
<td>850</td>
<td>35.9</td>
<td>3.8</td>
<td>4.1</td>
</tr>
<tr>
<td>900</td>
<td>37.5</td>
<td>3.9</td>
<td>4.1</td>
</tr>
</tbody>
</table>

4.2.3 Dielectric properties

Dielectric studies of the PZT (52/48) pellet were carried out to analyse its response to an applied ac voltage (1V) as a function of both temperature and frequency using AC technique of CIS. This technique enables to separate the real and imaginary components of electrical parameters and hence provides a true picture of the material properties. Figure 4.6 (a) and (b) show the dielectric constant ($\varepsilon_r$) and dielectric loss (tanδ) of the PZT (52/48) ceramics as a function of temperatures for various frequencies between 100 Hz and 1 MHz. The dielectric constant ($\varepsilon_r$) increases gradually with rise in temperature and reached a maximum value ($\varepsilon_r^{\text{max}}$) at a particular temperature known as Curie temperature ($T_c$). This general feature is same for all frequencies and the value of ($\varepsilon_r^{\text{max}}$) at $T_c$ decreases with increasing frequencies. Further, the value of $\varepsilon_r$ is larger at low frequency and the value of $T_c$ shifts towards the higher temperature side with decrease in frequency. It indicates that on heating, the dielectric constant gradually becomes frequency dependent [73]. In disparity, the dielectric loss increases with increase in frequency and temperature.
Figure. 4.6: (a) Dielectric constant vs. temperature, (b) Dielectric loss vs. temperature of PZT(52/48) ceramics for various frequencies (100 Hz- 1MHz).

4.2.4 Impedance analysis

Figure. 4.7 (a) and (b) show the complex impedance spectrum (Z’ vs. Z” called Nyquist Plot) of PZT (52/48) ceramic measured at different temperatures as function of frequency (range from 100 Hz to 1 MHz). The effect of temperature on impedance behavior of the material sample becomes clearly visible with rise in temperature. The impedance spectrum is characterized by the appearance of semicircular arcs whose pattern of evolution changes with rise in temperature. Each semicircular arc in the impedance pattern can be attributed to a parallel combination of resistance and capacitance. As temperature rises, the arcs progressively become semicircular with a shift in the center of their arc towards origin of the complex plane plot.

The presence of a single semicircular arc indicates that the electrical processes in the material arise basically due to the contribution from bulk material (grain interior) [74, 75]. The electrical process at these temperatures may be attributed to intragrain phenomena. The shift of the origin of the semicircular arc towards the origin of the complex plane plot indicates a decrease in the resistive behavior of the sample which is attributed to the grain boundary conduction with rise in temperature [76].
The real part of impedance ($Z'$) of the PZT ceramics under consideration exhibits a low frequency dispersion (not shown) due to polarization. At higher frequencies, it becomes almost independent of both frequency and the temperature. The same variation has been found in the case of imaginary part of impedance ($Z''$) of the PZT ceramics with frequency at lower temperatures. This supports the increase in ac conductivity with temperature. The initial decrease in $Z'$ with frequency may be due to a slow dynamic relaxation process in the materials which may probably due to space charges that releases at higher frequencies.
The variation of imaginary part of impedance ($Z''$) with frequency at higher temperatures is shown for the PZT ceramic compound in Figure. 4.8 which exhibits some peaks. These peaks shift towards higher frequencies on increasing temperature in a broadening manner with the decrease in peak height. It indicates a thermally activated dielectric relaxation process in the materials and shows the reduction in the bulk resistance with temperature. But peaks have not been found at low temperatures (not shown) which may be due to the weak current dissipation in the material or may be beyond the frequency of measurement. A significant broadening of the peaks with increase in the temperature suggests the presence of temperature dependent relaxation process in the materials. These dispersion curves appear to merge at higher frequency. This behavior is again due to the presence of space charge polarization at lower frequencies and its elimination at higher frequencies.

### 4.2.5 DC conductivity studies

![Graph showing Arrhenius plot with activation energy ($E_a$) of 0.210 eV](image)

**Figure. 4.9:** Activation energy ($E_a$) of perovskite PZT (52/48) ceramics derived by fitting to the Arrhenius equation.
Figure. 4.9 shows the temperature dependence of dc conductivity of PZT (52/48) ceramics in the temperature range from 598 K to 773 K. The Arrhenius plot has been obtained by plotting the logarithm of dc conductivity $\sigma$, versus the inverse temperature $1000/T$. The activation energy of the sample was found out using the relation

$$\sigma = \sigma_o \exp(-E_a/k_B T)$$  \hspace{1cm} (4.1)

in which $k_B$ is the Boltzmann constant and $\sigma_o$ is the pre exponential factor. The estimated value of activation energy of the PZT (52/48) sample is 0.210 eV. The type of temperature dependence of dc conductivity indicates that the electrical conduction in the material is a thermally activated process. In perovskite ferroelectric sample, the ionization of oxygen vacancies creates the conducting electrons, which are easily thermally activated. It clearly suggests that the conduction in the high temperature is due to oxygen vacancies.

### 4.2.6 Ferroelectric properties

Figure. 4.10: (a) & (b) Hysteresis loop behavior of the PZT (52/48) ceramic for various applied electric fields.

The electric-field dependence of polarization (ferroelectric hysteresis loop) studies were carried out for different applied voltages (0.5 - 4 kV) at room temperature and the loops are shown in Figure. 4.10 (a) and (b). Table 4.2 shows the saturation polarization ($P_s$), remnant polarization ($P_r$) and coercive field ($E_c$) determined from the
ferroelectric hysteresis loop obtained at various applied voltages for PZT (52/48) ceramics. The remnant polarization and coercive field increase with increase in applied voltage from 0.5 kV to 4 kV. The maximum remnant polarization of the sample is 1.65 µC/cm² with the coercive electric field of 8.73 kV/cm and at the applied voltage of 4 kV.

Table 4.2: Remnant polarization ($P_r$) and saturation polarization ($P_s$) and coercive field ($E_c$) determined from the measured hysteresis loop for PZT (52/48) ceramics

<table>
<thead>
<tr>
<th>Applied Voltage (kV)</th>
<th>Remnant Polarization ($P_r$) (µC/cm²)</th>
<th>Saturated Polarization ($P_s$) (µC/cm²)</th>
<th>Coercive field ($E_c$) (kV/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.14</td>
<td>0.79</td>
<td>1.35</td>
</tr>
<tr>
<td>2</td>
<td>0.48</td>
<td>2.0</td>
<td>3.65</td>
</tr>
<tr>
<td>3</td>
<td>0.81</td>
<td>3.33</td>
<td>5.60</td>
</tr>
<tr>
<td>4</td>
<td>1.65</td>
<td>5.27</td>
<td>8.73</td>
</tr>
</tbody>
</table>

4.3 CONCLUSION

The PZT powder was synthesized by sol-gel method using citric acid as a complexing reagent. The prepared powder was calcined at 600 °C, 700 °C, 800 °C, 900 °C and 1000 °C for 3 hours. The phase formation of PZT was confirmed by XRD, TGA/DTA and FT-IR. The XRD pattern indicates that the perovskite PZT powders were free of pyrochlore phase at 900 °C. The estimated average particle size of the PZT powders was found to be around 200 - 300 nm from SEM micrographs for the powder samples calcined at 900 °C. The broad XRD peaks clearly indicate the presence of nano crystalline particles. From the XRD patterns, the crystallite size was calculated with the help of Scherrer’s formula. The crystallite size was found to increase with the increase in the calcined temperature. The band gap energy was calculated from the results of UV-vis DRS and the band gap was found to decrease with increase in calcined temperature.
The impedance studies of the sample have been used to analyze the electrical conductivity properties with increase in temperature. The dielectric results indicate the decrease in dielectric constant with increase in frequency while the dielectric loss increases with increase in frequency. The activation energy of the sample calculated from the Arrhenius’s plot is 0.210 eV. The remnant polarization ($P_r$) and coercive electric fields ($E_c$) are found to be 1.65 µC/cm$^2$ and 8.73 kV/cm respectively from the ferroelectric loop measured at room temperature.