CHAPTER – 9
DIELECTRIC, FERROELECTRIC AND PIEZOELECTRIC CHARACTERISTICS OF SAMARIUM MODIFIED LEAD TITANATE CERAMICS.
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1.1 Introduction

Among the many ferroelectric oxides with perovskite structure of general formula $\text{ABO}_3$ (A = mono or divalent, B = trivalent – hexavalent ions), some are in the forefront both in areas of research as well as in industrial applications. Lead titanate is an important member of the family of perovskite structured materials that exhibits useful dielectric, piezoelectric and electromechanical properties. The lead titanate ceramics (PT) are very useful in high temperature and high frequency applications [1,2]. PT based ceramic sensors, which can detect human conditions in a room have also been reported [3].

Ferroelectric phase transition of PT ceramics occurs at 490 °C. Above this temperature its crystal structure is cubic and below the curie point the cubic phase changes to tetragonal phase. Due to this phase change a change in cell dimension is also produced and consequently, a strong internal stress may be induced. This stress renders PT ceramics fragile when cooled through curie temperature [4,5]. Also Pure PT ceramics have low resistivity ($10^7$-$10^8 \ \Omega \cdot \text{cm}$) which is due to vacancies caused by loss of lead during
9.2 Experimental

Sintered disks of samarium modified lead titanate ceramics were smoothened by grinding with alumina powder in aqueous medium to make surfaces flat and parallel. The disks of 12-13 mm in diameter and about 1
mm thick were electrode by applying fired-on silver paste on the both sides and fired at 800 °C. Dielectric constant and tangent loss as function of temperature and frequency were measured by automated measurement setup described in chapter 4. The dielectric constant and the ac conductivity were calculated from the measured capacitance and tangent loss of the sample, using the equation (9.1) and (9.2) respectively [16]

\[ \varepsilon = \frac{C}{\mu A t} \]  \hspace{1cm} (9.1)  
\[ \sigma_{ac} = \omega \varepsilon_0 \tan \delta \]  \hspace{1cm} (9.2)  

where \( C \) is the capacitance, \( t \) the thickness, \( A \) the area of the plates, \( \omega \) the frequency, \( \varepsilon' \) the dielectric constant, \( \varepsilon_0 \) permittivity of the free space \((8.854 \times 10^{-12})\) and \( \tan \delta \) the tangent loss.

A ceramic is agglomeration of individual crystallites which are distributed randomly resulting in zero net dipole moment. By applying strong electric fields, the dipoles can be made to orient in the direction of the applied field, giving ceramic the net dipole moment and the process is called poling. In the present studies, the samples of samarium modified lead titanate ceramics were poled by the application of the D.C. field of 20 to 30 kV/cm at 150 °C for 30 minutes in silicone oil and cooled under the application of field. Berlincourt meter was used for \( d_{33} \) measurements.

### 9.3 Dielectric characteristics

#### 9.3.1 Effect of samarium substitution

Room temperature dielectric constant \((\varepsilon')\) increases with increase in samarium doping (figure 9.1). This increase in dielectric constant is attributed to decrease in crystal tetragonality with increase in samarium addition which results in increase in polarization and hence the dielectric constant. Increase in dielectric constant with decrease in tetragonality has been reported in the literature \([12,17-19]\). Dielectric constant increases with increase in grain size \([20]\). Dielectric constant is also expected to increase with increase in density.
density of these samarium modified ceramics decreases with the increase in samarium substitution while as the bulk density increases with the increase in samarium substitution. Substitution of samarium reduces lattice tetragonality which in turn reduces the internal stress developed when cooled through the cure temperature.

The total polarization in ceramics and glasses involve a short range motion of charge. The various polarization mechanisms include, electronic polarization, atomic polarization, and dipole polarization and interfacial polarization. The electronic and atomic polarizations are predominant at very high frequency ranges of $10^{12}$ and $10^{12} - 10^{13}$ Hz, respectively. Dipolar polarization contributes to the dielectric properties in $10^2 - 10^4$ Hz. It is also referred in texts as the orientational polarization. The mechanism of dipolar polarization is divided into two categories. First, molecules containing the permanent dipole moment rotate against elastic restoring force about the equilibrium position. The second mechanism is an especially important contribution to the room temperature dielectric behaviour of glasses and ceramics. It involves rotation of dipole between two equilibrium positions which gives rise to non-linear polarization behaviour of the ferroelectric materials [21].

**9.3.2 Room temperature electric parameters**

Figures 9.2 and 9.3 show dependence of dielectric constant and tangent loss at room temperature ($30^\circ$C) on frequency of the applied a.c. field respectively for various concentrations of samarium (2 – 20 mol%) in PT ceramics. Small decrease of 10 –15% is observed in all samples within a frequency range of 100Hz to 1MHz. Similar behaviour is observed in case of tangent loss (Fig.9.3). The decrease in dielectric constant can be expressed by Kramers Kronig relation [22]:

$$\varepsilon'(\omega) - \varepsilon_\infty = A_4 \omega^{-1}$$

(9.3)
where \( \varepsilon' \) is the dielectric constant measured at frequency \( \omega \) (\( \omega = 2 \pi f \)) and \( \varepsilon'' \) is the dielectric constant measured at high frequency and exponent \( s = 1 \). Equation (9.3) can be expressed in the form \( \log(\varepsilon'(-\omega) - \varepsilon) = (1-s) \log \omega + \log A \). A plot of \( \log(\varepsilon'(-\omega) - \varepsilon) \) versus \( \log \omega \) shows the result as shown in figure 9.4.

From this it is observed that variation of dielectric constant is consistent with equation (9.3) with \( s = 0.96, 0.95, 0.91, 0.94 \) and proportionality constant \( A = 124, 86, 118, 55 \) for 20 mol\%, 10 mol\%, 5 mol\% and 2 mol\% samarium respectively. This dielectric dispersion seems to be due to hopping of charge carriers with random distribution of hopping distances and potential wells [23] and dispersion due to space charge is unlikely because of the high room temperature resistivity of all samples. The decrease in tangent loss with frequency (figure 9.3) seems also due to the hopping conduction. A.C conductivity at room temperature of these ceramics as a function of frequency is worked out using equation (9.2). Figure 9.5 shows variation of \( \log \sigma_{\omega} \) versus \( \log \) of frequency. This variation of conductivity is very well represented by the relation [24]:

\[
\sigma_{\omega}(\omega) = A_2 \omega^s
\]

Proportionality constant \( A_2 \) computed from figure 9.5 works out to be \( 2.11 \times 10^{-8}, 1.06 \times 10^{-9}, 0.63 \times 10^{-9} \) and \( 6.3 \times 10^{-9} \) for 20 mol\%, 10 mol\%, 5 mol\% and 2 mol\% samarium compositions respectively.

**9.3.3 Phase transition**

Dielectric constant shows peak at transition temperature in all samarium modified lead titanate samples. Figures 9.6 to 9.9 show variation of dielectric constant with temperature of 2, 5, 10, 20 mol\% samarium modified samples respectively. Tangent loss does not show peak in any of the compositions studied here. Figures 9.10-9.12 shows the effect of temperature on dielectric loss of various compositions of samarium modified lead titanate ceramics. Dielectric constant does not show much dependence on frequency and temperature below transition temperature but the effect of
both frequency and temperature becomes pronounced as the temperature approaches the transition temperature. If one concentrates on dielectric constant measured at single frequency of 1kHz, it is observed that the room temperature dielectric constant increases with the increase in samarium substitution (figure 9.1) while as the maximum dielectric constant ($\varepsilon'_\text{max}$ i.e., dielectric constant at transition temperature) decreases with the increase in samarium substitution. The decrease in $\varepsilon'_\text{max}$ implies that the substitution of samarium reduces dipole moment of the lattice and lowers peak dielectric constant. Figure 9.13 shows dielectric constant at 1kHz versus temperature of all compositions. The transition temperature is found to decrease with increase in samarium substitution. This decrease in transition temperature is attributed to decrease in crystal tetragonality caused by samarium substitution, which reduces the internal stress and which in turn reduces the transition temperature [25]. A linear decrease of transition temperature of 12 °C/mol of samarium addition is observed in these ceramics (figure 9.14). Linear decrease in transition temperature has been observed in lanthanum and calcium modified ceramics [18, 26, 27]. Xue et al [28] has also reported linear decrease in Curie temperature in Sm$_2$O$_3$ and (Gd$_2$O$_3$ + Nd$_2$O$_3$) modified lead titanate ceramics studied in composition range of 6-14 mol%. Width of the peak in dielectric constant versus temperature increases in compositions with higher samarium content, thereby indicating diffused phase transition. The degree of diffuseness of the transition is studied by using expression [29]:

$$\frac{1}{\varepsilon'} - \frac{1}{\varepsilon_{\text{max}}} = C(T-T_c)^\gamma$$  \hspace{1cm} (9.5)

where $\varepsilon'$ is the dielectric constant at temperature $T$ and $\varepsilon_{\text{max}}$ is the maximum dielectric constant at transition temperature $T_c$. The value of $\gamma$ is the degree of diffuseness which lies in the range of $1 < \gamma <= 2$. $\gamma = 1$ represents ideal Curie Weiss behaviour while $\gamma$ between 1 and 2 indicates diffused transition [27]. The value of $\gamma$ is measured from the slope of line $\log(1/\varepsilon') - (1/\varepsilon_{\text{max}})$ versus $\log(T-T_c)$, as drawn in figure 9.15. The value $\gamma$ is found to be 1.21, 1.25, 1.35
are 1.41 for 2 mol%, 5 mol%, 10 mol% and 20 mol% of samarium addition respectively. The value $\gamma > 1$ suggests diffused transition [30]. This diffuseness is due to the compositional fluctuations and structural disordering in the arrangement of cations in one or more crystallographic sites in the structure [31,32]. This suggests a microscopic heterogeneity in the samples with local curie points. Diffuse phase transition is also reported in calcium modified PT ceramics [27].

9.4 Ferroelectric studies

The spontaneous polarization of a ferroelectric material can be measured by hysteresis loop by using Sawyer-Tower circuit by the application of the a.c. field. Initially at smaller applied field, the dielectric displacement increases linearly, since the crystal behaves like a normal dielectric. As the field is increased, the number of domains switch to the positive side and the displacement increases rapidly. As more and more dipoles get aligned with the field, the polarization increases slowly and finally saturates. When the field is reversed the polarization decreases as the dipoles slowly reverse their direction. However, at zero field all the dipoles do not reverse their direction and the net polarization does not go to zero. This is called the remanent polarization. Presence of the remanent polarization in the hysteresis loop is a sure sign of the ferroelectricity. The negative field intercept at which polarization becomes zero is called the coercive field.

Figure 9.16 (a-d) shows the hysteresis loops of the samarium modified lead titanate ceramics recorded at room temperature. As is seen from the hysteresis loops, it is evident that the samarium substitution significantly affects the shape and size of the loop and the numerical values of the polarization and coercive field. Figure 9.17 shows the effect of samarium substitution on the numerical values of polarization and coercive field. In 2 mol% samarium containing sample, the values are very small, which suggests that there is stiffness to orientation of the domains. This may be due
to the small grain size and greater tetragonality in this composition. The value of the spontaneous polarization, remanent polarization and coercive field is found to decrease with the increase in samarium concentration in the samples with 5 to 20 mol % samarium (fig. 9.17). Spontaneous polarization is expected to decrease because the incorporation of samarium in the lattice reduces lattice tetragonality, which causes smaller unit cell displacements. Abram et al [33] reports that in displacive type ferroelectrics, the spontaneous polarization is related to the atomic displacements. Also, the spontaneous polarization is expected to decrease with increasing samarium content since crystal tetragonality decreases, which is due to smaller relative displacement of the unit cell contents as reported by Mendiola et al [34]. Decrease in the coercive field is attributed to the decreasing tetragonality and increasing grain size both of which facilitate the orientation of the domains. Decrease in the coercive field and the remanent polarization with decreasing c/a ratio is reported in lanthanum modified lead titanate ceramics [26]. Decrease in the coercive field with the increase in lanthanum concentration is also reported in lanthanum modified ceramics and thin films [26,35].

9.5 Piezoelectric coefficients

Piezoelectric longitudinal charge coefficient \( d_{33} \) shows dependence on the samarium substitution and poling field as is suggested by figure 9.18. Non-linear increase in \( d_{33} \) is observed with increase in samarium substitution. Piezoelectric voltage coefficient \( g_{33} \) is calculated by using the following expression [36]:

\[
g_{33} = \frac{(d_{33})}{(\varepsilon_0c^2)} \quad \text{.........} \quad (9.6)
\]

Increase in \( d_{33} \) in Sm-doped ceramics has been reported by Xue et al [28] which is consistent with observations reported here. However, magnitude of \( d_{33} \) is slightly less in the samples considered here which may be due to difference in B-site dopants and lower poling field used here. Almost similar values of \( d_{33} \) are reported in \( \text{PbO}_{0.88}\text{SmO}_{0.8}(\text{TiO}_{0.99}\text{MnO}_{0.02})\text{O}_3 \) by Duran et al [16].
Generally, very high values of $d_{33}$ are found in calcium modified lead titanate ceramics. Frutos and Jiminez [37] has reported saturated $d_{33}$ value of $110 \text{pC/N}$ in calcium modified lead titanate ceramics. They have attributed this increase in $d_{33}$ to the increased $180^\circ$ domain reversal with increase in calcium concentration. Frutos et al [38] have reiterated their result with the addition that the contribution due to stress caused by the poling field has to be taken into account. Since, in the $180^\circ$ domain orientation is facilitated by the decreasing crystal tetragonality so, the piezoelectric charge coefficients arising due to $180^\circ$ domain polarization seems to be reasonable to explain our results.

9.6 Conclusion

Dielectric constant at room temperature increases with increase in samarium substitution. Decrease in conductivity with increase in frequency is attributed to hopping of charge carriers with random distribution of hopping wells. Phase transition is observed in all samples. Transition temperature decreases @12 $^\circ$C/mol% with increase in samarium concentration which is due to decrease in internal stress in compositions containing higher samarium concentration. Nature of phase transition is diffused with degree of diffuseness ($\gamma$) equal to 1.21, 1.25, 1.35 and 1.41 for samples containing 2, 5, 10 and 20 mol % of samarium respectively. This suggests a microscopic heterogeneity in the samples with local curie points. Spontaneous polarization, remanent polarization and the coercive field decreases in the samples with the samarium concentration of 5 to 20 mol%. Non-linear increase in $d_{33}$/$g_{33}$ with increase in samarium concentration is observed.
References

Fig. 9.1 Grain size and room temperature dielectric constant Vs samarium substitution.
Fig. 9.2 Dielectric constant at room temperature Vs frequency.
Fig. 9.3 Dielectric loss at room temperature vs frequency.
Fig. 9.4 Log($\varepsilon'(\omega) - \varepsilon_\infty$) Vs Log frequency.
Fig. 9.5 Log of conductivity Vs log of frequency.
Fig. 9.6 Dielectric constant Vs temperature for 2 mol % Sm substituted composition.
Fig. 9.7 Dielectric constant vs. temperature for 5 mol % Sm substituted composition.
Fig. 9.8 Dielectric constant Vs temperature for 10 mol % Sm substituted composition.
Fig. 9.9 Dielectric constant Vs temperature for 20 mol % Sm substituted composition.
Fig. 9.10 Dielectric loss Vs temperature for 5 mol % Sm substituted composition.
Fig. 9.11 Dielectric loss Vs temperature for 10 mol % Sm substituted composition.
Fig. 9.12 Dielectric loss Vs temperature for 20 mol % Sm substituted composition.
Fig. 9.13 Dielectric constant measured at 1kHz. Vs temperature.
Fig. 9.14 Effect of samarium substitution on transition temperature.
Fig. 9.15 Log\{\frac{1}{\epsilon'}-\frac{1}{\epsilon_{\text{max}}}\} Vs Log (T-T_c)
Fig. 9.16 Continued on next page
Fig. 9.16 P-E loops of samarium modified lead titanate ceramics recorded at room temperature a) 20 mol% Sm, b) 10 mol% Sm, c) 5 mol% Sm and d) 2 mol% Sm.
Fig. 9.17 Effect of samarium substitution on polarization and coercive field.
Fig. 9.18 $d_{33}$ and $g_{33}$ Vs samarium substitution.