CHAPTER -11

SUMMARY OF THE RESULTS AND COMPARATIVE STUDY OF LANTHANUM AND SAMARIUM MODIFIED LEAD TITANATE CERAMICS.
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11.1 Summary of results of lanthanum modified lead titanate ceramics.

11.1.1 Preparation.

Lead titanate ceramics modified with lanthanum, molybdenum and iron bearing molecular formula \( \text{Pb}_{1-x}\text{La}_x\text{Ti}_{1-y}\text{Mo}_y\text{Fe}_y\text{O}_3 \) where \( x = 0.02, 0.05, 0.10, 0.15 \) and \( 0.20 \) and \( y = 0.02 \) were prepared by solid state reaction technique. Oxides of \( \text{Pb}, \text{La}, \text{Ti}, \text{Mo} \) and \( \text{Fe} \) were weighed accurately according to the above mentioned molecular formula, with 2-3\% additional \( \text{PbO} \), and mixed by ball milling for 48 hours in aqueous medium. The mixed powder was calcined at 900 °C for 2 hours and subsequently grounded to remove the hard aggregates formed during calcination. The free flowing powder so formed was granulated and pressed into pallets of 1-2 mm thickness and 15 mm diameter and sintered at 1200 °C in lead rich atmosphere.

Examination of X-ray diffraction patterns of the above said lanthanum modified lead titanate ceramics was carried out which confirms the formation of single phase in all compositions. Lattice parameters ‘a’, ‘c’ and lattice tetragonality ‘c/a’ show dependence on the amount of lanthanum substitution. There is sharp decrease in ‘c’ and gradual increase in ‘a’ and almost linear decrease in ‘c/a’ with the increase in lanthanum substitution. X-ray density
decreases with the increase in lanthanum substitution which is reasonable because lanthanum atom replacing lead atom is lighter than lead. Experimental density is observed to increase from 92% to 97% of the X-ray density with the increase in lanthanum content. Grain size is also influenced by the lanthanum substitution; the grain size showing increase from 1 to 2.8 micrometer when lanthanum content is changed from 2 to 20 mol%.

11.1.2 Dielectric, ferroelectric and piezoelectric characteristics.

Dielectric dispersion was observed in all the samples and the magnitude of dispersion was about 10-15%. Dielectric constant of poled ceramics was found to decrease with poling which is attributed to increase in 90° domain switching due to poling treatment. Room temperature dielectric constant increases with the increase in lanthanum substitution. The dielectric constant shows peak at transition temperature in all the samples while the dielectric loss does not show any peak. The peak dielectric constant i.e., dielectric constant measured at transition temperature is found to decrease with the increase in lanthanum substitution. The width of peak at transition temperature is found to increase with the increase in lanthanum substitution, indicating the diffused nature of the phase transition. The diffuseness factor ($\gamma$) works out to be 1.34, 1.39, 1.45 and 1.68 for 2 mol%, 5 mol%, 15 mol% and 20 mol% respectively for these La modified PT ceramics. The phase transition is supposed to be diffused if $1<\gamma\leq 2$. Transition temperature is found to decrease @ 14 °C/mol% with the increase in lanthanum substitution. Spontaneous and remanent polarizations remain suppressed in low lanthanum containing samples. However, polarization increases sharply in samples containing greater than 5 mol % of lanthanum and shows peak in 15 mol % lanthanum containing samples. Coercive field decreases continuously with the increase in lanthanum content and is attributed to increase in domain rotation and orientation facilitated by the decreasing tetragonality and increasing grain size.
Electromechanical thickness coupling factor ($k_1$) shows significant compositional dependence. It is found to increase from 0.16 for 2 mol% to 0.61 for 15 mol % composition, but thereafter it decreases. Electromechanical planar coupling factor ($k_p$) does not show much compositional dependence and remains almost constant around 0.11. Non observance of zero $k_p$ is attributed to coarse grain and compositional effects on electrostrictive coefficients. Piezoelectric longitudinal charge coefficient ($d_{33}$) increases from 39 pC/N to 88 pC/N when lanthanum content is changed from 2 to 15 mol %. The decreasing trend in $d_{33}$ is observed when the lanthanum content is increased beyond 15 mol%. The transverse piezoelectric charge coefficient ($d_{31}$) remains almost constant at -11 pC/N irrespective of lanthanum content. The hydrostatic charge ($d_{h}$) and voltage ($g_{hi}$) coefficients also show peak in 15 mol % lanthanum containing sample.

11.1.3 Microhardness

Microhardness decreases with the increase in load in the load range of 0.1 to 0.8 N and tends to attain saturation at loads greater than 0.8 N. The decrease in microhardness with the increase in load is explained on the basis of Newtonian resultant pressure as proposed by Hays and Kendall's law ($P-W = K_2 d^2$). The load independent value of microhardness worked out on application of Hays and Kendall's law is consistent with the saturated value of the microhardness in every sample. The load independent value of the microhardness increases linearly from 1481 MN/m$^2$ to 4176 MN/m$^2$ when the lanthanum content is increased from 2 to 20 mol%. Well defined and measurable cracks are observed to originate from the corners of the indentation impression at a load of 1 N and above. Crack length is found to increase with the increase in load. However, crack length at a given load decreases with the increase in lanthanum concentration. Fracture toughness is found to increase with load in the low load region with a tendency to attain saturation at higher loads. Magnitude of fracture toughness at a given load increases with increase in lanthanum substitution. The brittleness index is
observed to be high in the low-load region which decreases rapidly with increase in load in the case of 2 mol% lanthanum modified sample. However, small decrease in $B_r$ in low load region with tendency to achieve saturation at higher loads is observed in the case of 20 mol% lanthanum modified composition. The internal stress measured by the microindentation technique decreases with increase in lanthanum substitution. This is due to the fact that the increase in lanthanum substitution decreases lattice tetragonality which in turn decreases the internal stress developed during para-to-ferroelectric phase transition.

11.2 Summary of results of samarium modified lead titanate ceramics.

11.2.1 Preparation.

Samarium modified lead titanate ceramics bearing composition $\text{Pb}_{1-x}\text{Sm}_x\text{Ti}_9\text{Fe}_{0.02}\text{W}_{0.02}\text{O}_3$ with $x=0.02, 0.05, 0.10, 0.20$ were prepared by solid state reaction method. Oxides of lead, samarium, titanium, iron and tungsten were weighed according to the above said molecular formula and mixed using ball milling method. The mixed powder was calcined at 900°C for two hours. The calcined powder was pressed into pallets of 1-2 mm thickness and 15 mm diameter and sintered at 1250°C for three hours. The samples were sintered at 1250°C for 3 hours in lead rich atmosphere to reduce the loss of lead. X-ray diffraction studies confirm formation of single phase in all sintered compositions. Lattice constants ‘a’ and ‘c’ calculated from X-ray diffraction studies show almost no change in the former but a significant decrease in the latter with the increase in samarium substitution. The decrease in ‘c’ indicates that the unit cell gets compressed along the c-axis with increase in samarium substitution. Lattice tetragonality ($c/a$) is found to decrease with the increase in samarium substitution. Theoretical density of the samarium modified lead titanate ceramics decreases with the increase in samarium substitution which could be due to the fact that the samarium atom replacing the lead atom is lighter than lead atom. Experimental density
increases with the increase in samarium substitution. It is due to the fact that the samarium substitution reduces lattice tetragonality which reduces the internal stress \( T_s \propto c/a-1 \) and thereby facilitates formation of denser microstructure and reduced porosity. Grain size also increases from 0.2 to 1.5 micrometer when the samarium substitution is increased from 2 to 20 mol %.

11.2.2 Dielectric, ferroelectric and piezoelectric characteristics.

Dielectric constant at room temperature increases with increase in samarium substitution. This increase in dielectric constant is attributed to decrease lattice tetragonality with increase in samarium substitution which increases the polarization and hence the dielectric constant. Dielectric dispersion of 10-15% is observed in all the compositions of samarium modified lead titanate ceramics. This dielectric dispersion is well expressed by Kramer's Kronig relation \( \varepsilon'(\omega) - \varepsilon_\infty = A_1\omega^{-1} \). Dispersion due to space charge is unlikely because the room temperature resistivity of the samples is very high, so the most probable reason seems to be the hopping of charge carries with random distribution of hopping distances and potential wells. Conductivity at room temperature shows frequency dependence and is well represented by the relation \( \sigma_{ac}(\omega) = A_2\omega^\gamma \). Phase transition is observed in all samples. Transition temperature decreases @12 °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 samarium concentration of 5 to 20 mol%. Non-linear increase in \( d_{33} / g_{33} \) with increase in samarium concentration is observed.
11.2.3 Microhardness.

The microhardness decreases nonlinearly in the load range $0.1 - 0.8$ N and attains saturation thereafter up to the maximum applied load of $10$ N. Decrease in microhardness in the load range $0.1 - 0.8$ N is explained on the basis of Hay's and Kendall's law. The load-independent value of microhardness as calculated on application of Hay's and Kendall's law is consistent with the saturated microhardness value as seen at loads greater than $0.8$ N. Well defined and measurable cracks were seen at loads of $1$ N and above up to the maximum applied load of $10$ N. The crack length increases with the increase in load more rapidly in samples with a low Sm content compared to that of the samples with a high Sm content. In low Sm-substituted ceramics, the brittleness index is observed to be high in the low-load region which decreases rapidly with load and attains almost a saturation value at higher applied loads. However, brittleness index is found to be almost load independent in case of $20$ mol% Sm-substituted ceramics. The internal stress measured by the microindentation technique decreases with decrease in crystal tetragonality (c/a).

11.3 Comparative study of lanthanum and samarium modified lead titanate ceramics.

Lanthanum modified lead titanate ceramics bearing composition $\text{Pb}_{1-x}\text{La}_x\text{Ti}_{1.2}\text{Mo}_y\text{Fe}_7\text{O}_{3}$ where $x = 0.02, 0.05, 0.1, 0.15$ and $0.20$ and $y = 0.02$ and samarium modified lead titanate ceramics bearing composition $\text{Pb}_{1-x}\text{Sm}_x\text{Ti}_{1.2}\text{W}_y\text{Fe}_7\text{O}_{3}$ where $x = 0.02, 0.05, 0.1$ and $0.20$ and $y = 0.02$ were mixed, calcined and shaped under similar conditions. However, best sintering conditions for La-modified ceramics was found to be $1200$ °C for two hours whereas for Sm-modified ceramics it was found to be $1250$ °C for three hours. Bulk density was found to increase with the increase in substitution in both samarium and lanthanum modified ceramics considered in the present work. Maximum density attained was $97\%$ and $96\%$ of the theoretical density in...
lanthanum and samarium modified ceramics respectively. Lattice constant 'a',
'c' and lattice tetragonality 'c/a' is affected by the substitution of both
lanthanum as well as samarium. Lattice tetragonality and lattice constant 'c'
decrease with increase in substitution in both the compositions. This
indicates that with increase in substitution (La or Sm), the unit cell contracts
along the C-axis. The grain size increases from 1 to 2.8 µm in case La-
modified ceramics and 0.25 to 1.5 µm in case of Sm-modified ceramics when
the amount of substitution is increased from 2 to 20 mol%. Dielectric
dispersion of 10-15% was observed in both samarium and lanthanum
modified ceramics. Room temperature dielectric constant measured at 1 kHz
increases from 243 to 437 and 257 to 397 in case of lanthanum and
samarium modified lead titanate ceramics respectively. In 20 mol% La
composition dielectric constant is 437 and in case of 20 mol% Sm it is 397.
Higher dielectric constant of 437 in case of 20 mol % La modified composition
in comparison to only 397 for 20 mol % Sm composition may be due to lower
c/a ratio of the former with respect to latter.

From the study of dependence of dielectric constant on temperature,
phase transition is observed in all compositions of both La and Sm modified
lead titanate ceramics. Transition temperature is found to decrease with the
increase in substitution. Transition temperature decreases at the rate of 14
°C/mol% and 12 °C/mol% substitution of La and Sm-modified lead titanate
ceramics respectively. The dielectric constant attains peak at the transition
temperature and the peak dielectric constant decreases with the increase in
substitution. In La-modified lead titanate ceramics the peak dielectric
constant at 2 and 20 mol % is 18861 and 2001 respectively while as in 2 and
20 mol% Sm-modified ceramics the peak dielectric constant is 7269 and 2232
respectively. The width of the peak at the transition temperature, both for La
and Sm-modified lead titanate ceramics, increases with the increase in
frequency of measurement. The effect of frequency of the applied a.c. field
becomes more pronounced in samples containing higher La or Sm content.
The phase transition in both La and Sm - modified ceramics considered here is diffused. The degree of diffuseness (γ) worked out for La-modified lead titanate ceramics is 1.34, 1.39, 1.45 and 1.68 for 2 mol%, 5 mol%, 15 mol% and 20 mol% La containing samples respectively while as the same for Sm-modified ceramics is 1.21, 1.25, 1.35 and 1.41 for 2, 5, 10 and 20 mol % Sm containing samples respectively. This indicates that the phase transition is diffused in both La and Sm-modified lead titanate ceramics considered here; however it is more diffused in case of La-modified ceramics compared to Sm-modified ceramics.

Spontaneous and remnant polarization is significantly low in low La or Sm containing compositions, implying that there is stiff opposition to orientation and rotation of domains. Spontaneous and remnant polarization attain peak in 15 mol % La-modified lead titanate ceramics considered here, while as there is a non-linear decrease in spontaneous and remnant polarization in Sm-modified ceramics when the samarium substitution is ≥ 5 mol%. Coercive field decreases with the increase in substitution, both in case of La and Sm - modified ceramics. Its value decrease from 66 to 7.7 kV/cm in case of La-modified lead titanate ceramics and 48 to 9 kV/cm in case of Sm-modified lead titanate ceramics when the quantum of substitution is changed from 2 to 20 mol%.

Electromechanical thickness coupling factor (k_t) shows dependence on lanthanum substitution in La-modified lead titanate ceramics and maximum value of 0.61 is attained in case of 15 mol% La composition. Electromechanical planar coupling factor (k_p) remains almost constant around 0.11 irrespective of the amount of lanthanum substitution. Piezoelectric constant d_{33} increases from 39 pC/N for 2 mol% La composition and reaches to a maximum of 88pC/N for 15 mol% La composition, while as d_{31} remains almost constant around -11pC/N. Non-linear increase of d_{33} from 14 to 56 pC/N when poled at 20 kV/cm and 16 to 69 pC/N when poled at 30kV/cm was
observed in Sm-modified lead titanate ceramics with samarium substitution changed from 2 to 20 mol%. However, in case of La-modified lead titanate ceramics, $d_{33}$ increases from 39pC/N for 2 mol% La composition, attains maximum value of 88pC/N for 15 mol% La composition thereafter it decreases to 74 pC/N for 20 mol % La composition.

Microhardness studies, using Vicker's microindentation technique, show non-linear decrease in microhardness with the increase in load in low load region (0.1 - 0.8N) with tendency to attain saturation at loads beyond 0.8N in both La and Sm-modified ceramics considered here. The decrease in microhardness in the low load region is explained on the basis of Hays and Kendall's law of Newtonian resultant pressure. Load independent value of microhardness obtained on application of Hays and Kendall's Law increases from 1481 to 4176 MN/M$^2$ in La-modified lead titanate ceramics, while as the same increases from 1858 to 3143 MN/M$^2$ in case of Sm-modified lead titanate ceramics when the lanthanum or samarium substitution is increased from 2 to 20 mol%. While as, the increase is linear in case of La-modified ceramics, it is non-linear in the case of Sm-modified lead titanate ceramics. The microhardness becomes almost independent of load at loads greater than 0.8 N up to the maximum applied load of 10 N. This saturated value of microhardness is consistent with the load independent value of microhardness obtained using Hay's and Kendall's Law in both La and Sm-modified ceramics considered here. Well-defined and measurable cracks were seen associated with the indentation impressions of 1N and above. Crack length in both La and Sm-modified lead titanate ceramics increases with the increase in load but at a given load the crack length decreases with the increase in substitution of Sm or La. The crack length, corresponding to any given load considered here, at a given substitution level for the same load is higher in La-modified lead titanate ceramics compared to that of Sm-modified lead titanate ceramics. This indicates that the La-modified ceramics are more brittle as compared to Sm-modified lead titanate ceramics. Fracture
toughness shows similar behaviour in both ceramic series studied here. Nonlinear decrease in internal stress evaluated using microindentation technique is observed in both La and Sm-modified lead titanate ceramics studied here.

Summing up the distinctive features exhibited by La and Sm substituted lead titanate ceramics, one may outline the same as follows:

1. Best sintering condition for La-modified ceramics was found to be 1200 °C for two hours whereas for Sm-modified ceramics it was found to be 1250 °C for three hours.

2. While the grain size increases from 1 to 2.8 μm in case of La-modified ceramics, it increases from 0.25 to 1.5 μm in case of Sm-modified ceramics when the amount of substitution is increased from 2 to 20 mol%.

3. Room temperature dielectric constant measured at 1 kHz increases from 243 to 437 while as it increases from 257 to 397 in case of lanthanum and samarium modified lead titanate ceramics respectively when the substitution level is increased from 2 to 20 mol%.

4. Transition temperature decreases at the rate of 14 °C/mol% in the case La-modified lead titanate ceramics. However, the transition temperature decreases at the rate of 12 °C/mol% for Sm-modified lead titanate ceramics.

5. Phase transition is diffused in both La and Sm-modified lead titanate ceramics considered here. However, the degree of diffuseness (γ) for La-modified lead titanate ceramics is 1.34, 1.39, 1.45 and 1.68 for 2 mol%, 5 mol%, 15 mol% and 20 mol% La containing samples respectively while as γ for Sm-modified ceramics is 1.21, 1.25, 1.35 and 1.41 for 2, 5, 10 and 20 mol% Sm containing samples respectively. Indicating that the phase transition is more diffused in case of La-modified ceramics.
6. Non-linear increase of $d_{33}$ from 16 to 69 pC/N, on increase of Sm substitution from 2 to 20 mol%, when poled at 30kV/cm was observed in Sm-modified lead titanate ceramics. However, in case of La-modified lead titanate ceramics $d_{33}$ increases from 39pC/N for 2 mol% La composition, attains maximum value of 88pC/N for 15 mol% La composition and thereafter it decreases to 74 pC/N for 20 mol% La composition. In this respect, La and Sm modified lead titanate ceramics exhibit different behaviour.

7. Load independent value of microhardness obtained on application of Hays and Kendall's Law increases from 1481 to 4176 MN/M$^2$ in La-modified lead titanate ceramics, while as the same increases from 1858 to 3143 MN/M$^2$ in case of Sm-modified lead titanate ceramics when the lanthanum or samarium substitution is increased from 2 to 20 mol%. However, the increase is linear in case of La-modified ceramics and non-linear in the case of Sm-modified lead titanate ceramics.