ABSTRACT

A considerable amount of work, in the last few decades, has been carried out to substitute polycrystalline materials in place of single crystals for device applications. Of them, the crystallites in the perovskite structure of ABO_3-type (A = mono- or divalent ions and B = tri- to hexavalent ions) are quite prominent. The lead zirconate-titanate (PZT), a solid solution of ferroelectric $PbTiO_3$ ($T_C = 490^0C$) and anti-ferroelectric $PbZrO_3$ ($T_C = 230^0C$) belonging to this type, has been found to be one of the excellent materials in the area of electro- and optoceramics and particularly so the La-doped PZT (PLZT). The characteristics of these ceramics have been known to be very sensitive to the method of synthesis, mixing the raw materials, calcination time and temperature, sintering temperature and method, etc. Till 1971, PLZT was considered as just an opaque ferroelectric material. But the fact that the compound with the same composition turned out to be a good optical ceramic, just by adopting the hot pelletisation instead of the conventional cold and dry pelletisation technique, should serve as a classic example to illustrate how the above said factors do affect the properties of ceramics. The quality of PZT ceramics prepared by different chemical methods are also found to be quite superior compared to that of the PZT prepared by solid-state reaction techniques. Sol-gel process has been one such process known for maintaining purity and homogeneity during the formation of compounds. In certain ferroelectric materials, high dielectric constant has been obtained with proper densification. Sintering has been known to be one of the important criteria to achieve high densification. Further, focusing on the PZT/PLZT, its selection for variety of applications depends on Zr/Ti ratio and the La concentration. In view of the above, in the first part of the present study, an attempt has been made to characterise PLZT(x/65/35) prepared through sol-gel route and sintering the pellets at different temperatures.

Further, it has also been known that, like any other ferroelectric ceramics, the properties of PLZT could very well be altered by the substitution of another dopant either at A- or B-site. In the second part of the current work, the effect of paired dopants (9% La +D, D = alkali ions viz., Li, Na, K) on PZT with Zr/Ti ratio 65/35 [PLZT (9/65/35)] (which figures near the morphotropic phase boundary) has been studied. It may be mentioned here that the observations made in this part of the investigation shall serve as a reference material for further investigations, as the effect of the alkali dopants in PLZT (9/65/35) on various structural and electrical properties does not find a place in the literature. The following are the important studies carried out in the present work on both singly and doubly doped PZT ceramics:

The complex compounds were prepared through sol-gel technique, precisely known as Pechini method. The compounds were sintered at different temperatures in PbO environment. The shrinkage and porosity fractions of the compounds were evaluated. The actual densities of the compounds were determined.

Preliminary structural studies were carried out, on the compounds at room temperature using X-ray diffraction technique over a wide range of Bragg angle 2θ. The reflection peaks were indexed and lattice parameters were determined from the observed d-values. The particle size and the theoretical density were calculated from the X-ray results.

The dielectric parameters (dielectric constant and loss tangent) of the compounds as a function of frequency at room temperature and as a function of temperature at 10 kHz frequency were measured using GR 1620-AP capacitance measuring assembly. Diffusivity parameters of all the compounds were estimated. From the dielectric parameters, the ac conductivity and the activation energy of the compound were derived. Using KEITHLEY 617 programmable electrometer was used to measure the dc resistivity as a function of applied field at room temperature and as a function of temperature with a constant electric field. The effects of sintering on all the above dielectric

parameters were examined. The piezoelectric strain coefficients were measured for all the samples sintered at on particular temperature using Berlincourt piezometer.

X-ray studies revealed that the majority of the compounds belong to the rhombohedral and a few of them belong to cubic crystal systems. It was observed that the dielectric parameters were strongly dependent on La concentration as well as the alkali concentration. The transition temperature was found to increase with the increase of the concentration of the second dopant. For majority of the compounds, the degree of diffuseness was found nearer to 2 that indicated the phase transition was of second-order. The resistivity of the compounds was in the order of 10^9 Ω-cm. The alkali dopants affected the piezoelectric strain coefficients considerably.