ABSTRACT

Lead zirconate titanate ceramics are of interest, because they have spontaneous polarization and a high Curie temperatures. The complex $Pb(ZrTi)O_3$ compound (generally referred to as PZT) is fabricated from the perovskite ferroelectric $PbTiO_3$ (T_c = 490°C) and anti-ferroelectric $PbZrO_3$ (T_c = 230°C). It crystallizes in the perovskite structure of ABO_3-type in which A-sites are occupied by the Pb^{+2} ions while Zr^{+4} and Ti^{+4} ions are accommodated at the B-sites. PZT has been found to be very important and interesting ferroelectrics particularly for electro-ceramic applications. It has also been found that the homogeneous lead lanthanum zirconate titanate (PLZT) powders synthesized by sol-gel technique near the morphotropic phase boundary (MPB) have very interesting and promising piezoelectric and pyroelectric properties for device fabrications.

A considerable amount of efforts have been done on modified PZT, based on various synthesis techniques and various substitutes in the A-site and B-site of the PZT unit cell, leading to considerable changes in their electrical and mechanical properties, so as to make them suitable for industrial applications such as transducer, computer memory and display, light valves, electro-optical modulators, sensors etc. A large number of charge neutral or deficient compounds have been prepared by generating vacancies with suitable substitution (e.g. supervalent or subvalent) in A-site or B-site or in the oxygen lattice. These modifications could be done by addition of small quantities of the tri or pentavalent oxides (e.g. lanthanum, neodynium, tantalum or niobium).

As not much work on the effect of double doping with different La, alkali or Bi ions at Pb site have been done so far, we therefore, have considered important to prepare high purity, chemically homogeneous PZT powders with pairs of dopants partially substituting Pb in their crystal structure by sol-gel method and to study their structural, electrical, pyroelectric and piezoelectric properties, for device applications.

The following polycrystalline materials were synthesized for our present investigation :

Group A : $Pb_{1-x}La_x(Zr_yTi_{1-y})_{1-x/4}O_3$

where x = 0.07 , 0.08 , 0.09 , 0.10 ; y = 0.53

Group B : $Pb_{1-x}(La_{1-z/3}D_z)_x(Zr_yTi_{1-y})_{1-x/4}O_3$

where x = 0.10 , y = 0.53 , z = 0.0, 0.1, 0.3, 0.5, 0.7

D = Na , K , Li , Cs , Tl .

Group C : $Pb_{1-x}(La_{1-z}Bi_z)_x(Zr_yTi_{1-y})_{1-x/4}O_3$

where x = 0.10 , y = 0.53 , z = 0.0, 0.1, 0.3, 0.5, 0.7

The present thesis is mainly concerned with synthesis, testing and studies of structural electrical, pyroelectric and piezoelectric properties of the proposed compounds.

we have made use of Pechini method for the synthesis of pure as well as modified PLZT powders. The room temperature structural study of pure and modified PLZT compounds have been under taken using powder diffraction technique with CuKα radiation (λ = 0.15418 nm) in a wide range of Bragg angle. The X-ray diffraction patterns suggest that there is no change in the basic crystal structure of PZT on single doping (La^{3+}) or double doping (La^{3+} and alkali ions (e.g. Na^+, K^+, Li^+, Cs^+, Tl^+)or Bi^{3+}) with different concentrations. The preliminary structural analysis indicates that all the above pure and modified PLZT compounds have a tetragonal perovskite-type structure.

Study of the electrical properties (dielectric constant, loss, ac conductivity, and dc resistivity) of the compounds have provided an interesting information about the ferroelectric/paraelectric phase transition. Based on dielectric measurements, it has been found that doping elements play an important role on diffuse phase transition and majority of the doped samples show extremely diffuse phase transition (DPT) and relaxation behavior The values of γ calculated for the samples, ranging from 1 (normal Curie-Weiss behavior) to 2 (completely disordered). The values of activation energy for the samples in the temperature range 100-250°C were found to be very low. The nature of variation of specific resistivity with temperature of the PZT compounds containing various amount of single (La) or pair of dopants (La, alkali ions) was found to be very similar except in the low temperature

region. At low temperature changes in specific resistivity of PLZT compounds with doping concentration were observed. The pyroelectric coefficient for the pure and alkali ions modified PLZT ceramic samples was measured. The combination of large pyroelectric coefficients with relatively high Curie temperatures should make these materials attractive for pyroelectric detector applications. The piezoelectric parameters (coupling coefficient, frequency constant, mechanical quality factor and figure of merit) of the compounds at room temperature are also influenced by double doping. Since the mechanical quality factor, has come down below 100 in most of the compositions, these ceramics are suitable for use in phonograph pickup elements.