Abstract

Because of their potentially low cost and greater durability under adverse atmospheric conditions lead zirconate-titanate (PZT) ceramics have come into prominence during the last couple of the years. Present market trends continue to show that the future of ferroelectrics ceramics is bright and continue to get even brighter as the transition is made from passive to electrically active smart materials. Undoubtably, La modified PZT (PLZT) are destined to be leading candidates in this arena due to its potential applications in the areas of high dielectric constant capacitors, infrared pyroelectric detectors, piezoelectric sensors, actuators, etc. Modification of the PZT system by the addition of lanthanum has a marked effect on several physical properties of the material.

It is found that the properties of PZT are very sensitive to its compositional fluctuations near the morphotropical phase boundary (MPB), particle size, doping, calcinations and sintering temperature. Depending upon the specific requirements a large number of charge neutral and charge deficient compounds have been prepared in the past with suitable substitutions (namely, supervalent or subvalent) at different sites of PZT or in the oxygen lattice. Doping enables us to tailor material properties. It can drastically change the device parameters. PLZT itself is a doped material, combines a multitude of improved properties which makes the material smart and intelligent over a wide variety of applications from high dielectric capacitors, tranducers to sensors acuators, - MEMS to IC. This was the driving force to study a complex PZT system so that desirable changes can be achieved as per our requirements.

Through a large amount of work has been carried out in the past on the modified PLZT with its various Zr/Ti ratios, the effect of trivalent ions (Bi, Sb, Al, Ga, Fe) substitution at the Pb/La-site of PLZT has not been studied so far. It is, therefore, considered important to prepare high-purity, homogenous trivalent ions (partially substituted at the Pb/La-site in the structure) modified PLZT (8% La) powders with Zr/Ti = 65/35, 60/40 by sol-gel/ solid-state method and to study their effect on the structural, electrical, piezo-and pyroelectric properties.

The following polycrystalline materials have been synthesized by chemical (sol-gel) and mechanical solid-state methods for the present investigations:

- La- modified PZT (PLZT), with general formula:

  $Pb_{1-x}La_x(Zr_yTi_{1-y})_{1-x/4}O_3$ where x = 0.08 and y = 0.65 and 0.60

- Trivalent ions-modified PLZT (PLDZT) with general formula:

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

where D = Bi (Bismuth), Fe (Iron), Sb (Antimony), Ga (Gallium), Al (Aluminium);

x = 0.08,y = 0.65 and 0.60, z = 0.0, 0.3, 0.6, 0.9 and 1.0

Though it is well known that sol-gel technique provides better homogeneity and enhances material properties, it is cost effective and the reaction process is very sensitive to moisture. So the attempt has been made to optimize the conditions of solid-state technique (multiple grinding steps for about three hours through dry and wet medium,

double calcination process and finally sintering) by which the material properties can be achieved comparable to the sol-gel derived one.
The structural and microstuctural properties of the above compounds have been investigated using XRD, SEM, TEM and SAED. The room temperature XRD patterns of the compounds have been recorded using X-ray powder diffractometer over a wide range of Bragg angles with CuK_α and CoK_α radiation (λ = 1.5418 A^o and 1.7902 Å).
The microstructures of the samples have been analysed by TEM and SEM. The d_{hkl} observed from SAED and XRD are very much comparable, which confirms the presence of crystalline phase in the materials. It is also observed from TEM that most of the particles of the ceramic powders are spherical. The particles are well dispersed and the average particle size is about ~15-30 nm.
The polycrystalline grains are distributed almost uniformly and homogeneously throughout the sintered sample surface as observed from the SEM micrographs. Also, the clear grains of average size 2-5μm are observed which are separated from each other by a distinct boundary.
The temperature and frequency dependent dielectric properties of the above compounds have been studied. The dielectric parameters- ε (dielectric constant) and tanδ (tangent loss) of the compounds have been measured using a HIOKI LCR 3532 hitester with a two terminal sample holder. The permittivity increases gradually to a maximum (ε_{max}) value with the increase of temperature up to transition temperature (T_c) and then it decreases for all the pure and trivalent modified PLZT compounds. The shift in transition temperature is observed on increasing doping concentration. It is difficult to generalize the variation of the maximum dielectric peak values for the modified samples. The value of dielectric constant at T_c is found to be depended on the type of the trivalent dopant (D) and their concentration. Maximum dielectric constant (~18,000) achieved with Bi doping for both 65:35 and 60:40 Zr/Ti ratios. With Al doping for Zr/Ti = 65/35 almost the same value of dielectric constant is noted as in the case of Bi doping. But in the case of other modifiers (Sb, Fe, Ga), PLZT gives very low dielectric constant. The dielectric constants of the 65/35 series are observed to be fairly high compared to those of the 60/40 series for all the modifiers. The tanδ value of the samples is found to reach a maximum value before attaining a constant value. Similar temperature dependent variation of tanδ is also found by others.
A concentration dependent broadening of dielectric peaks have been observed for all the samples indicating the important characteristic of a disorder perovskite structure with diffuse phase transition. From the various experiments, it is found that a diffuse phase transition occurs in all such cases where compositional fluctuations and/or substitutional disordering in the arrangement of cations in one or more crystallographic sites of the structure are created. This leads to microscopic heterogeneity in the compounds, and it can be distributed at different local Curie point. The values of diffusivity (γ), calculated for all the samples are found to be between 1 and 2 that confirms the diffuse phase transition in the materials. The results confirm that the doping concentration controls the diffuseness of the phase transition. The broadening of the dielectric peak and decrease in ε_{max} can also be attributed to the variation of grain size.
The room temperature hysteresis loop of the modified samples has been taken up to confirm the presence of ferroelectricity in them. The room temperature value of P_r and E_c

of the samples are recorded using the modified Sawyer and Tower circuit. The square shape (memory type) of the hysteresis loop of PLZT changes with increasing of trivalent ion concentration. It is observed that double doping at the A-site of PZT has greatly influenced the shape of the loop, values of P_r and E_c

Piezoelectric strain coefficient d_{33} was measured at room temperature using Piezo Meter (PM35 M/S Take-Control, UK) at frequency 100 Hz and 1 Newton pressure. The sensing and actuation property of the samples has been tested using a piezo sensing system by giving a mechanical vibration to the samples with its intimate bonding to the carbon composite cantilever beam. It is observed that the doping influences the piezoelectric parameters and a most described output for the sensor applications is also preferred from the modified samples.

Since PLZT is that kind of material in which a better piezo property is instigated along with a enhance pyroelectric property. This has influenced/interested us to perform the pyroelectric measurements on the poled samples using a laboratory-fabricated experimental set-up based on Byer and Roundy technique. The phase transition temperatures obtained for the compounds from these pyroelectric measurements are very closed to that obtained from the dielectric studies. This confirms the correctness of our experimental results as well as the reproducibility of the experimental data. It is found that PLZT has a relatively high pyroelectric coefficient with Zr/Ti = 60/40. The high value of P^T with this ratio is also observed for Bi and Ga doping while with other substituents (Fe, Sb, Al) it gives diverse results (i.e., lower P^T value with Zr/Ti = 60/40 and higher with 65/35).

Impedance study is the only measurement, which provides convincing information/evidence on microstructure as well as electrical properties without any ambiguity. The change in microstructure really affects the system properties. This has been confirmed by the complex impedance study (CIS). Using this (CIS) method of study the complex impedance, complex modulus, complex permittivity, d.c and a.c conductivity of all the samples has been estimated. The presence of grain boundary resistance of the system is an evident from the complex impedence (nyquist) plots. The drastic fall in impedance value at high temperature introduces a fairly high conductivity to the material. A substantial increase in conductivity is achieved by a particular doping concentration at high frequency and at maximum temperature.

In general, present results point out that the doping plays a key role to control the physical properties of the materials. Though in some way physical properties depend on the combined effects of powder processing steps and structural modifications, the major influence of the doping material and their concentration. By suitably selecting the nature and amount of doping materials, the samples with desired physical properties can be prepared.