Abstract

There has been a considerable interest in the solid solutions of lead zirconate-titanate, $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) with a perovskite structure due to its possible applications in the areas of high dielectric constant capacitors, infrared pyroelectric detectors, piezoelectric sensors and non-volatile ferroelectric memories etc. A considerable amount of works has been done on modified PZT ceramics prepared from high-temperature solid-state reaction technique. It is found that the properties of PZT are very sensitive to its compositional fluctuations near the morphotropical phase boundary (MPB), particle size, doping, calcination and sintering temperature. In recent years, sol-gel processing of ceramics has attracted greater interest because of its inherent advantages as compared to other conventional processing techniques. The sol-gel process confers low calcination and sintering temperature, a high degree of molecular mixing, chemical homogeneity and control of stoichiometry. In addition, smaller particle size offers a higher rate of densification both due to an increase in the driving forces for sintering and due to a smaller distance of mass transport needed to fill the pores permitting the lowering of sintering temperature and the achievement of the fine grain ceramics.

A large number of charge neutral and charge deficient compounds have been prepared in the past with suitable substitution (namely, supervalent or subvalent) at different sites of PZT or in the oxygen lattice. In most of the complex PZT/PLZT systems, broadened dielectric peak or diffuse phase transition with relaxation character has been observed.

Though a large amount of work has been carried out on the modified PZT with its various Zr/Ti ratio, the effect of rare-earth and/or alkali ions substitution at Pb-site have not been studied so far with Zr/Ti = 60/40. It is, therefore, considered important to prepare high-purity, homogeneous PZT powders with rare-earth and/or alkali ions (partially substituted at Pb-site in the structure) by sol-gel method and to study their effect on the phase transition and ferroelectric properties. The crystal structure, microstructures, thermal, electrical (dielectric, polarisation), pyroelectric and piezoelectric properties of the compounds have been studied.

The following polycrystalline materials have been synthesized for our present investigation:

1. Rare-earth modified PZT (PRZT)

   $(Pb_{1-x}R_x)(Zr_yTi_{1-y})_{1-x/4}O_3$, where R = La, Pr, Nd, Sm, Eu, Gd, Dy, Er, Yb;

   x = 0.07, 0.08, 0.10 and y = 0.60

2. Lanthanum modified PZT (PLZT)
   $(Pb_{1-x}La_x)(Zr_yTi_{1-y})_{1-x/4}O_3$, where x = 0.00, 0.03, 0.05, 0.07, 0.08, 0.10, 0.12, 0.14 and y = 0.60
3. Alkali modified PLZT (PLAZT)
   $Pb_{0.92}(La_{1-x}A_x)_{0.08}(Zr_{0.60}Ti_{0.40})_{0.98+0.04x}O_3$
   where x = 0.0, 0.1, 0.3, 0.5, 0.7 and
   A = Li, Na, K and Cs.

The studies of XRD, SEM, TEM and SAED properties of the compounds have been done.

The room temperature XRD of the compounds have been obtained using x-ray powder diffractometer over a wide range of Bragg angle with CuK_α radiation (λ = 1.5418 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 the particles of the ceramic powders are spherical. The particles are well dispersed and the average particle size is about ~120 Å.

The grain distribution is found almost uniform and distributed homogeneously throughout the sintered surface as observed from SEM study.

The studies of the temperature and frequency dependence of dielectric properties of the above compounds have been discussed. The ε and tanδ of the compounds have been measured using the GR 1620AP capacitance measuring assembly with a three-terminal sample holder. The ε increases gradually to a maximum (ε_{max}) value with increase of temperature up to transition temperature (T_c) and then it decreases for all the rare-earth doped PZT. The dielectric peaks do not show any systematic trend with the rare-earth ion concentration except lanthanum doped PRZT. However, it was found decreasing with increase of La concentration in PLZT. It is difficult to generalize the variation of the dielectric peak values for PLAZT samples. The value of dielectric constant at T_c is found to depend on the type of the second (alkali ion) dopant in the PLAZT ceramics. It is observed that the dielectric peaks have been broadened with the increase of doping concentration for all the samples (PRZT, PLZT and PLAZT), indicating the important characteristic of a disordered 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 γ (diffusivity), calculated for all the samples are found to be between 1 and 2 that confirm the diffuse phase transition in the materials. It is observed that the doping concentration controls the diffuseness of the phase transition. The values of γ for PRZT do not show any trend. For the PLZT compounds, γ value increases with increasing La content. From dielectric measurements, it is found that doping elements play an important role in diffuse phase transition and majority of the doped samples shows extremely diffuse phase transition (DPT). The broadening of the dielectric peak and decrease in ε_{max} can also be attributed to the variation of grain size. The tanδ value of the samples is found to reach a maximum value before attaining a constant value. Similar temperature variation of tanδ is also found by others.

The temperature variations of P_r and E_c of the samples are recorded using the modified Sawyer and Tower circuit. The hysteresis loop changes from linear to memory type with increasing of alkali ion concentration for the samples of PLAZT. It is observed that double doping has greatly influenced the values of P_r and E_C. Moreover, from the polarisation study we can classify the PLAZT ceramics as soft material. They can be used as memory element and phonographic peak-up elements.

The piezoelectric coefficients/ parameters are measured on the poled samples using HP 4194A Impedance/Gain Phase Analyser and Berlincourt d_{33} piezo meter at 25 Hz. It is seen that the piezoelectric parameters are influenced for the double doped materials.

The pyroelectric measurements on the poled samples are performed using laboratory-fabricated experimental set-up based on Byer and Roundy technique. The phase transition temperatures for the compounds obtain from these pyroelectric measurements are in good agreement with that obtains from the dielectric studies.

Finally, our overall results point out that the major control over the final properties of the ceramic depends on the combined effects of powder processing technique and final densification. By suitably selecting the kind and amount of doping pairs, one can obtain samples with desired dielectric properties. The pair of doping in Pb-sites creates more structural disorder in PZT system and hence more diffuse phase transition.