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Synthesis And Characterization Of Ta Doped Lead Zirconate Titanate

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Abstract

Lead zirconate titanate (PZT) powder of composition $Pb(Zr_{0.65}Ti_{0.35})O_3$ was modified by incorporation of Tantalum (Ta^{+5}) in a wide composition range (5-25 at%) by chemical co-precipitation method using PbO, Zr_2O_3, TiO_2 and Ta_2O_5. X-ray diffraction patterns of the samples showed the formation of a single phase and confirm the formation of a rhombohedral phase of all the samples after sintering. SEM analysis showed well developed, uniform and loosely packed grains. Both the linear particle size and the grain size were found to decrease with Ta doping. In dielectric studies, the transition temperature was found to decrease whereas ε is found to increase with the increasing concentration of Ta. All these results suggest that this Ta doped PZT may be suitable for device applications.

Keywords— Lead zirconate titanate (PZT), Ta doped, dielectric constant, dielectric loss

I. INTRODUCTION

Perovskite structured oxides due to their high demand in electronic industries are materials of research interest for the past few decades. Lead Zirconate Titanate $Pb(ZrTi)O_3$ (PZT), ceramics is the major promising material among them. The material has been studied intensively since the discovery of the miscibility of lead titanate and lead zirconate in the 1950s. Due to their excellent dielectric, pyroelectric, ferroelectric, piezoelectric and electro-optic properties they find variety of applications in high energy capacitors, non-volatile memories (FRAM), ultrasonic sensors, infra red detectors, electromechanical transducer materials, temperature sensors, ferroelectric memories, electro optic devices among others. Ferroelectric and piezoelectric properties of PZT depend on many parameters, including the composition, crystallographic structure, grain size and preferential orientation. The microstructure and electrical properties of PZT depend on the starting material and the method of synthesis [1]. In the last two decades an extensive research has been carried out on the chemical synthesis of nanostructured PZT employing various techniques like hydrothermal, co-precipitation [2] and sol–gel.

Perovskite Pb(Zr-Ti)O_3, (PZT) Lead Zirconate Titanate has a general formula ABO_3, (A = mono or divalent, B = tri to hexavalent ions) is a solid solution of ferroelectric (FE) $PbTiO_3$ (T_C = 490 °C) and antiferroelectric (AFE) $PbZrO_3$ (T_C = 230 °C) in different Zr/Ti ratios. Its A-site (Pb^{2+}) occupying the cubo-octohedral interstices described by the BO_6 site octahedral and has tetragonal, rhombohedral and orthorhombic phases at room temperature, depending on the value of Zr/Ti ratio. The structure of PZT above Curie temperature (Tc), is cubic over whole range of compositions, and has no electric dipole moment. At T<Tc, Ti/Zr ion shifts from its central location along one of several allowed directions which distorts crystal lattice into a perovskite structure and produces a permanent electric dipole. In the case of PZT, the lattice distortion may be either tetragonal or rhombohedral, depending on the Zr/Ti molar ratio.

The phase diagram of PZT (Fig.1) shows two morphotropic boundaries (MPB) at 95/5 and 53/47 Zr/Ti ratio, where it undergo phase transition from orthorhombic to low temperature rhombohedral and high temperature rhombohedral to tetragonal phases, respectively.

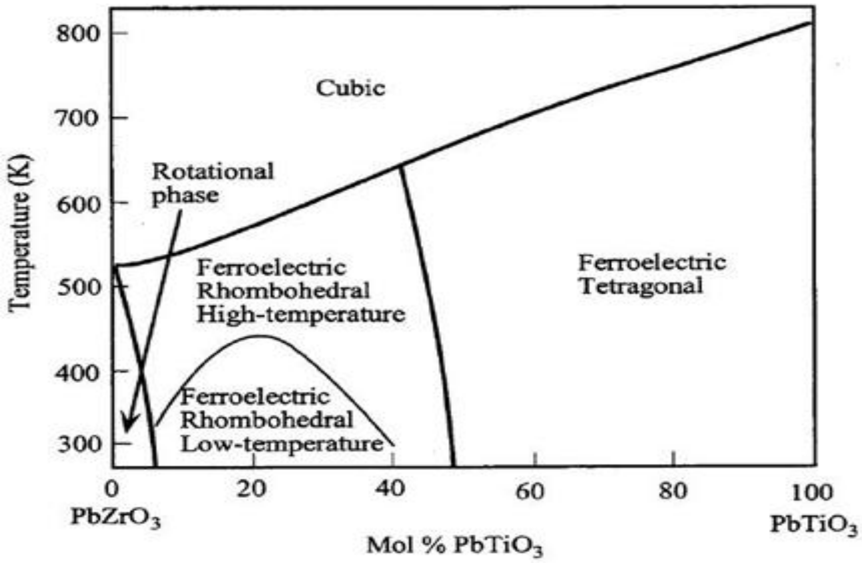

Fig 1 Phase diagram of PZT

This phase boundary is of immense technological importance since the dielectric constant (ε), piezoelectric constant (d_{ij}), and electromechanical coupling coefficient (k) all show maximum response in the vicinity of the MPB [3]. All these compositions show cubic phase above transition temperature. PZT compositions show significant merit, when they are doped with foreign ions. Its dielectric and piezoelectric properties change, depending on the site occupied by the foreign ion in ABO_3 perovskite structure. Dopants are classified as isovalent, acceptors or donors [4]. Donors (trivalent ion at A-site and pentavalent ion at B-site) reduces the concentration of intrinsic oxygen vacancy created due to PbO evaporation, which in turn increases bulk resistance of sample. Higher-valence foreign cations (donors), such as La^{3+} for A-site modification or Nb^{5+} for B-site modification, are compensated by negatively charged defects such as Pb vacancies. Acceptors (monovalent at A-site and trivalent at B-site) introduces oxygen vacancies to maintain charge neutrality, due to which domain walls gets pinned and space charges are introduced, so reduces grain resistance and inhibits domain motion [5], also acceptor-doped PZT shows poor hysteresis loop and low dielectric constant. Lower-valence foreign cations (acceptors), such as Li+ for A site modification or Fe^{3+}, Mn^{3+}, Ni^{2+} for B site modification, are compensated by positively charged defects, such as oxygen vacancies, to maintain the overall electroneutrality. Isovalent (divalent at A-site and tetravalent at B-site) doping tends to reduce the Curie temperature [6] and increases the density of PZT ceramic, which in turn effect the electrical properties.

In the present work, we have prepared Tantalum (Ta^{5+})-doped PZT (65/35) in a wide composition range (5-25 at%). Structural and electrical characterizations were carried in order to study the effect of doping on the phase formation behavior and electric properties.

II. EXPERIMENTAL

Generally interstitial ions do not occur in PZT perovskite structure due to its high packing density. Since Ta^{+5} has an ionic radius of 0.064 nm, which is relatively close to that of Zr^{4+} (0.086 nm) and Ti^{4+} (0.0745 nm), it seems that Ta^{5+} occupies B-site in the ABO_3 perovskite structure. This B-site vacancy can be formulated as: $Pb(Zr_{0.65}Ti_{0.35})_{1-x/5}Ta_xO_3$. Powder samples of the PZTT system were prepared according to the formula $Pb(Zr_{0.65}Ti_{0.35})_{1-x/5}Ta_xO_3$ for x = 0.05, 0.10, 0.15, 0.20, 0.25. The analytical grade reagents PbO, Zr_2O_3, TiO_2 and Ta_2O_5 were balled milled in double distilled water for 2-3 hrs in order to get a homogeneous mixture. The filtered powder was then kept in an oven (for 24 hr) at 150ºC for drying and then calcined at 900ºC for 6 hrs. Then these powders were pressed into pellets of diameter 10 mm and thickness 1–2 mm using PVA as binder under a pressure of 2×10^8 N/m^2 using a uniaxial hydraulic press. Finally, the pellets were sintered at 1100ºC for 4 hrs [8].

The formation and quality of pellets were checked by X-ray diffraction (XRD) technique at room temperature using an X-ray powder diffractometer (Brueker D8 Advance) with Cu Kα radiation (λ= 0.15418 nm) over a wide range of Bragg angles (20^o -70^o) with scanning speed 2^o/min operated at 30 KV and 20 mA. The microstructure and the composition analysis were investigated using an energy dispersive x-ray spectrometer ((EDX) also known as EDS) attached to the field emission scanning electron microscope (FEI, Quanta 200) at different spots on the samples by applying accelerating potentials of 20 kV and 15 kV. For electric and dielectric measurements the flat polished surface of the sintered pellets were then electroded with air drying ultrafine, high purity silver paste and fired at 120 ºC for 30 min. Measurements of dielectric constant (ε) and dielectric loss was done using HIOKI 3532-50 Hi- Tester LCR meter at frequencies from 1 KHz to 1 MHz, and at temperatures from room temperature to 400 ^{o}C was done. A laboratory-made three-terminal sample holder was used which compensated for any stray capacitance.

III. RESULTS & DISCUSSION

Fig. 2 shows the X-ray diffraction (XRD) patterns of the powder samples. The sharp and single (unsplit) peaks of the X-ray diffraction profiles of all the reflections of complex PZTT suggest better homogeneity and the formation of single phase desired compound. Absence of the splitting in the XRD patterns, therefore, indicates that there is no coexistence of mixed ferroelectric phases in the entire range of modified compositions. This can be attributed to the greater homogeneity of the prepared powders which restricts compositional fluctuations in the sintered ceramics [11]. All the reflections were indexed over a wide 2θ range with a standard computer program. The average linear particle size (*P*) of the compounds was calculated from strong and medium intensity peaks using Scherrer's equation $P = (0.9\lambda)/\beta_{1/2}\cos\theta$, where $\beta_{1/2}$ is Full Width at Half Maximum intensity.

Fig. 3 shows the variation of particle size with dopant (Ta) concentration in PZTT. This shows that the average linear particle size decreases with increase in dopant concentration (Ta) for all values of x, except x= 0.10, for which P is large. The decrease in particle size by Ta doping may be due to occupation of Ta^{+5} ion at B site replacing Zr^{4+}/Ti^{4+} ion, where it act as acceptor. The acceptor dopant in ABO$_3$ perovskite lattice introduces oxygen vacancy to maintain charge neutrality [9, 10], due to this oxygen vacancy domain walls gets pinned and reduces grain size. Also these oxides get precipitated at the grain boundary that subsequently resists the grain growth. SEM micrographs of the PZTT pellets sintered at 1100˚C are shown in figures 4 (*a-e*). The sintered pellets have been found to have a grain size more than powder samples and of the order of nanometers and uniform grain distribution.

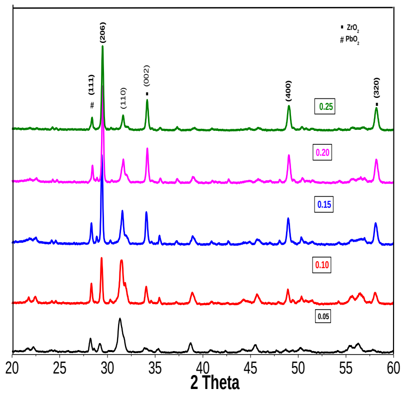

Fig. 2 XRD plots of PZTT

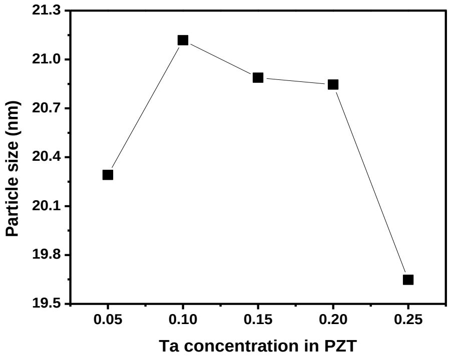

Fig 3 Particles size (nm) vs Ta concentration

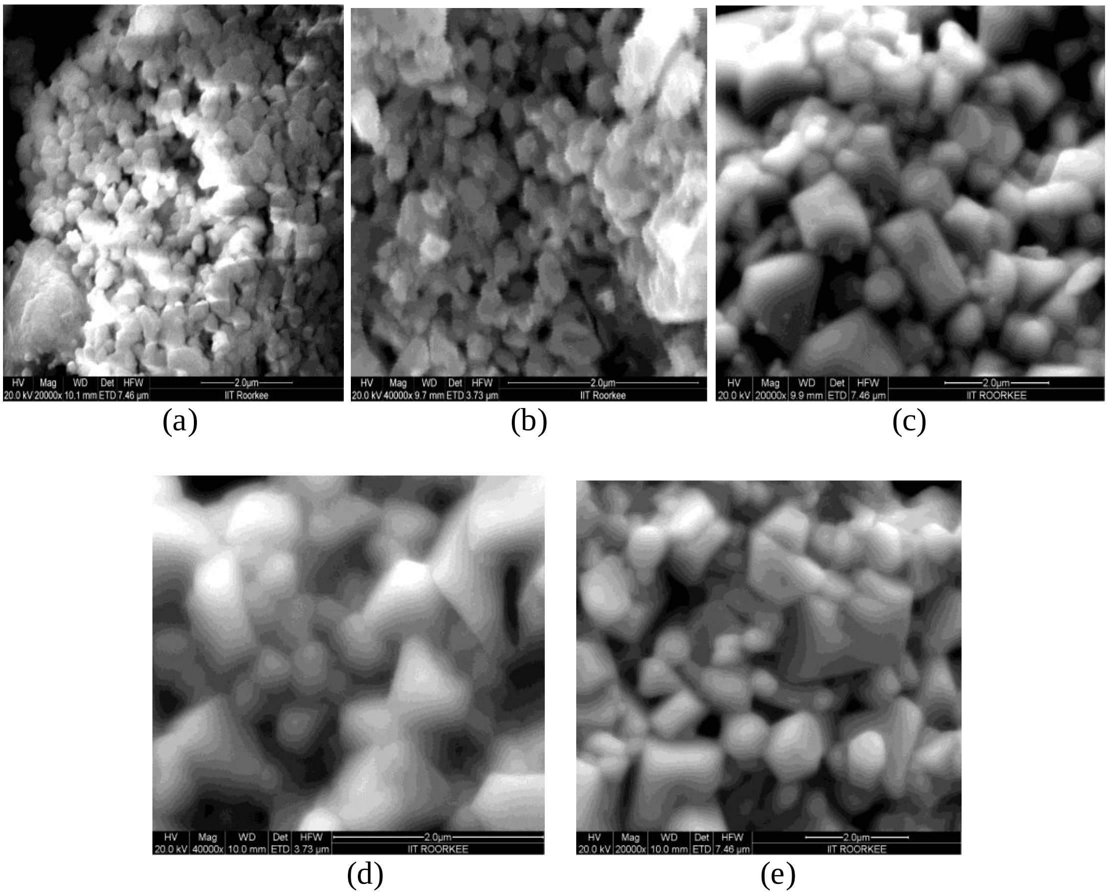

Fig. 4 SEM of sintered PZTT pellets for (a) x = 0.05, (b) x = 0.10, (c) x = 0.15, (d) x = 0.20 and (e) x = 0.25

Well developed and uniform-shaped grains are observed in all the compositions, which confirm the formation of a single phase in all the samples. PZTT, $x = 0.05$, 0.10

shows uniform, loosely packed and crack-free grains at the surface with some porosity; in the PZTT, $x = 0.15$, 0.20, and 0.25, the porosity is observed to decrease, and shows uniformly and tightly packed grains at the surface, with no visible porosity. Both the linear particle size and the grain size are found to decrease with Ta doping. The reason may be that Ta is expected to occupy the B site, which may result in decreasing grain and particle size.

The temperature dependent dielectric properties of various Ta doped PZT compositions are shown in Fig. 5. It shows the variation of dielectric constant (ε) with temperature measured at 1 MHz. As in a normal ferroelectric ε increases gradually to its maximum value (ε_{max}) with increase of temperature up to the transition temperature and then it decreases for all the values of x (x=0.05, 0.10, 0.15, 0.20, 0.25), indicating the ferroelectric phase transition in PZTT. Qualitatively, the broadened peaks of PZTT indicate that the phase transition is of diffuse type which is an important characteristic of disordered perovskites. The broadening of the dielectric peak is attributed to disorder in the arrangement of cations on one or more crystallographic sites in the structure, leading to a microscopic heterogeneity in the composition and thus in a distribution of local Curie points [9]. Symmetric dielectric peaks are observed in all the compositions and the width of the peak is found to increase with Ta doping; also the peak dielectric constant (ε_{max}) and the transition temperature (Tc) were found to decrease with Ta doping, upto x = 0.15, except for $x = 0.10$, which shows maximum dielectric constant and transition temperature, and also after x= 0.15, dielectric constant increases. This may be due to the reason that, at lower doping Ta successfully replaced the B-site ion and at higher doping (greater than x= 0.15) it remained insoluble [10]. When the amount of Ta in PZTT is increased, Tc is expected to vary with composition (x). It is noticed that Tc is continuously shifted to lower temperatures with increasing x as can be seen in Table-1. This decrease in Tc with increase in x can be explained by the fact that, Ta ion and intrinsic defects such as oxygen and Pb vacancies, acts as source of random electric field distributions which reduces Tc. Smaller the grain size and hence high density of grain boundary concentration which in turn increases the random field strength and shifts Tc to lower value [12]. The Tc is found to be independent of measured frequency, but maximum dielectric constant is decreasing with increase in frequency.

Figure 6 shows the dielectric loss of different Ta doped PZT compositions as a function of temperature. From the graph it is found that the dielectric loss increases with temperature.

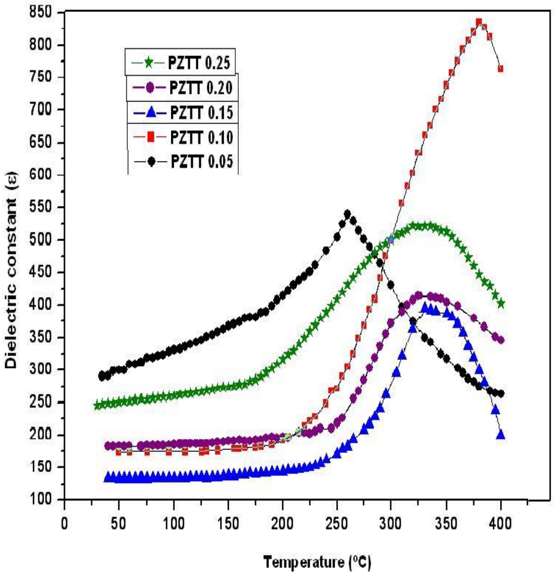

Fig.5. Plot of Dielectric constant vs. Temperature of PZTT at varying dopant concentration @ 1 MHz

In general the dielectric loss contribution for the polar substances comes from dipole losses and electric conduction losses [13]. Fig 7 shows the variation of dielectric constant (ε) of PZTT as a function of frequency at room temperature (30 °C) and hence show a typical characteristic of a normal dielectric. By increasing the frequency, electron hopping cannot follow electric field fluctuations.

TABLE I The variation of E_{MAX} and Transition Temperature with dopant concentration

S. No.	**Samples**	**Dielectric constant (ε_{max})**	**Transition temperature(Tc)**
1.	$x = 0.05$	540	260
2.	$x = 0.10$	836	380
3.	$x = 0.15$	395	330
4.	$x = 0.20$	414	325
5.	$x = 0.25$	523	320

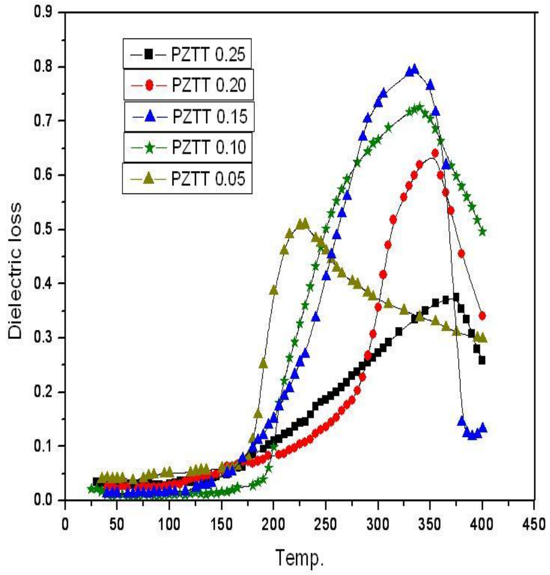

Fig. 6 Plot of Dielectric loss vs temperature of PZTT with varying dopant concentrations at 1 MHz

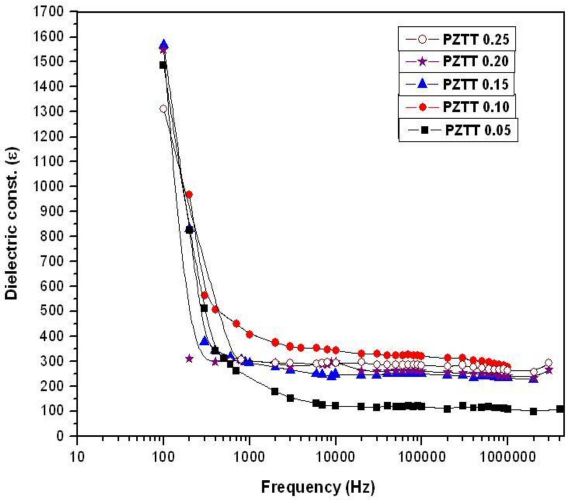

Fig 7 Plot of dielectric constant vs Frequency at room temperature (30 °C)

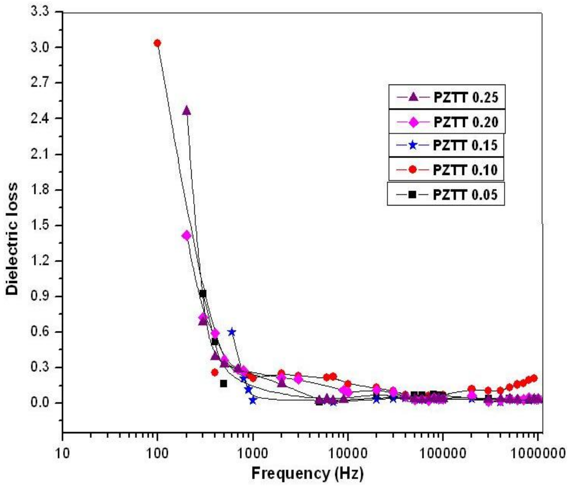

Fig 8 Plot of Dielectric loss vs Frequency at room temperature (30 °C)

Fig 8 shows the variation of dielectric loss as a function of frequency at 30 °C and hence shows a typical characteristic of a normal dielectric. Low frequency region corresponds to high resistivity (due to grain boundaries) a large amount of energy is needed for electron transfer [15]. At high frequency which corresponds to low resistivity, less amount of energy is needed for electron transfer, so the dielectric loss is less.

IV. SUMMARY

Ta doped PZT samples were prepared through the chemical route and the effect of Ta doping on structural, microstructure, dielectric and ferroelectric properties of the PZT (65/35) system was investigated. The analysis carried out on crystal structure shows the formation of a single phase. XRD studies confirm the formation of a rhombohedral phase of all the samples after sintering with the appearance of ZrO_2 peak, because the sintering was done in absence of PbO powder, so during sintering some of the PbO got evaporated from the samples, which caused the appearance of ZrO_2 peaks. There is a slight decrease in the grain size and average linear particle size with increasing concentrations of Ta^{+5}. In dielectric studies, the transition temperature is found to decrease whereas ε is found to increase with the increasing concentration of Ta. It is finally concluded that these compounds are suitable for the preparation of high value capacitors and may be good candidates for device applications.

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