

Dielectric Properties of Nanostructured PZT Synthesised by Chemical Methods

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ABSTRACT

In this study, the dielectric behaviour of smart material, lead zirconate titanate (PZT), which is important for wide industrial applications, has been explored. Two samples of nanostructured $Pb(Zr_{0.52}Ti_{0.48})O_3$ ceramic powders were prepared by hydroxide co-precipitation and aqueous solution method (water bath technique). The XRD pattern of the powder exhibited the presence of major tetragonal and minor rhombohedral crystalline phases indicating the mixed-phase composition, which is close to the morphotropic phase boundary (MPB). SEM analysis revealed good homogeneity of the materials. The plot of real part versus imaginary part of the complex impedance was observed nearly a semicircle, indicating that the samples are good dielectric materials, whose resistance decreases considerably with the increase of temperature. Similar to the normal ferroelectric materials, the dielectric constant (ϵ) of PZT has been found to be increasing gradually with temperature and attains a maxima (ϵ_{max}). The detailed analysis for the shift in peak temperature and dielectric constant were carried out.

Keywords: PZT, lead zirconate titanate, nanostructured PZT, smart materials, ceramic powders, ferroelectric ceramic materials, perovskite structure, memory devices, ferroelectric materials perovskite phase, perovskite

1. INTRODUCTION

Dielectric relaxation spectroscopy is a popular and powerful technique for studying the relaxation dynamics of almost any kind of material. The dielectric, elastic, and piezoelectric properties of ferroelectric materials are dependent on frequency and amplitude of the driving field. Materials exhibiting piezoelectricity as well as nonlinear dielectric behaviour are named as ferroelectric materials¹. These types of materials have wide range of applications² as sound wave detectors, electromechanical transducers, phonograph pickups, microphones, accelerometers, biomedical field, capacitors, etc.

During the last two decades extensive work³ have been realised about the chemical preparation

of nanostructured ferroelectric ceramic materials such as lead zirconate titanate (PZT), with general formula $Pb(Zr_{1-x}Ti_x)O_3$. Most of the piezoelectric ceramics, and in particular PZT, is in the perovskite (ABO_3 : A= Pb^{2+} at corners, B= Ti^{4+} or Zr^{4+} at body centre and O at face centre) structure. To obtain the materials with desired electrical properties, a perovskite structure is required. One of the necessary conditions for obtaining perovskite phase is to maintain the stoichiometric composition of the perovskite. In the particular case of PZT, the largely debated area around the morphotropic phase boundary (MPB) at composition near to $x \sim 0.52$ depends on the processing method used⁴. Noheda⁵, *et al.* found that the room temperature structure of PZT close to MPB is monoclinic (Space Group, Cm). Thus, the current

view is that instead of MPB (at which tetragonal, P4 mm and rhombohedral, R3m phases are in a thermodynamical equilibrium), there is a morphotropic phase (Cm) separating the two phases. However, in case of large composition fluctuation, one really has both rhombohedral and tetragonal phases present in the same sample and the phase fraction of these two phases is sensitive to the sample preparation technique⁶. However, the volatile *PbO* tends to be deficient in the PZT material, obtained by conventional solid state reactions when annealed at high temperature. Therefore, the choice of a convenient synthesis route is a key to obtain a higher control over the properties of the PZT.

Several wet chemical routes have been developed to improve the control over the stoichiometry and morphological characteristics of the multicomponent oxides and were applied to synthesize PZT⁷⁻⁹. The co-precipitation route is an efficient method for advanced material synthesis. By this method the powder calcinations temperature can be lowered and the powder obtained has high homogeneity. Guifford¹⁰, *et al.* reported PZT preparation by co-precipitation using NH_4OH and oxalic acid as precipitants at 700 °C. But *PbO* phase is still found in the powder calcined at 600 °C. In this paper, a different preparation method of PZT powder in aqueous medium at lower temperature is presented which could avoid the loss of *PbO* and lead to fine, nanostructured and homogeneous PZT powder. The studied composition ($Pb(Zr_{0.52}Ti_{0.48})O_3$), was close to the MPB which corresponds to maximum of electromechanical response¹¹. The phase transition between antiferroelectric (AFE) and ferroelectric (FE) phases in PZT can be induced by varying temperature, electric field or hydrostatic pressure¹². Therefore, it has been thought worthwhile to study the structural and dielectric properties of PZT prepared by different chemical routes by varying temperature and frequency.

2. EXPERIMENTAL DETAILS

2.1 Sample Preparation

Two methods have been adopted for the preparation of nanostructured PZT samples. The starting materials

used were analytical grade $PbNO_3$, $ZrOCl_2 \cdot 8H_2O$ and $TiCl_4$. The precipitant was ammonia solution.

In the first method (PZT-1), a fresh $ZrO(OH)_2 \cdot xH_2O$ was precipitated from $ZrOCl_2 \cdot 8H_2O$ (dissolved in doubly distilled water) by reaction with cold NH_4OH in water at 2-5 °C with constant stirring. It was filtered and washed with distilled water to get rid of chloride ions and other byproduct impurities^{13,14}. Similar method was followed to obtain $TiO(OH)_2 \cdot xH_2O$ from aqueous $TiCl_4$ solution. These $ZrO(OH)_2 \cdot xH_2O$ and $TiO(OH)_2 \cdot xH_2O$ were dissolved in HNO_3 and then mixed with an aqueous $Pb(NO_3)_2$ solution in requisite amounts corresponding to one mole of $Pb(Zr_{0.52}Ti_{0.48})O_3$.

In another method of preparation (PZT-2), a freshly prepared aqueous solution of $ZrOCl_2 \cdot 8H_2O$ was added dropwise to an aqueous solution of $PbNO_3$ with constant stirring in a water bath maintained at temperature 50-60 °C. It was followed by the addition of a mixture of H_2O_2 and $TiCl_4$ solution with constant stirring. Finally, the solution was taken out and processed further.

Dropwise addition of aqueous ammonia solution was carried out to both the above solutions and these were maintained at $pH \sim 9$. The precipitates so obtained were washed several times for eliminating other ions. After drying at 100 °C for 12 h, the white powders were crushed and calcined at 450 °C and 550 °C for 4 h.

3. CHARACTERISATION

The sintered powder samples were subjected to XRD studies with a typical wavelength of 1.54 Å (Cu Ka-radiation). The diffractometer (ISO DEBYLEX, 2002) was operated at 30 kV and 20 mA. The scanning speed of the diffractometer was 3°min⁻¹. The diffraction angle 2θ was varied from 20-80°. SEM images obtained using FEI Quanta 200, Netherland SEM, of the polished and gold-coated sample pellets were used to study the surface morphology of the prepared material.

The prepared powder was mixed with an appropriate amount of PVA as a binder and then palletised (10 mm dia × 1.5 mm thickness) for dielectric

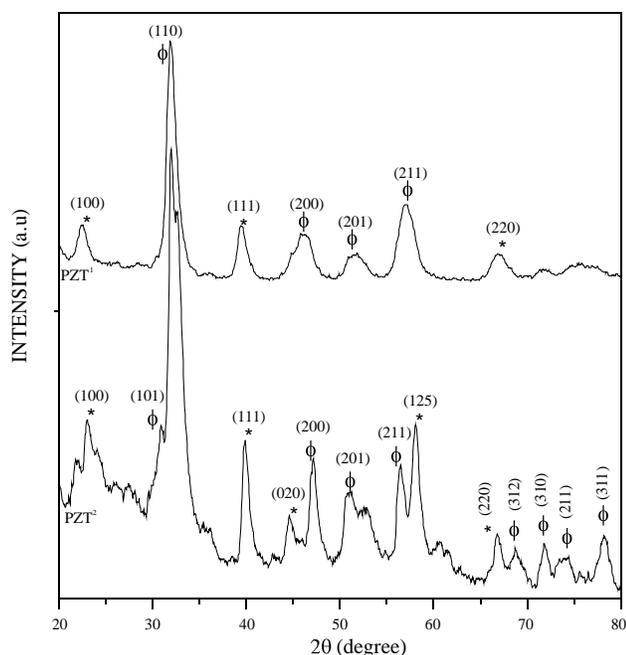


Figure 1. XRD patterns of synthesised PZT (ϕ Tetragonal, *rhombohedral).

measurements. An impedance analyser, HP 4192A LF has been used for the dielectric studies in the frequency range 1 kHz to 13 MHz.

4. RESULTS AND DISCUSSION

4.1 X-Ray Diffraction

The XRD indexing results imply the presence of a major tetragonal crystalline phase and a minor rhombohedral phase (Fig. 1) indicating mixed-phase composition close to the MPB. Crystallite size (t) was calculated using Scherrer formula [Eqn. (1)] and was found to be ~ 8 nm and ~ 10 nm for samples PZT-1 and PZT-2 respectively.

$$t = 0.89\lambda/\beta \cos\theta \quad (1)$$

where β is the excess line broadening and θ is the Bragg angle.

4.2 Scanning Electron Microscopy

SEM images (Fig. 2) clearly revealed that the material contains agglomeration of particles with well-defined grain boundaries having variable grains size nearly $0.1 \mu\text{m}$. Also, the SEM-EDAX analysis revealed good homogeneity of the material.

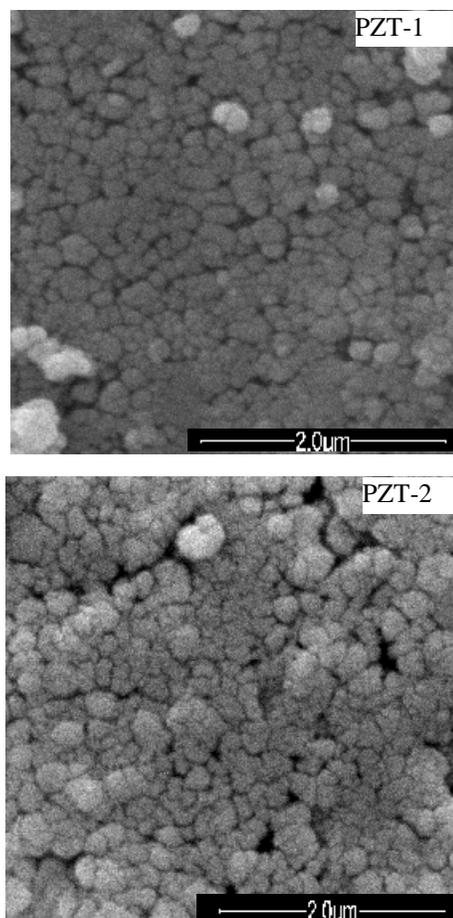


Figure 2. SEM images of the calcined PZT samples.

4.3 Dielectric Measurement

The impedance is a complex function and is dependent on frequency, which can be expressed by the following equation:

$$Z^*(\omega) = Z(\omega) + j Z(\omega) \sin\theta \quad (2)$$

The plot of real part versus imaginary part of the complex impedance were nearly semicircle (Fig. 3) indicating the sample to be a good dielectric whose resistance decreases considerably with temperature. The resistance of the sample prepared by coprecipitation (PZT-1) was found to be very less compared to that prepared by water bath technique (PZT-2) which may be due to the difference in the grain size. A capacitor consisting of lossy dielectric may be represented by an equivalent circuit which consists of a pure capacitance and a resistance¹⁵. In an alternating current the charge stored in a dielectric has both real (ϵ' , in phase) and imaginary (ϵ'' , out

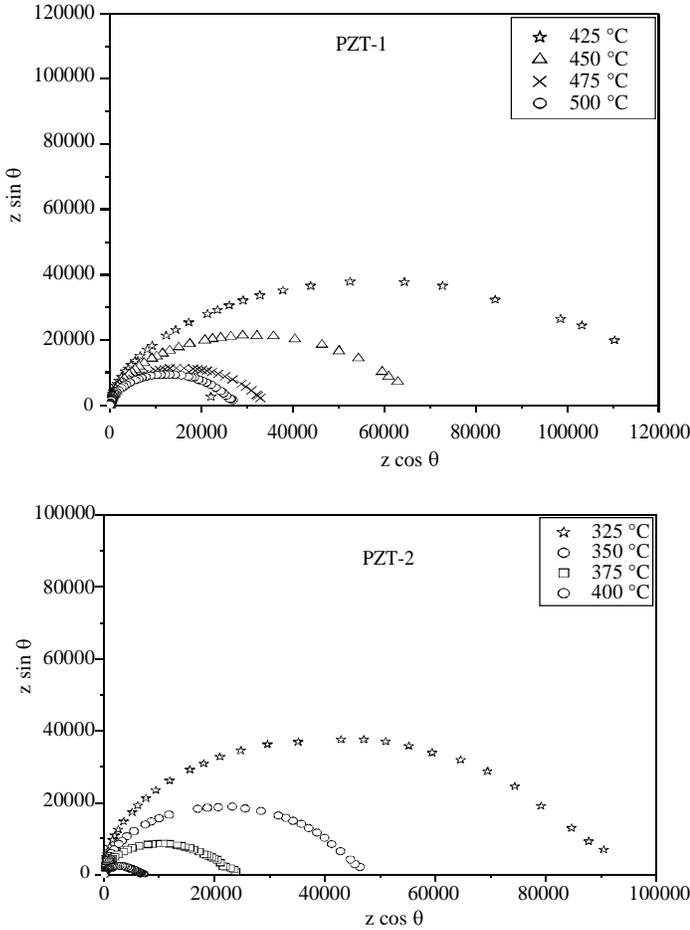


Figure 3. Plot of imaginary part versus the real part of impedance at various temperatures.

of phase) components. Impedance of the dielectric-electrode system can be expressed as

$$Z^* = \frac{1}{j\omega C} = \frac{1}{j\omega \epsilon^* C_o} \quad (3)$$

where the dielectric constant (ϵ^*) [Eqn (4)] is a complex quantity of which the imaginary part is a measure for the dielectric losses of the material.

$$\epsilon^* = \epsilon' - j\epsilon'' \quad (4)$$

Both the real and imaginary parts incorporate the electronic, ionic, and orientational contributions to the polarisation¹⁵. The imaginary part is proportional to the energy absorbed by the material from the alternating field. As in normal ferroelectric materials, the dielectric constant (ϵ') of PZT is found to be increasing gradually with temperature and attains

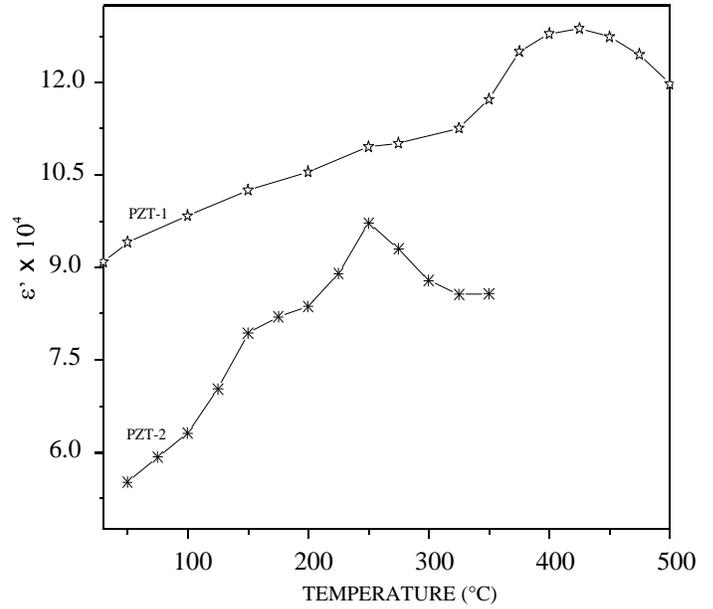


Figure 4. Real part of dielectric constant versus temperature at 500 kHz.

a maxima (ϵ'_{\max}) at the temperature¹⁶ (T_{\max}). The plot of the real part of dielectric constant (ϵ') as a function of temperature for PZT pellet is shown in the Fig. 4. Peaks in the dielectric constant plots are attributed to the phase transition from the ferroelectric tetragonal to the antiferroelectric rhombohedral structure¹⁷. In ferroelectrics, there will be more than one orientational state for the dipoles in the absence of electric field and these switchover from one state to other under the external electric field. As the PZT is heated from a low-temperature ferroelectric state to the antiferroelectric state, a structural change occurs in the unit cell, usually with a contraction in the direction of the polar axis. Intergranular stresses vanish and a domain relaxation occurs. The ferroelectric ceramic has been showing high dielectric constants, of the order of 10^5 , implying high capacitance.

It was found that the values of ϵ'_{\max} the dielectric peak temperatures were distributed between 456-406 °C as the frequency were varied from a lower value to a higher value in kHz range for sample PZT-1. In the case of PZT-2 sample, the dielectric peak temperature was 250 °C for all the frequencies in the kHz range and the peak height decreased as frequency increased. But no shift in peak temperatures was found as observed in the case of PZT-1 sample.

The shift in ε'_{\max} as a function of temperature and frequency indicate a relaxor type of behaviour for the material. The frequency dispersion of dielectric peaks in relaxors may be due to the onset of relaxation of the polar clusters present above the transition temperature. At a given frequency, the smaller clusters relax at lower temperature while the bigger clusters relax at higher temperature. This will produce a peak in dielectric constant (ε') versus temperature plot. By increasing the measuring frequency, the relaxation of smaller clusters occurs at lower temperatures because of their smaller relaxational time, producing shift in the peak¹⁷. This slow relaxational dynamics may be due to the correlated motion of Pb^{2+} ions about their displaced sites. As the length of the clusters increases over which the dipoles are correlated, the relaxation frequency decreases. The difference in the dielectric phase transition in both the cases may be due to the crystallite size difference. If the crystallite size is large, and as a result of diffuse phase transition, the characteristic peak on ε' versus temperature curve broadens.

The frequency shift of the dielectric modulus (M'') will be substantial for a distributed relaxation. So an M'' -based analysis can be expected to give a better separation between the dipole relaxations and conduction dominated losses than one based on ε'' . The reason for this is that the dispersion curves often reveal more details and hence, provide a better evaluation of the complex data like overlapping peaks. The imaginary part of M'' converts the low frequency steady increase in ε'' to a specific conduction peak. The position of loss maxima can be found easily from $(d \ln M'' / d \ln \omega = 0)$. The plot of M'' as a function of frequency at different temperatures is shown in Fig. 5. In the temperature range 375-500 °C, the relaxation frequency is found to be distributed between 7-100 kHz, confirming the relaxor type behaviour for the material for PZT-1. For PZT-2, the peak appears at a lower temperature (200 °C) and the peak height is found to be decreasing with the increase in temperature. This may be due to the presence of more small clusters than bigger ones in the sample.

It is proposed that competing ferroelectric and antiferroelectric interactions are responsible for

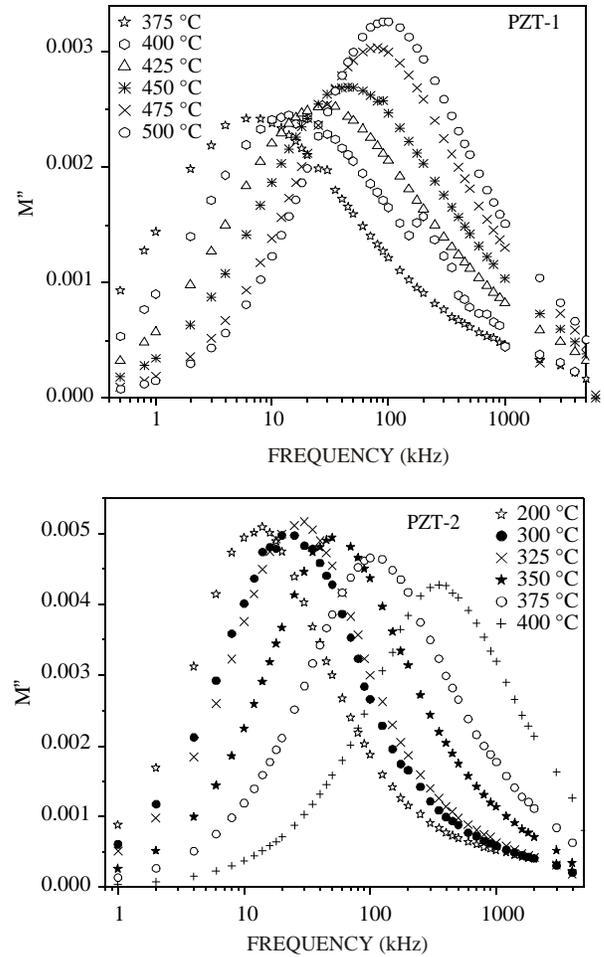


Figure 5. Frequency dispersion of imaginary part of dielectric modulus.

the relaxor ferroelectric behaviour. Also, the increase in the linear coupling between the strain and polarisation enhances the thermal hysteresis associated with the antiferroelectric to ferroelectric transition. The ferroelectric and antiferroelectric phase transitions in PZT are caused by two competing instabilities in the low frequency polar modes at the zone centre and the zone boundary respectively. Depending on the temperature one of the two instabilities dominate, giving rise to pure ferroelectric or antiferroelectric phase with definite stability fields. The imaginary part of the dielectric constant (ε'') is proportional to the absorption of energy by the material from the alternating field. The dielectric loss is the ratio of imaginary to real part of the complex permittivity¹⁸ and is given as

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'} = \frac{M''}{M'} \quad (5)$$

It was found that with increase in frequency, $\tan \delta$ and ϵ' decrease and showed a typical characteristic of normal dielectric. The value of $\tan \delta$ is found to be decreasing with increase in frequency (Fig. 6) and attains a constant value of nearly 0.08 around 400 kHz in both the cases. The dielectric loss was found to be very large at low frequencies for PZT-2 sample. It is observed that a phase transition occurs around 345 °C in both the cases. Loss rapidly

increased on further increase in temperature while the $\tan \delta$ value is almost constant just before this phase transition. For PZT-1 sample the constant value was around 0.034 and for the other sample it was nearly 0.1. The sample PZT-1 shows room temperature conductivity around $4 \times 10^{-6} \Omega^{-1}\text{cm}^{-1}$ and a linear dependence with the frequency. Whereas PZT-2 exhibits, a conductivity $\sim 1 \times 10^{-5} \Omega^{-1}\text{cm}^{-1}$ and found to be independent of frequency.

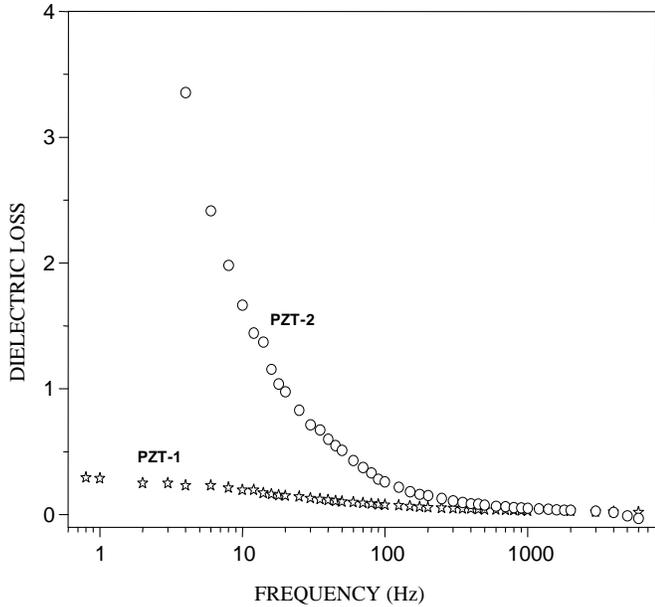


Figure 6. Plot of dielectric loss versus frequency at room temperature.

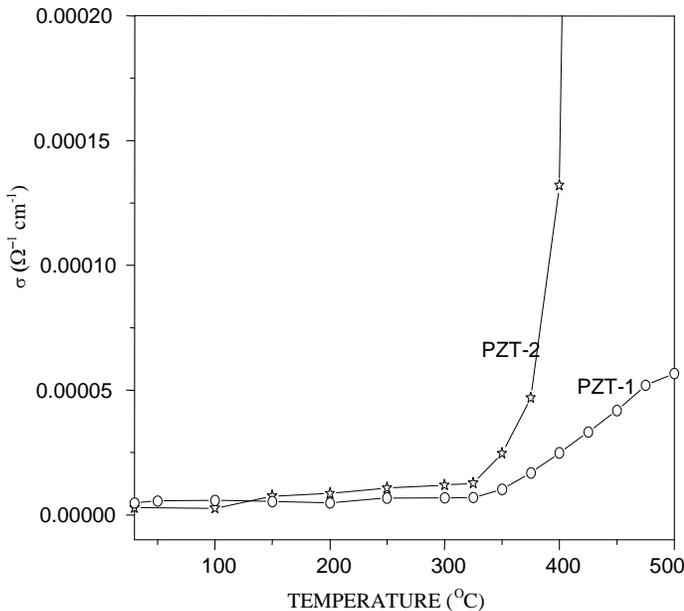


Figure 7. Plot of conductivity versus temperature.

In both the cases, conductivity (Fig. 7) and $\tan \delta$ transitions occur at 345 °C. This implies that the samples are moderate conductors and the effect of electrode polarisation is negligible and the Curie temperature of the prepared samples is 345 °C. Conductivities of both PZT samples have been showing nonlinear variation with temperature similar to a semiconductor whereas it is a linear function of frequency. The conductivity can be expressed by the Arrhenius relation as

$$\sigma = \sigma_0 e^{\frac{-E_a}{kT}} \quad (6)$$

where σ_0 is a constant and E_a is the activation energy. The PZT-2 sample exhibits sharp increase in the conductivity after the phase transition.

5. CONCLUSIONS

Chemical routes for the synthesis of nanostructured PZT are technically simple and economical. The crystallite size of the prepared materials are found to be 6-8 nm (PZT-1), 10-12 nm (PZT-2), and the surface morphology study implies well-defined grain boundary. Detailed dielectric measurements have been carried out and various impedance-related functions such as dielectric constant (ϵ'), $\tan \delta$, dielectric modulus (M''), and conductivity (σ) have been studied as a function of temperature and frequency. The observed Curie temperature (T_c) has been found to be ~ 345 °C. The high dielectric constant and low loss at room temperature makes the material suitable for memory devices. Studies on the frequency dispersion indicate a relaxor type of behaviour for the material. The peaks in the dielectric constant plots are attributed to the transition from ferroelectric to antiferroelectric phase and

are associated with the change from tetragonal to rhombohedral structures. The ferroelectric ceramics are known to show high dielectric constants, which are of the order of 10^5 , implying high capacitance. The interesting dielectric properties of the prepared PZT makes it suitable for actuator and capacitor applications also.

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