



## ELECTRICAL AND PIEZOELECTRIC STUDIES OF Ba (Zr,Ti) O<sub>3</sub> CERAMICS

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### ABSTRACT

$x\text{BaZrO}_3 - (1 - x) \text{BaTiO}_3$  (BZT) solid solutions were synthesized by solid state reaction method at different mole percentages of  $x$  (5% - 30%). These samples were characterized by measuring the dielectric constant with temperature at different frequencies. Curie-Weiss fitting of these samples suggests displacive type ferroelectric nature of the samples. Frequency and temperature dependent of AC conductivity for the samples reveal mode of charge transport is multiple hopping process follows the Johnsher power law and thermally activated relaxation process follows the Arrhenius law. The relaxation parameters ( $E_a$ ) were calculated from the Arrhenius fitting on the samples. Doped  $\text{BaTiO}_3$  can exhibit competitive piezoelectricity in comparison with lead titanate zirconate ceramic. Piezoelectric coefficient of the samples decreases with increase of  $\text{BaZrO}_3$  content as well as with increase of field. Pyroelectric coefficients were calculated from the spontaneous polarization measurement as a function of temperature and they were observed to be decrease with increase of  $\text{BaZrO}_3$  content. Figure of merit of the samples suggests that these samples has good pyroelectric efficiency.

**Key words:** Dielectric, AC conductivity, Piezoelectricity and pyroelectricity

### INTRODUCTION:

Different ferroelectric materials possess interesting electrical and structural properties. Among all ferroelectric materials  $\text{BaTiO}_3$  is an excellent material with numerous promising applications such as capacitors and piezoelectric transducers. It undergoes, rhombohedral -to-orthorhombic, orthorhombic – to – tetragonal and tetragonal – to- cubic transformations [1]; above the transition temperature, the crystal symmetry becomes insufficient for piezoelectricity. Pure  $\text{BaTiO}_3$  has lower piezoelectric properties than lead titanate zirconate. However, doped  $\text{BaTiO}_3$  can improve the piezoelectric properties in comparison with lead titanate zirconate ceramic having reduced hysteresis loss in comparison with “soft” compositions [2]. Many pyroelectric and piezoelectric detectors based on  $\text{BaTiO}_3$  operate close to the transition temperature [3]. Hence it is desirable to lower the transition temperature towards room temperature. The phase transition temperature can be altered by B-site ion substitution. In the present work we report results of studies on higher ionic radius  $\text{Zr}^{+4}$  dopant substituted for  $\text{Ti}^{+4}$ . The change in the phase transition behaviour, Hysteresis, Piezoelectricity and Pyroelectricity are studied. An understanding of the results obtained is also presented. Frequency and temperature dependent of AC conductivity for the samples reveal mode of charge transport is multiple hopping process follows the Johnsher power law and thermally activated relaxation process follows the Arrhenius law. The relaxation parameters ( $E_a$ ) were calculated from the Arrhenius fitting on the samples.

### Synthesis method:

BZT ceramic system prepared through solid state reaction synthesis by taking organic and carbonates. Initially calcination of the given system was done at 800oC in the form of square pellet followed by grinding. To obtain the densification, samples made into circular pellets using PVA and sintered at 1400oC-1450oC.

### RESULTS AND DISCUSSION:

#### Dielectric studies:

Temperature dependent of dielectric constant of all the samples at 1kHz frequency was studied by using HP 4192A Impedance analyzer and the heating rates was maintained 2.5°C/min. Figure 1(a) shows that phase transition temperature of the BZT samples decreases with increasing Zr concentration.

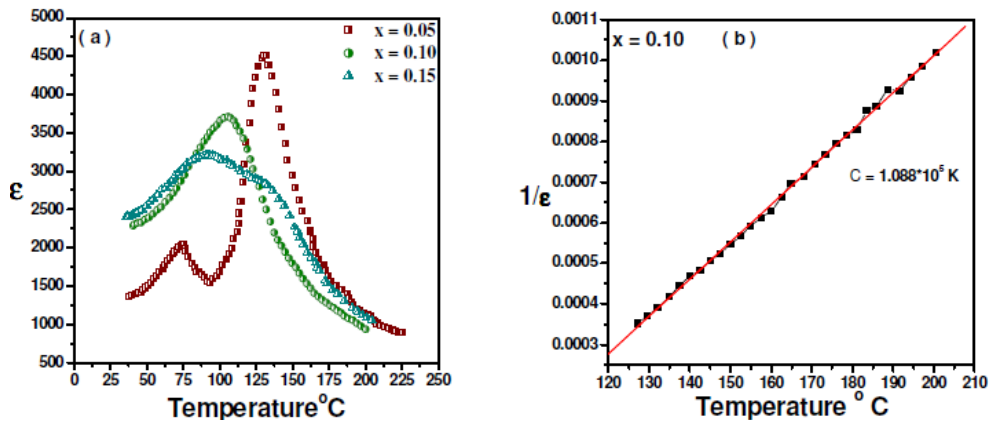


Figure 1.(a) Dielectric constant versus temperature plot. (b) Curie – Weiss fitting plot.

concentration lowers the phase transition temperature and raise the other two transition temperatures of pure BaTiO<sub>3</sub>. Deviation in normal Curie –Weiss law suggests the change from normal to diffuse phase transition leads to relaxor nature of the samples. Order of the Curie – Weiss constant 10<sup>5</sup>K (Figure 1(b)) suggests that these materials shows displacive nature of ferroelectricity [4].

**AC conductivity studies:**

AC conductivity of the sintered BZT samples was calculated from admittance of the samples

$$\sigma = \frac{Y' t}{A} \dots\dots\dots (1)$$

Where *Y'* is the admittance, *t* is thickness and *A* is area of the sample.

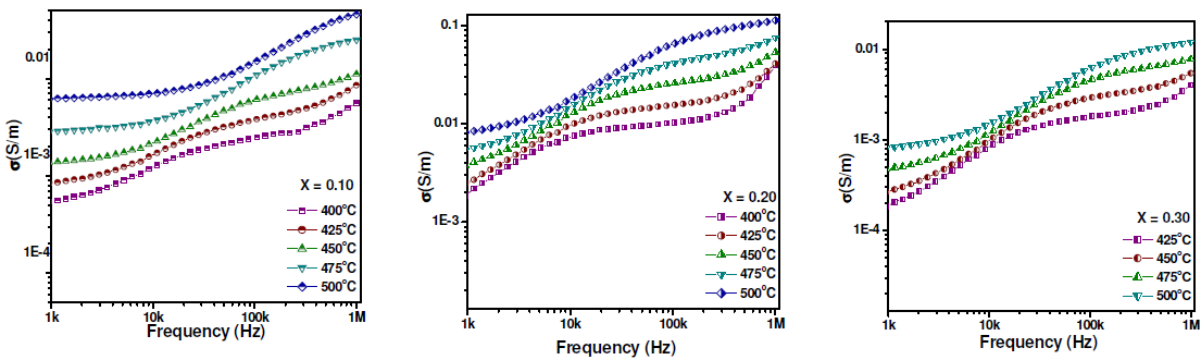


Figure 2. Sigma versus Frequency plot.

Figure 2. shows the variation of AC conductivity with frequency at different temperatures C for BZT ceramics. At low temperatures the frequency dependence of ac conductivity shows the dispersion throughout the frequency range of measurement. At higher temperature  $\sigma_{dc}$  remains almost constant in the low frequency region as a result frequency independent plateau is seen, whereas the dispersion of conductivity is observed in the higher frequency region. The Johnson power law is used to fit the ac conductivity of the material as follows:

$$\sigma = \sigma_{dc} + A\omega^n \dots\dots\dots (2)$$

where  $\sigma_{dc}$  is frequency independent conductivity that related to dc conductivity, A is the temperature dependent pre- exponential factor and n is the frequency exponent. The value of n varies between 0 and 1 [5]. The calculated frequency exponent ' n ' values are given in table1-2. The value of ' n ' reduced at higher temperatures with increasing concentration of Zr indicating an increase in the disorderness in the system. The cross over from the frequency independent region to frequency dependent region shows the onset of the conductivity relaxation i.e transition from long range hopping to the short range ionic motion. The onset of the conductivity relaxation shifts to higher frequency side with increasing temperature implies different conduction mechanisms involved in the samples [6]. The value of  $\sigma_{dc}$  decreases with increasing Zr

concentration in BaTiO<sub>3</sub> throughout the frequency range. At higher temperatures the  $\sigma_{dc}$  increases with temperature confirming negative temperature coefficient of resistance behaviour. Thermally activated electrical conductivity of the present prepared samples at different frequencies was calculated using equation ( 1 ) as shown in figure.3 and it follows the Arrhenius law .

$$\sigma = \sigma_0 e^{\frac{-E_a}{KT}} \dots\dots\dots ( 3 )$$

where  $\sigma_0$  is a pre-exponential factor and  $E_a$ ,  $K$  and  $T$  are respectively the activation energy for conduction, Boltzmann's constant and the absolute temperature. The activation energy for conduction ( $E_a$ ) of samples could be calculated from the slope of the straight line obtained from  $\ln\sigma$  vs  $1000/T$  plot. For each frequency in the plot, occurrences of different slopes of the different temperature regions suggest the presence of multiple conduction processes in the sample with different activation energies. In low temperature region the a.c. conductivity depends significantly on the frequency. At lower temperatures and higher frequencies, it is observed to be independent of temperature. However, with the increase in temperature, the dielectric relaxation takes place and the dependency of conductivity on frequency gets

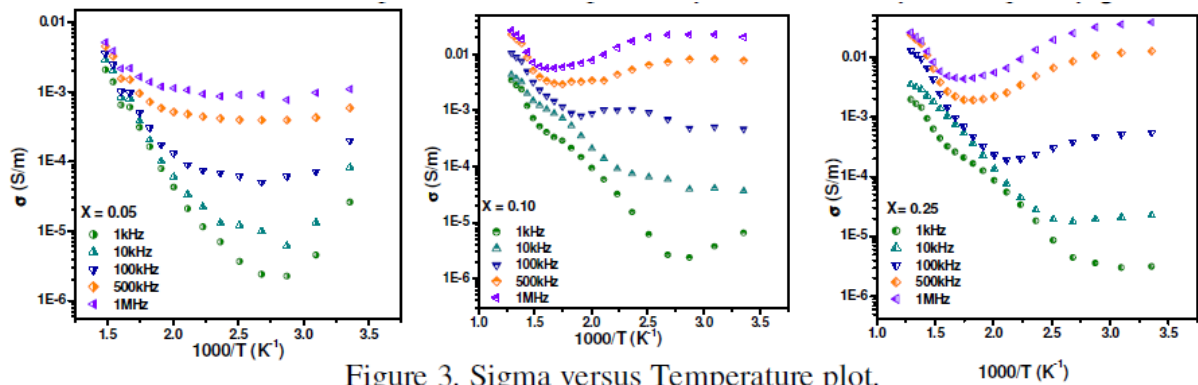


Figure 3. Sigma versus Temperature plot.

reduced. It is noted that the conductivity curves are found to merge at higher temperatures and at these temperatures the onset of intrinsic conductivity takes place [7].

Table 1:  $n_1, n_2$  and  $n_3$  values of  $X = 0.05$  sample

X=0.05	$n_1$	$n_2$	$n_3$
400	0.21861	0.36074	0.69706
425	0.22191	0.33818	0.83611
450	0.25194	0.18397	0.66617
475	0.36149	0.16481	0.29811
500	0.38184	0.27025	0.19679

**Piezoelectric and Pyroelectric studies:**

Figure. 4(a) shows the temperature dependent of polarization versus electric field measurement was carried out on the sintered samples in the unpoled state. Beyond the 20 mol% of Zr, the paraelectric phase increases in amount at room temperature and this results in the decreasing polarization values for Zr contents greater than 20 mol%. At 30 mol% of Zr content, the curve is almost lossy elliptical loops and no hysteresis is observed.

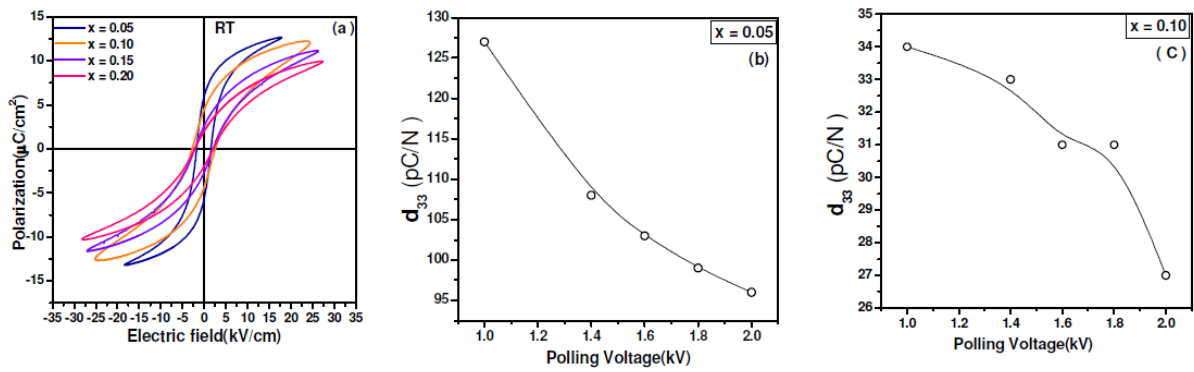


Figure. 4(a) P versus E plot. 4 (b-c). d33 versus Polling voltage plots.

It points out the degradation of ferroelectric nature of the samples. Polarization of the samples at the absence of electric field decreases from  $x = 0.0574 \text{ C/m}^2$  for  $x = 0.05$  to  $0.0199 \text{ C/m}^2$  for  $x = 0.20$  with increasing temperature. It may be due to the discontinuity of the order parameter of the ferroelectric samples (i.e. polarization) across the grain and grain boundary of the sample. Here the observed ferro – para phase transition temperature where the polarization becomes zero is slightly higher than the observed value of transition temperature in the dielectric measurement.

Table 2:  $n_1, n_2$  and  $n_3$  values of  $X = 0.10$  sample

X=0.10	$n_1$	$n_2$	$n_3$
400	0.40936	0.22644	0.60007
425	0.23566	0.24051	0.45078
450	0.1439	0.45042	0.27188
475	0.09905	0.53572	0.22976
500	0.05965	0.47141	0.44835

To measure the piezo electric coefficient, initially the samples were poled at room temperature under DC field of 2kV/cm using a stabilized power supply. Piezoelectric coefficient measurement of the poled samples was done by using Piezo meter PM100 system. Figure shows the piezoelectric properties of the sintered samples versus electric poling field. Piezoelectric coefficient values for  $x = 0.05$  is 120pC/N, for  $x = 0.10$  is 26pC/N.  $d_{33}$  of the samples decreases with increasing polling (figure 5). This may be due to grain size which affects the coercive field values by changes in the domain wall motion occurs during polling process [8].

pyro electric coefficient of the present samples is determined from the temperature dependence of the spontaneous polarization using following equation [9].

$$p = \partial P_s / \partial T \dots\dots\dots (2)$$

where  $p$  is pyro electric coefficient,  $P_s$  is the spontaneous polarization. Figure 4 shows the pyroelectric coefficient versus temperature graph for the BZT samples. It is observed from the graph that pyro electric coefficient has a peak similar to the temperature dependent of the dielectric constant curve. pyro electric coefficient peak is less than the of transition temperatures observed in dielectric measurements. Pyro electric peak could not be observed

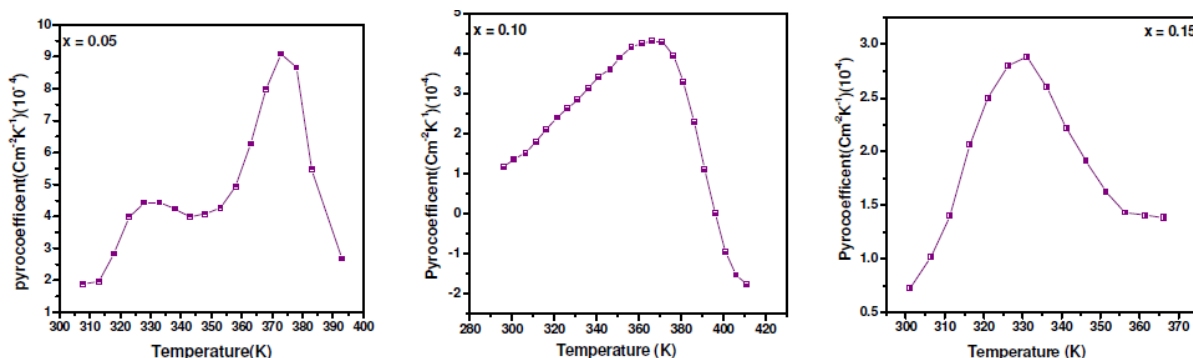


Figure .5. Pyrocoefficient versus Temperature plots.

#### Conclusions:

The BZT ceramic samples were prepared by Solid state reaction method. The phase transition temperature decreases with doing concentration. Deviation in the Curie – Weiss law suggests that these materials show diffuse phase transition behavior. Frequency dependent of conductivity obeys the universal power law. Temperature dependent of AC conductivity shows intrinsic and extrinsic regions having different activation energies. Decrease in  $d_{33}$  with increasing doping concentration as well as polling voltage. From the pyroelectric measurement these materials (BZT) has good efficiency for pyroelectric devices.

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