Dielectric And Electrical Properties Of Barium Zirconate Titanate Ceramics

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ABSTRACT
Ferroelectric zirconium doped barium titanate (BZT) has been prepared by using solid state reaction technique. The XRD and SEM data confirmed the presence of the desired BZT phase. All the samples showed dispersion relation with frequency and there were shift of the transition temperatures to lower values with zirconium contents. The frequency dependence of ac conductivity curves of the doped samples were fitted using the relation $\sigma(f) = \sigma_0 + A(T) f^{\alpha(T)}$. At lower frequency range, the curve was not well fitted suggesting the contribution of small ac conductivity due to electrode polarization effect along with dc conductivity; however at higher frequency the curves were well fitted indicating the frequency dependence of ac conductivity at higher frequency. Frequency dependent of ac conductivity indicates that conduction occurs due to hopping of small polarons among the localized states. It was also reported that changes in ac conductivity with Zr contents in the samples.

Keywords: Solid state method, ferroelectric, dielectric constant, ac conductivity.

1. Introduction:
Multi-component ferroelectric materials having perovskite structures have been widely used in many multi-functional devices. The Barium titanate a well known ferroelectric material with perovskite structure have many useful properties such as high dielectric constant, low coercive field, high polarization etc. and have been utilized in many devices such as multilayered capacitors, positive temperature coefficient thermistors, piezoelectric transducers and a variety of electro-optic devices [1]. Various types of additives are usually mixed to the Barium Titanate powder in order to obtain better performance and good control over the grain sizes and electrical properties of the ceramics. It has been found that the dielectric property of the Barium Titanate polycrystalline depends on the type of additives and density and grain growth during sintering. Thus, additives that change microstructure can modify the dielectric properties of Barium Titanate ceramics. Study on the effect of Zr addition to Barium titanate shows that the Zr addition shifts the Curie point at lower temperature and depressed dielectric peak. Zr$^{+4}$ ions can substitute for Ti$^{+4}$ ions in isovalent. Zirconia particles with BT can form core-shell structures. The temperature stability in the dielectric properties can be achieved by the formation of core-shell grains [2]. Barium titanate based multilayered capacitors can be modified to exhibit temperature stable dielectric behaviour over temperature range-55°C to 125°C. The stability may be either the result from chemical substitution in the ceramics, from a small-grained microstructure or from the presence of core-shell-grains [3]. Remarkable changes occur in various characteristics when there is homovalent or heterovalent substitution of barium or titanium ions [2,4,5]. Many researchers have interested in the solid state solution Ba(Zr$_x$Ti$_{1-x}$O$_3$) with different concentrations x=0.0, 0.1, 0.2 and 0.3. It is also reported that Zr substitution of BT affects the transition temperatures. In this paper we have studied the dielectric properties as a function of temperature and frequency up to 1MHz and ac conductivity of BZT ceramics by solid state method.

2. Experimental Technique:
For the preparation of zirconium doped barium Titanate with general formula Ba(Zr$_x$Ti$_{1-x}$O$_3$) (x=0.0, 0.1, 0.2 and 0.3) the materials used were analytical grade barium carbonate (BaCO$_3$), titanium dioxide (TiO$_2$) and zirconium oxychloride (ZrOCl$_2$). We have used BaCO$_3$ and TiO$_2$ as parent material and ZrOCl$_2$ as additive. The samples with x=0.0, 0.1, 0.2 and 0.3 hereafter called as BTO, BZT1, BZT2 and BZT3 respectively. The required amount of the materials are mixed, homogenized, dried and grinded to fine powder in an agate mortar with pestle for few hours with distilled water. The grinded powder is heated at 700°C for 2 hours and twenty minutes. Then the thermal treated powder were pressed into circular discs of 15mm diameter and 1-2mm thickness at a pressure of 3×10$^8$ N/m$^2$ using hydraulic press. Polyvinyl alcohol was used as a binder to prepare the pellet which was burnt out at high temperature. The pellets were sintered at the optimizing temperature of
3. Results and discussion:
3.1 Structural and micro-structural properties:
As evident from figure 1, the samples are crystalline. The diffraction peaks of BTO and BZT1 correspond to tetragonal and orthorhombic phases while the diffraction peaks of BZT2 and BZT3 corresponds to cubic phases. The lattice constants calculated from the XRD peaks of the four samples are reported in Table 1. The crystallite sizes of the samples were also calculated from the major peaks using the Scherer’s formula [6]. The calculated values are reported in Table 1. As evident from the Table 1, the crystallite size was found to decrease with increase in Zr content. It was observed that with the increase in Zr content, the phase transition from tetragonal to orthorhombic and orthorhombic to cubic. As evident from the figure 1, the diffraction peaks was found to be shifted to lower angles with increase in Zr content. It was expected that the shifting of peak indicates the increase in the lattice parameters. It may be attributed due to the replacement of smaller ionic radius Ti$^{4+}$ (0.74) by larger ionic radius Zr$^{4+}$ (0.86) as reported by other workers’ Zr doped BaTiO$_3$ thin films [7]

The Scanning electron micrographs of BTO, BZT1, BZT2 and BZT3 are shown in figure 2(a–d). As evident from figure 2, all the samples show well crystalline surface morphology.

3.2 Dielectric properties:
The variation of dielectric constant ($\varepsilon$) and dissipation factor (tanδ) of BTO, BZT1, BZT2 and BZT3 at room temperature are shown in figure 3. Both dielectric constant ($\varepsilon$) and dissipation factor (tanδ) show decreasing trend with increase in frequency. The dielectric constant decreases with power law in the low frequency range. This may be attributed due to the effects of space charge polarization or Maxwell-Wagner type interfacial polarization. The fall in the dielectric arises from fact that polarization does not occur instantaneously with the application of the electric field because of inertia. The delayed response to alternating electric field leads loss and decline in dielectric constant. At low frequencies, all type of polarizations contributes. While those polarizations with large relaxation times ceases to respond at higher frequency and hence dielectric constant decreases. While studying the behaviour of the dielectric constant with frequency, at low frequencies, the non-uniform charge accumulation at the grain boundaries mainly due to oxygen vacancies. These dipoles due to non-uniform charge accumulation at grain boundaries do not respond at higher frequencies thereby reducing the dielectric constant. Same type of frequency dependent dielectric behavior is found in many ferroelectric materials [8,9]. At high frequency regions, the dielectric constant of the BZT samples slightly decrease linearly with increase in frequency. The high dielectric loss at low frequency in these samples is confirmed due to presence of non-uniform charge accumulation at the grain boundaries. Two mechanisms are associated with relation to dielectric loss [10]. One is resistive loss and another one is relaxation loss. In case of resistive loss, energy is consumed by the mobile charges in the ceramics. In relaxation loss mechanisms, relaxation of dipoles dissipate energies. Loss tangent (dielectric loss) obeys a decreasing tendency with increase in zirconium content. In high frequencies, dielectric loss is independent of frequency. At room temperature the dielectric loss decrease from 0.18 to 0.078 with increase in Zr content.
Figure 4 shows variation of dielectric constant($\varepsilon$) and dissipation factor with temperature for four samples at 105KHz. As evident from Fig4, the samples BTO and BZT1 showed the dielectric anomaly peaks at 135°C and 125°C. The dielectric anomaly peak of BZT1 is lower than that of BTO. The existence of the anomaly peaks in dielectric and dissipation factor shows the ferroelectric to paraelectric phase transitions. The transition temperature was found to decrease with Zr content. The samples BZT2 and BZT3 do not show the anomaly peaks. The absence of the anomaly peaks in these samples is in consistent with the XRD studies as we do not expect ferroelectricity in BZT with cubic structure.

Figure 5 and figure 6 shows the variation of the dielectric constant and dissipation factor with temperature at different frequencies for all the samples.

3.3 AC Conductivity:
The frequency and temperature dependence of ac conductivity is useful method for gaining insight the electrical conduction mechanism of ferroelectric materials. The measured conductivity of the materials as a function of frequency can be described by the relation [11].

$$\sigma(f) = \sigma_{dc} + \sigma_{ac}(f) = \sigma_{dc} + A(T)f^{n(T)}$$

Where $\sigma_{dc}$ and $\sigma_{ac}$ are dc and ac conductivity of the material, $A(T)$ is thermally activated constant that determines the polarizability strength and $n(T)$ is a constant that determines the degree of interaction between the ions and lattice[12]. The ac conductivity of the various samples are calculated using the relation $\sigma_{ac} = \omega\varepsilon\varepsilon_0\tan\delta$.

The figure 7 shows the variation of $\sigma_{ac}$ with frequency at room temperature. As evident from the figure 7, the ac conductivity increase with increase in frequency. The rate of increase of conductivity is more for $x=0.1$ sample as compared to other samples. At low frequencies the conductivity is linearly independent on frequency and this may be attributed to the dc conductivity of the samples ($\sigma_{dc}$). When frequency is further increased, the conductivity is increased rapidly. The experimentally observed values of the samples using relation 1 were fitted and fitted parameters are reported in table 2.

It may be noted that at lower frequency range the experimental and theoretical values are not in good agreement. This may be attributed to the presence of space charge polarization at the sample-electrode interface and grain boundaries. However at higher frequency the curves are well fitted. It may be attributed to hopping of small polarons among the localized states. Hopping conduction is favoured in ionic lattice in which the same kind of cations exists in two oxidation states. In case of small polaron model, the ac conductivity increases with increase in frequency [13]. As evident from table 2, the BZT1 sample shows higher conductivity compared to other samples. In BTO, the maximum number of Ti$^{+4}$ and Ti$^{+3}$ ions are available on the B sites of the perovskite. When the concentration of Zr is increased, the number of electron hopping sites might have been decreased thereby decreasing the conductivity. The decrease in ac conductivity may also be attributed to the decrease in grain sizes of the samples as observed in section 3.1 and 3.2.

4. Conclusion
The single phase BZT powders are obtained from the mixed oxide method at 1300°C for 4 hours in free air. There is change in crystal structure from tetragonal (BTO) to orthorhombic for $x=0.1$ and then to cubic above $x=0.2$ in the samples. The diffraction peaks were found to be shifted to lower angles as Zr content is increased. The grain sizes of all the samples range from 90.8 to 47.4nm. The phase transition temperature was found to be reduced systematically as zirconium content is increased. Ac conductivity was found maximum for BZT1 compared to the other samples.

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Reference

Fig 1: XRD patterns of the Different samples of BTO, BZT1, BZT2 and BZT3

Fig 2: SEM images of different samples of BTO(a), BZT1(b), BZT2(c) and BZT3(d)
Fig3: Variation of Dielectric constant ($\varepsilon$) and dissipation factor (tan $\delta$) with frequency

Fig4: Variation of dielectric constant ($\varepsilon$) and dissipation factor (tan $\delta$) with temperature

Fig5: Temperature dependence of dielectric constant ($\varepsilon$) of BTO, BZT1, BZT2 and BZT3.
Fig6: Temperature dependence of dissipation factor (tan\(\delta\)) of BTO, BZT1, BZT2 and BZT3.

Fig7: AC conductivity (\(\sigma_{ac}\)) with frequency for BTO, BZT1, BZT2 and BZT3 at room temperature.
Table 1: Showing the lattice parameters and crystallite sizes for the different samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>Cell Volume (10^6 pm³)</th>
<th>Grain size from XRD data (nm)</th>
</tr>
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<tbody>
<tr>
<td>BTO</td>
<td>3.991</td>
<td>3.991</td>
<td>4.051</td>
<td>64.54</td>
<td>91.8</td>
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<tr>
<td>BZT1</td>
<td>7.538</td>
<td>5.671</td>
<td>5.585</td>
<td>241.46</td>
<td>87.8</td>
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<tr>
<td>BZT2</td>
<td>4.038</td>
<td>4.038</td>
<td>4.038</td>
<td>65.85</td>
<td>81.7</td>
</tr>
<tr>
<td>BZT3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>47.7</td>
</tr>
</tbody>
</table>

Table 2: Dielectric constant (ε), ac conductivity and fitting parameters of the different composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dielectric constant (ε)</th>
<th>Dissipation factor ( tanδ )</th>
<th>σac (Sm⁻¹) (10⁻⁴)</th>
<th>σdc (Sm⁻¹) (10⁻⁶)</th>
<th>A(T) (10⁻¹⁰)</th>
<th>n</th>
</tr>
</thead>
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<tr>
<td></td>
<td>10KHz</td>
<td>100KHz</td>
<td>1MHz</td>
<td>10KHz</td>
<td>100KHz</td>
<td>1MHz</td>
</tr>
<tr>
<td>BTO</td>
<td>1144</td>
<td>1099</td>
<td>1133</td>
<td>0.045</td>
<td>0.027</td>
<td>0.029</td>
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<tr>
<td>BZT1</td>
<td>1804</td>
<td>1615</td>
<td>1680</td>
<td>0.067</td>
<td>0.08</td>
<td>0.080</td>
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<tr>
<td>BZT2</td>
<td>1237</td>
<td>1201</td>
<td>1232</td>
<td>0.023</td>
<td>0.020</td>
<td>0.024</td>
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<tr>
<td>BZT3</td>
<td>1526</td>
<td>1415</td>
<td>1429</td>
<td>0.067</td>
<td>0.047</td>
<td>0.048</td>
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