A study of enhanced structural, microstructural and dielectric behaviour of aliovalent ions doped \( \text{BaZr}_{0.05}\text{Ti}_{0.95}\text{O}_3 \) ceramic

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Abstract. The lead-free ceramics are considered to be the best substitutes for lead based ceramics which have tremendous harmful effects regarding environmental pollution. In this concern, the lead-free ceramics have been widely attracted by research communities. In the present study we have prepared lead free \( \text{BaZr}_{0.05}\text{Ti}_{0.95}\text{O}_3 \) perovskite ceramics with various doping concentrations of \( \text{Gd}^{3+} \) ions by the conventional solid-state reaction method. The perovskite phase formation was studied by x-ray diffraction which indicate the transformation of crystal symmetry from orthorhombic to tetragonal structure for the \( \text{Gd}^{3+} \) ions doped samples. The scanning electron microscopy studies revealed the modification in grain size on doping Gd ions also the energy dispersive X-ray spectra have been obtained to study the compositional variations. The dielectric and loss studies have been performed in the large range of temperature and frequency. The low dielectric loss and high dielectric constant suggests possible applications in memory devices and ceramic capacitors. Temperature coefficient of capacitance plots have also been plotted.

1. Introduction

\( \text{BaTiO}_3 \) (BT), a commonly known perovskite was commercially used for acoustic and ultrasonic generation and detection though its Curie temperature was quite low (i.e. 120 °C) [1-6]. Soon it was replaced by another perovskites like \( \text{PbTiO}_3 \) and \( \text{Pb(Zr, Ti)}_3 \text{O}_3 \) [7-13]. Though the lead based ceramic compounds have proved to be extremely good as far as the industrial needs are concerned but, the toxicity of Pb restricts its practical applications. Thus, in recent years the need for lead free perovskite ceramics caused a reconsidered interest in \( \text{BaTiO}_3 \) based ceramics [14-18]. The structural and dielectric properties of \( \text{BaTiO}_3 \) can be modified to a large extent by the addition of some aliovalent ions (heterovalent dopants) such as \( \text{La}^{3+}, \text{Ce}^{3+}, \text{Nb}^{5+}, \text{Nd}^{3+}, \text{Pr}^{3+}, \text{Eu}^{3+}, \text{Er}^{3+}, \text{Gd}^{3+}, \text{Mg}^{2+}, \text{Sn}^{4+} \) etc. on \( \text{Ba}^{2+} \) or \( \text{Zr}^{4+} \) on \( \text{Ti}^{4+} \) sites that forms the solid solution [19-26]. Among various compositions \( \text{Zr}^{4+} \) with ~15% substitution in \( \text{Ba(Zr, Ti)}_3 \text{O}_3 \) (BZT) undergoes three structural phase transitions (rhombohedic to orthorhombic, orthorhombic to tetragonal and tetragonal to cubic) like \( \text{BaTiO}_3 \), also the Curie temperature decreases [27-30]. After thorough investigation of literature, out of the several rare earth ions our focus was on Gd whose ionic radius is 0.91Å. The incorporation of rare-earth (Gd\(^{3+}\)) ions into
the BT host system was studied by Borah et al. in 2014 [31]. The results of their study revealed that Gd$^{3+}$ ions greatly manifest dielectric relaxation and carrier conduction mechanisms. The dielectric constant showed a decreasing trend with doping content and with increasing frequency. However, in the low-frequency region due to the combined result of orientational polarization and electrical conduction the loss tangent (tan δ), was found to be quite high in the doped samples as compared to their un-doped counterpart. In another study the amphoteric nature of Gd$^{3+}$ ions were discussed by Li et al. in 2012 [32]. According to the study because of the mediocre ionic radius of Gd$^{3+}$ ion, it may replace the A-site ions or B-site ions. After the analysis of XRD patterns they revealed that different substitution sites of Gd$^{3+}$ ions could be affected by amount of Gd$_2$O$_3$ doping. Gd$^{3+}$ tended to occupy Ba-site when Gd$_2$O$_3$ concentration was less than 0.25 mol%. On further increasing concentration of Gd$_2$O$_3$ doping amount to 0.3 mol%, Gd$^{3+}$ ions get substituted into both the Ba- and Ti-sites as a result of which an improvement on dielectric constant of BaTiO$_3$-based ceramics is seen. They used self-compensation model to discuss the dielectric behaviour. Reddy et al. in 2011[33] gave a detailed study of dielectric studies properties when Gd$^{3+}$ ions are doped at A site of BaZr$_{1-x}$Ti$_{x}$O$_3$ ceramic. The microstructural investigation on the sintered ceramics showed that Gd doping significantly reduced the grain size of pure BZT ceramics. Change in the Gd concentration had minor influence on the grain size and on morphology. The Curie temperature (Tc) significantly decrease with an increase in the Gd content. However, the maximum value of dielectric constant at T_c was seen for 2 mol% Gd and on further increase in Gd content the dielectric constant at T_c decreased. They reported that the dielectric constant was significantly improved as compared to that of undoped BZT ceramic. Hence it is concluded that the tunable dielectric materials with good dielectric properties can be prepared by doping BZT with Gd.

In the present study we have chosen 5 mole % Zr$^{4+}$ doped BT i.e. BaZr$_{0.05}$Ti$_{0.95}$O$_3$ as base material. This composition of BZT shows normal ferroelectric behavior and also the presence of morphotropic phase boundaries give special features by improving the piezoelectric properties. Further we have chosen Gd$^{3+}$ as an heterovalent ion which can replace Ba$^{2+}$ ions at A-site as according to the formula Ba$_{1-x}$Gd$_{2x/3}$Zr$_{0.05}$Ti$_{0.95}$O$_3$. Thus, the objective of the present work is to study the influence of Gd$^{3+}$ ions doping on the dielectric properties of BaZr$_{0.05}$Ti$_{0.95}$O$_3$.

2. Materials and methods
The perovskite samples of pure and Gd doped Barium Gadolinium Zirconium Titanate with formula Ba$_{1-x}$Gd$_{2x/3}$Zr$_{0.05}$Ti$_{0.95}$O$_3$ (x=0.00, 0.01, 0.02) were prepared by conventional high temperature solid state reaction method. For the sake of convenience, we will mention the samples as BZT, BGZT1 and BGZT2 for x = 0.00, 0.01 and 0.02 respectively. The starting raw materials were BaCO$_3$, TiO$_2$, ZrO$_2$ and Gd$_2$O$_3$ (all from Merck) all were more than 99% pure. The stoichiometric ratio of all the chemicals were thoroughly mixed in an agate mortar in dry and wet mixing with appropriate amount of Acetone for 5 hours. After proper mixing the samples were calcined at 1200°C for 4 hours at a heating rate of 5 °C per minute. A small amount of polyvinyl alcohol was added to the calcinated powders for the fabrication of pellets which were sintered at 1250 °C. The circular disc shaped pellets were prepared by applying uniaxially a pressure of 200 MPa. A preliminary study on compound formation and structural parameters was carried out using an X-ray diffraction (XRD) technique with an X-ray powder diffractometer. The XRD pattern of the calcinated powder was recorded at room temperature PANalytical X’pert pro with Cu-Kα radiation (1.5405 Å) in a wide range of Bragg’s angles 2θ (20 ≤ 2θ ≤ 80). The dielectric constant and dielectric loss were measured on N4L-NumetriQ LCR meter (model PSM1735).

3. Results and Discussions
3.1 Structural characterization
The X-ray diffraction patterns of BZT, BGZT1 and BGZT2 ceramic specimen are shown in figure 1. After a keen analysis by X’pert Highscore software, the Perovskite structure was identified for all the specimens at room temperature. The peaks of BGZT1 and BGZT2 specimens seems to move slightly towards right (higher 2θ). The lattice parameters from the XRD data were calculated using Checkcell
software shown in inset. The structural evolution of the specimens with these compositional changes can be readily understood in terms of the ionic radii of the cations at A-site ($r_{\text{Ba}^{2+}} = 1.61$ Å and $r_{\text{Gd}^{3+}} = 0.91$ Å) and B-site ($r_{\text{Ti}^{4+}} = 0.605$ Å and $r_{\text{Zr}^{4+}} = 0.72$ Å). The splitting of peaks at $2\theta = 45^\circ$ for BGZT1 and BGZT2 show the tetragonal symmetry indicating the ferroelectric phase at room temperature. However, for the BZT sample the crystal symmetry was observed to be orthorhombic at room temperature. The inset shows the variation of d-spacing and cell volume both these values decrease with increasing concentration of Gd.

**Figure 1.** XRD plots of BZT, BGZT1 and BGZT2 at room temperature. The inset is variation of d-spacing and cell volume with composition.

### 3.2 Microstructural studies

Figure 2(a)-(c) reveal the scanning electron microscopic images of BZT, BGZT1, BGZT2 samples. The non-uniform distributions of the irregular shaped grains are observed in all the ceramics. The microstructural modifications in terms of grain size can be seen in the pictures. The average grain sizes were decreased sharply with Gd addition accompanied with uniform grains. As significant from the figures the average grain size for BZT is ~20µm whereas for BGZT1 and BGZT2 it reduces to ~2µm. However, no remarkable change in the density of the ceramics with the variation of Gd concentration in the BZT system. The compositional characterization was done by Energy dispersive X-ray spectroscopy (EDX) which is shown in inset of figure 2. Table 1 shows the calculated and EDX derived composition of BZT, BGZT1 and BGZT2 ceramics. There exist small variation in both the data which is possibly due the deficiency of oxygen during sintering at high temperature.
Figure 2. SEM micrographs of (a) BZT (b) BGZT1 (c) BGZT2 ceramics. The insets show EDX spectrum showing the elemental composition of the ceramics.

Table 1. Calculated and EDX derived composition of BaGdZr0.05Ti0.95O3 ceramic.

| Element | BZT | BGZT1 | BGZT2 |
|---------|-----|-------|-------|
|         | Wt.% calculated | Wt.% from EDX | Wt.% calculated | Wt.% from EDX | Wt.% calculated | Wt.% from EDX |
| Ba      | 57.59 | 57.65 | 56.39 | 56.45 | 56.17 | 56.11 |
| Zr      | 1.48  | 1.59  | 1.50  | 1.55  | 1.52  | 1.46  |
| Ti      | 18.52 | 18.12 | 18.57 | 18.55 | 18.60 | 18.46 |
| O       | 22.41 | 22.64 | 22.96 | 22.85 | 22.90 | 23.12 |
| Gd      | -     | 0.58  | 0.60  | 0.81  | 0.85  |       |

3.3 Dielectric studies
We have done the dielectric studies and dielectric loss studies of Gd doped BZT as a function of temperature at various frequencies. But these results were reported in our earlier publication [34] so here, we only report the dielectric study as function of frequency at various temperatures. Figure 3 (a-c) illustrated the frequency dependent dielectric studies of BZT, BGZT1 and BGZT2 ceramics at various temperatures from room temperature to temperature above phase transition. We have noticed an inverse relation between dielectric constant and frequency i.e. $\varepsilon'$ decreases with increasing frequency. All the ferroelectric materials follow this behaviour. At lower frequencies the values of dielectric constant are higher while in the higher frequency region the dielectric constant drops and attains a saturation. To understand this behaviour Debye gave a modified law for the dipoles oscillating in AC fields [35]:

$$\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + i\omega\tau^\alpha}$$

where $\varepsilon_0$ and $\varepsilon_\infty$ are the low and high-frequency values of $\varepsilon$, $\omega$ (=2$\pi$f) is the cyclic frequency, $f$ is the frequency of measurement, $\tau$ is the relaxation time and $\alpha$ measures the distribution of relaxation time. According to this relation at lower frequencies the relaxation time is quite high so the dipoles get sufficient time to follow the electric field resulting in high value of $\varepsilon'$. With increasing frequency, the dipoles begin to lag behind the field as a result of which decrease in $\varepsilon'$ values are seen. At much higher frequencies due very short relaxation times the dipoles could not orient themselves in the direction of the applied electric filed and hence reduction in the dielectric values are seen.

The inset in figure 3 shows the dielectric loss as function of frequency for the samples. The dielectric loss of the samples is less than 0.2 and for BZT and BGZT2 the value is even less than 0.1 which show good thermal stability for practical applications. The dielectric loss is attributed to the presence of oxygen vacancies which are commonly seen in the oxide perovskites. The dielectric loss curves follow the similar trend as seen in the dielectric constant vs. frequency plots. The curves are more dominant at
lower frequencies than higher frequencies. At higher frequencies the dipoles could not follow the applied AC fields because of infinitesimally small relaxation time. In BZT at some frequencies between $10^2$-$10^4$ Hz a small hump is seen indicating dielectric relaxation in the sample however, in BGZT1 and BGZT2 samples this kind of relaxation is not seen.

Figure 3. Variation of dielectric constant with frequency at various temperatures from room temperature to Tc. The inset shows the corresponding dielectric loss values. (a) BZT (b) BGZT1 (c) BGZT2.

The capacitance and dissipation factor of ceramic capacitors are significantly affected by doping concentrations. The permittivity/capacitance of ferroelectrics is generally temperature dependent and varies especially near to the Curie temperature. In order to measure the degree of capacitance variation with temperature, the temperature coefficients of capacitance (TCC) near phase transition temperature were calculated using the formula [36]:

$$\text{TCC}(\%) = \frac{C(T) - C(T_c)}{C(T_c)} \times 100\%$$

Where $C(T)$ is capacitance at the temperature $T$ and $C(T_c)$ the reference value of the capacitance at phase transition temperature ($T_c$). The TCC(%) measured at 100kHz frequency is represented as a function of the temperature for BZT, BGZT1 and BGZT2 in figure 4. In case of doped samples, the variation of capacitance is less than 25% from 40°C-160°C. The corresponding temperature interval of 120°C is considered as a ceramic with good stability which is a fundamental property of all devices for energy storage application. Analysis of the plots suggests that the TCC of BGZT2 sample is almost close to the temperature stability specifications for X8R and X9R capacitors, which state that the capacitance change should fit within ±15% of the tolerance limit for long temperature range.
Figure 4. Temperature coefficient of capacitance with temperature.

3.4 Conductivity studies

Figure 5 shows the variation of AC conductivity of BZT, BGZT1 and BGZT2 samples with temperature (40℃-160℃ that corresponds to the temperature nearby phase transition) measured at 100kHz. Here, ac conductivity was evaluated from dielectric data by employing the following relation [37]:

\[ \sigma_{ac} = \omega \varepsilon_0 \varepsilon' \tan(\delta) \]  \hspace{1cm} (3)

where, \( \sigma_{ac} \) is the ac conductivity, \( \omega = 2\pi f \) is the angular frequency and \( \varepsilon_0 \) is the absolute permittivity. It is apparent from the figure that in low temperature regime the ac conductivity depends significantly on the frequency. However, the increase in temperature, where marked dielectric relaxation takes place, reduced gradually the frequency dependence of \( \sigma_{ac} \) so that the conductivity was mainly determined by temperature. At still higher temperatures (near phase transition) there was a deviation probably due to the onset of dielectric phase transition. The ac conductivity found to increase with temperature at lower frequencies however, at higher frequency we could not find much variation in conductivity. Near Curie temperature, the domain structure breaks up, carriers become free and take part in conduction mechanism. Interpretation of different theoretical models concludes that ac conductivity originates from migration of ions by hopping between neighbouring potential wells at lower temperatures which eventually give rise to dc conductivity at high temperatures. Oxygen vacancies are the most mobile charge carriers in oxide ferroelectrics and play an important role in the conduction process in most dielectric ceramics. Around the oxygen vacancy, long range potential wells may be formed, there can be large number of titanium centres within each potential well surrounding the oxygen vacancy. Conduction electrons created by the ionization of oxygen vacancies can cause hopping of electrons between Ti\(^{4+}\) and Ti\(^{3+}\) [38-40]. The figure also indicates that the introduction of Gd\(^{3+}\) ions has slightly increased the conductivity probably due to the presence of oxygen vacancies.
4. Conclusion

The performance characteristics of ceramic capacitors are greatly determined by the properties of the dielectric material. Thus, from the present study we conclude that lead free ceramic samples of Gadolinium doped Barium Zirconium Titanate samples have been synthesized successfully by the conventional solid-state reaction method. The XRD technique has confirmed the perovskite phase with orthorhombic structure for BZT and tetragonal for BGZT1 and BGZT2. The microstructural studies reveal that the shape, size and distribution of BZT has got modified by addition of Gd$_2$O$_3$ in it and reduced from 20µm to 2µm. The dielectric values found to decrease for the doped samples but the dielectric loss for these samples is little larger. Also, the variations in temperature effected capacitance and dissipation factor of ceramic capacitors are found. The conductivity values are increased for doped samples.

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