# Glassy behavior study of dysprosium doped barium zirconium titanate relaxor ferroelectric

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**Research Article**

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**Abstract:** We report the glassy behavior of dysprosium doped barium zirconium titanate single phase perovskite ceramics with general formula $Ba_{1-x}Dy_{2x/3}Zr_{0.25}Ti_{0.75}O_3$ prepared by solid-state reaction method. Temperature and frequency dependent dielectric studies of the ceramics reveal relaxor behavior. A non-Debye relaxation, which is analogous to the magnetic relaxation in spin-glass system, is observed clearly around temperature of dielectric permittivity maximum ($T_m$). Frequency dependence of $T_m$ governed by production of polar nano-regions is analyzed using Debye relation, Vogel–Fulcher (V–F) relation and power law. A clear change in dynamic behavior is observed by power parameter which is related to growth of interactions between polar nano-regions with different composition. Various parameters like activation energy for relaxation, freezing temperature, relaxation frequency, etc., are determined after non-linear curve fitting. Temperature dependence of dielectric constant at temperatures much higher and lower than $T_m$ is analyzed by two exponential functions, which gives an idea about the production of polar clusters at high temperature and distribution of freezing temperatures at lower temperature. Various other associated parameters are calculated by non-linear curve fitting and their significance has been explained.

**Keywords:** diffuse phase transition; transition temperature; dielectric properties; relaxors; polar nano-regions

## 1 Introduction

Relaxor ferroelectrics (RFE) with complex perovskite structure are of great interest due to their wide application in the fabrication of devices such as multilayer ceramic capacitors, electrostrictive actuators, electromechanical transducers and in the fundamental understanding of ferroelectric systems. Relaxor materials are characterized by a diffuse phase transition with strong frequency dispersion of dielectric permittivity, where temperature of dielectric permittivity maximum ($T_m$) shifts to higher temperature with increasing frequency. Relaxor behavior in ferroelectric materials normally results from compositional inheritance, disorder or frustration. This behavior has been observed and studied most extensively in disorder $ABO_3$ perovskite ferroelectric. Three essential ingredients of relaxor ferroelectric are the existence of lattice disorder, evidence of existence of polar nanodomains at temperatures much higher than $T_m$ and existence of domains as islands in a highly polarisable host lattice. Relaxor behavior has been usually explained by various theoretical models, such as dipole inhomogeneity, order–disorder, micro–macro domain transition, super-paraelectricity, dipolar glass and local random field [1–6]. In spite of continuous fundamental investigations on relaxor ferroelectrics in

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recent years, the nature of their extraordinary properties has not yet been understood completely and they are still the subject of intensive research. Vieland *et al.* [7,8] have proposed dipolar glass model and successfully explained the frequency dispersion of $T_m$ with the Vogel–Fulcher (V–F) relation. Although the relationship is widely used for RFEs, it has some shortcomings in explaining the dielectric relaxation for certain RFEs [9]. Later, Cheng *et al.* [10] have proposed a more reasonable super exponential relation named power law to explain the relation between frequency and $T_m$.

Barium zirconium titanate solid solution system $BaZr_xTi_{1-x}O_3$ (BZT) has received special attention in recent years due to its potential as a lead-free high strain material and a high-permittivity dielectric material [11]. It is well known that $BaTiO_3$ (BT) presents three phase transitions, i.e., rhombohedral-to-orthorhombic at 183 K, orthorhombic-to-tetragonal at 268 K, and tetragonal-to-cubic at 393 K [12]. When $Ti^{4+}$ ion is substituted by $Zr^{4+}$ ion in BT, temperature of ferroelectric-to-paraelectric phase transition decreases, while temperature of ferroelectric-to-ferroelectric phase transition increases, resulting in a pinched phase transition (for $0.10 < x < 0.15$) at temperatures between 345 K and 365 K [13–15]. Consequently, a broad peak is obtained in a plot of permittivity versus temperature. For higher zirconium concentrations ($x > 0.15$) only a rhombohedral-to-cubic phase transition is observed. Furthermore, the phase transition of this system changes from a "normal" ferroelectric to a typical relaxor behavior by increasing zirconium concentration (until $x = 0.75$) [16–21] which is caused by the inhomogeneous distribution of $[ZrO_6]$ clusters into the titanium (Ti) sites and/or by the mechanical stresses on the grains [19]. A polar cluster like behavior is obtained for Zr-rich BZT compositions ($x > 0.75$) [17]. Present composition $BaZr_{0.25}Ti_{0.75}O_3$ is chosen as the host material because it shows relaxor behavior and detailed optical, structural and dielectric studies have been reported by Ref. [22].

It has been well reported that small amounts of impurity ions can dramatically modify the properties of BZT ceramics. The selection of dopants or substitutions at different atomic sites is based on many factors, including (i) charge neutrality, (ii) tolerance factor $t = (r_A + r_o)/\sqrt{2}(r_B + r_o)$ where $r_A$ and $r_B$ are the radii of A and B site ions respectively and $r_o$ is

the ionic radius of oxygen, and (iii) solubility/ miscibility. Aliovalent cations incorporated in perovskite lattice serve as donors or acceptors, which can affect the electrical characteristics greatly, even though solubility remains at a trace level [23–25]. Trivalent rare earth cations have been widely used in the modification of barium titanate based ceramics owing to their special electronic structure and their moderate ionic radii, which allows them being incorporated in both A and B sites in $ABO_3$ lattice [23,26,27]. Hence, interesting microstructural and dielectric response features have been observed. For instance, the temperature of phase transition is drastically decreased by addition of rare-earth ions and a relaxor-type behavior is induced [28], in a manner similar to the effects of an increment of zirconium. Both the diffusivity of the phase transition and the degree of relaxor behavior increase with the rise of the rare earth content [29–33]. It is widely accepted that the behavior of the polar regions in the material is key to the behavior of RFE [34,35]. Therefore, it is interesting to study the behavior of the polar regions in the present material. In this context, it aims to study the relaxor behavior of the $Ba_{1-x}Dy_{2x/3}Zr_{0.25}Ti_{0.75}O_3$ ceramics using some theoretical models. Temperature dependence of dielectric constant and frequency dependence of dielectric constant of these REFs at temperatures higher and lower than $T_m$ have been analyzed using Cheng's model [10].

## 2　Experimental

The samples with general formula $Ba_{1-x}Dy_{2x/3}Zr_{0.25}Ti_{0.75}O_3$ ($x = 0.0$, 0.01, 0.025, 0.05) were prepared through solid-state reaction route. The compositions were prepared from $BaCO_3$ (S.D. Fine Chem., Mumbai), $Dy_2O_3$ (S.D. Fine Chem., Mumbai), $TiO_2$ (E. Merck India Ltd.) and $ZrO_2$ (Loba Chem., Mumbai). All the chemicals had more than 99% purity. The raw powder was thoroughly mixed with agate mortar using IPA. The homogenous mixture was calcined in air successively at 1300 ℃ for 6 h and 1350 ℃ for 4 h with intermediate mixing and grinding. The detailed synthesis and characterization were reported elsewhere [36]. For electrical property measurements, the disks were pressed uniaxially at 200 MPa with 2 wt% PVA solution added as binder

and then sintered at 1350 ℃ for 6 h. Silver electrodes were applied to the opposite disk faces and heated at 700 ℃ for 5 min. Dielectric measurement was carried out over the frequency range 50 Hz to 1 MHz using a Hioki LCR meter connected to computer. The dielectric data was collected at an interval of 3 ℃ while heating at a rate of 0.5 ℃/min.

# 3 Result and discussion

It has been reported that dysprosium doped BZT behaves as a strong relaxor which is revealed from the increased value of diffuseness and frequency dispersion of $T_m$ [36]. For a clear picture, temperature dependence of dielectric constant curve for all compositions is presented in Fig. 1. Table 1 provides the $\gamma$ values and experimental values of $T_m$ of all the samples. Dielectric study reveals a diffuse phase transition behavior along a frequency dependent transition temperature, which is the characteristic of relaxor ferroelectric. Relaxor behavior and

the diffuseness of ferroelectric phase transition in these materials can be explained as a consequence of $Dy^{3+}$ substitution for A-site $Ba^{2+}$ ions in $Ba_{1-x}Dy_{2x/3}Zr_{0.25}Ti_{0.75}O_3$ (BDZT) compounds. For every two $Dy^{3+}$ substituting for $Ba^{2+}$ ions, only one A-site vacancy is created, producing compositional fluctuation on a microscopic scale. In the same way, presence of $Dy^{3+}$ ions in A site and its interaction with A-site vacancies can originate lattice distortion of perovskite structure. Lattice distortion and compositional fluctuation originating from vacancy inclusions in $Ba_{1-x}Dy_{2x/3}Zr_{0.25}Ti_{0.75}O_3$ structure can explain the diffusion of the ferroelectric phase transition and the relaxor behavior observed in these compounds [37].

**Table 1 Parameters obtained from the temperature dependent dielectric study of $Ba_{1-x}Dy_{2x/3}Zr_{0.25}Ti_{0.75}O_3$**

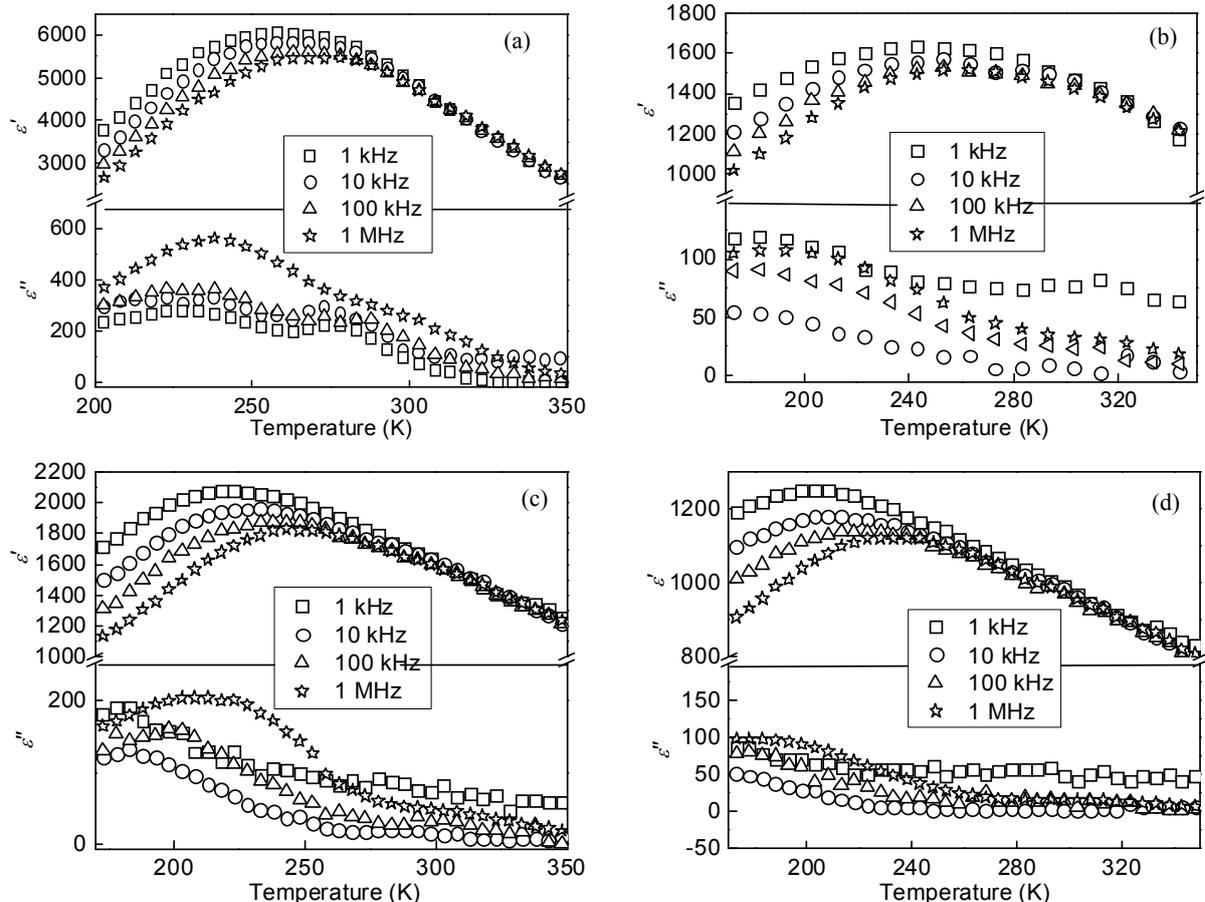| Sample | $T_m$ (K) | $T_{cw}$ (K) | $\Delta T_m$ (K) | $\gamma$ |
|---|---|---|---|---|
| $x = 0.0$ | 273 | 361 | 88.321 | 1.71 |
| $x = 0.01$ | 263 | 341 | 77.7 | 1.80 |
| $x = 0.025$ | 248 | 317 | 69.4 | 1.83 |
| $x = 0.05$ | 227 | 293 | 65.8 | 1.91 |



Fig. 1 Temperature dependent real and imaginary parts of permittivity of $Ba_{1-x}Dy_{2x/3}Ti_{0.75}Zr_{0.25}O_3$ at various frequencies: (a) $x = 0.0$, (b) $x = 0.01$, (c) $x = 0.025$, (d) $x = 0.05$.

Normal ferroelectrics exhibit a sharp ferroelectric to paraelectric phase transition. In contrast, relaxor materials posses a diffuse phase transition over a broad temperature range. Zhi *et al*. [1] have demonstrated that relaxors deviate from the Curie–Wiess law at temperature above temperature of dielectric maximum $T_m$ and they exhibit non-Debye relaxation cumulating in polarization freezing at a temperature below $T_m$. Since relaxors typically operate at temperature within the transition, material behavior strongly depends on temperature and frequency of applied electric load. Transition temperature is often tailored to a specific application by mixing additional dopants. Cross [4] has proposed a more completed picture of relaxor behavior. He postulated that nanoscale size polar regions form with decreasing temperature. These small regions have an energy barrier so they fluctuate with thermal agitation in a manner analogous to super para-magnetism. Each region's dipole moment has random orientation; the macroscopic polarization is zero but system's RMS dipole moment is non zero. Initially, the relaxor obeys Curie–Weiss relationship with a very high Curie temperature. With further cooling, thermal fluctuation slows and interaction between regions freezes polarization in a manner similar to magnetic spin glasses. Materials deviate from the Curie–Weiss relationship and possess strong frequency dependence. Eventually, the materials develop a permanent remnant polarization and large domains develop as in a normal ferroelectric. Later, Bokov and Ye [38] have reported that at high temperature relaxor ferroelectrics exist in a non-polar paraelectric (PE) phase, which is similar in many respects to the PE phase of normal ferroelectrics. Upon cooling they transform into the ergodic relaxor (ER) state in which polar regions of nanometer scale with randomly distributed directions of dipole moments appear. This transformation which occurs at the so-called Burns temperature ($T_B$) cannot be considered a structural phase transition because it is not accompanied by any change of crystal structure on the macroscopic or mesoscopic scale. Nevertheless, the polar nano-regions (PNRs) affect the behavior of crystal dramatically, giving rise to unique physical properties. For this reason the state of crystal at $T < T_B$ is often considered as new phase different from PE. At temperatures close to $T_B$, the PNRs are mobile and their behavior is ergodic. On cooling, their dynamics slows down enormously and at a low enough temperature, $T_f$ (typically hundreds degrees below $T_B$),

the PNRs in canonical relaxors become frozen into a non-ergodic state, while average symmetry of crystal still remains cubic. Similar kind of non-ergodicity is characteristic of a dipole glass (or spin glass) phase. Existence in relaxors of an equilibrium phase transition into a low temperature glassy phase is one of the most interesting hypotheses which have been intensively discussed [38]. Freezing of dipole dynamics is associated with a large and wide peak in the temperature dependence of the dielectric constant ($\varepsilon$) with characteristic dispersion observed at all frequencies practically available for dielectric measurements. In analogy with spin glasses, such a behavior of the dynamic susceptibility in disordered ferroelectric is supposed to be concerned with existence of broad spectrum of relaxation times. In general, for relaxor materials the dispersion observed near $T_m$ is associated with the volume distribution of polar regions and interaction between them [30]. Thus it indicates that the dielectric polarization is of relaxation type in nature such as dipolar glasses. Thus, one can use the frequency dependence of $T_m$ to get insight into the temperature dependence of relaxation time, which is directly related to volume distribution of polar regions. Hence, to understand behavior of polar regions in BDZT system, glassy nature of BDZT system has been studied using some theoretical models.

## 3. 1   Frequency dependence of $T_m$ and relaxor behavior

It is generally considered that Debye model is based on the assumption of a single relaxation time [39]. However, the erroneous pre-exponential factor and activation energy observed in Debye medium (where the polar regions are free to rotate and can be frozen only at $0\,\mathrm{K}$) suggest that there exists some interaction between the polar regions in RFEs. For Debye medium, the relation between $\omega$ and $T_m$ can be described by following equation:

$$\omega = \omega_0 \exp\left(-\frac{T_0}{T_m}\right) \qquad (1)$$

where $\omega$ is the applied or probing frequency; $\omega_0$ is the attempt frequency of a dipole or Debye frequency; and $T_0$ is the equivalent temperature of activation energy for the relaxation process. Experimental data are fitted to the above equation in Fig. 2 and fitting parameters are given in Table 2.
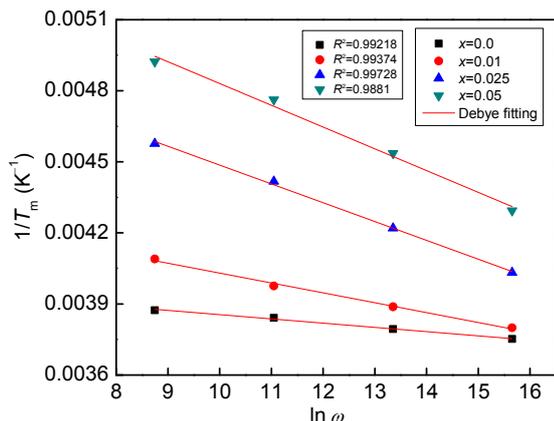
Fig. 2   Fitting for relaxation behavior using Debye model of $Ba_{1-x}Dy_{2x/3}Zr_{0.025}Ti_{0.75}O_3$.

**Table 2   $T_0$ and $\omega_0$ from the fitting parameters of Debye relation for $Ba_{1-x}Dy_{2x/3}Zr_{0.25}Ti_{0.75}O_3$ relaxors**

| Sample | $\omega_0$ (Hz) | $T_0$ (K) |
|---|---|---|
| $x = 0.0$ | $5.895 \times 10^{97}$ | $5.58 \times 10^4$ |
| $x = 0.01$ | $1.9 \times 10^{52}$ | $2.7 \times 10^4$ |
| $x = 0.025$ | $2.48 \times 10^{31}$ | $1.4 \times 10^4$ |
| $x = 0.05$ | $1.025 \times 10^{27}$ | $1.08 \times 10^4$ |

According to Debye relaxation process, all dipoles in the system relax with the same relation time (which is called a single-relaxation-time approximation). The single-relaxation-time model of Debye assumes a simple exponential decay of relaxation function and a single relaxation time for some process, which typically strongly diverges from the experimental observations. Such a distribution of relaxation time implies that the local environment seen by individual dipoles differs from site to site. It does not consider contributions from interactions among the relaxing species, entropic or enthalpic effects of mixing. As it is mentioned that Debye model has limitations, two models have been used to analyze the frequency dependence of $T_m$ for RFEs, i.e., V–F and power law.

To analyze the frequency dependence of $T_m$, one can use V–F law, which is given by

$$\omega = \omega_0 \exp\left(-\frac{T_0}{T_m - T_f}\right) \qquad (2)$$

where $T_f$ is the freezing temperature of the polar regions in the material. Fitting curves are shown in Fig. 3 and fitting parameters $\omega_0$, $T_0$ and $T_f$ are given in Table 3. Values of $\omega_0$ are in all ranges and $T_f$ are found to be different in different compositions. This indicates that all polar clusters in these systems do not

freeze at the same temperature rather than a range of temperatures. Similar contradiction has also been observed by Cheng *et al.* [10]. The pre-exponential factor $\omega_0$ gives an idea about the size and degree of interaction between polar clusters in RFEs. The larger is the size of the polar clusters, the stronger is the interaction between them and hence the smaller is the value of $\omega_0$ [9].

A new power exponential relation characterizing the glassy behavior of relaxor ferroelectrics was introduced by Cheng *et al.* [10]:

$$\omega = \omega_0 \exp\left[-\left(\frac{T_0}{T_m}\right)^p\right] \qquad (3)$$

where $\omega_0$ is the attempt frequency of the polar regions; $T_0$ is the equivalent temperature of the activation energy for the relaxation process; and $p > 1$ is associated with the degree of relaxation of material. The smaller is the value of $p$, the stronger is the dielectric relaxation of the material. For $p = 1$, Eq. (2) reduces to Debye relation and no relaxation phenomena exist. For high value of $p = \infty$, the system behaves like normal. Figure 4 shows the fitting curve of Eq. (3) and the fitting parameters are given in Table 4. Pre-exponential factor $\omega_0$ gives an idea about the size and degree of interaction between polar clusters in
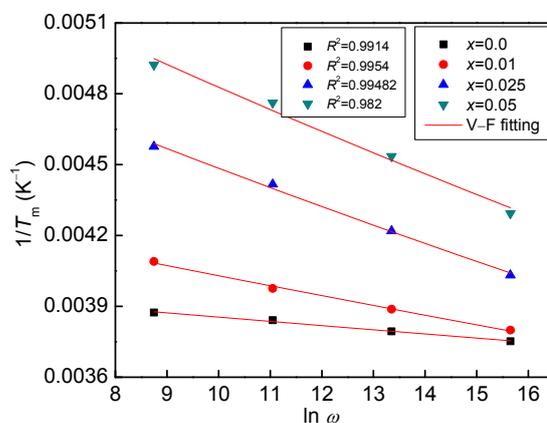


Fig. 3   Fitting for relaxation behavior using V–F model of $Ba_{1-x}Dy_{2x/3}Zr_{0.025}Ti_{0.75}O_3$.

**Table 3   Values of $\omega_0$, $T_0$ and $T_f$ from V–F law**

| Sample | $\omega_0$ (Hz) | $T_0$ (K) | $T_f$ (K) |
|---|---|---|---|
| $x = 0.0$ | $3.84 \times 10^{25}$ | $2617(\pm 1)$ | $207(\pm 1)$ |
| $x = 0.01$ | $1.58 \times 10^{24}$ | $4503(\pm 1)$ | $150(\pm 1)$ |
| $x = 0.025$ | $3.18 \times 10^{21}$ | $5857(\pm 1)$ | $142(\pm 1)$ |
| $x = 0.05$ | $5.04 \times 10^{13}$ | $1563(\pm 1)$ | $134(\pm 1)$ |

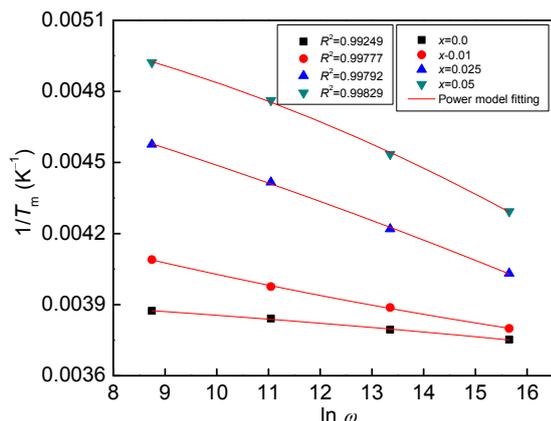Fig. 4   Fitting for relaxation behavior using power law of $Ba_{1-x}Dy_{2x/3}ZrO_{0.25}Ti_{0.75}O_3$.

**Table 4    Fitting parameters of power law**

| Sample | $\omega_0$ (Hz) | $T_0$ (K) | $p$ |
|--------|------------|-----------|-----|
| $x = 0.0$ | $1.56 \times 10^{23}$ | $293(\pm1)$ | 34 |
| $x = 0.01$ | $2.37 \times 10^{22}$ | $305(\pm1)$ | 27 |
| $x = 0.025$ | $5.25 \times 10^{19}$ | $312(\pm1)$ | 21 |
| $x = 0.05$ | $7.14 \times 10^{11}$ | $322(\pm1)$ | 19 |

RFEs. The larger is the size of polar clusters, the stronger is the interaction between them and hence the smaller is the value of $\omega_0$ [10]. Thus, dielectric behavior of RFEs below $T_m$ may be governed by the rate of growth of polar clusters with temperature. Therefore, it is essential to study the dielectric behavior at temperatures much higher and lower than that of $T_m$ to visualize the relaxation mechanism in present system.

## 3. 2   Dielectric behavior above $T_m$

Cheng *et al.* [10] have suggested a dual mechanism behavior to explain the dielectric behavior of relaxor ferroelectrics. They believed that there are two polarization processes around $T_m$, which affect the dielectric properties of an RFE. Dielectric behavior of these RFE materials above $T_m$ is basically governed by the thermally activated flips of polar regions. The dielectric behavior at temperatures much higher than $T_m$ ( $\varepsilon_H$ ) is investigated through the exponential relation   proposed by Cheng *et al.* [10] which is given below:

$$\varepsilon_H(T) = \varepsilon_\infty + \exp(\alpha_H - \beta_H T) \tag{4}$$

where $\alpha_H (>0)$ and $\beta_H (>0)$ are constants whose values are generally larger than zero; $\varepsilon_\infty$ is dielectric constant at high frequency. From the dielectric theory,

$\varepsilon_H$ should be static dielectric constant and is associated with dipole moment of polar regions in materials. Value of $\alpha_H$ is associated with the highest possible concentration of the polar regions while $\beta_H$ is associated with the production rate of the polar regions with decreasing temperature. For $\beta_H = 0$, the equation characterizes the Debye medium, hence $\beta_H$ indicates the degree of relaxation. If the degree of relaxation is strong, value of $\beta_H$ is small. Since $\varepsilon_H$ is generally much higher than $\varepsilon_\infty$, the above relation can be expressed as

$$\varepsilon_H(T) \approx \exp(\alpha_H - \beta_H T) \tag{5}$$

The experimental data have been fitted to Eq. (5) which is shown in Figs. 5(a)–5(d) and the fitting parameters are listed in Table 5. Value of $\alpha_H$ is associated with the highest possible concentration of the polar regions while $\beta_H$ is associated with production rate of polar regions with decreasing temperature.

**Table 5    Values of $\alpha_H$ and $\beta_H$ from Eq. (5)**

| Sample | $\alpha_H$ | $\beta_H$ |
|--------|-----------|-----------|
| $x = 0.0$ | 8.874(8) | 0.0129(2) |
| $x = 0.01$ | 7.751(3) | 0.0049(4) |
| $x = 0.025$ | 7.533(8) | 0.0056(8) |
| $x = 0.05$ | 6.945(3) | 0.0031(2) |

## 3. 3   Dielectric behavior below $T_m$

It has been mentioned earlier that there is a broad distribution of freezing temperatures of the polar regions in the low temperature region. It is worthy to have a qualitative analysis of the behavior of polar clusters at temperatures much below $T_m$. It has been reported that below $T_m$ the relation between dielectric constant and frequency can be expressed as

$$\varepsilon_L(\omega) = \varepsilon_\infty + A(\ln \omega_0 - \ln \omega) \tag{6}$$

where $A$ is an intrinsic parameter that depends on temperature and is independent of frequency; $\omega_0$ is relaxation frequency which is independent of temperature. Thus, the low temperature dielectric response depends mainly on the temperature dependence of $A$ and hence on the freezing process of the polar regions.

Equation (6) can be modified as

$$\varepsilon_L(\omega) = B(T) + A(T)\ln \omega \tag{7}$$
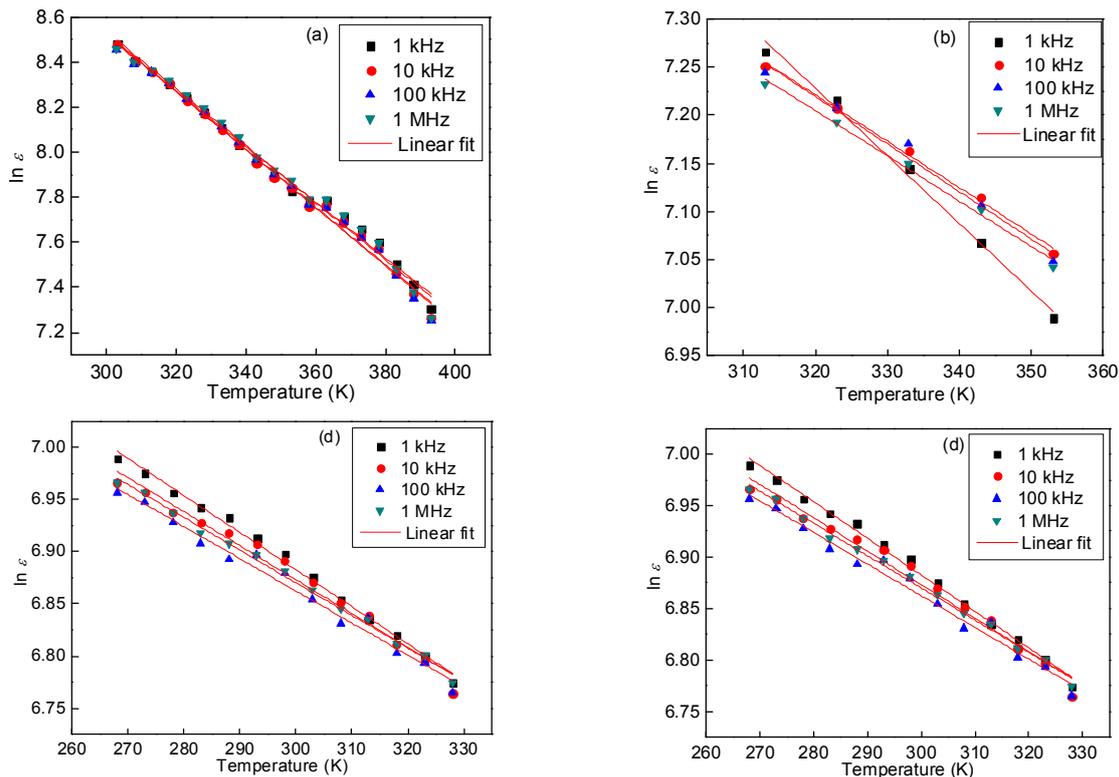
where $B(T)$ is given by

Fig. 5    Plots of $\ln\varepsilon$ versus temperature at different frequencies for $Ba_{1-x}Dy_{2x/3}Zr_{0.25}Ti_{0.75}O_3$: (a) $x = 0.0$, (b) $x = 0.01$, (c) $x = 0.025$, (d) $x = 0.05$.

$$B(T) = \varepsilon_\infty + A(T)\ln\omega_0 \qquad (8)$$

Values of $A$ and $B$ are obtained by fitting frequency dependence of $\varepsilon$ at different temperatures using Eq. (7) shown in Figs. 6(a)–6(d). Again by fitting $A$ and $B$ to Eq. (8), as shown in Figs. 7(a)–7(d) we obtain the values $\varepsilon_0$ and $\omega_0$ given in Table 6. Temperature dependence of parameter $A$, reflecting the degree of dispersion of the dielectric constant at temperatures much lower than $T_m$, can be fitted to the following empirical super exponential relation:

$$A(T) = \exp\left[\alpha_L + \left(\frac{T}{\beta_L}\right)^{1+\delta}\right] \qquad (9)$$

where $\alpha_L$, $\beta_L$ and $\delta$ ($0 \leqslant \delta \leqslant 1$) are positive constants. Figure 8 shows the fitting of $A(T)$ versus $T$ and it is clear that Eq. (9) can indeed express the temperature dependence of $A(T)$ at low temperature.

**Table 6   Values of $\omega_0$, $\varepsilon_\infty$, $\alpha_L$, $\beta_L$ and $\delta$ from Eq. (8) and Eq. (9)**

| Sample | $\omega_0$ (K) | $\varepsilon_\infty$ | $\alpha_L$ | $\beta_L$ | $\delta$ |
|---|---|---|---|---|---|
| $x = 0.0$ | $4.6\times10^{24}$ | 2372.8 | 1.88(7) | 442.40(2) | 0.602(6) |
| $x = 0.01$ | $2.25\times10^{22}$ | 1337.8 | 2.80(9) | 219.50(7) | 0.640(1) |
| $x = 0.025$ | $6.7\times10^{21}$ | 1250.6 | 4.39(4) | 748.10(5) | 0.678(3) |
| $x = 0.05$ | $3.2\times10^{19}$ | 2992.3 | 2.17(2) | 118.73(1) | 0.891(4) |

The fitting parameters are listed in Table 6.

Following conclusion can be drawn from the parameters $\omega_0$, $p$, $\delta$, $\beta_L$, $\alpha_H$ and $\beta_H$, which are obtained from different relations used above in $Ba_{1-x}Dy_{2x/3}Zr_{0.25}Ti_{0.75}O_3$ ceramics. The compounds behave as a strong relaxor due to incorporation $Dy^{3+}$ ion in place of $Ba^{2+}$, indicating that there is a broad distribution of the volume of polar regions around $T_m$. In other way, it can be understood that there is a broad distribution of relaxation time of the polar regions in the material. $\omega_0$ obtained from V–F and power law agrees with other reported relaxor materials, which confirms the existence of some interaction between polar clusters unlike general or orientation glasses [40]. Different values of $T_f$ obtained from V–F law indicate that all the polar clusters do not freeze at the same temperature and there is a broad distribution of freezing temperature. It can be concluded that the concentration of polar regions decreases with increases in Dy content as $\alpha_H$ value decreases. It is also observed that the $p$ values, reduce drastically with an increase in Dy content. Value of $\delta$ (indicates the degree of dielectric relaxation) increases with Dy content, leading to the increase of frozen rate of polar
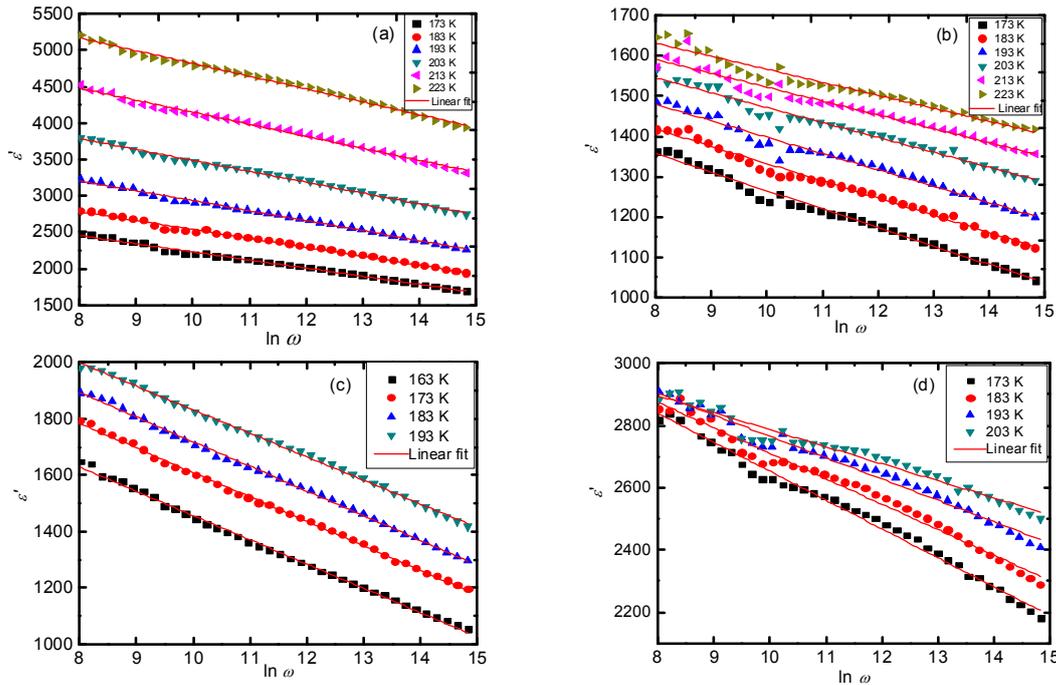
Fig. 6　Frequency dependence of dielectric constant of $Ba_{1-x}Dy_{2x/3}Zr_{0.25}Ti_{0.75}O_3$ ceramics: (a) $x=0.0$, (b) $x=0.01$, (c) $x=0.025$, (d) $x=0.05$.
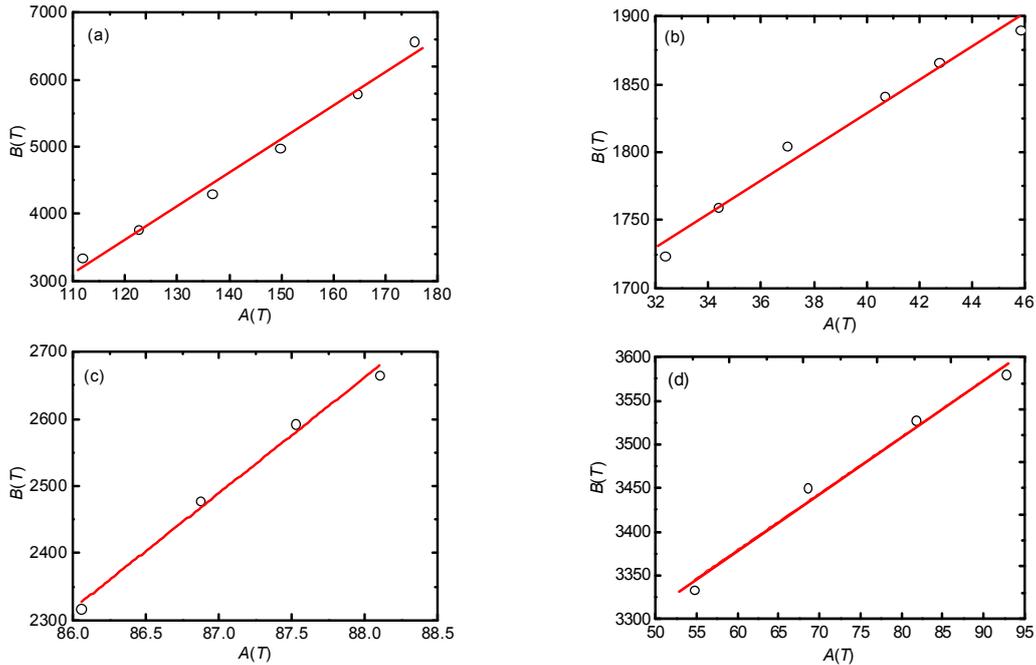


Fig. 7　Linear relation between $A$ and $B$ for $Ba_{1-x}Dy_{2x/3}Zr_{0.25}Ti_{0.75}O_3$ ceramics: (a) $x=0.0$, (b) $x=0.01$, (c) x = 0.025, (d) $x=0.05$.

regions. Variation of $\beta_L$ also confirms the increment of dielectric relaxation within the system.

## 4　Conclusions

The glassy behavior of $Ba_{1-x}Dy_{2x/3}Zr_{0.25}Ti_{0.75}O_3$ ($x=$

0.0, 0.01, 0.025, 0.05) ceramics have been studied in detail by using empirical relation and various models like Debye, V–F and power law. It is revealed from the fitting parameters that power law explains the relaxation mechanism much better than V–F law and Debye relation. Freezing temperature of the polar
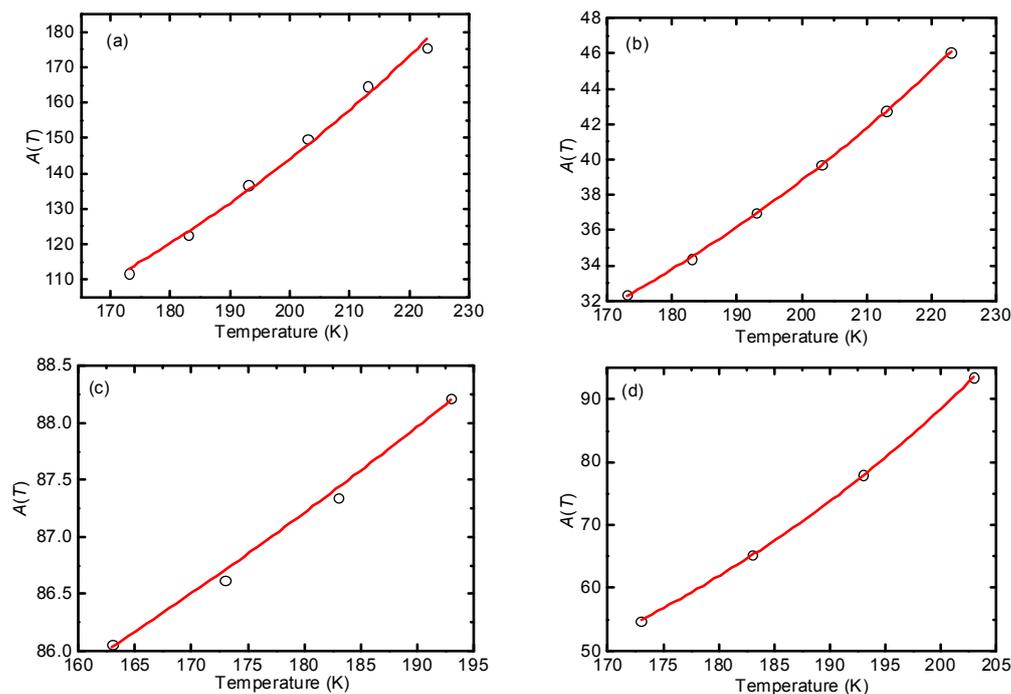
Fig. 8    Fitting of temperature dependence of *A* for $Ba_{1-x}Dy_{2x/3}Zr_{0.25}Ti_{0.75}O_3$ ceramics: (a) *x* = 0.0, (b) *x* = 0.01, (c) *x* = 0.025, (d) *x* = 0.05.

nano-regions using V–F relation is estimated by non-linear curve fitting. By observing the variation of dielectric constant with temperature at temperature much higher and lower than $T_m$, it is suggested that both the rate of production of polar clusters and distribution of freezing temperature of the polar clusters are associated with different profiles of the degree of dielectric relaxation of the materials. Decrease in the value of $\beta_H$ with increase in Dy in the system shows that relaxation phenomenon increases with addition of Dy.

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