

Phase transition and dielectric study in $\text{Ba}_{0.95}\text{Dy}_{0.05}\text{TiO}_3$ ceramic

M R PANIGRAHI* and S PANIGRAHI

Department of Physics, National Institute of Technology, Rourkela 769 008, India

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Abstract. Temperature and frequency dependence dielectric permittivity of $\text{Ba}_{0.95}\text{Dy}_{0.05}\text{TiO}_3$ ceramic has been studied in the temperature range of 100–350 K at the frequencies, 1 kHz, 10 kHz, 100 kHz and 1 MHz. Diffuse phase transition and frequency dispersion is observed in the permittivity-vs-temperature plots. This has been attributed to the occurrence of relaxor ferroelectric behaviour. The observed relaxor behaviour has been quantitatively characterized based on phenomenological parameters. A comparison with the Zr doped BaTiO_3 has also been presented. The microstructure of as-sintered samples shows a dense and almost uniform micrograph without any impurity phases; the grains are almost spherical with random orientation.

Keywords. BDT; ferroelectric; dielectric; relaxor.

1. Introduction

Perovskite-based ferroelectric materials attract considerable interest owing to the rich diversity of their physical properties and possible applications in various technologies like memory storage devices (Kington *et al* 1996), micro-electromechanical systems (Polla and Francis 1996), multilayer ceramic capacitors (Sakabe *et al* 1986), and recently in the area of opto-electronic devices (Walker and Mckee 1996). These useful properties have most often been observed in lead based perovskite compounds, such as PMN, PST, PLZT (Setter and Cross 1980; Cross 1987; Lu and Calvarin 1995). The enhanced properties of these compounds are attributed to their relaxor behaviour, observed in doped (mixed) perovskites. However these compositions have obvious disadvantages of volatility and toxicity of PbO. Therefore, much effort has been made towards investigating environmental friendly 'Pb-free' ceramic materials. Specifically, BaTiO_3 and its isovalent substituted materials are promising candidates for microwave and opto-electronic applications.

The effect of substitution on dielectric relaxation, ferroelectric phase transition and electrical properties of BaTiO_3 has been extensively studied (Maglione and Belkaoumi 1992; Lin and Wu 1990). On partial substitution of dopants like Ca, Sr, Zr (Victor *et al* 1994; Tiwari *et al* 1995; Zhi *et al* 2002), the variation of ϵ around T_c gets broadened out both in ceramics and single crystal samples. Broadening increases with increasing concentration of the dopant, as also does the deviation from Curie–

Weiss behaviour at temperatures above the peak temperature (T_m) of the $\epsilon - T$ variation. The observed broadening in $\epsilon - T$ variation has generally been attributed to the presence of nano-regions resulting from local composition variation over length scale of 100–1000 Å. Different nano-regions in a macroscopic sample transform at different temperatures giving rise to a range of transformation temperatures, the so-called 'Curie range'. Thus the compositional fluctuation (Cross 1987; Tiwari *et al* 1995), in an otherwise compositionally homogenous system leads to diffuse phase transition (DPT). In compositionally homogenous systems quenched random disorder breaks the long range polar order at unit cell level, leading to broad $\epsilon - T$ response (Setter and Cross 1980). Such materials exhibit slow relaxation dynamics and hence have been termed ferroelectric relaxors (Setter and Cross 1980; Cross 1987; Lu and Calvarin 1995). A series of impurity doped BaTiO_3 systems such as Sn, Ce, Zr etc. have shown ferroelectric relaxor behaviour. Among these the Zr-substituted BaTiO_3 ceramics have received renewed attention due to its enhanced properties both in single crystals and ceramics (Zhi *et al* 2002). In the present investigation, we have studied the ferroelectric relaxor behaviour in lower concentration Dy substituted BaTiO_3 , i.e. $\text{Ba}_{0.95}\text{Dy}_{0.05}\text{TiO}_3$ ceramics, by monitoring the variation of its dielectric permittivity in the temperature range of 60–350 K and frequency range of 1 kHz to 1 MHz. Till date only limited work has been carried out for Dy doping in BaTiO_3 (Payne and Tennery 1965; Tura and Mitoseriu 2000) ceramics like its effect on dielectric and structural properties. Detailed structural and dielectric studies have been carried out. The data has been quantitatively analysed in terms of parameters characterizing the relaxor behaviour.

*Author for correspondence (manash_123india@yahoo.co.in)

2. Experimental

Dysprosium modified barium titanate ceramics, with the formula $\text{Ba}_{0.95}\text{Dy}_{0.05}\text{TiO}_3$ was prepared by conventional solid-state reaction technique. High purity powders of BaCO_3 , TiO_2 and Dy_2O_3 were hand-milled for more than 3 h with acetone in an agate mortar for homogeneous mixing of powders. High energy ball milling of homogeneous powder mixture was carried out in a planetary ball mill (Model P5, M/s Fritsch, Germany). Milling was done at room temperature in Zirconia vial (volume 250 ml) using 40 balls of 10 mm diameter made of same material. The powder mixture was milled for 2 h. The powder of the compounds was conventionally calcined at 1400°C for 4 h in an electrical furnace. The calcined powders were once again thoroughly mixed and ground for 2 h, mixed with 2 wt.% of PVA binder and pressed into disk-shaped pellets of 10 mm diameter and finally the green ceramics were sintered at 1450°C for 6 h. The ceramics were structurally characterized by a PANalytical X'pert-MPD X-ray diffractometer (XRD). Scanning electron microscopy (SEM) of Jeol JSM 6480LV was used to observe the microstructure of the ceramics. Platinum-coated targets were used for the investigation. The compositions of the elements in the target were identified using energy dispersive spectrometry (EDS) attached to an SEM of Jeol JSM 6480LV. An electron beam of 10 kV and $57\ \mu\text{A}$ was used for the above study. The average grain size was measured through scanning electron microscope. Dielectric measurement was carried out over frequency range 1 kHz to 1 MHz using an LCR meter connected to PC. The dielectric data was collected at an interval of 5°C while heating at a rate of 0.5°C per min.

3. Results and discussions

3.1 Structural studies

The results of X-ray diffraction characterization of the as-prepared $\text{Ba}_{0.95}\text{Dy}_{0.05}\text{TiO}_3$ and BaTiO_3 samples are shown in figure 1. The figure shows that the $\text{Ba}_{0.95}\text{Dy}_{0.05}\text{TiO}_3$ ceramic is in single tetragonal perovskite phase and the other two phases present are Dy_2TiO_5 ($2\theta = 30.884^\circ$) and Dy_2O_3 ($2\theta = 60^\circ$). Majority of the dysprosium might have entered the barium site. The SEM micrograph of $\text{Ba}_{0.95}\text{Dy}_{0.05}\text{TiO}_3$ ceramic is shown in figure 2. Well shaped grains of sizes ranging from 400–900 nm can be seen. The theoretical and experimental wt% of different elements in the sample is well comparable.

In the higher resolution micrograph one can see that it is rich in nano contrast regions of 2–5 nm apparent sizes. The detailed features of these nano contrasts are typical to the presence of strained regions (Hirsch *et al* 1969), not due to any secondary phase inclusions. Since these regions were found to change contrast simultaneously

during tilt, these might originate from strain fields due to some defect, like tiny dislocation loops extending just to few lattice sites with their burger vectors parallel. The occurrence of these defect features in $\text{Ba}_{0.95}\text{Dy}_{0.05}\text{TiO}_3$ will lower its structural correlation length as compared to BaTiO_3 in which no such features were found. The 'structural correlation length' is basically a measure of the effective extent to which the long range order of an atomic arrangement gets limited as a result of the cumulative effect of all types of defect features, which somehow either interrupt the chemical order or produce strain in the lattice. Beyond this extent the atoms do not scatter coherently and contribute to the width of the diffraction maxima. Thus the structural correlation length may be used as a measure of comparison of defects present in two similar types of structures. Thus to compare the presence of defects in the bulk samples of $\text{Ba}_{0.95}\text{Dy}_{0.05}\text{TiO}_3$ and BaTiO_3 , structural correlation lengths were calculated from the half-widths of the first sharp diffraction peak (FSDP), after applying instrumental broadening and $K\alpha_2$ corrections. These were $\sim 33\ \text{\AA}$ and $\sim 26\ \text{\AA}$ respectively for $\text{Ba}_{0.95}\text{Dy}_{0.05}\text{TiO}_3$ and BaTiO_3 . The interlayer separation with an effective periodicity, R (the atom-void distance (Elliott 1991)), was $2.04\ \text{\AA}$ and $3.10\ \text{\AA}$

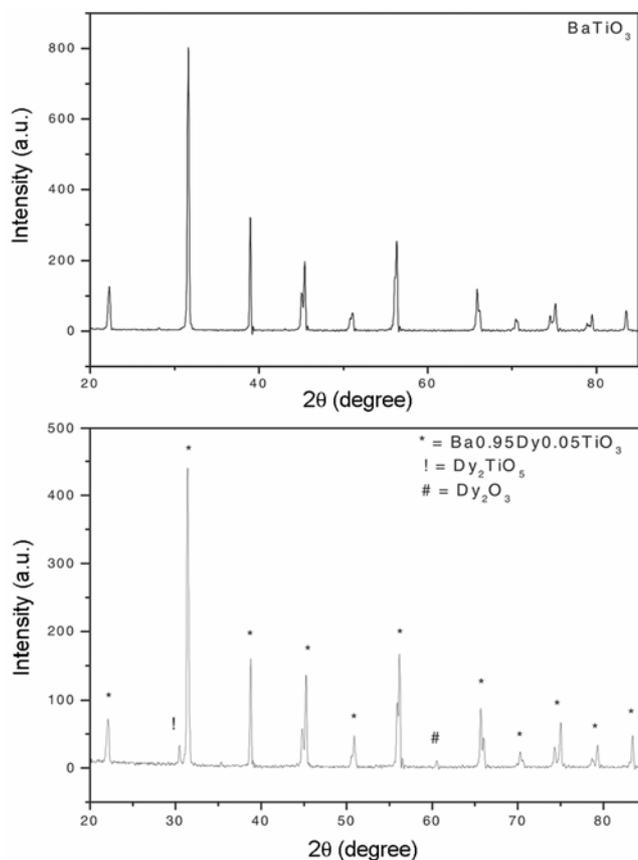


Figure 1. XRD pattern of BaTiO_3 and $\text{Ba}_{0.95}\text{Dy}_{0.05}\text{TiO}_3$ ceramics showing different phases present.

for $Ba_{0.95}Dy_{0.05}TiO_3$ and $BaTiO_3$ ceramics respectively for FSDP. It should be noted that the size of even the smallest grain, as seen through SEM, is at least an order of magnitude larger than the structural correlation length.

3.2 Dielectric studies

The temperature dependence of the dielectric permittivity of $Ba_{0.95}Dy_{0.05}TiO_3$ ceramic is shown in figure 3. Unlike $BaTiO_3$ the transition is quite diffuse. The paraelectric to ferroelectric phase transition temperature (T_c) as compared to that of the $BaTiO_3$, has decreased. The three phase transitions which are observed in $BaTiO_3$ have merged into one round peak in $\epsilon - T$ variation. The results obtained can be described as:

(i) There is a broad peak around $T_m = 200$ K in the $\epsilon - T$ curve. With increasing frequency T_m increases, while the magnitude of the peak decreases.

(ii) There is a strong dielectric dispersion in radio frequency region around and below T_m in the $\epsilon - T$ curve.

The above described features of ($\epsilon - T$) variations shown in figure 3 are similar to the observations by other workers (Hirsch *et al* 1969; Cross 1987; Victor *et al* 1994; Lu and Calvarin 1995; Zhi *et al* 2002) for various lead based

and lead free ferroelectric relaxor materials. In order to further confirm the relaxor behaviour, the quantitative characterizations as described in the following have been done.

3.3 Permittivity variation in the high temperature side

It is known that dielectric permittivity of a normal ferroelectric above Curie temperature follows the Curie–Weiss law described by

$$\epsilon = \frac{C}{(T - T_0)} \quad (T > T_0), \quad (1)$$

where T_0 is the Curie–Weiss temperature and C is the Curie–Weiss constant.

Figure 4 shows the inverse of ϵ as a function of temperature at 10 kHz and its fit to the experimental data by Curie–Weiss law. A deviation from Curie–Weiss law starting at T_{dev} can be clearly seen. The parameter ΔT_m , which is often used to show the degree of deviation from the Curie–Weiss law is defined as:

$$\Delta T_m = T_{C-W} - T_m, \quad (2)$$

where T_{CW} denotes the temperature from which the permittivity starts to deviate from the Curie–Weiss law and T_m represents the temperature of the dielectric maximum. The T_{CW} as determined from the Curie–Weiss fit, is $T_{CW} = 141$ K, and ΔT_m is thus found to be = 6.15 K at 10 kHz. For such relaxor behaviour a modified Curie–Weiss law has been proposed by Uchino and Nomura, (1982) to describe the diffuseness of the phase transition. This is defined as:

$$\frac{1}{\epsilon} - \frac{1}{\epsilon_m} = (T - T_m)^{\gamma} / C, \quad (3)$$

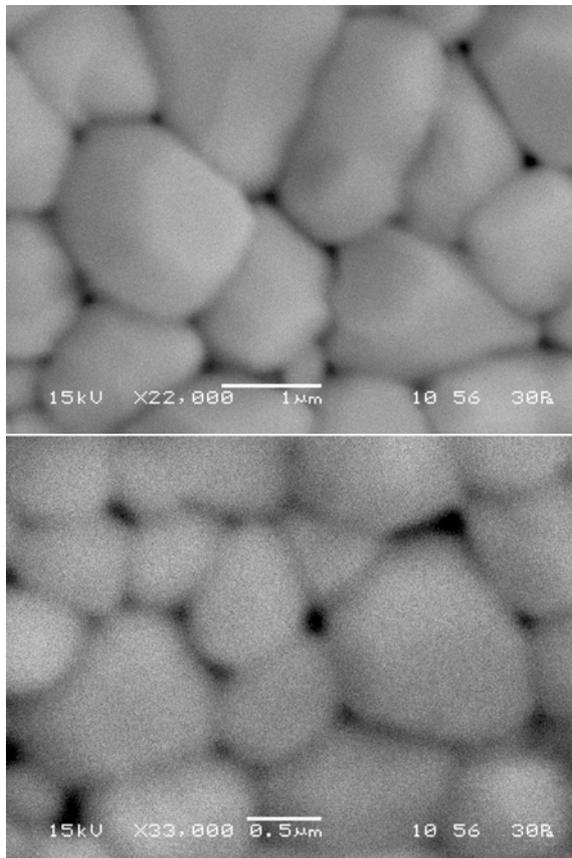


Figure 2. SEM micrograph of $Ba_{0.95}Dy_{0.05}TiO_3$ ceramic at different resolutions.

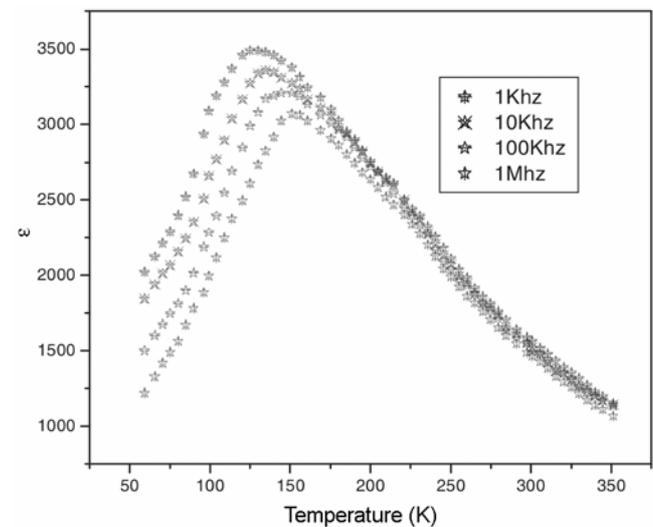


Figure 3. Relative permittivity vs temperature curve at different frequencies.

where γ and C are assumed to be constant. The parameter γ gives information on the character of the phase transition. Its limiting values are $\gamma = 1$ and $\gamma = 2$ in expression (3) of the Curie–Weiss law, $\gamma = 1$ is for the case of a normal ferroelectric and the quadratic dependence is valid for an ideal ferroelectric relaxor respectively (Ang *et al* 2002; Zhi *et al* 2002). Thus the value of γ can also characterize the relaxor behaviour. The plot of $\ln(1/\varepsilon - 1/\varepsilon_m)$ as a function of $\ln(T - T_m)$ is shown in the figure 5. The exponent γ , determining the degree of the diffuseness of the phase transition, is obtained from the slope of $\ln(1/\varepsilon - 1/\varepsilon_m)$ versus $\ln(T - T_m)$ plot. We obtained the value of the parameter γ to be 2.08, which is very close to 2, suggesting that the prepared ceramic is a relaxor ferroelectric (Uchino and Nomura 1982; Ang *et al* 2002). Yet another parameter, which is used to characterize the degree of relaxation behaviour in the frequency range of 100 Hz to 100 kHz, is described (Ang *et al* 2002) as:

$$\Delta T_{\text{relax}} = T\varepsilon_m(100 \text{ kHz}) = T\varepsilon_m(1 \text{ kHz}).$$

The value of ΔT_{relax} was determined to be 14.63 K for the present sample. The above characterization done on the basis of Curie–Weiss law and the value of empirical parameters like ΔT_m , γ and ΔT_{relax} suggest that the permittivity of $\text{Ba}_{0.95}\text{Dy}_{0.05}\text{TiO}_3$ ceramic follows Curie–Weiss law only at temperatures much higher than T_m . Thus the large deviation from the Curie–Weiss behaviour, large relaxation temperature γT_{relax} , and $\gamma = 2.08$, suggest that $\text{Ba}_{0.95}\text{Dy}_{0.05}\text{TiO}_3$ is a relaxor ferroelectric.

The broadening of the phase transition is better illustrated by plotting the reduced dielectric constant ($\varepsilon/\varepsilon_m$) as a function of reduced temperature (τ) at different frequencies (figure 6). The full width of the plot has very little dispersion over a wide frequency range similar to the observation made in other relaxor materials (Tyunina *et al* 1999).

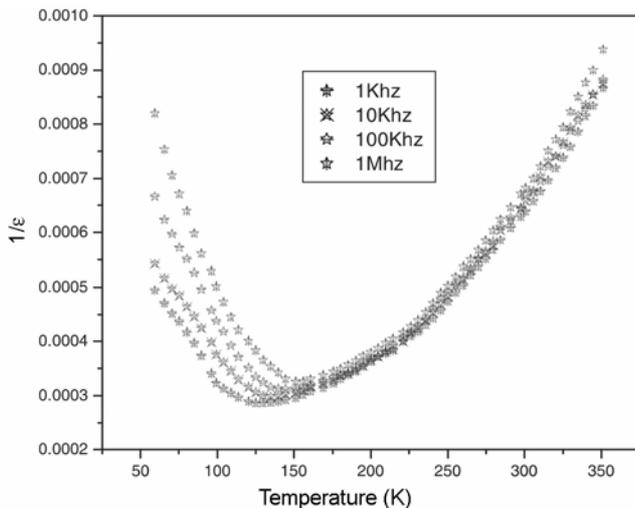


Figure 4. Inverse relative permittivity vs temperature curve at different frequencies.

The frequency dependency of T_m is shown in figure 7 as $\ln f$ vs $1000/T_m$. The observed frequency dependence of T_m was empirically evaluated using Vogel–Fulcher’s relationship given by:

$$f = f_0 \exp\left[\frac{-E_a}{k_B(T_m - T_f)}\right],$$

where f is the attempt frequency, E_a the measurement of average activation energy, k_B the Boltzman constant, T_f the freezing temperature of polarization fluctuation and f_0 is the pre exponential factor. The fitting parameters for the compositions are $E_a = 0.1109$ eV, $T_f = 113$ K, $f_0 = 7.1 \times 10^{11}$ Hz. The fitting parameters having close agreement with the data of Vogel–Fulcher’s relationship suggests that the relaxor behaviours in the systems are analogous to that of a dipolar glass with polarization fluctuations above a static freezing temperature.

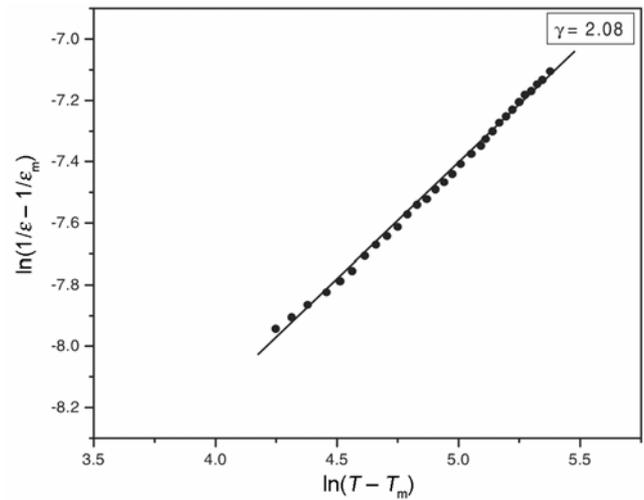


Figure 5. The plot of $\ln(1/\varepsilon - 1/\varepsilon_m)$ as a function of $\ln(T - T_m)$.

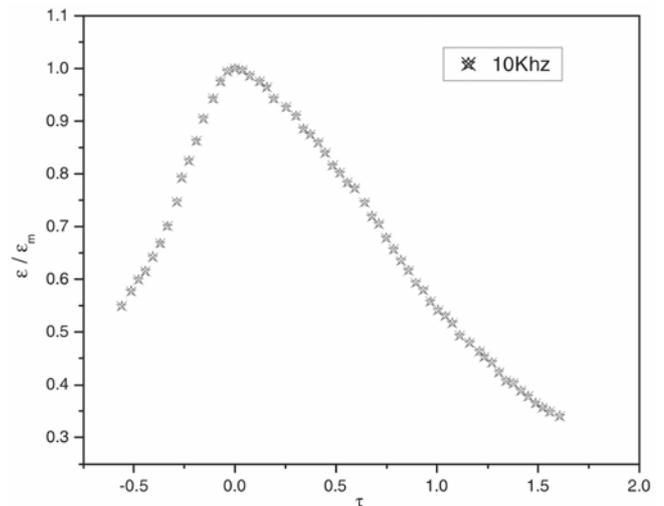


Figure 6. The plot of reduced dielectric constant ($\varepsilon/\varepsilon_m$) as a function of reduced temperature (τ) at different frequencies.

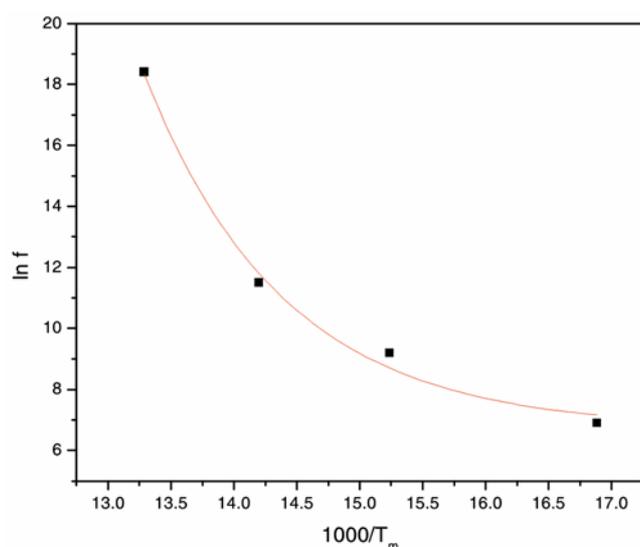


Figure 7. Frequency dependence of T_m for $Ba_{0.95}Dy_{0.05}TiO_3$ ceramic. The symbols and solid line indicate data points and fit to Vogel–Fulcher relationship, respectively.

The occurrence of relaxor in Zr substituted barium titanate (Ravez *et al* 1991; Ravez and Simon 2000; Zhi *et al* 2002) has been attributed to the existence of nanopolar region due to Zr doping. The replacement of Ti^{4+} by Zr^{4+} ions is known in the classical ferroelectric (Ravez *et al* 1991; Ravez and Simon 2000). The increasing substitution decreases the Curie temperature, which is related to the ionic radius of the dopant. In $BaZr_{0.3}Ti_{0.7}O_3$ (BZT) (Ravez *et al* 1991; Ravez and Simon 2000; Zhi *et al* 2002) where the ionic radius of Zr^{4+} (0.88 Å) is higher than Ti^{4+} (0.605 Å) by 0.275 Å the $T_c = 280$ K is lower than that of the pure $BaTiO_3$ ($T_c = 395$ K). For $Ba_{0.95}Dy_{0.05}TiO_3$, in the present study, $T_c = 133$ K, which is much lower than that of the Zr doped one; whereas the ionic radius of Dy^{3+} (0.91 Å) is not much different than the ionic radius of Zr^{4+} .

It can be seen from the comparative structural study of $Ba_{0.95}Dy_{0.05}TiO_3$ and $BaTiO_3$ using XRD and SEM, that nano scale defect features are present in $Ba_{0.95}Dy_{0.05}TiO_3$. It appears that substitution of Dy causes nano-scale compositional heterogeneity due to presence of defects (Ravez *et al* 1991; Ravez and Simon 2000; Tyunina *et al* 1999; Ravez and Simon 1997) creating nano polar domains. It has been suggested that polar nano-domains are responsible for the relaxational behaviour in PMN and PLZT (Victor *et al* 1994) systems. The substitution of Dy ions tends to make the distance between off center Ti dipoles larger thus weakening the correlation between these dipoles. The mismatch in the size of Ti and Dy ions will cause substitutional distortion of the oxygen octahedra, giving rise to local electric-field and strain-

field. Also the ferroelectric behaviour of $Ba_{0.95}Dy_{0.05}TiO_3$ depends on the competitions between long-range ordering owing to strong correlation of the off center Ti dipoles and the random fields induced by Dy doping. Thus the existence of these fields leads to the destruction of long-range ferroelectric ordering and nanopolar coherent domains are formed giving rise to the relaxor behaviour.

4. Conclusions

Based on the X-ray diffraction and dielectric studies of $Ba_{0.95}Dy_{0.05}TiO_3$ ceramic it can be concluded that Dy substitution in $BaTiO_3$ forms a perovskite tetragonal phase structure at room temperature. The occurrence of diffuse phase-transition and strong frequency dispersion of maxima in the permittivity versus temperature, strongly indicate the relaxor behaviour for this $Ba_{0.95}Dy_{0.05}TiO_3$ ceramic. The quantitative characterization and comparison of the relaxor behaviour based on empirical parameters (ΔT_m , γ , γT_{dif} and ΔT_{relax}) confirms its relaxor behaviour.

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