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Review paper

Relaxor behavior in $(Ba_{1-3x/2}Bi_x)(Zr_yTi_{1-y})O_3$ ceramics

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Abstract

New ferroelectric ceramics Bi-BZT of ABO_3 perovskite type were synthesized in the $(Ba_{1-3x/2}Bi_x)(Zr_yTi_{1-y})O_3$ system by solid state reaction route. The effect of the substitution of barium by bismuth in the A cationic site on structural and dielectric properties was investigated. The dielectric constant was studied in the temperature range from 20 K to 320 K at frequencies ranging from 0.2 to 100 kHz. A clear relaxor behavior was observed for samples with $x \geq 0.075$ and $y = 0.1$. In this case the value of the relaxation parameter $\gamma \approx 2$ estimated from the linear fit of the modified Curie–Weiss law, indicates the relaxor nature of the Bi-BZT ceramics. The dielectric relaxation rate follows Vogel–Fulcher relation with an activation energy of 0.26 eV and 0.27 eV, an attempt frequency $f_0 = 3.4 \times 10^{12}$ Hz and 5.7×10^{12} Hz and a static freezing temperature $T_{VF} = 98$ K and 94 K respectively for $x = 0.075$ and $x = 0.1$.

Keywords: C. Dielectric properties; Relaxor ferroelectric; BZT ceramics; Vogel–Fulcher

Contents

1. Introduction

Barium titanate $BaTiO_3$ based materials have received considerable attention in electromechanical, electronic, microwave applications [1,2] and in electro-optic devices [3]. In particular, there is a renewed interest in the environmental friendly lead-free perovskite $Ba(Zr_yTi_{1-y})O_3$ (BZT) as a substitute for $Ba_{1-x}Sr_xTiO_3$ (BST) in these applications due to its high dielectric constant value combined with relatively low dissipation and large voltage tunability of the dielectric constant, as well as a good chemical stability [4–6]. Depending on the Zr content, this material can exhibit either a normal ferroelectric or relaxor

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behavior [7–13]. The relaxor state is characterized by a strong dispersion of the dielectric constant for temperatures below the maximum permittivity temperature T_m, by a shift of T_m towards higher values when the frequency is increased and by a deviation from the Curie–Weiss law in the paraelectric phase around T_m [12].

The relaxor behavior can also be induced by the substitution of the A cation sites in BST system by Bi^{3+} ions. This is, for example, the case of the study reported recently on $(Sr_{0.4}Ba_{0.6})_{0.925}Bi_{0.05}TiO_3$ [14], on BST system [15] and on $SrTiO_3$ system [16] which showed relaxor-type properties. Other studies have focussed on the effect of doping on the dielectric properties of the ferroelectric relaxor BZT [17–19].

Recently we investigated the effect of heterovalent atoms substitution of the B site BZT and reported a relaxor behavior in the $Ba[Zr_xTi_{1-x-y}](Zn_{1/3}Nb_{2/3})_yO_3$ system [20]. Therefore it would be interesting to investigate the effect of the substitution of Ba by other entities such as Bi in the BZT system. Thus, one goal of the present work was the study of the structural, dielectric and ferroelectric properties of $(Ba_{1-3x/2}Bi_x)(Zr_yTi_{1-y})O_3$ (Bi-BZT) ceramics as function of Bi content. The Bi-BZT system is obtained by the substitution of barium by bismuth in BZT. The value of y was chosen to be below the threshold value for the onset of relaxor behavior in $BaZr_yTi_{1-y}O_3$.

2. Materials and methods

In this work $(Ba_{1-3x/2}Bi_x)(Zr_yTi_{1-y})O_3$ ceramics samples with $x = 0.025$, 0.05, 0.075 and 0.1 and $y = 0.1$ (referred to as Bi-BZT) were prepared by the conventional solid-state reaction method [14,15], using stiochiometric proportions of high purity $BaCO_3$ (Fluka, 99%) ZrO_2 (Acros Organics, 99%), TiO_2 powders (Prolabo, 99%) and Bi (Prolabo, ≥99%). Appropriate quantities of these precursors were weighed, thoroughly mixed in an agate mortar and pestle, and subsequently calcined at 1398 K in alumina crucibles under an air atmosphere for 10 h. After cooling, the obtained powder was ground, and then pressed into pellets of 13.5 mm diameter and approximately 1.5 mm thickness, under a uniaxial pressure of 35 MPa. The pellets were then sintered at 1498 K for 4 h in air.

The X-ray diffraction (XRD) patterns were recorded at room temperature on the powder samples, in a Philips X'Pert system, with a Kα radiation (λ = 1.54056 Å), at 40 kV and 30 mA, a step of 0.04° and an integration time of 1 s per step. Microstructures were examined by scanning electronic microscopy using a Jeol JSM5500 microscope.

For the dielectric measurements, the sample electrodes were obtained by painting both sides of the pellets with low firing-temperature silver paint. The dielectric properties of the samples were then measured as a function of temperature from 20 K to 320 K and at different frequencies (200 Hz, 500 Hz, 1 kHz, 5 kHz, 10 kHz, 50 kHz and 100 kHz) using a helium closed cycle cryostat (ARS DE-202) and a Keithley LCZ3300 meter.

3. Results and discussion

3.1. X-ray diffraction analysis

XRD patterns of Bi-BZT ceramics with $x = 0.025$, 0.05, 0.075 and 0.1 sintered at 1498 K are shown in Fig. 1. As revealed by the XRD patterns all the peaks of the X-ray diagrams are attributed to the perovskite phase. However, a careful examination of the XRD patterns reveals that for $x = 0.1$, there are two small peaks at 2 Theta = 29.162° and 28.0145° related respectively to Bi_2O_3 (JCPDS reference 74-1374) and to $BaBiO_3$ (JCPDS reference 78-0599). This result shows that the solubility of bismuth in the $BaZr_{0.1}Ti_{0.9}O_3$ compound is limited for $x > 0.075$. The analysis of the X-ray diffraction diagrams shows that the diffraction peaks shift to lower angles with increasing Bi content, as evidenced by the enlarged view of the (0 0 2) peak shown in the inset. This shift, observed although the ionic radius of Bi^{3+} (1.03 Å) is lower than that of Ba^{2+} (1.42 Å), can be attributed to the fact that each three Ba atoms are substituted by 2 Bi atoms in the lattice. The sample with $x = 0.025$, shows the tetragonal perovskite structure with c/a determined value of 1.0077. On the other hand, samples with $x = 0.05$, $x = 0.075$ and $x = 0.1$ show cubic-type perovskite structure. The lattice parameter of Bi-BZT ($y = 0.1$) samples, listed in Table 1, increases with the Bi content. These results are in good agreement with those reported [14] for $(Sr_{0.4}Ba_{0.6})_{0.925}Bi_{0.05}TiO_3$ and [21] for $(Sr_{1-1.5x}Bi_x)TiO_3$ ceramics. In addition, the XRD peaks are intense and very narrow suggesting a good crystallinity of the samples.

Fig. 2 shows the SEM micrographs of $(Ba_{1-3x/2}Bi_x)(Zr_yTi_{1-y})O_3$ ceramics with different Bi contents. The microphotographies show a homogeneous microstructure and well-developed grain morphology and microstructure. The average grain size increases with the increase in Bi content (x) between 1 μm for $x = 0.025$ and 4 μm for $x = 0.1$. This increase in grain size can be associated to the higher grain-growth rate caused by

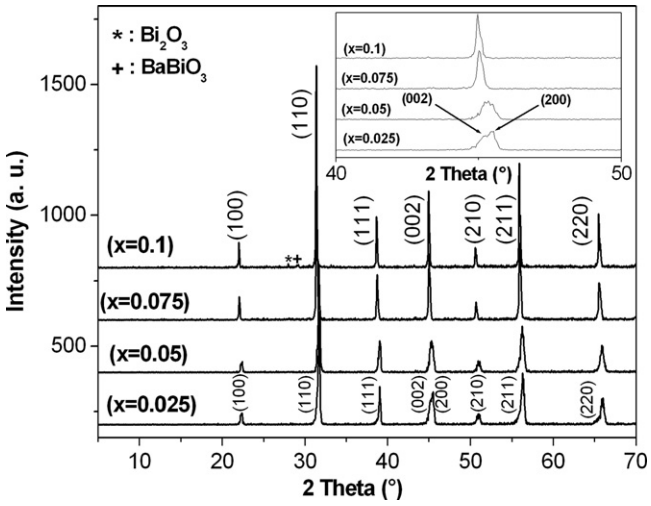

Fig. 1. X-ray diffraction patterns for $(Ba_{1-3x/2}Bi_x)(Zr_yTi_{1-y})O_3$ ceramics with $y = 0.1$ sintered at 1498 K.

Table 1
Structure and lattice parameters of different compositions in the system $(Ba_{1-3x/2}Bi_x)(Zr_yTi_{1-y})O_3$.

Composition (x)	Structure	(Å)
0.025	Tetragonal	$a = 3.9876$ and $c = 4.0184$
0.05	Cubic	4.0149
0.075	Cubic	4.0258
0.1	Cubic	4.0297

good diffusion of the smaller Bi^{3+} ion in place of larger Ba^{2+} ion. A similar result was reported [22] in the substitution of the Zr^{2+} ion by Ti^{4+} in the BZT.

3.2. Dielectric properties

Fig. 3 shows the temperature dependence of the dielectric constant and loss-tangent of Bi-BZT samples at 200 Hz, 500 Hz, 1 kHz, 5 kHz, 10 kHz, 50 kHz and 100 kHz. The dielectric constant increases gradually to a maximum value with the increase in temperature and then decreases smoothly indicating a phase transition. For $x \geq 0.075$, the maximum of the dielectric constant and the corresponding temperature (T_m) depend upon the measurement frequency. A clear signature of the relaxor behavior is observed: a shift of T_m towards higher temperatures with increasing frequency and a strong dispersion of the dielectric constant when the temperature is below T_m. These observations suggest a transition from a normal ferroelectric to a relaxor-like behavior for higher Bi content ($x \geq 0.075$). The results also show that T_m decreases with increasing values of x, implying that the Bi substitution in $BaZr_{0.1}Ti_{0.9}O_3$ affects the transition temperature T_m. The same relaxor behavior is also revealed by the temperature dependence of the loss-tangent. As shown in Fig. 3(a)–(c), the dielectric losses above T_m are smaller for samples with higher Bi contents. For example, at 1 kHz and 300 K, $\tan(\delta)$ is equal to 0.016 for $x = 0.05$, 0.008 for $x = 0.075$. These values are higher than that for $x = 0.1$ sample ($\tan(\delta) \sim 0.003$) at the same temperature.

It is known that the dielectric constant of a normal ferroelectric follows the Curie–Weiss law above the Curie temperature (T_C) as described by Eq. (1):

$$\frac{1}{\varepsilon'} = \frac{T - T_0}{C}, \quad (T > T_C), \tag{1}$$

where C is the Curies–Weiss constant and T_0 is the Curie–Weiss temperature. However, a clear deviation from Curie–Weiss law is observed around T_m as shown in Fig. 4(a) for $x = 0.075$ and Fig. 4(b) for $x = 0.1$

The phase transition feature of the samples with $x = 0.075$ and 0.1 was fitted using the modified Curie–Weiss law given by

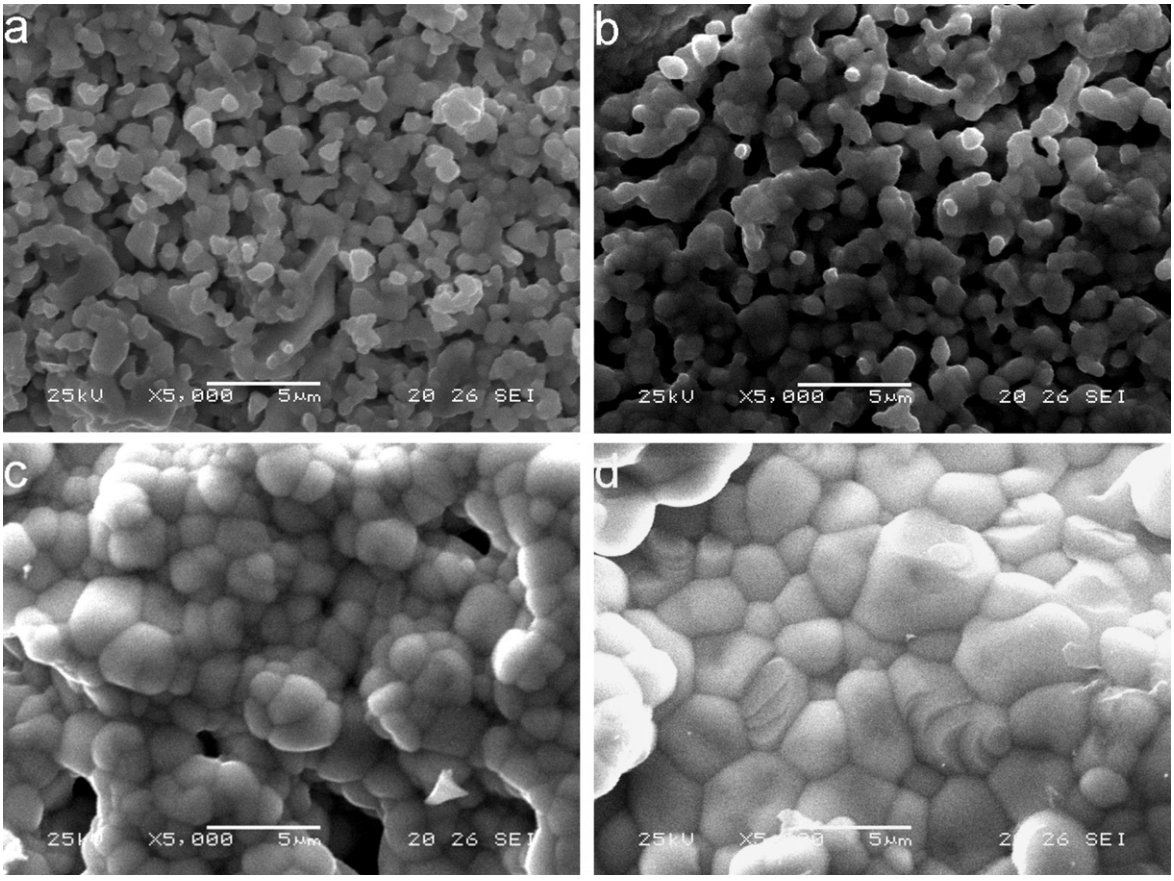

Fig. 2. SEM micrographs of $(Ba_{1-3x/2}Bi_x)(Zr_yTi_{1-y})O_3$ for (a) $x = 0.025$, (b) $x = 0.05$, (c) $x = 0.075$ and (d) $x = 0.1$.

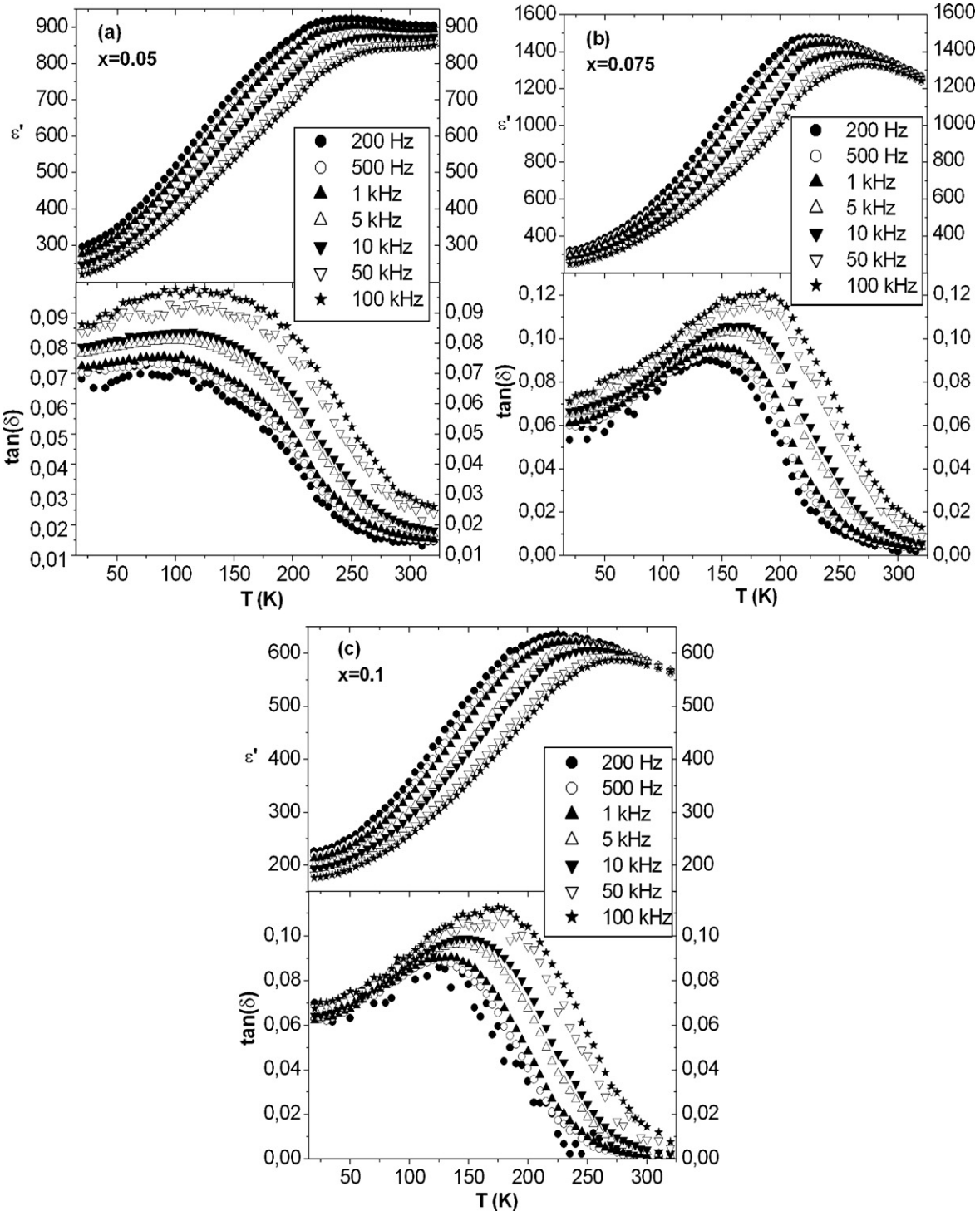

Fig. 3. Temperature and frequency dependence of the dielectric constant and loss-tangent of $(Ba_{1-3x/2}Bi_x)(Zr_yTi_{1-y})O_3$ ceramics for (a) $x = 0.05$, (b) $x = 0.075$ and (c) $x = 0.1$.

Eq. (2) [23,24]:

$$\frac{1}{\varepsilon'} - \frac{1}{\varepsilon'_m} = \frac{(T - T_m)^\gamma}{C'}, \tag{2}$$

where C' and γ are assumed to be constant and ε'_m is the maximum value of the dielectric constant. The parameter γ yields information on the degree of diffuseness of the ferroelectric to paraelectric transition. For $\gamma = 1$ a normal Curie–Weiss law is obtained, while $\gamma = 2$ describes a completely diffuse phase transition [23–25].

The plot of $\ln((1/\varepsilon') - (1/\varepsilon'_m))$ as a function of $\ln(T - T_m)$ at 100 kHz is shown in Fig. 5 for different values of x. The exponent γ, determining the degree of the phase transition diffuseness, is obtained from the slope of $\ln((1/\varepsilon') - (1/\varepsilon'_m))$ versus $\ln(T - T_m)$ plot. The values of γ obtained from the linear

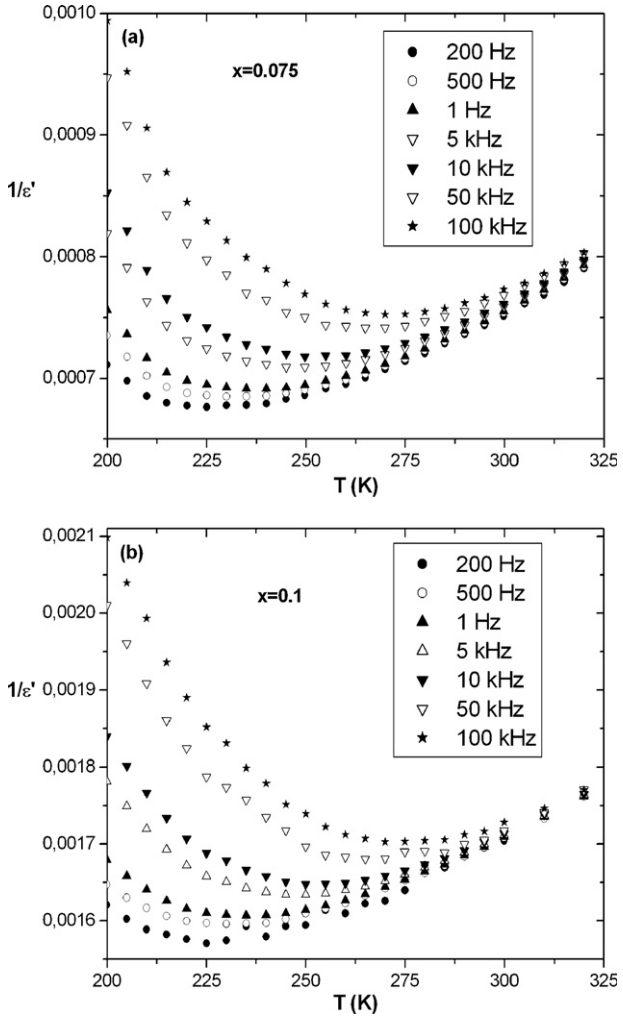

Fig. 4. Temperature dependency of $1/\varepsilon'$ of $(Ba_{1-3x/2}Bi_x)(Zr_yTi_{1-y})O_3$ ceramics for (a) $x = 0.075$ and (b) $x = 0.1$.

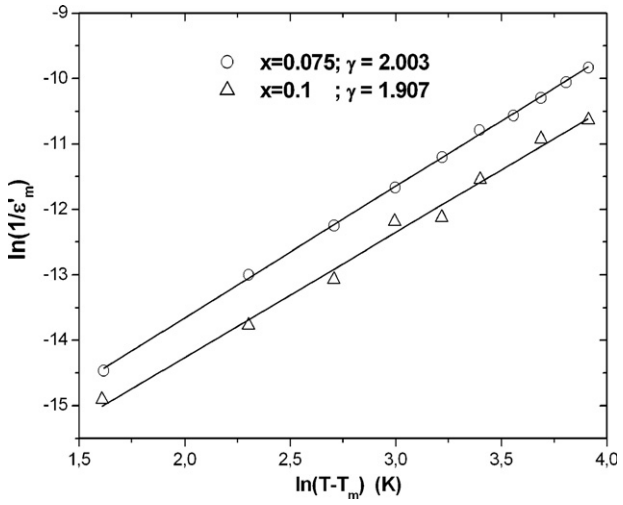

Fig. 5. Plot of $\ln(1/\varepsilon' - 1/\varepsilon_m)$ as a function of $\ln(T - T_m)$ of $(Ba_{1-3x/2}Bi_x)(Zr_yTi_{1-y})O_3$ at 100 kHz for $x = 0.075$ and 0.1 (symbols: experimental data; solid line: fit).

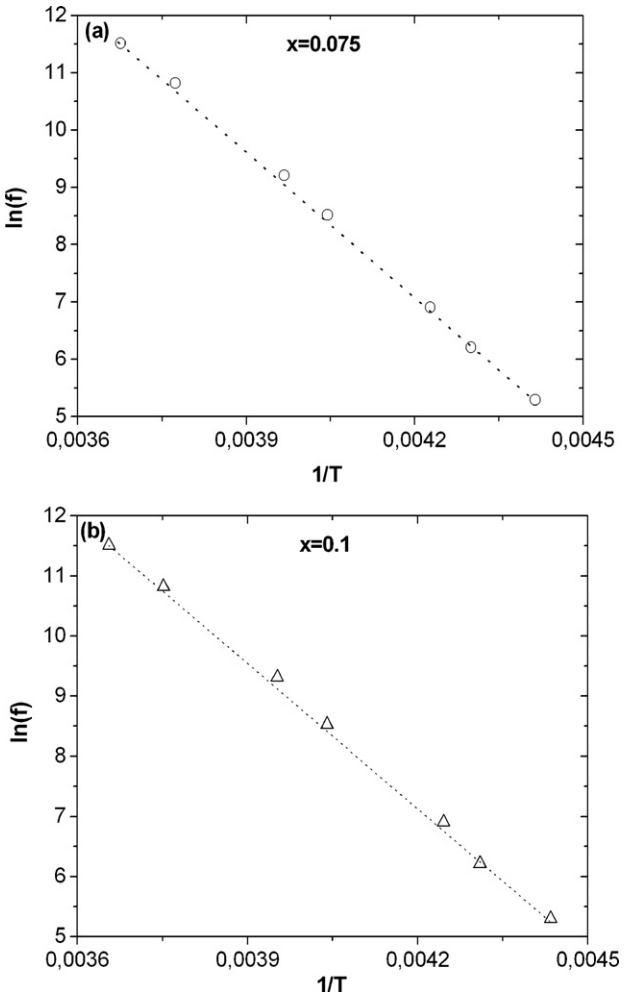

Fig. 6. Plot of $\ln(f)$ as a function of $1/T_m$ of $(Ba_{1-3x/2}Bi_x)(Zr_yTi_{1-y})O_3$ for (a) $x = 0.075$ and (b) $x = 0.1$.

fit of the experimental data are 2.0 and 1.9 respectively for $x = 0.075$ and $x = 0.1$. The obtained values of the parameter γ are higher than 1. These results show a clear deviation from the normal Curie–Weiss behavior around T_m, giving evidence that the prepared ceramic is a relaxor ferroelectric [26,27]. To illustrate the degree of the deviation from the Curie–Weiss law and to characterize the degree of relaxation behavior in the frequency range of 100 Hz to 100 kHz, another parameter [28] given by Eq. (3) was used:

$$\Delta T_{relax} = T[\varepsilon'_m\,(100\,\text{kHz})] - T[\varepsilon'_m\,(200\,\text{Hz})]. \quad (3)$$

The value of ΔT_{relax} was determined to be 45 K for both $x = 0.075$ and $x = 0.1$. The above characterization done on the basis of Curie–Weiss law and the value of empirical parameters like γ and ΔT_{relax} suggest that the dielectric permittivity of Bi-BZT ceramic follows the Curie–Weiss law only at temperatures much higher than T_m. Thus the large deviation from the Curie–Weiss behavior, large relaxation temperature ΔT_{relax}, and γ close to 2 all suggest that Bi-BZT is a relaxor ferroelectric.

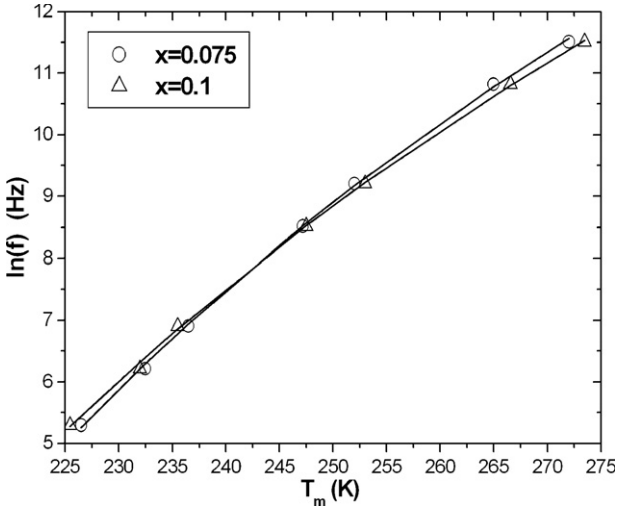

Fig. 7. Plot of ln(f) as a function of T_m for the sample of $(Ba_{1-3x/2}Bi_x)(Zr_yTi_{1-y})O_3$ ceramic for $x = 0.075$ and 0.1 (symbols: experimental data; solid line: Vogel–Fulcher law fit).

Fig. 6 shows the plot of ln(f) as a function of $1/T_m$ of the samples with $x = 0.075$ and $x = 0$. This curve clearly indicates that the data cannot be fitted with a simple Debye equation model given by Eq. (4):

$$f = f_0 \exp\left(\frac{-E_a}{kT_m}\right), \quad (4)$$

where f_0 is the attempt frequency, E_a is the activation energy for the relaxation and k is Boltzmann's constant. As in the case of spin glass systems, the experimental data was therefore fitted using the Vogel–Fulcher model given by Eq. (5) [23,24,29]:

$$f = f_0 \exp\left[\frac{-E_a}{k(T_m - T_{VF})}\right], \quad (5)$$

where T_{VF} is the characteristic Vogel–Fulcher temperature (static freezing temperature), the other parameters are as defined above.

As shown in Fig. 7 (solid line), this model accounts well for the data, suggesting that the relaxor behavior in the present Bi-BZT system is analogous to a spin glass with polarisation fluctuations above T_{VF}. The obtained Vogel–Fulcher parameters are $E_a = 0.26$ eV, $T_{VF} = 98$ K and $f_0 = 3.43 \times 10^{12}$ Hz for $x = 0.075$ and $E_a = 0.27$ eV, $T_{VF} = 94$ K and $f_0 = 5.66 \times 10^{12}$ Hz for $x = 0.1$. These values of parameters are very close and are in agreement with those reported for BZT relaxors [4,8]. These parameters suggest that the Bi content of $x = 0.075$ in the Bi-BZT system is sufficient to make it a good relaxor material.

4. Conclusions

Perovskite $(Ba_{1-3x/2}Bi_x)(Zr_yTi_{1-y})O_3$ ceramic samples with $x = 0{,}025$, 0.05, 0.075 and 0.1 and $y = 0.1$ have been prepared trough solid state reaction route at a temperature of 1498 K which is lower compared to that of BZT prepared by the same route. The room temperature XRD study suggests that for $x \leq 0.075$, these ceramics have single-phase perovskite type structure. Dielectric measurements show that the temperature T_m decreases with increasing x and that the ferroelectric behavior samples with $0.075 \leq x \leq 0.1$ is a relaxor-like behavior. The experimental T_m data points are in good agreement with the Vogel–Fulcher relation. The value of the Bi content of $x = 0.075$ is sufficient to make the BZT a good relaxor material.

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