Relaxor dielectric behavior in BaTiO₃ substituted BiFeO₃–PbTiO₃ multiferroic system

Naveen Kumar¹ · Narayan Bastola² · Sanjeev Kumar¹ · Rajeev Ranjan²

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Abstract (0.9 – x)BiFeO₃–xPbTiO₃–0.1BaTiO₃ for 0.20 ≤ x ≤ 0.24 ceramic sample was prepared by conventional solid state reaction method. X-ray diffraction analysis confirmed the existence of morphotropic phase boundary (MPB) between monoclinic (Cc) and tetragonal (P4mm) phases. Dielectric measurements revealed the diffusive and dispersive relaxor-like behavior for all the composition in the vicinity of MPB. A broad dielectric maximum was observed in temperature dependent real part of dielectric permittivity for all the compositions. The relaxor-like character was quantified by using Vogel–Fulcher relationship, which yielded activation energy of 0.190–0.225 eV, characteristic frequency of the order of 10¹² Hz and freezing temperature ranging 189.0–200.5 °C. The low remnant polarization and high coercive field suggests that the polarization in nanodomains is weakly coupled, which limits the long range ordering of dipoles and alters the system from normal ferroelectric to relaxor ferroelectric. The high value of tetragonal strain (c/a ~ 1.16) results in a weak piezoelectric response for all the ceramic compositions.

1 Introduction

Ferroelectric (FE) materials with relaxor dielectric behavior are widely used for potential applications like sensors, capacitors, actuators and piezoelectric transducers due to

wide range of transition temperature and also due to its high permittivity [1–4]. Relaxor ferroelectrics (RFEs) are characterized by the broadening of temperature dependent dielectric maximum and dispersion of dielectric permittivity at different frequencies near the temperature of dielectric maximum [5]. There exists spontaneous polarization even at a temperature higher than the maximum temperature over which the structural transition takes place in normal ferroelectrics [6]. BiMeO₃–PbTiO₃ binary systems (Me = Sc³⁺, Fe³⁺ or mixed ions (Ni_{1/2}Ti_{1/2}), (Mg_{1/2}Ti_{1/2}) with an average 3+ valence state) possess high Curie temperature (T_c) and become a suitable member for the potential applications [7–10]. In the family of PbTiO₃ based piezo ceramics, BiFeO₃–PbTiO₃ (BF–PT) has the highest value of T_c [8]. Also BF–PT solid solutions possess very high c/a (~1.187) at MPB [8–11]. The displacement of B-site cations (Ti, Fe) and strong hybridization between Bi/Pb and O anions is the reason for high tetragonality (c/a) and high Curie temperature (T_c) in this system [12–14]. It is possible to use BF–PT at high temperature but high tetragonality limits the application due to the presence of internal strain caused by stresses. These stresses don't allow the domain switching, due to which ceramic sample cannot be poled completely below the breakdown voltage [15]. The d₃₃ value of BF–PT is 50 pC/N at MPB, which is much lower than other reports present on BiMeO₃–PbTiO₃ solid solutions [16]. Although it is hard to obtain mechanically robust and dense ceramics of BF–PT, due to negative temperature expansion gradient and high tetragonal distortion when sintered at high temperature [17, 18]. Strategies are being made to improve piezo-response by site engineering and also by defect engineering with improved method of preparation by specific temperature processing. For example, introduction of BaZrO₃ and PbZrO₃ improved the piezoreponse of BiFeO₃–PbTiO₃ [19, 20]. Also BiScO₃–BaTiO₃,

✉ Sanjeev Kumar
sanjeev04101977@gmail.com

¹ Department of Applied Sciences, PEC University of Technology, Chandigarh 160012, India

² Department of Materials Engineering, Indian Institute of Science, Bengaluru 560012, India

Fig. 1 XRD patterns of $(0.90 - x)\text{BiFeO}_3\text{-}x\text{PbTiO}_3\text{-}0.10\text{BaTiO}_3$ for $x = 0.20\text{--}0.24$

$\text{Bi}(\text{Ni}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{-BaTiO}_3$, $\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{-BaTiO}_3$ binary solid solutions exhibit improved piezoelectric properties [21–23]. The present studies on $\text{BiMeO}_3\text{-PbTiO}_3$ system reveals that the increase or decrease in ‘c/a’ ratio subsequently increase or decrease the Curie temperature T_c [24]. The reports present on $\text{BiFeO}_3\text{-PbTiO}_3\text{-BaTiO}_3$ ternary system show high remnant polarization ($P_r \sim 60 \mu\text{C}/\text{cm}^2$) and high piezoelectric coefficient ($d_{33} = 100 \text{ pC/N}$) [25], which motivated us to choose this system for further studies. The main objective of present work is to

investigate specifically the structural and dielectric properties of ternary $(0.9 - x)\text{BiFeO}_3\text{-}x\text{PbTiO}_3\text{-}0.1\text{BaTiO}_3$ with $x = 0.20\text{--}0.24$ compound within MPB region.

The present work also adopted the method of site engineering by substitution of Ba at Pb site forming a ternary system $(0.90 - x)\text{BiFeO}_3\text{-}x\text{PbTiO}_3\text{-}0.10\text{BaTiO}_3$ with $x = 0.20\text{--}0.24$. This compositional series is being prepared by conventional mixed oxide route. The main purpose of this investigation is to obtain a highly dense electrically insulated ceramic within MPB region with improved ferroelectric and dielectric properties. The phase transformations are studied by Rietveld refinement method and dielectric studies reveal the relaxor like dielectric behavior, which is not observed in BF–PT.

2 Experimental

$(0.90 - x)\text{BiFeO}_3\text{-}x\text{PbTiO}_3\text{-}0.10\text{BaTiO}_3$ ceramics were prepared by conventional solid state reaction route with $x = 0.20\text{--}0.24$ using analytical grade high purity powders of Bi_2O_3 , Fe_2O_3 , PbO , TiO_2 and BaCO_3 . The powders were thoroughly mixed in a planetary ball mill (P5, Fritch) for 10–12 h and then dried and calcined at 800°C for 2 h. The calcined powder then mixed with 2% polyvinyl alcohol and then uniaxially compressed into small discs (thickness = 1 mm, diameter = 13 mm) and sintered in a range of $920\text{--}1020^\circ\text{C}$ in alumina crucible plate surrounded by powder of same composition as a spacer. After sintering the pellets were crushed and annealed at 700°C for 1 h to remove the strain generated during sintering and milling. Powder XRD pattern at room temperature was collected with Rigaku (Japan) powder diffractometer using Cu K_α source with nickel filter. The sintered pellets were silver electroded for hysteresis loops between polarization and electric field were measured with Precision Premier II loop tracer (Radiant). Dielectric measurements were carried by Novocontrol (Alpha AN) impedance analyzer. The longitudinal piezoelectric coefficient d_{33} measurement was carried out by using Piezotest PM 300.

Table 1 Refined structural parameters of monoclinic (Cc) and tetragonal phases (P4mm) of $(0.90 - x)\text{BiFeO}_3\text{-}x\text{PbTiO}_3\text{-}0.10\text{BaTiO}_3$ with $x = 0.20\text{--}0.24$

Space subgroup	Monoclinic (Cc)				
Pb (wt%)	20	21	22	23	24
a (Å)	9.777316	9.773978	9.769102	9.762426	9.759645
b (Å)	5.612700	5.611489	5.612964	5.619437	5.623404
c (Å)	5.631406	5.628358	5.628525	5.625953	5.625254
Space subgroup	Tetragonal (P4mm)				
a (Å)	3.865601	3.866278	3.868350	3.861906	3.863624
c (Å)	4.498729	4.495141	4.498793	4.496086	4.491859

Fig. 2 The temperature dependent real part of dielectric permittivity and dielectric loss for $(0.90 - x)\text{BiFeO}_3\text{-}x\text{PbTiO}_3\text{-}0.10\text{BaTiO}_3$, **a** $x = 0.20$, **b** $x = 0.21$, **c** $x = 0.22$, **d** $x = 0.23$ and **e** $x = 0.24$

3 Results and discussions

Figure 1 shows the XRD patterns of the $(0.9 - x)\text{BiFeO}_3\text{-}x\text{PbTiO}_3\text{-}0.10\text{BaTiO}_3$ with $x = 0.20\text{--}0.24$ ceramic compositions. All the compositions show morphotropic phase boundary (MPB) in this system. In the vicinity of MPB, XRD pattern confirms both monoclinic (Cc) and tetragonal (P4mm) phases. Although space group of BiFeO_3 is believed to be R3c and that of PbTiO_3 is P4mm at room temperature, but Rietveld refinement studies using FULLPROF gives the best fit using Cc + P4mm model. The lattice parameters

of both the phases are shown in Table 1. Both tetragonal (P4mm) and lower symmetry monoclinic (Cc) phases are also observed for $x > 0.3$, $0.10 \leq x \leq 0.27$ and $x = 0.27$ in $(1 - x)\text{BiFeO}_3\text{-}x\text{PbTiO}_3$ binary systems [8, 26]. Noheda et al. reported the existence of monoclinic phase in MPB region [27]. They suggested that the existence of monoclinic phase in MPB region is like a bridge between rhombohedral and tetragonal phase based on polarization rotation model. There is one more report available on the existence of monoclinic phase in MPB region [28]. They reported the existence of monoclinic phase in MPB region based on adaptive phase theory, according to

Fig. 3 The temperature dependent imaginary part of dielectric permittivity for $(0.90 - x)\text{BiFeO}_3\text{-}x\text{PbTiO}_3\text{-}0.10\text{BaTiO}_3$. **a** $x = 0.20$, **b** $x = 0.21$, **c** $x = 0.22$, **d** $x = 0.23$ and **e** $x = 0.24$

which the existence of nanodomains give rise to coherent scattering, which further results in additional peaks in the diffraction pattern with different intensities. Similar results are observed in the diffraction pattern of the

present ceramic composition for $(0.9 - x)\text{BiFeO}_3\text{-}x\text{PbTiO}_3\text{-}0.10\text{BaTiO}_3$ with $x = 0.20\text{--}0.24$.

The temperature dependent dielectric permittivity (ϵ') and dielectric loss ($\tan\delta$) for $(0.90 - x)$

Fig. 4 The maximum dielectric temperature T_m as a function of $\ln \nu$ fitted with V–F relationship for $(0.90 - x)\text{BiFeO}_3 - x\text{PbTiO}_3 - 0.10\text{BaTiO}_3$. **a** $x = 0.20$, **b** $x = 0.21$, **c** $x = 0.22$, **d** $x = 0.23$ and **e** $x = 0.24$

$\text{BiFeO}_3 - x\text{PbTiO}_3 - 0.10\text{BaTiO}_3$ ($x = 0.20 - 0.24$) in the frequency range 500 Hz–100 kHz is shown in Fig. 2. As the measuring frequency is increased, the peak value of dielectric permittivity shifts towards higher temperatures. Also the peak value of dielectric permittivity (ϵ'_{max}) decreases with increasing frequency which clearly confirms the relaxor like dielectric behavior of the system. It indicates that the doping of Ba at Pb site not only shifts the maximum temperature T_m but also decreases the peak value of permittivity at higher frequencies. The dispersion of dielectric permittivity can also be clearly seen in Fig. 3, in which the imaginary part of dielectric permittivity shifts with increasing temperature when measured at different frequencies.

If it is assumed that dynamic orientations of polar clusters are initiated above the static freezing temperature (T_f), then this dielectric phenomenon is analogous to spin or dipolar glasses [29]. Therefore in this case the dielectric relaxation or shifts in dielectric maximum temperature as a function of frequency can be understood by using Vogel–Fulcher model [30], which can be expressed as

$$\nu = \nu_o \exp[-E_a/k(T_m - T_f)] \quad (1)$$

Here, T_m is the maximum temperature of dielectric permittivity at various frequencies, T_f is the static freezing temperature, E_a is the activation energy and ν_o is the Debye frequency. The reorientation of the dipolar nano-domains are no longer thermally activated at static freezing

Table 2 Compositional dependence of activation energy, freezing temperature, Debye frequency, remnant polarization, coercive field and piezo coefficient for $(0.90 - x)$ BiFeO₃-xPbTiO₃-0.10BaTiO₃ for $x = 0.20$ – 0.24

Material	E_a (eV)	T_f (K)	ω_0 (Hz)	P_r ($\mu\text{C}/\text{cm}^2$)	E_c (kV/cm)	d_{33} (pC/N)
0.66BF–0.24PT–0.10BT	0.2047	196.21	1.54×10^{12}	11.2	37.47	34
0.67BF–0.23PT–0.10BT	0.1945	189.09	0.99×10^{12}	10.58	37.06	27
0.68BF–0.23PT–0.10BT	0.1942	192.78	0.63×10^{12}	10.34	35.41	12
0.69BF–0.21PT–0.10BT	0.2240	200.50	4.62×10^{12}	7.54	29.72	8
0.70BF–0.20PT–0.10BT	0.2134	193.25	2.64×10^{12}	7.34	29.66	3

temperature T_f . The data is fitted by using Eq. (1), Fig. 4 shows the plot between $\ln(\nu)$ and maximum temperature T_m , where the solid line is the V–F fit and the dotted points are the experimentally calculated data. The values of activation energy E_a , Debye frequency ν_0 and freezing temperature T_f are tabulated in Table 2, for all the compositions. The close agreement of data with V–F relationship confirms the relaxor like behavior in the present $(0.90 - x)$ BiFeO₃-xPbTiO₃-0.10BaTiO₃ ($x = 0.20$ – 0.24) system, which is same as the spin glass behavior with polarization fluctuations above T_f . It is also well known that the origin of polar nano-domain regions in the Pb based perovskite (ABO₃) materials is due to chemical disordering of A-site and B-site atoms. The dynamic motion of polar nano-domain regions is considered to be the reason for relaxor like dielectric behavior. XRD pattern also confirms the presence of extra reflections, which may be due to the twinning of ground state rhombohedra (R3m) of BaTiO₃ [31]. These nanotwin domain regions may be responsible for dispersion of dielectric permittivity.

The electric field dependence of the electrical polarization (P-E hysteresis loops) measured at 50 Hz at room temperature for $(0.9 - x)$ BiFeO₃-xPbTiO₃-0.10BaTiO₃ with $x = 0.20$ – 0.24 is shown in Fig. 5. It is well established that the effect of polarization in piezoceramics or ferroelectrics is nearly linked with the structural distortion and the chemical bonding of atoms which is involved in structural stability. Cohen showed that the origin of ferroelectricity in the materials which exhibit perovskite (ABO₃) structures like PbTiO₃ and BaTiO₃ is mainly due to A–O bonding [32]. In BF–PT, the Bi–O and Pb–O hybridization is mainly responsible for ferroelectricity [33–35]. The doping of Ba at Pb site in BF–PT system increases the Pb–O bond and this effect disrupts the perovskite structure and leads to the interaction between Ti and O ions due to weakly tied part of the perovskite structure resulting in polarization in the system. The remnant polarization also increases as the PT content increases as shown in the inset of Fig. 5.

Levin et al. have reported the large tetragonal distortion in BF–PT binary system, which occurs due to the displacement of A-site cations (Bi/Pb) [36]. The high tetragonal distortion with elevated ‘c/a’ ratio (~ 1.16) have been observed for all the compositions. This elevated distortion also deteriorates the piezoelectric properties.

High ‘c/a’ ratio in the ceramic sample generates internal stresses, which obstruct the domain switching [37], when the sample is poled at higher fields, resulting in low value of piezoelectric coefficient. The piezoelectric coefficient (d_{33}) value is higher for the compositions with higher remnant polarization. The piezoelectric coefficient (d_{33}) is given in Table 2.

4 Conclusions

In summary, $(0.9 - x)$ BiFeO₃-xPbTiO₃-0.10BaTiO₃ with $x = 0.20$ – 0.24 ceramics were successfully prepared by solid state reaction method. It was observed that the BaTiO₃ substitution stabilizes the monoclinic (Cc) and tetragonal (P4mm) phases and drove the MPB of BF–PT to lower BiFeO₃ ($x = 0.24$) content. The larger cation size of Ba induced the structural changes in BF–PT system and shifts the transition temperature towards the lower temperature and the dielectric studies revealed the Vogel–Fulcher type relaxor freezing below the maximum temperature T_m which result in a relaxor ferroelectric behavior relative to normal ferroelectric as observed in pure BF–PT binary system. On the other hand BaTiO₃

Fig. 5 P-E loops of $(0.9 - x)$ BiFeO₃-xPbTiO₃-0.10BaTiO₃ for $x = 0.20$ – 0.24 , inset shows the variation of polarization with increasing PbTiO₃ content

introduction in BF–PT system merely affected the tetragonal distortion and c/a ratio reduced from ~ 1.18 to ~ 1.16 in the MPB region for all the compositions. Still the value of tetragonal distortion is very high and it limited the piezo response. It had been observed from the P-E loops that remnant polarization increased with increasing PT content.

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