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Structural, dielectric and ferroelectric properties of $Ba_{1-x}(Bi_{0.5}Na_{0.5})_xTiO_3$ ceramics

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Abstract

Lead free $Ba_{1-x}(Bi_{0.5}Na_{0.5})_xTiO_3$ ($x=0$, 0.02, 0.04, 0.06, 0.08, 0.1) ferroelectric ceramics were synthesized by conventional solid state reaction technique. Sintering was done at 1200 °C for 2 h in air atmosphere. The final products have tetragonal symmetry with decreasing c/a ratio confirmed by X-ray diffraction analysis. The grain size varies between 300 nm to 1000 nm for $x=0$ to 0.1. With increase in $Bi_{0.5}Na_{0.5}TiO_3$ [BNT] content, the room temperature permittivity decreases whereas the Curie temperature (T_c) increases and its highest value was found to be 155 °C for 10 mol% of BNT addition. The ceramics show stable and low dielectric loss characteristics. The remnant polarization (P_r) and the coercive field (E_c) increases monotonously with increase in BNT content. The highest value of $2P_r$ ($=17\ \mu C/cm^2$) and $2E_c$ ($=22$ Kv/cm) was obtained for $x=10$ mol% BNT addition.
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Keywords: A. Powders: solid state reaction; B. Grain size; C. Ferroelectric properties; D. Perovskite

1. Introduction

In recent years, a considerable interest has arisen in lead-free ceramics due to the restriction of the use of lead, on the ground of human health and environmental protection. Barium titanate ($BaTiO_3$, BT) displays superior dielectric, ferroelectric, piezoelectric, pyroelectric, and electro–optical properties [1–3]. It possesses ferroelectric–paraelectric transition around its Curie temperature ($T_c=120$ °C) [4]. This phenomenon is widely used in BT-based ceramics. It is the main component used in different electro-ceramic devices such as Multi-Layer Capacitors (MLCs), ferroelectric memory devices, and also in various applications utilizing its piezoelectric properties and Positive Temperature Coefficient of Resistance property (PTCR) [5–7]. It is well known that BT-based electronic devices perform at temperatures less than its Curie temperature (<120 °C). In order to fulfill the demands of special applications functioning at a temperature above 120 °C, $PbTiO_3$ (PT) is usually added to the BT ceramics to shift the T_c to higher temperature. Since lead had been prohibited to be used in electronic devices, hence some other kinds of perovskite-type compounds [8–10] were doped into BT to replace the traditional PT, in order to increase the Curie temperature of BT-based ceramics.

$(Bi_{0.5}Na_{0.5})TiO_3$ (BNT) was developed by Smolenskii et al. [3], a kind of perovskite-type ferroelectric material that possess Curie temperature ($T_c=320$ °C) and remnant polarization ($P_r=38.1\ \mu C/cm^2$) and coercive field ($E_c=73$ kV/cm) at room temperature. As it can form solid solutions with BT, it is considered to be a good material which may raise phase transition temperature of BT. The compositions of $(1-x)Bi_{0.5}Na_{0.5}TiO_3-xBaTiO_3$ has been studied by many researchers [11–16] and found that these compositions have a rhombohedral (F_α)–tetragonal (F_β) morphotropic phase boundary (MPB) around $x=0.06-0.07$, where it shows outstanding piezoelectric and dielectric properties. It was considered to be a superior lead-free candidate to replace widely used lead-contained materials to increase the Curie temperature of $BaTiO_3$-based ceramics [17–19]. The investigations of lead-free $(1-x)BaTiO_3-xNa_{0.5}Bi_{0.5}TiO_3$ ceramics with different electrical properties are of great scientific and practical interest, particularly its dielectric properties [20–23].

In the present work, a systematic study of structural, dielectric and ferroelectric properties of $Ba_{1-x}(Bi_{0.5}Na_{0.5})_xTiO_3$ [BNBT], ($x=0$, 0.02, 0.04, 0.06, 0.08, and 0.1) series

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was done, which was synthesized by solid state reaction method.

2. Experimental

Polycrystalline ceramics with composition of $Ba_{1-x}(Bi_{0.5}Na_{0.5})_xTiO_3$ [BNBT], ($x=0$, 0.02, 0.04, 0.06, 0.08, and 0.1) were synthesized by conventional solid-state reaction technique. The raw materials Bi_2O_3 (99.5%, Himedia, India), Na_2CO_3 (99.9%, Qualigens, India) $BaCO_3$ (98.5%, Himedia, India) and TiO_2 (99%, Himedia, India) were used as the starting materials. The powders taken in stoichiometric ratios were ground well in agate mortar in acetone medium for 4 h. An extra amount of 3 wt% Bi_2O_3 and Na_2CO_3 were added to initial mixture to compensate the losses of bismuth and sodium as they are volatile above 820 °C and 850 °C respectively. The resultant mixture was then calcined at 1050 °C for 2 h. The X-ray diffraction (XRD) pattern of ceramics was recorded using X-ray powder diffractometer (Bruker D8 Advance) with Cu(K_α) ($\lambda=1.5402$ Å) radiation, over a wide range of Bragg angle ($20^\circ \le 2\theta \le 70^\circ$) with a scanning speed of $1^\circ\,min^{-1}$ at room temperature. The calcined powders were grounded again until the grains reached a fine form and pressed into discs of thickness 1.2 mm and diameter 10 mm by Hydraulic press. These pellets were sintered at 1200 °C for 2 h in air and then slowly cooled down to room temperature. Field effect scanning electron microscopy (FESEM) was used to study the morphology of the samples. Silver paste was applied to both flat surfaces of the sintered samples to act as electrode. The dielectric measurements were done by using an automated HIOKI 3532-50 Hi Tester LCR Meter as a function of temperature (range from room temperature to 500 °C) with heating rate of $2\,^\circ C\,min^{-1}$ and PSM 1735 LCR Hi tester (ranges of 1 Hz–35 MHz) was used to measure dielectric constant and dielectric loss as a function of frequency at room temperature.

The remnant polarization (P_r), and coercive field (E_c), were determined from P–E hysteresis loops at room temperature using modified Sawyer-Tower Circuit.

3. Results and discussion

3.1. Phase identification and microstructure studies

The phase and crystal structural characteristics of the solid solution were investigated by XRD. Fig. 1 shows XRD pattern of the ceramics with 0, 2, 4, 6, 8 and 10 mol% of BNT. It indicates the formation of single phase solid solution with perovskite structure. At room temperature, BT has a tetragonal structure and BNT has a rhombohedral structure. There is splitting in peak for 2θ, 42°–50° (2 0 0) and (0 0 2) shown in Fig. 1(c), which confirms the existence of tetragonality symmetry, but it decreases as BNT contents increases. The tetragonality factor c/a as a function of BNT-doping concentration is shown in inset of Fig. 1 (b). The tetragonality factor c/a and volume decreases with increasing BNT content because the ionic radii of Na^+ ($r_{12}=1.39$ Å) and Bi^{3+} ($r_{12}=1.34$ Å) are smaller than the ionic radii of Ba^{2+} ($r_{12}=1.61$ Å) [24]. Thus distortion and deformation of the structure took place when Bi^{3+} and Na^+ ion were substituted at A-site (Ba^{2+} ion).

The FESEM images obtained from the surface of sintered samples are shown in Fig. 2(a–f). The morphologies of the prepared samples are dense and uniform. The average grain size calculated by linear interception method was in the range 300 nm–1000 nm. The considerable increase in grain size with increasing BNT contents may be due to the increase of liquid phase at grain boundaries. The apparent densities lies in the range 92% to 96% of theoretical densities calculated from the molecular weight and lattice parameters. Energy dispersive X-ray analysis (EDS) as shown in the Fig. 2(g) for $x=0.08$ confirmed that all the samples are nearly in stoichiometry ratio.

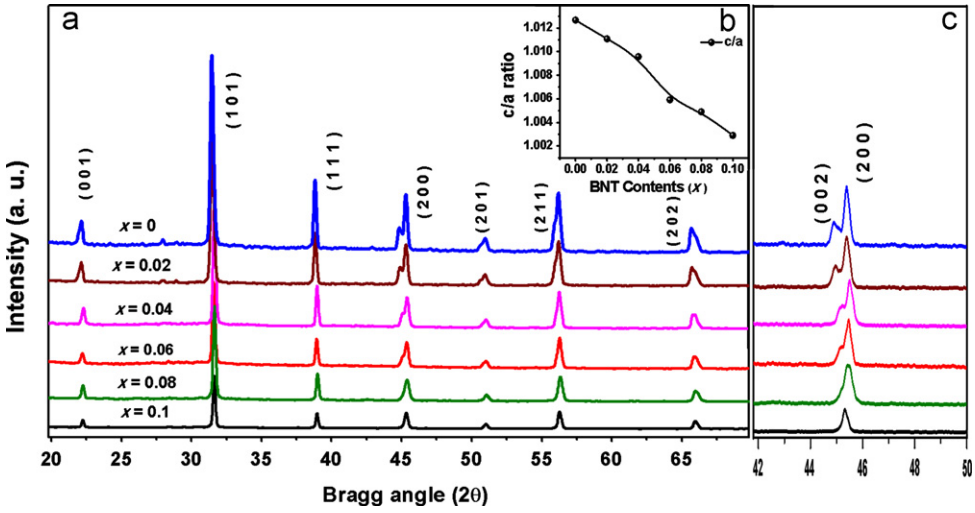
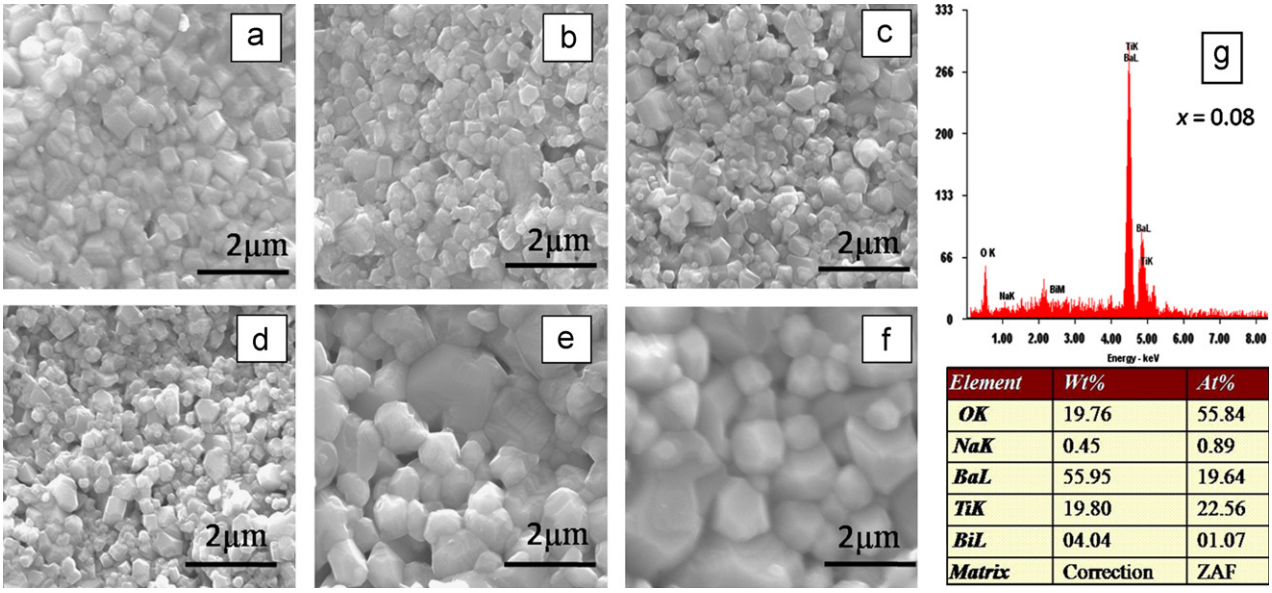


Fig. 1. X-ray diffraction pattern for various compositions in the system $Ba_{1-x}(Bi_{0.5}Na_{0.5})_xTiO_3$ for (a) 2θ, 20°–70°, (b) c/a ratio and (c) 2θ, 42°–50°.



Element	Wt%	At%
OK	19.76	55.84
NaK	0.45	0.89
BaL	55.95	19.64
TiK	19.80	22.56
BiL	04.04	01.07
Matrix	Correction	ZAF

Fig. 2. SEM Micrograph for (a) $x=0$, (b) $x=0.02$, (c) $x=0.04$, (d) $x=0.06$, (e) $x=0.08$, and (f) $x=0.1$ in the system $Ba_{1-x}(Bi_{0.5}Na_{0.5})_xTiO_3$, and (g) energy dispersive X-ray spectrum for $Ba_{1-x}(Bi_{0.5}Na_{0.5})_xTiO_3$, $x=0.08$.

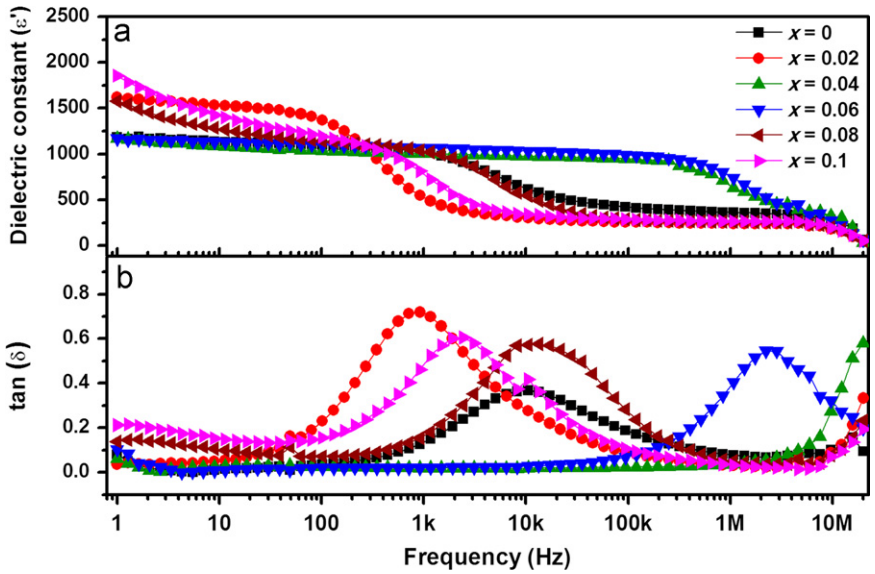


Fig. 3. Variation of (a) dielectric constant (b) dielectric loss, with frequencies for various compositions in the system $Ba_{1-x}(Bi_{0.5}Na_{0.5})_xTiO_3$.

3.2. Dielectric properties

Fig. 3(a) and (b) shows variation of dielectric permittivity (ε') and loss tangent ($\tan\delta$) with frequency at room temperature. A relatively high value of dielectric constant at low frequencies may be due to the presence of all types of polarizations (i.e. electronic, ionic, dipolar, interfacial, etc.), which is a characteristic of a ferroelectric material. Dielectric permittivity initially showed a sharp decrease with the increase in frequency up to 10 kHz and then became almost saturated up to 1 MHz. The large value of ε' at low frequency may be attributed to the presence of space charge effect. We find that the dielectric loss have a peak at a frequency where the applied field has the same period of relaxation for a particular polarization process.

Temperature dependent dielectric permittivity (ε') of the ceramics with different BNT content is shown in Fig. 4(a–f). The $\varepsilon' - T$ curves of the BNBT ceramics exhibit broad dielectric peaks around T_m, which is one of the most important characteristics of a disordered perovskite structure with diffuse phase transition. This broadening is considered to be due to compositional fluctuation, and/or substitutional disordering in the arrangement of cations in one or more crystallographic sites of the structure, which leads to microscopic or nanoscopic heterogeneity in the compounds, with different Curie points [25,26].

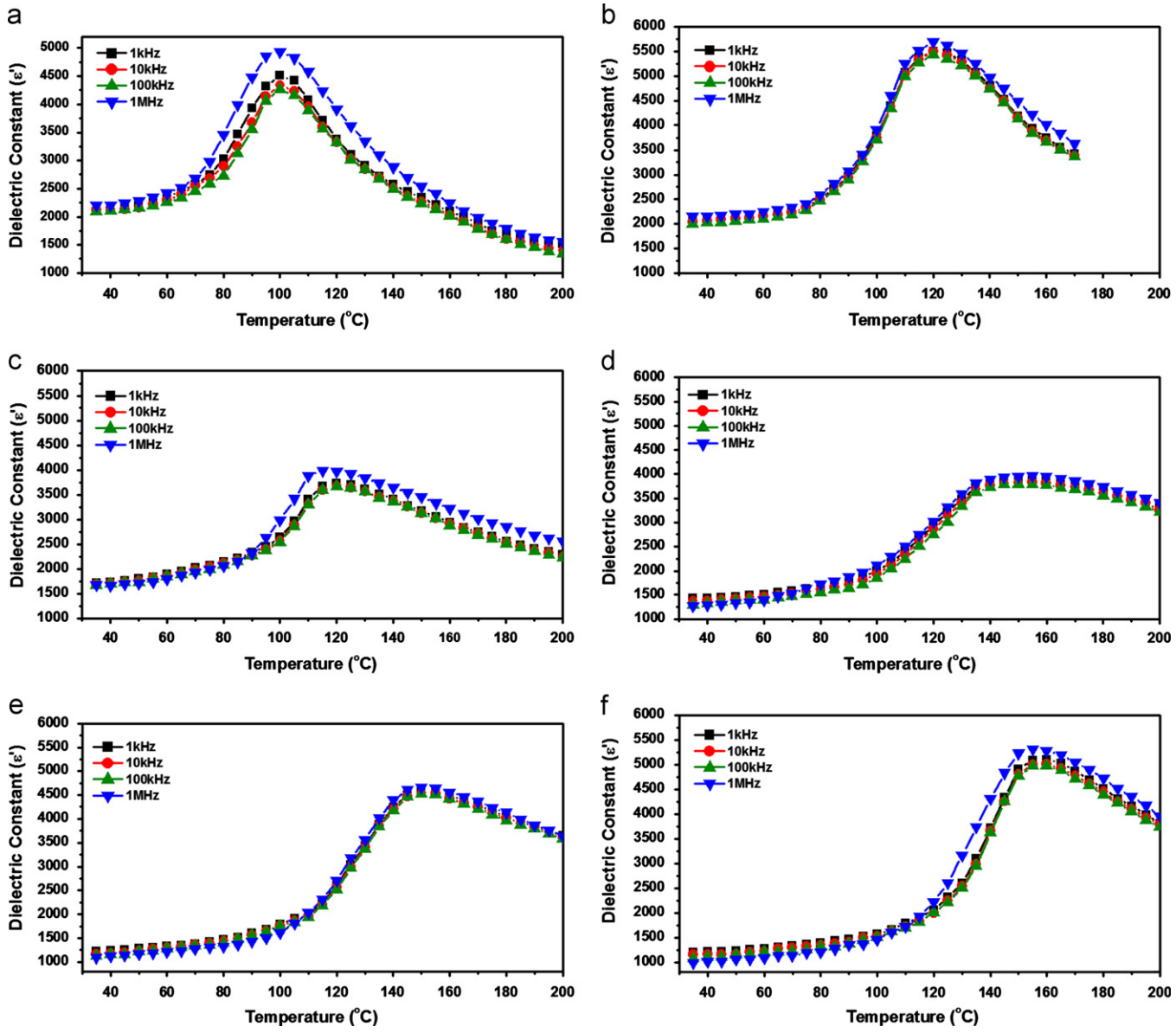


Fig. 4. Variation of dielectric constant (ε') with temperature at different frequencies for (a) $x=0$, (b) $x=0.02$, (C) $x=0.04$, (d) $x=0.06$, (e) $x=0.08$, and (f) $x=0.1$ respectively in system $Ba_{1-x}(Bi_{0.5}Na_{0.5})_xTiO_3$.

These fluctuations may be at A-site which is occupied by Ba^{2+}, alkali elements (Bi^{3+}, Na^{+}) or at B-site occupied by Ti^{4+}, in ABO_3 type of compounds.

In order to further characterize the dielectric dispersion and diffuseness of the phase transition, a modified Curie–Weiss law proposed by Uchino and Nomura [27] was employed

$$1/\varepsilon' - 1/\varepsilon'_{max} = A(T - T_m)^{\gamma}$$

where $\varepsilon'_{\max}$ is the maximum value of dielectric constant at the phase transition temperature (T_m), and γ is the degree of diffuseness. Normal ferroelectric have $\gamma=1$ and relaxor ferroelectrics have $1 \le \gamma \le 2$. Plots of $\ln(1/\varepsilon' - 1/\varepsilon'_{max})$ as function of $\ln(T - T_m)$ at 1 kHz of the BNBT ceramics are shown in Fig. 5. By least-square fitting to the experimental data of the modified Curie–Weiss law the value of γ was determined, which lies between from 1.5 and 1.9. This suggests that the degree of the diffuseness of the phase transition increases with increasing BNT contents, which confirm the second order phase transition. We can also see that the temperature corresponding to permittivity maxima known as Curie temperature (T_c) of the ceramics was found to increase from 100 °C to 155 °C as BNT content increases from 0 to 10 mol%. This may be explained as follows. In BT–BNT the Bi_2O_3 has melting point 820 °C so it becomes volatile at our working temperature (1200 °C), because the Bi–O bonds are weak. So A–O bonds were weakened, due to this Ti–O bonds were strengthened. As a result the interactions between Ti^{4+} and O^{2-} became strong as a result Ti^{4+} could not resume its position unless the tetragonality was wrecked at higher temperature, hence the Curie temperature of BT–BNT

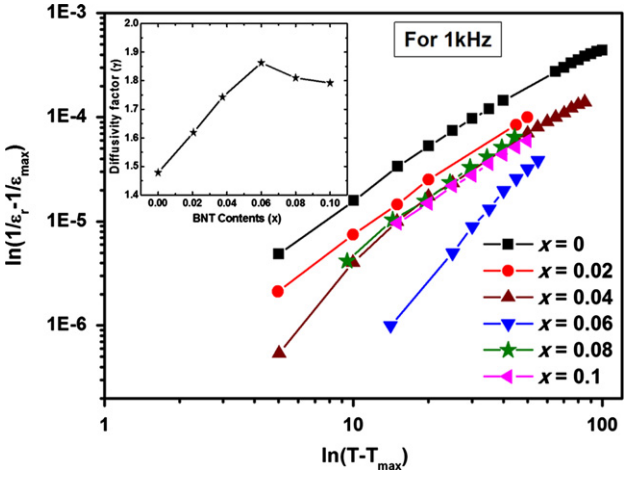


Fig. 5. Variation of $\left(1/\varepsilon'-1/\varepsilon'_{max}\right)$ with $(T-T_m)$ for $x=0$, 0.02, 0.04, 0.06, 0.08, 0.1 in the system $Ba_{1-x}(Bi_{0.5}Na_{0.5})_xTiO_3$ for 1 kHz (inset shows variation of diffusive factor with BNT contents).

ceramics increased. Moreover in perovskite-type (ABO_3) structure, A-site ion is at the center of oxygen dodecahedron, and the oxygen octahedron is held down directly by A-site ions. Hence replacement of A-site ion influence Ti-O bonds, as a result the Curie temperature T_C of materials is going to be increased [23,28]. The tan δ–T curve of all the samples are shown in Fig. 6(a–f), which exhibit a very low dielectric loss

Fig. 7 shows the variation of room temperature dielectric permittivity (ε'_{RT}), tan δ and Curie temperature (T_c) with BNT contents at frequency 1 kHz. It is clear that as the BNT content increases from 0 to 0.1, the room temperature dielectric permittivity decreases from 2200 to about 980, Curie temperature (T_c) of the ceramics is found to increase monotonously from 100 °C to 155 °C. Dielectric loss is very low (between 0.02–0.042), which kept almost constant throughout the temperature range 30–200 °C which indicates that the ceramics have stable dielectric loss.

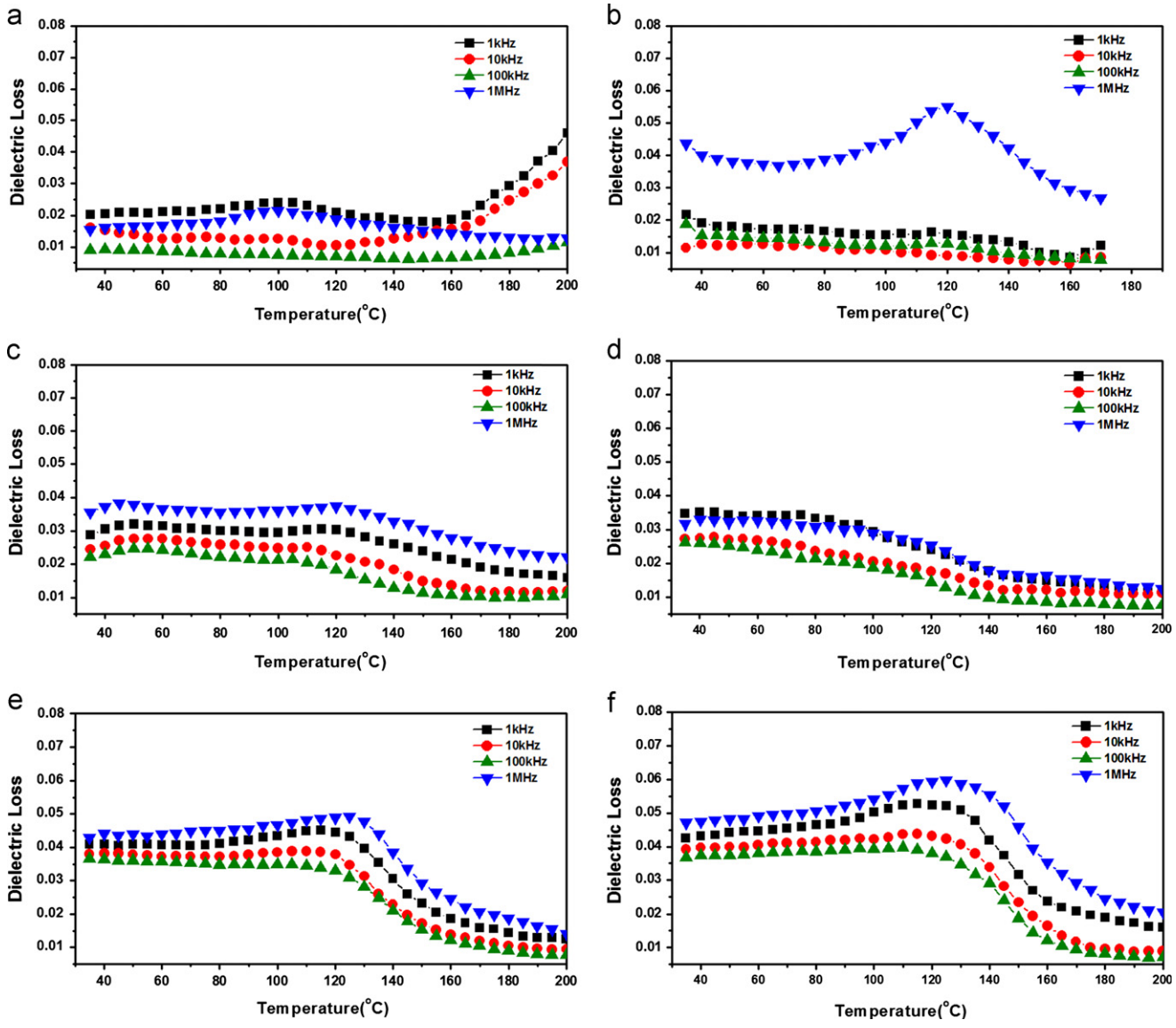


Fig. 6. Variation of dielectric loss (tan δ) with temperature at different frequencies for (a) $x=0$, (b) $x=0.02$, (C) $x=0.04$, (d) $x=0.06$, (e) $x=0.08$, and (f) $x=0.1$ respectively in system $Ba_{1-x}(Bi_{0.5}Na_{0.5})_xTiO_3$.

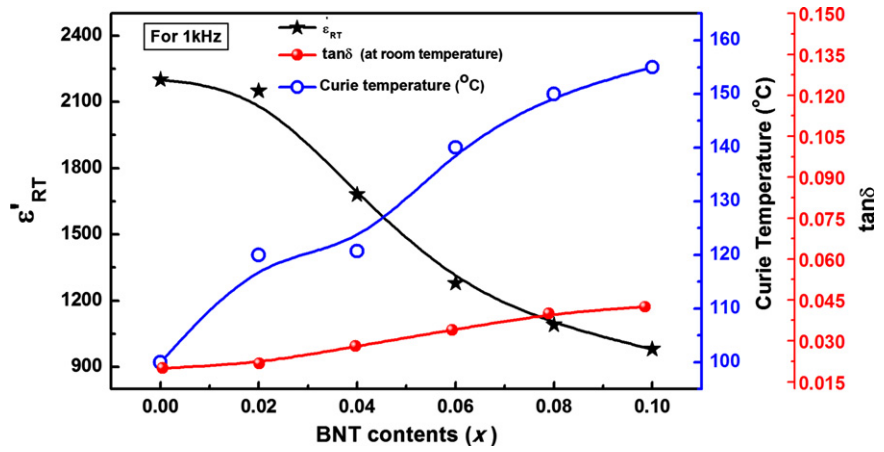


Fig. 7. Variation of room temperature dielectric permittivity (ε'_{RT}), dielectric loss (tan δ), and Curie temperature (T_c) with BNT contents at1 kHz.

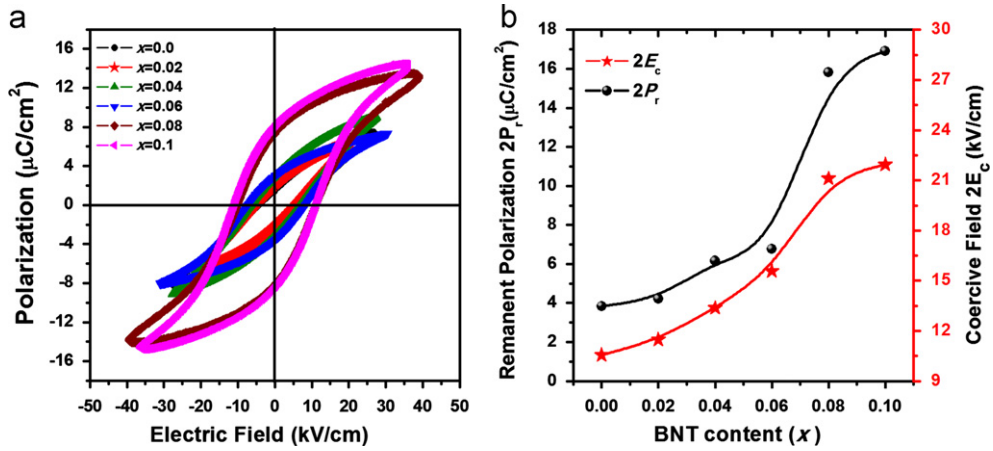


Fig. 8. (a) *P–E* hysteresis loops, and (b) variation of $2P_r$ and $2E_c$ of the $Ba_{1-x}(Bi_{0.5}Na_{0.5})_xTiO_3$ ceramics with $x=0$, 0.02, 0.04, 0.06, 0.08 and 0.1 of BNT at room temperature.

3.3. Ferroelectric properties

P–E hysteresis loops of the ceramics with different BNT content at room temperature is shown in Fig. 8(a). Ferroelectric properties are affected by composition, its homogeneity, defects, external field and orientation of domains, which eventually contribute to the materials response. Uniform oriented domain structures actually increase the ferroelectric properties. As observed from the hysteresis curves, remnant polarization increases monotonously as the BNT contents is increased with $2P_r$ (Fig. 8(b)) values 3.9, 4.2, 6.2, 6.8, 15.8 and 17 μC/cm^2 for $x=0$, 0.02, 0.04, 0.06, 0.08 and 0.1 respectively. The maximum value of remnant polarization here is 17 μC/cm^2 (for $x=0.1$), which is much better than as reported earlier by Gao, et al. [29] and Huang, et al. [30]. Coercive field ($2E_c$) is also found to increase monotonously from 10.5 to 22 kV/cm with increasing BNT contents from $x=0$ to 0.1, which indicates that the domain reorientation and rotation is gradually hindered as BNT is increased. This variation in remnant polarization and coercive field with BNT addition is considered to be the result of distortion and deformation of the crystal structure.

4. Conclusion

Polycrystalline lead-free ceramics, $Ba_{1-x}(Bi_{0.5}Na_{0.5})_xTiO_3$, were prepared by solid-state reaction method. The solid solutions have a single-phase perovskite structure, lattice constant c/a ratio decreased as BNT increases. The incorporation of BNT into $BaTiO_3$ not only improved ferroelectric properties but also increased the Curie temperature (T_C) monotonously from 99 °C to 155 °C. The ceramics have stable and low dielectric loss characteristic. Both the remnant polarization ($2P_r$), and the coercive field ($2E_c$), increased monotonously with increasing BNT. The maximum value of remnant polarization was 17 μC/cm^2 for 10 mol% of BNT.

Acknowledgments

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