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Dielectric and ferroelectric properties of $(1-x)BaTiO_3$–$xBi_{0.5}Na_{0.5}TiO_3$ ceramics

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Abstract

Lead-free $(1-x)BaTiO_3$–$xBi_{0.5}Na_{0.5}TiO_3$ ($x = 0.01$, 0.02, 0.05, 0.1, 0.2, 0.3) ferroelectric ceramics were fabricated by the conventional ceramic technique. Sintering was made at 1200 °C for 2–4 h in air atmosphere. The crystal structure was investigated by X-ray diffraction. The dielectric and ferroelectric properties were also studied. Room temperature permittivity was found to decrease as $Bi_{0.5}Na_{0.5}TiO_3$ (BNT) content increases. Only the sample with 0.3 mol BNT was found to have relaxor behaviour. The T_c shifted slightly only for BNT addition lower than 0.1 mol. The highest T_c (about 150 °C) was obtained for 0.2 mol BNT addition. The remanent polarization, P_r, decreases whereas the coercive field, E_c, increases monotonously as the BNT content increases.

Keywords: C. Ferroelectric properties; C. Dielectric properties; Ceramics

1. Introduction

$BaTiO_3$ (BT) and $Bi_{0.5}Na_{0.5}TiO_3$ (BNT) are two attractive lead-free materials, which were considered to be the candidates to replace the widely used lead-containing perovskite materials because of lack of lead pollution during the production process. BT is a typical ferroelectric material with perovskite structure. It has good piezoelectric and ferroelectric properties, but relatively low Curie temperature, $T_c = 120$ °C, along with a secondary phase transition at about 5 °C [1,2], which would lead to lower temperature stability. For use of $BaTiO_3$ based lead-free ferroelectric materials, it is necessary to increase the T_c and shift the temperature of the secondary phase transition. BNT is a ferroelectric material which has relatively high Curie temperature, $T_c = 320$ °C, a relative large remanent polarization, $P_r = 38$ μC/cm^2, and coercive field, $E_c = 73$ kV/cm, at room temperature [3]. Nevertheless, pure BNT is hard to be poled for its large coercive field and relatively large conductivity. To improve its properties, several solid solutions of BNT with $SrTiO_3$ [4], $La_2(TiO_3)_3$ [5], $NaNbO_3$ [6], and $BaTiO_3$ [7] have been investigated. Among the BNT-based system, $(1-x)Bi_{0.5}Na_{0.5}TiO_3$–$xBaTiO_3$ possesses a rhombohedral (F_α)-tetragonal (F_β) morphotropic phase boundary (MPB) at $x = 0.06$–0.07, where the system shows outstanding piezoelectric and dielectric properties [7]. Therefore, many researches are focused on compositions near the MPB [7–12], whereas few reports are involved with compositions close to $BaTiO_3$.

BNT is considered to be a suitable material to improve the electrical properties of $BaTiO_3$ based ceramics for its good ferroelectric properties. In this paper, the dielectric and ferroelectric properties of BT-based solid solution $(1-x)BaTiO_3$–$x(Bi_{0.5}Na_{0.5})TiO_3$ (abbreviated as BT–BNT100x) have been studied, and the ferroelectric and dielectric properties of the related ceramics have been characterized.

2. Experimental

$(1-x)BaTiO_3$–$x(Bi_{0.5}Na_{0.5})TiO_3$ ($x = 0.01$, 0.02, 0.05, 0.1, 0.2, 0.3) ceramics were prepared by the conventional powder processing route. Reagent grade TiO_2, Bi_2O_3, $BaCO_3$, and Na_2CO_3 mixed in stoichiometric proportions and milled in ethanol for 10 h were dried and calcined at 850 °C for 4 h. The

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calcined powders were reground, and then pressed into discs 20 mm in diameter and about 1 mm in thickness. The green discs were sintered at 1200 °C for 2–4 h in air atmosphere. Silver paste was fired on the surfaces of the discs as electrodes.

The crystal structure of the ceramics was determined by X-ray powder diffraction (XRD). Dielectric measurements were carried out by a TH2819 precision LCR Meter from room temperature to 180 °C, with a heating rate of 0.5 °C min^{-1}, at 100, 1k, 10k, and 100 kHz, respectively. The coercive field, E_c, and remanent polarization, P_r, were determined from D–E loops obtained by the modified Sawyer–Tower circuit.

3. Results and discussion

3.1. X-ray diffraction patterns of $(1-x)BaTiO_3$–$x(Bi_{0.5}Na_{0.5})TiO_3$ ceramics

The X-ray diffraction patterns of $(1-x)BaTiO_3$–$x(Bi_{0.5}Na_{0.5})TiO_3$ ($x = 0.01$, 0.1, 0.2, 0.3) ceramics sintered in air at 1200 °C for 2 h are shown in Fig. 1. All the BT–BNTx ceramics were of pure perovskite structure. At room temperature, $BaTiO_3$ is of tetragonal symmetry and $Na_{0.5}Bi_{0.5}TiO_3$ is rhombohedral. Their solid solutions were of tetragonal symmetry when the compositions were close to $BaTiO_3$. X-ray diffraction revealed that the crystal structure was influenced by BNT addition. (1 0 0), (2 0 0) and (0 0 2) peaks significantly reduce, and the peak of (0 0 1) gradually disappears as the content of BNT increases. The parameters a and c of the tetragonal structure being different, the combination of (1 0 0) and (0 0 1) peaks indicates that the difference between axes a and c reduces with the increase of BNT. Thus, distortion and deformation of the structure took place when Bi^{3+} and Na^+ ions were substituted into the site with Ba^{2+} ion, because the ionic radii of Bi^{3+} and Na^+ are smaller than the ionic radius of Ba^{2+}.

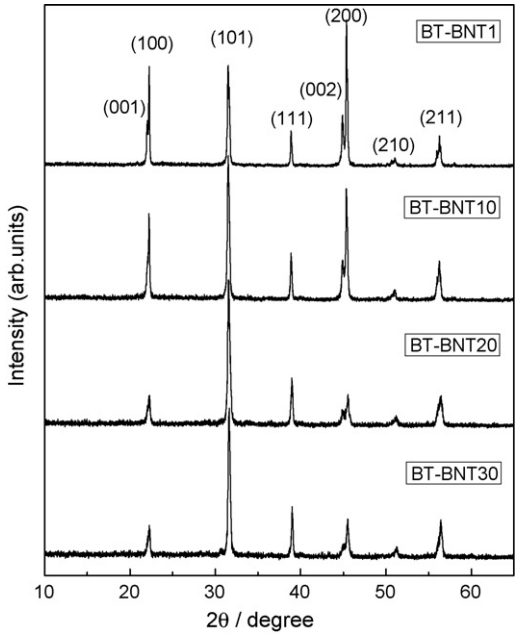

Fig. 1. X-ray diffraction patterns of the ceramics with different BNT content sintered at 1200 °C.

3.2. Dielectric properties of $(1-x)BaTiO_3$–$x(Bi_{0.5}Na_{0.5})TiO_3$ ceramics

Figs. 2 and 3 show the temperature dependence of the relative permittivity, ε_r, and the loss tangent, tan δ, of the ceramics with different BNT content, respectively. The ceramics with 0.01, 0.02, 0.05, and 0.1 mol BNT show normal ferroelectric characteristics, and the ε_r–T curves display a sharp shape near the Curie point (Fig. 2a–d). But in the ε_r–T curve of the ceramic with 0.05 mol BNT, a new broad peak appears near 32 °C (Fig. 2c). Similar peak can be found in the tan δ–T curve in the same position (Fig. 3c). This phenomenon indicates that a new phase transition occurred at a temperature near 32 °C. It is a ferroelectric–ferroelectric phase transition, for typical P–E hysteresis loops could be seen at a temperature below and over the transition point.

At 0.2 mol BNT content, the peaks of the ε_r–T curves near T_c broaden, much like that of relaxor ferroelectrics, but the position of the peaks keep unchanged at the different testing frequencies (Fig. 2e). At 0.3 mol BNT content, the peaks of the ε_r–T curves near T_c were broader, and the maximum of the permittivity decreases as the measurement frequency increases and the maximum permittivity temperature, T_m, is shifted slightly towards high temperatures as well (Fig. 2f). These characteristics indicate that the ceramic with 0.3 mol BNT shows relaxor ferroelectric properties. This phenomenon resulted from the high substitutions of Na^+ and Bi^{3+} ions for Ba^{2+} ions, which distort the unit cell, change the dipolar moment, and induce strain in the lattice. The more cations co-occupy the same lattice of unit cell, the more the chemical composition and crystal structure are inhomogeneous at the nanometer scale, therefore the relaxation characteristic is more evident [13].

The Curie temperature, T_c, of the ceramics was found to shift slightly in the temperature range between 114 and 126 °C, which is very near the T_c of the pure BT, when the addition of BNT is not higher than 0.1 mol. T_c did not shift monotonously to high temperature as expected when the BNT content is increased. The highest Curie temperature, about 150 °C, was obtained when the addition of BNT is 0.2 mol. It is interesting that T_c did not shift to higher temperature but shifted to lower temperature, about 112 °C, when the addition of BNT increased from 0.2 to 0.3 mol (Fig. 4). This differs from previous results [14], where ceramics with 0.2 and 0.3 mol BNT sintered at <1200 °C showed relaxor ferroelectric properties, with maximum permittivity temperature, T_m, at about 180–200 °C, which shifted monotonously to high temperatures as BNT content increased.

The permittivity of the ceramics was affected to a large extent by BNT addition. As the BNT content increased from 0.01 to 0.3 mol, room temperature permittivity decreased from 3000 to about 1000. At 0.05 mol BNT addition, room temperature permittivity was higher than these of the ceramics with 0.02 and 0.1 mol BNT, due to a secondary phase transition near room temperature. The variation of the room temperature permittivity with the BNT content is summarized in Fig. 5.

The dielectric losses, tan δ, were also affected noticeably by BNT addition. As seen in Fig. 3, the tan δ–T curves of all the samples except that of the ceramic with 0.2 mol BNT change

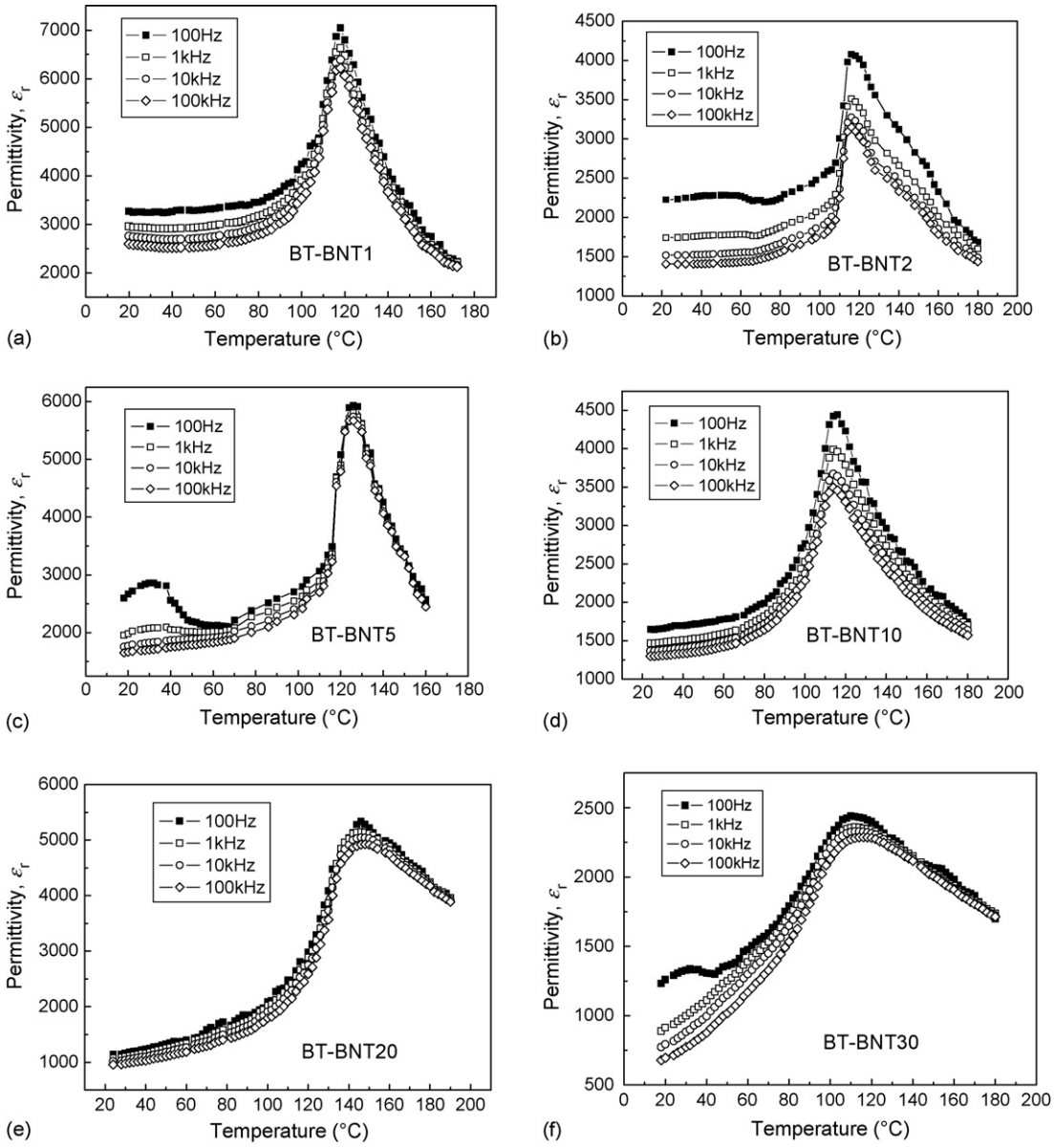

Fig. 2. Variation of the relative permittivity, ε_r, with the temperature, T, at the frequencies of 100, 1k, 10k, and 100 kHz.

remarkably with the temperature and the frequency. The tan δ of the samples with 0.01, 0.02, 0.05, 0.1, and 0.3 mol BNT decreased as the testing frequency and temperature increased. On the contrary, the tan δ of the ceramic with 0.2 mol BNT increased as the testing frequency increased, whereas of dielectric losses are smaller than for all other samples (Fig. 3e). In addition, the tan δ–T curves of the sample with 0.2 mol BNT exhibit a platform within the broad temperature range below 120 °C, which indicates it to have relatively stable and low dielectric losses.

3.3. Ferroelectric properties of $(1-x)BaTiO_3$–$x(Bi_{0.5}Na_{0.5})TiO_3$ ceramics

Fig. 6 shows the P–E hysteresis loops of BT–BNT2, BT–BNT5, BT–BNT10, and BT–BNT20 at room temperature. As observed from the hysterisis curves, BNT exerts significant influence on the loops shape and polarization value. The remanent polarization, P_r, of all the samples decreased monotonously as the content of BNT increases (Fig. 7). The values of P_r are all lower than 7 μC/cm^2, and the maximum value, 6.8 μC/cm^2, was obtained when BNT content was 0.02 mol. Theoretically, P_r values should have decreased because of the decreasing relative displacement of unit cells. The decrease in P_r as BNT content increases suggests that the high substitutions of Na^+ with Bi^{3+} ions for Ba^{2+} ions would cause the decrease of the relative displacement of unit cells.

The coercive field, i.e. the field at which the domains begin to switch their polarity, is strongly influenced by the BNT addition. As seen in Fig. 7, the coercive field, E_c, increased monotonously from 4 to 11.2 kV/cm when the content of BNT increased from 0.01 to 0.3 mol, a possible index of domain

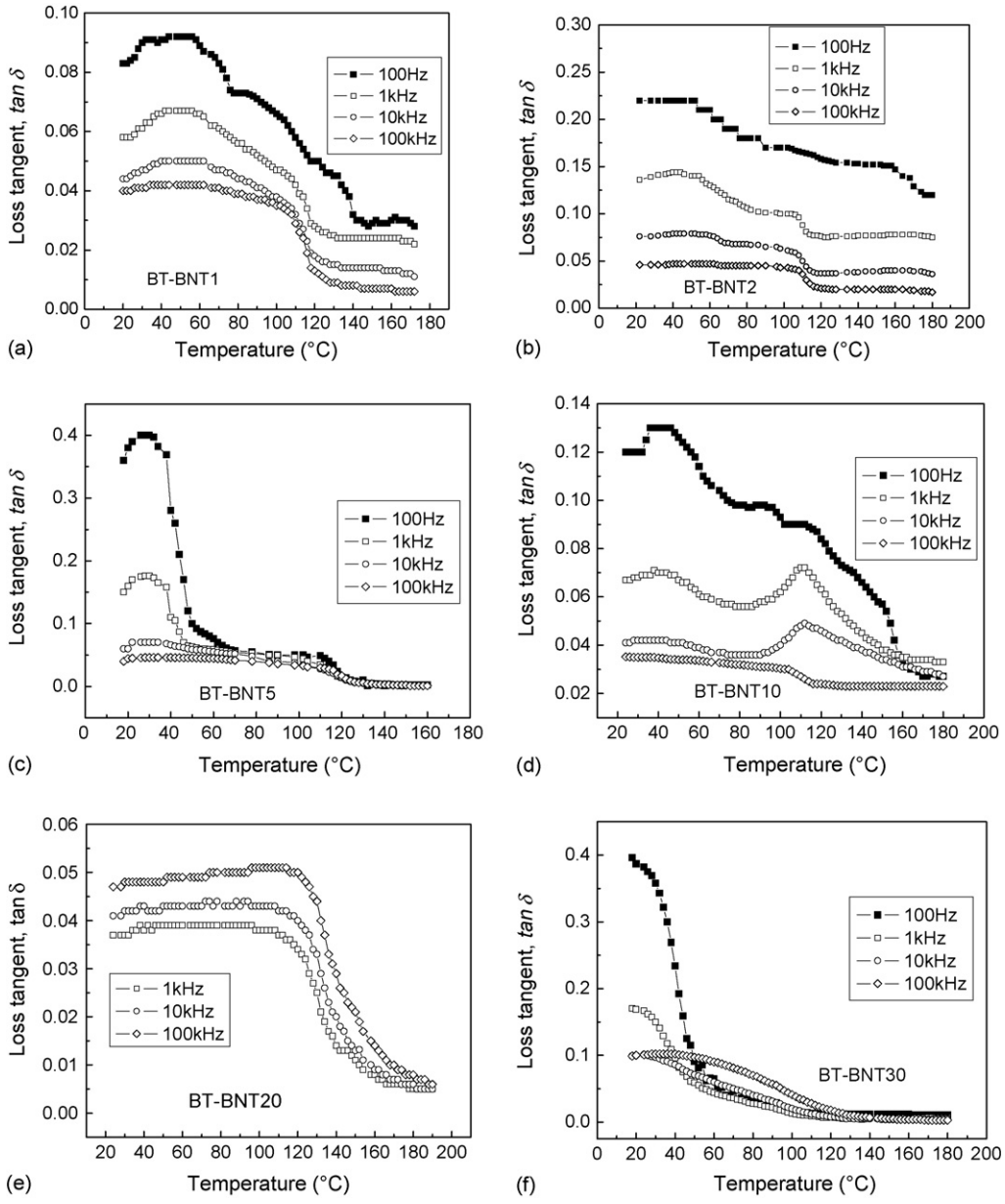

Fig. 3. Variation of the loss tangent, tan δ, with the temperature, T, at the frequencies of 100, 1k, 10k, and 100 kHz.

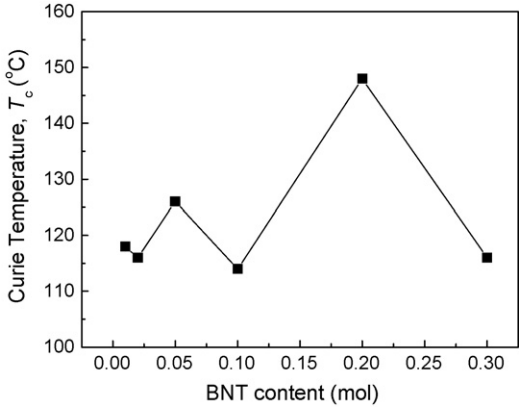

Fig. 4. Variation of Curie temperature, T_c, of the ceramics with different BNT content.

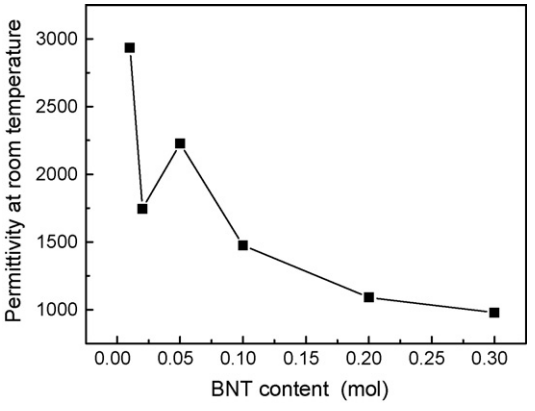

Fig. 5. Variation of the permittivity, ε_r, of the ceramics at room temperature with different BNT content at 1 kHz.

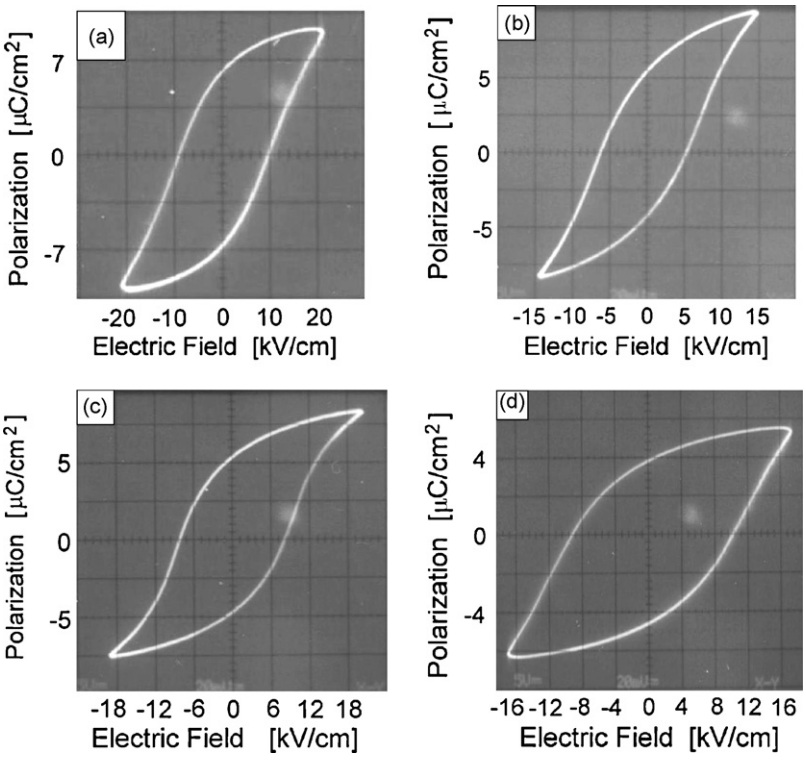

Fig. 6. *P–E* hysteresis loops of the ceramics with BNT of (a) 0.02 mol, (b) 0.05 mol, (c) 0.1 mol, and (d) 0.2 mol at room temperature.

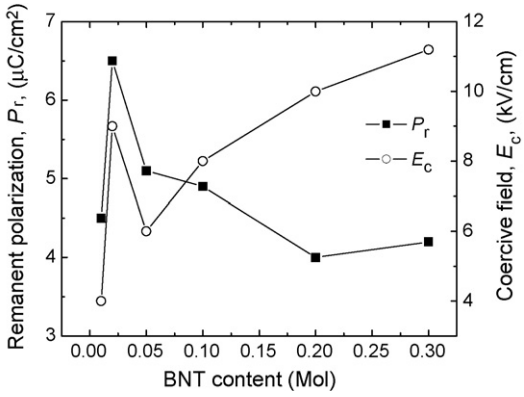

Fig. 7. Variation of the remanent polarization, P_r, and coercive field, E_c, of the ceramics with BNT content.

reorientation and rotation to be gradually hindered as BNT content increases.

4. Conclusions

$(1-x)BaTiO_3$–$x(Bi_{0.5}Na_{0.5})TiO_3$ ($x = 0.01, 0.02, 0.05, 0.1, 0.2, 0.3$) solid solutions with perovskite structure were prepared by a conventional ceramic fabrication technique. The addition of BNT affects to a large extent the dielectric and ferroelectric characteristics of the ceramics. The ferroelectric–paraelectric phase transition temperature does not shift monotonously to high temperature as BNT content increases. The Curie temperature, T_c, of the ceramics was found only shifting slightly near the T_c of the pure BT when the addition of BNT is not higher than 0.1 mol. It shifts to about 150 °C at 0.2 mol BNT addition, but shifts back to lower temperature, ~112 °C, as the BNT content increased to 0.3 mol. Relaxor ferroelectric characteristics were found at 0.3 mol BNT addition. The remanent polarization, P_r, becomes smaller and the coercive field, E_c, becomes larger compared to pure BT ceramics as BNT content increases.

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