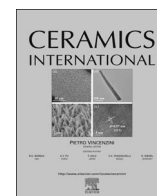




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Investigation of a new lead-free $(1-x-y)$ BNT- x BKT- y BZT piezoelectric ceramics

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ABSTRACT

Lead-free solid solutions $(1-x-y)\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3-x\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3-y\text{BaZr}_{0.05}\text{Ti}_{0.95}\text{O}_3$ ($0 \leq y \leq 0.25$ and $0.10 \leq x \leq 0.30$) were prepared by using a solid-state reaction method. The effect of y (BZT) and x (BKT) contents on phase, microstructure, and electrical properties was investigated. The XRD and Raman spectra exhibited co-existing rhombohedral and tetragonal phases throughout the entire compositional range with the tetragonal phase becoming dominant at higher y (BZT) and x (BKT) concentrations. While an increased in y (BZT) content promotes grain growth, the addition of x (BKT) suppresses it. The diffuseness exponent (γ) of ceramics increased from 1.82 to 1.92 and from 0.05 to 1.77 when increased of y (BZT) and x (BKT) contents, respectively, which showed the diffuse phase transition behavior. The change in P - E loops of ceramics was closely related to relative stability of long-range order. The results reflected a competition between compositions induced tetragonality and disorder. It appears that small amount of x (BKT) and y (BZT) favor ergodic behavior, which is indicative of increased disorder and stable PNRs at zero field conditions. However, with increased amount of x (BKT) and y (BZT), non-ergodic behavior is re-introduced, most likely due to increased tetragonality. The results indicated that the addition y (BZT) and x (BKT) significantly enhances the field-induced strain in $(1-x-y)\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3-x\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3-y\text{BaZr}_{0.05}\text{Ti}_{0.95}\text{O}_3$ ceramics.

1. Introduction

Piezoelectric materials are being widely used in a variety of applications such as actuators and sensors [1,2]. These applications are mostly based on PZT ceramics, which contain more than 60% lead. Lead is very toxic substance and environmentally problematic due to its high vapor pressure during sintering process [3,4]. Therefore, it is very urgent to develop lead-free piezoelectric ceramics with excellent properties to replace PZT based ceramics.

$\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BNT) lead-free based material have attracted great attention after the recent discovery of the large strain [5], which is associated with the reversible phase transitions between relaxor and ferroelectric [6]. However, high electric fields are required in this system, resulting in a low d_{33}^* (the large-signal piezoelectric coefficient) [7]. For improving piezoelectric properties, binary and ternary solid solutions based on BNT were developed and were shown to have electromechanical high performance at the MPB. $(1-x)\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3-x\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ (BNT-BKT) binary system between rhombohedral and tetragonal phases exhibits highest d_{33} of ~ 157 pC/N for $x = 0.20$ [5,6].

$(1-x)(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3-x\text{BaTiO}_3$ (BNT-BT) with $x = 0.06-0.07$ near the MPB has been well studied because of their improved electrical properties. However, $\text{Ba}(\text{Zr,Ti})\text{O}_3$ ceramics with 5% Zr content has better piezoelectric properties than that of BaTiO_3 [7]. Yu et al. reported that $\text{Ba}(\text{Ti}_{0.95}\text{Zr}_{0.05})\text{O}_3$ ceramics showed fairly satisfactory piezoelectric response, with the d_{33} value of 236 pC/N at room temperature [8]. In addition, the substitution of Zr^{4+} for Ti^{4+} ($r_{\text{Ti}^{4+}} = 0.605 \text{ \AA}$, $r_{\text{Zr}^{4+}} = 0.72 \text{ \AA}$) enhances structural lattice distortion and results in larger dipole moment inside the unit, both are beneficial to improve electrical properties [9,10]. Therefore, in this work, $(1-x-y)\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3-x\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3-y\text{BaZr}_{0.05}\text{Ti}_{0.95}\text{O}_3$ ($0 \leq y \leq 0.25$ and $0.10 \leq x \leq 0.30$) ceramics were prepared by the solid-state reaction method. The effects of y and x contents on microstructure, phase formation, electrical properties (dielectric, piezoelectric, P - E and S - E loops) were studied.

2. Material and methods

$(1-x-y)\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3-x\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3-y\text{BaZr}_{0.05}\text{Ti}_{0.95}\text{O}_3$

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($0 \leq y \leq 0.25$, fixed $x = 0.20$ and $0.10 \leq x \leq 0.30$, fixed $y = 0.10$) by using a solid-state reaction method. Bi_2O_3 (99.5%), Na_2CO_3 (99.5%), K_2CO_3 (98.0%), TiO_2 (99.5%), BaCO_3 (98.0%) and ZrO_2 ($> 99.95\%$) were chosen as the starting raw materials. For each composition, the oxides and carbonates were weighed according to the stoichiometric formula and ball milled again for 24 h. The slurries were subsequently dried and separately calcined at $850^\circ\text{C}/2\text{ h}$ for BNT, $850^\circ\text{C}/2\text{ h}$ for BKT and $1350^\circ\text{C}/2\text{ h}$ for BZT, respectively. The BNT, BKT and BZT calcined powders were then weighted and blended according to the formulas of $(1-x-y)\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3-x\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3-y\text{BaZr}_{0.05}\text{Ti}_{0.95}\text{O}_3$ (abbreviated to $(1-x-y)\text{BNT}-x\text{BKT}-y\text{BZT}$). The calcined powders were mixed with polyvinyl alcohol and pressed into discs of 10 mm in diameter and 1–2 mm in thickness. The green pellet were Sintered between 1000°C and 1200°C for 2 h in air at heating/cooling rate of $5^\circ\text{C}/\text{min}$.

Phase structure of the ceramics was identified using X-ray diffraction (XRD, Philip PW 3040/60 X'Pert Pro). The grain morphology of the samples was observed by means of scanning electron microscopy (SEM, Leol4555VP). For electrical characterization, samples were polished and painted with silver paste on the surfaces. Dielectric constant and loss of the ceramics for a wide variety of frequencies in the temperature range of $50\text{--}500^\circ\text{C}$ were measured using LCR meter (Agilent 4284A). The piezoelectric constant d_{33} values were measured using a quasi-static d_{33} -meter (Sinocera, YE2730A). The polarization-electric field (P - E) hysteresis loops and strain-electric field (S - E) hysteresis loops were measured using the ferroelectric test system (Radiant, PLC2-1014346).

3. Results and discussion

3.1. Crystal structure

The XRD patterns of the $1-x-y\text{BNT}-x\text{BKT}-y\text{BZT}$ ternary ceramics with different $y(\text{BZT})$ contents are presented in Fig. 1(a–c). The XRD peaks indicated pure perovskite phase and no secondary phases were found from the patterns for all samples, which indicated that the perovskite structure of the BNT-BKT-BZT ternary system is stable. It is well known that the rhombohedral structure is identified by (003)/

(021) peaks split at 2θ range of 38° to 41° and a single peak of (202) between 44° and 48° . While, the tetragonal structure is characterized by a single peak of (111) between 38° and 41° and split (002)/(200) peaks between 44° and 48° . At $y(\text{BZT})=0$, splitting of XRD peaks over the 2θ range of (003)/(021) and an asymmetry in the (202) peak over the range of 44° to 48° was detected, as seen in Fig. 1(b) and Fig. 1(c). When $y(\text{BZT})$ is increased, the (003)/(021) peak begins to merge into a single (111) peak and splitting of (202) peaks into (002) and (200) diffraction peaks can be observed. This indicated that the coexistence of rhombohedral and tetragonal phases, which is consistent with the nature of the polished specimen with an MPB composition. In the case of $x(\text{BKT})$ content increase, at $x = 0.10$, an asymmetry of a single (202) peak was observed between 38° and 41° and (003)/(021) peak at 2θ range of 44° to 48° presented an unclear splitting which indicated the coexistence of both rhombohedral and tetragonal phases. When $x(\text{BKT})$ is increased from 0.10 to 0.30, the peak at 2θ between 38° and 41° became more and (002) and (200) peaks at 2θ between 44° and 48° became more widely split, which suggested that the tetragonality of the ceramics was increased, as seen in Fig. 2. This result was similar to BNT-BKT-BLT and BNT-BKT-BF ceramics prepared by combustion technique [11,12]. Moreover, the peak at 2θ range of $38\text{--}41^\circ$ and $44\text{--}48^\circ$ gradually shifted toward lower angle with increasing $y(\text{BZT})$ and $x(\text{BKT})$ contents which indicated that the unit cell volume was enlarged. This is expected because the ionic radii of Ba^{2+} ($1.61\text{ \AA}$) and K^+ ($1.38\text{ \AA}$) are larger than that of Bi^{3+} ($1.17\text{ \AA}$) as well as of Na^+ ($1.18\text{ \AA}$) on A-site. Similar situation exists for Zr^{4+} ($0.72\text{ \AA}$) substituting for Ti^{4+} ($0.605\text{ \AA}$) on B-site [13,14].

The phase structure was confirmed by studying the Raman spectroscopy, which probes the local ionic configuration within a short length scale usually less than 10 nm. The observed Raman profiles of $1-x-y\text{BNT}-x\text{BKT}-y\text{BZT}$ ternary ceramics with differences $y(\text{BZT})$ contents are presented in Fig. 3(a) The Raman spectrum consisting of three main modes were perceived in the $1-x-y\text{BNT}-x\text{BKT}-y\text{BZT}$ system from 100 to 700 cm^{-1} , which were identical to other BNT-based ceramics [14,15]. The first Raman-active $\text{A}_1(\text{TO})$ mode at around 146 cm^{-1} is related to network modifiers or distorted octahedral $[\text{BiO}_6]$, $[\text{KO}_6]$ and $[\text{NaO}_6]$ clusters. The second Raman-active Ti-O mode at around

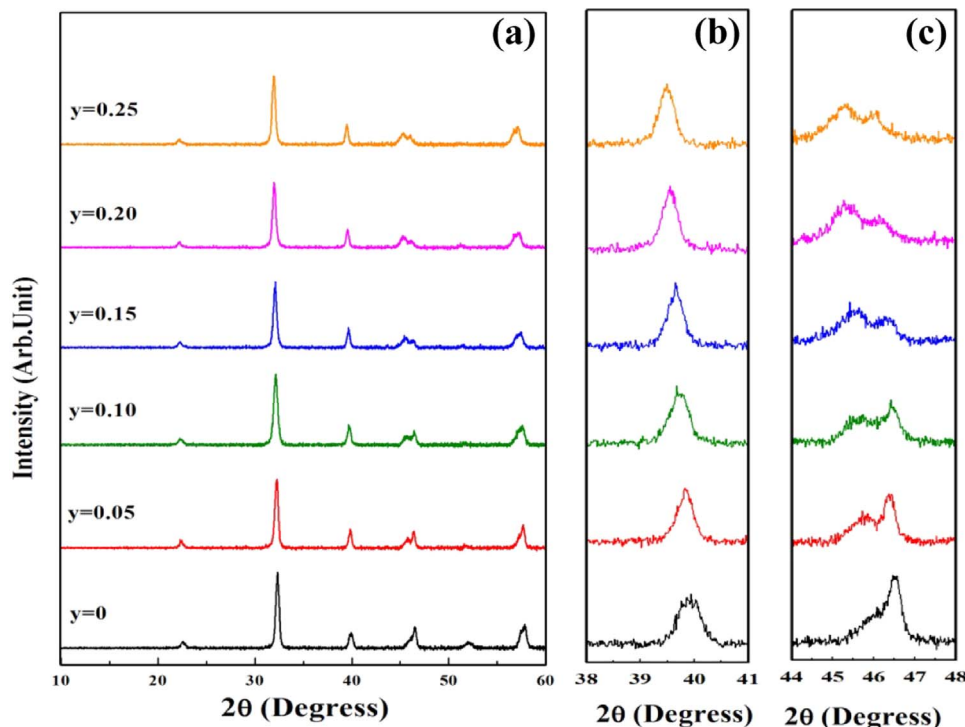


Fig. 1. X-ray diffraction patterns of $0.80-y\text{BNT}-0.20\text{BKT}-y\text{BZT}$ sintered ceramics in the 2θ range of (a) 10° to 60° , (b) 38° to 41° and (c) 44° to 48° .

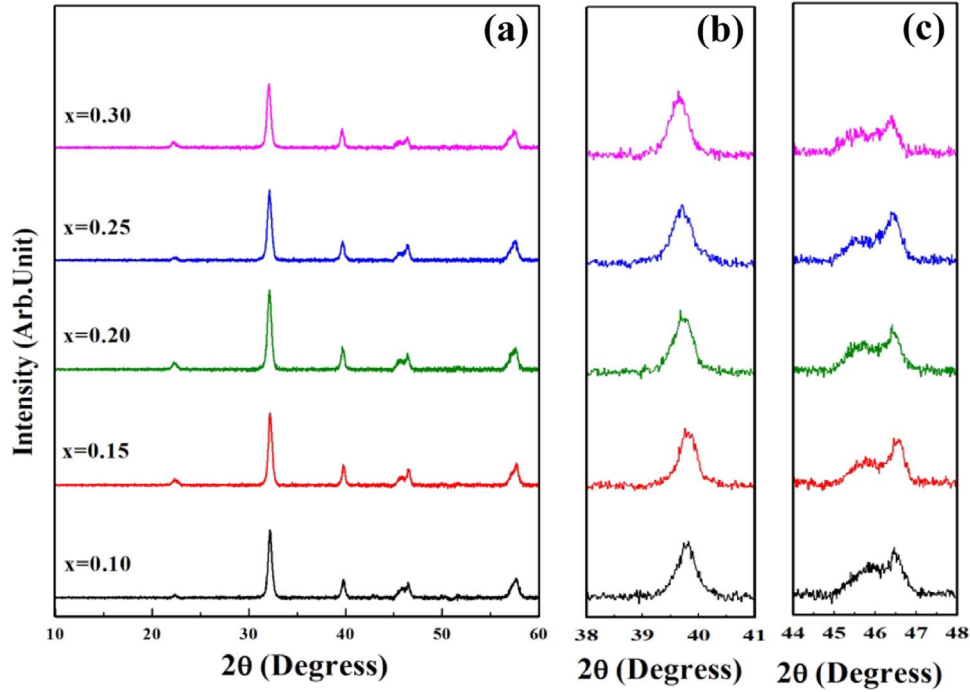


Fig. 2. X-ray diffraction patterns of 0.90-xBNT-xBKT-0.10BZT sintered ceramics in the 2θ range of (a) 10° to 60° , (b) 38° to 41° and (c) 44° to 48° .

279 cm^{-1} can be assigned to stretching from the bonds due to the presence of the octahedral $[\text{TiO}_6]$ cluster at short range. The mode shows anomaly at $y=0.05$ and starts splitting into two bands that shift apart with further increase in the BZT content to $y = 0.25$. The third Raman-active mode at around 542 cm^{-1} with low intensity is related to symmetric stretching vibrations of the octahedral $[\text{TiO}_6]$ cluster. This mode is common in materials with perovskite-type structure. However the Raman spectrum of the band over range of $450\text{--}650\text{ cm}^{-1}$ are split and the splitting become more into distinct bands with further increase of $y(\text{BZT})$ content. This can be attributed to the coexistence of rhombohedral and tetragonal phases. The result is in good agreement with that of the previously reported 0.80BNT-0.20BKT samples [16,17]. With an increase of $x(\text{BKT})$ content, the results are similar to that of increase of $y(\text{BZT})$ content, as shown in Fig. 3(b).

3.2. Microstructure

The SEM micrographs of $1-x-y\text{BNT}-x\text{BKT}-y\text{BZT}$ ceramics with y and x content are shown in Fig. 4(a–c) and Fig. 4(d–f), respectively. At $y(\text{BZT})=0$, the presented microstructure with rectangular-like grains. When $y(\text{BZT})$ is increased, the grain promotes a change to spherical-like grains and then re-enter the rectangular-like grains with increasing $x(\text{BKT})$ contents. The average grain size increased from $0.43\text{ }\mu\text{m}$ to $1.02\text{ }\mu\text{m}$ when the $y(\text{BZT})$ content was increased from 0 to 0.25. On the other hand, the grain size decreases from 0.64 to $0.54\text{ }\mu\text{m}$ with increase of $x(\text{BKT})$ content as listed in Table 1.

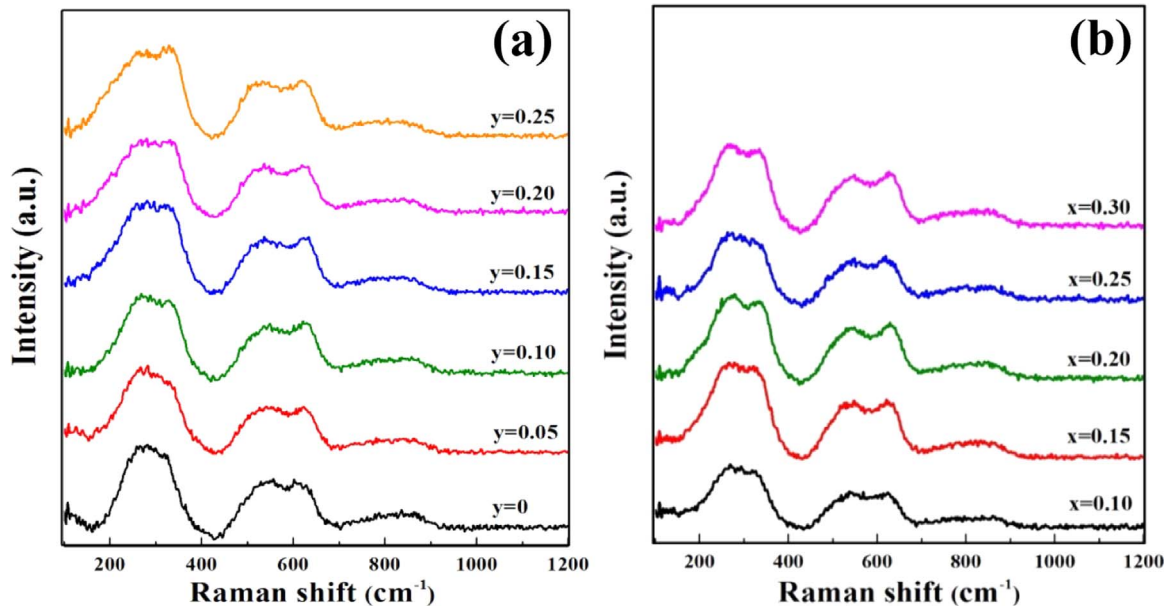


Fig. 3. Raman spectra of (a) 0.80-yBNT-0.20BKT-yBZT and (b) 0.90-xBNT-xBKT-0.10BZT ceramics at room temperature.

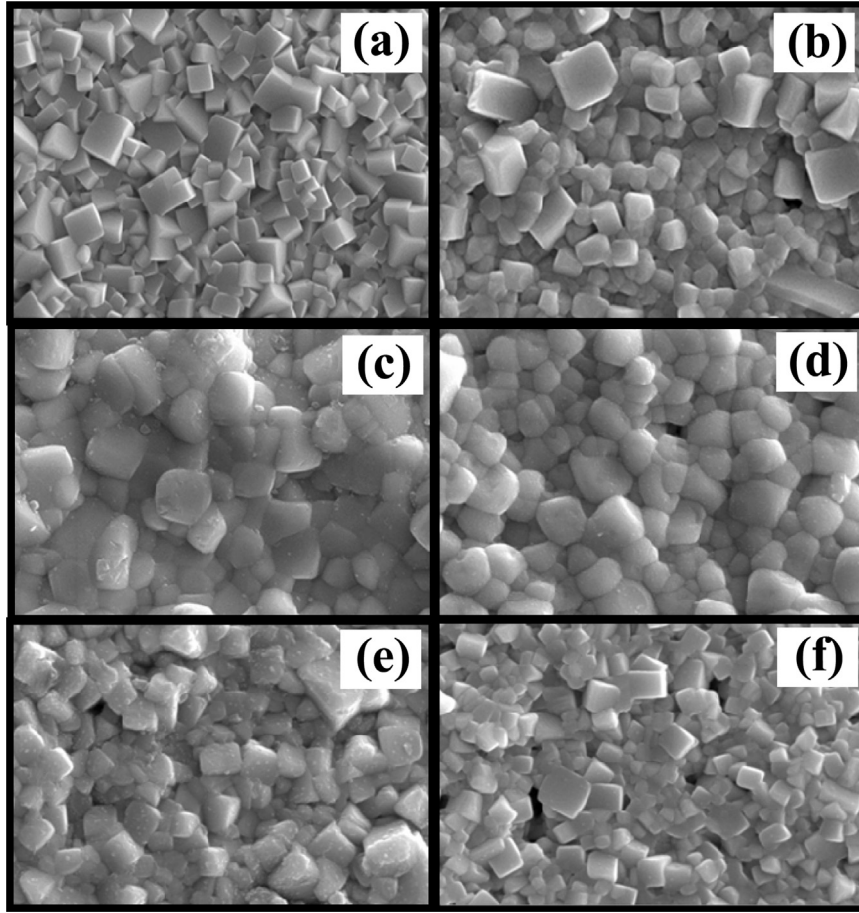


Fig. 4. SEM images of 1- x - y BNT- x BKT- y BZT sintered ceramics with (a) $y = 0$, (b) $y = 0.10$, (c) $y = 0.20$, (d) $x = 0.10$, (e) $x = 0.20$ and (f) $x = 0.30$.

3.3. Electrical properties

Fig. 5 and Fig. 6 show the temperature dependence of the dielectric constant (ϵ) and dielectric loss ($\tan\delta$) of 0.80- y BNT-0.20BKT- y BZT and 0.90- x BNT- x BKT-0.10BZT ceramics which were measured at different frequencies between 1 kHz and 1 MHz. The dielectric curves of all samples look similar. There are two dielectric anomaly peaks. The first anomaly was observed at a lower temperature which will be denoted by the “FA” and second broad dielectric constant peak at higher temperature which will be denoted by the “SA”. Both of the anomaly peaks were changed with addition y (BZT) and x (BKT) contents. When y (BZT) content increased from 0 to 0.25, T_{FA} gradually increased from 106 to 215 °C, and then decreased from 215 to 91 °C as listed in Table 1. The T_{SA} tended to reduce from 324 to 302 °C when

the y content increased from 0 to 0.25 (Table 1). In the case of increase x contents, T_{FA} gradually increased when the x content was increased up to 0.20, and then decreased as listed in Table 1. The T_{SA} tended to increase from 325 to 340 °C when there was increase of x content from 0.10 to 0.30 (Table 1). This indicated that the increase of y (BZT) and x (BKT) contents caused the increment and following reduction of T_{FA} . This behavior may be attributed to the coexistence of a mixed rhombohedral–tetragonal phase, which may have been twisting or bending the oxygen octahedron. These finding are similar to the observation in the BNKLLT-BCTZ [18] and BNT-BT [19] systems. Moreover, both T_{FA} and T_{SA} exhibit an obvious dependence on the frequency. With increasing frequency, T_{FA} moves to higher temperature regions and T_{SA} moves to lower temperature regions. However, when the temperature is higher or lower than T_{FA} and T_{SA} , the ϵ does

Table 1

P_r , P_{max} , E_c , T_{FA} , T_{SA} , ϵ_{SA} , γ , S_{Max} , S_{Neg} , S_{Max}/E_{Max} and d_{33} of 0.80- y BNT-0.20BKT- y BZT and 0.90- x BNT- x BKT-0.10BZT ceramic.

Compositions	P_r ($\mu\text{C}/\text{cm}^2$)	P_{max} ($\mu\text{C}/\text{cm}^2$)	E_c (kV/cm)	T_{FA} (°C)	T_{SA} (°C)	ϵ_{SA}	γ	Strain (%)		S_{Max}/E_{Max} (pm/V)	d_{33} (pC/N)
								S_{Max}	S_{Neg}		
$y=0$	21.6	30.5	25.2	106	324	4106	1.82	0.11	−0.02	220	184
$y=0.05$	3.0	31.4	5.1	80	340	3891	1.89	0.12	−0.007	240	185
$y=0.10$	18.8	24.5	28.0	215	320	5137	2.10	0.09	−0.02	180	202
$y=0.15$	18.9	23.5	27.8	97	324	4076	1.76	0.06	−0.01	120	200
$y=0.20$	17.7	20.5	31.5	94	318	4435	1.84	0.04	−0.01	80	192
$y=0.25$	16.0	22.6	23.0	91	302	3357	1.98	0.03	−0.01	60	187
$x=0.10$	7.6	11.3	30.6	146	325	3162	0.05	0.01	−0.009	20	62
$x=0.15$	21.2	30.6	26.1	200	343	5455	1.48	0.07	−0.01	140	194
$x=0.20$	23.1	32.2	19.1	215	320	5156	1.81	0.14	−0.04	280	240
$x=0.25$	11.6	17.3	27.4	214	336	3732	1.65	0.10	−0.01	200	85
$x=0.30$	8.9	15.0	8.0	205	340	3682	1.77	0.08	−0.003	160	76

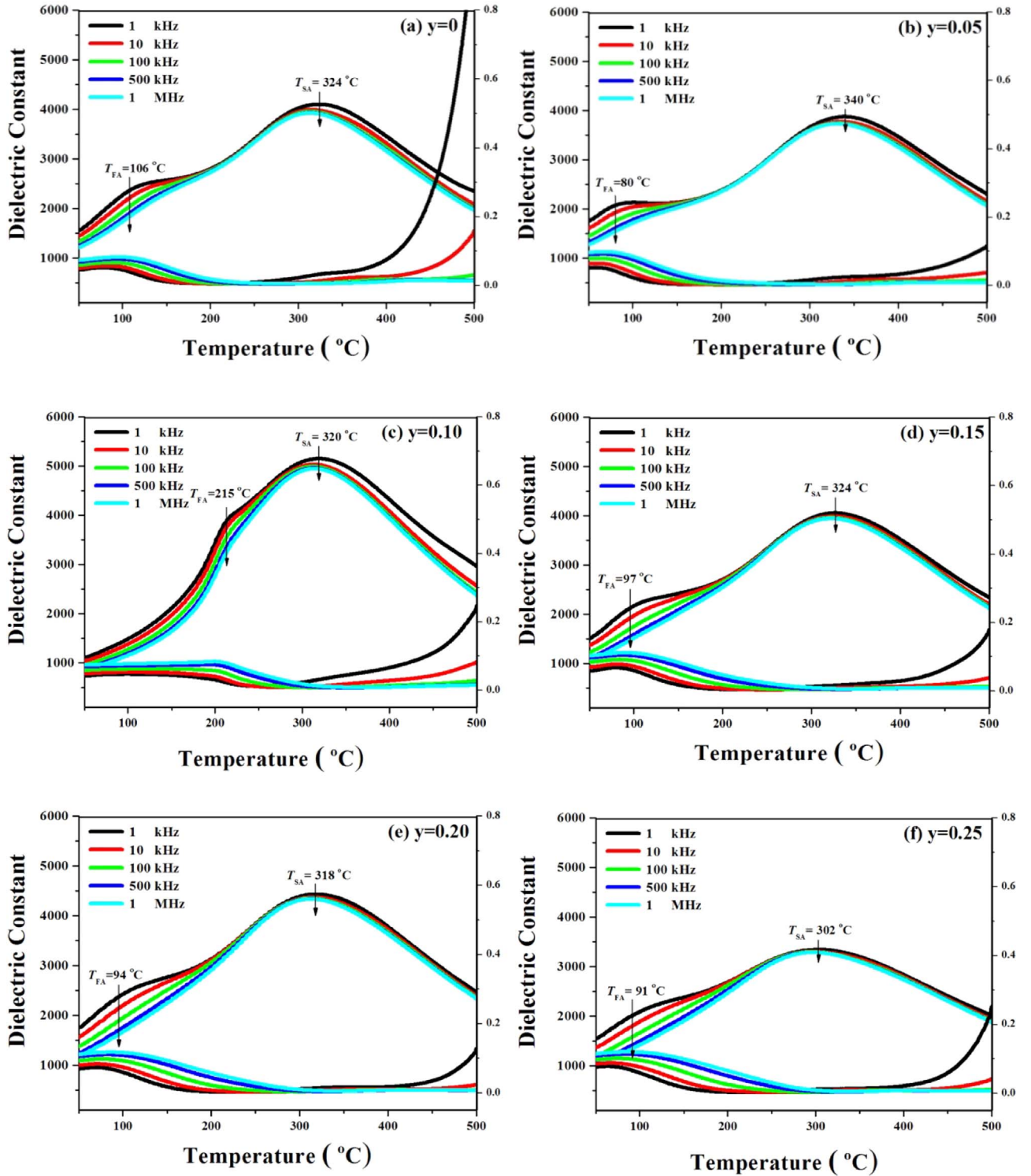


Fig. 5. Temperature dependence of dielectric properties in the BNT-BKT-BZT system: (a) 0.80BNT-0.20BKT-0BZT, (b) 0.75BNT-0.20BKT-0.05BZT, (c) 0.70BNT-0.20BKT-0.10BZT, (d) 0.65BNT-0.20BKT-0.15BZT, (e) 0.60BNT-0.20BKT-0.20BZT and (f) 0.55BNT-0.20BKT-0.25BZT.

not show any evidence shift with increasing frequency. The broad ϵ peaks (at T_{FA} and T_{SA}) and the character of the temperature dependence of ϵ (at T_{FA} and T_{SA}) show typical relaxor characteristics. The diffuseness exponent (γ) of ceramics increased from 1.82 to 1.92 and from 0.05 to 1.77 when increased of y (BZT) and x (BKT) contents, respectively, indicating that the BNT-BKT-BZT solid solutions are diffuse phase transition behavior. These results may imply an elevation of the relaxor feature. A relaxor phase transition similar to what is seen in these compositions has been observed in many ABO₃-type perovs-

kites and bismuth layer-structure compounds, such as $(1-x)\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3-x\text{BaTiO}_3$ [20], $\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3-\text{Bi}_{1/2}\text{K}_{1/2}\text{TiO}_3-\text{SrTiO}_3$ [21], $\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3-\text{Bi}_{1/2}\text{K}_{1/2}\text{TiO}_3$ [22], of which either the A-sites or B-sites are occupied by at least two cations. For the BNT-BKT-BZT ceramics, Na^+ , Bi^+ , Ba^+ and K^+ are randomly distributed in the 12-fold coordination sites, so the observed relaxor behavior is reasonably attributed to the disordering of the A-site cations and the compositional fluctuation. The maximum dielectric constant (ϵ) at T_{SA} increased from 4106 to 5137 when the y (BZT) content was increased up

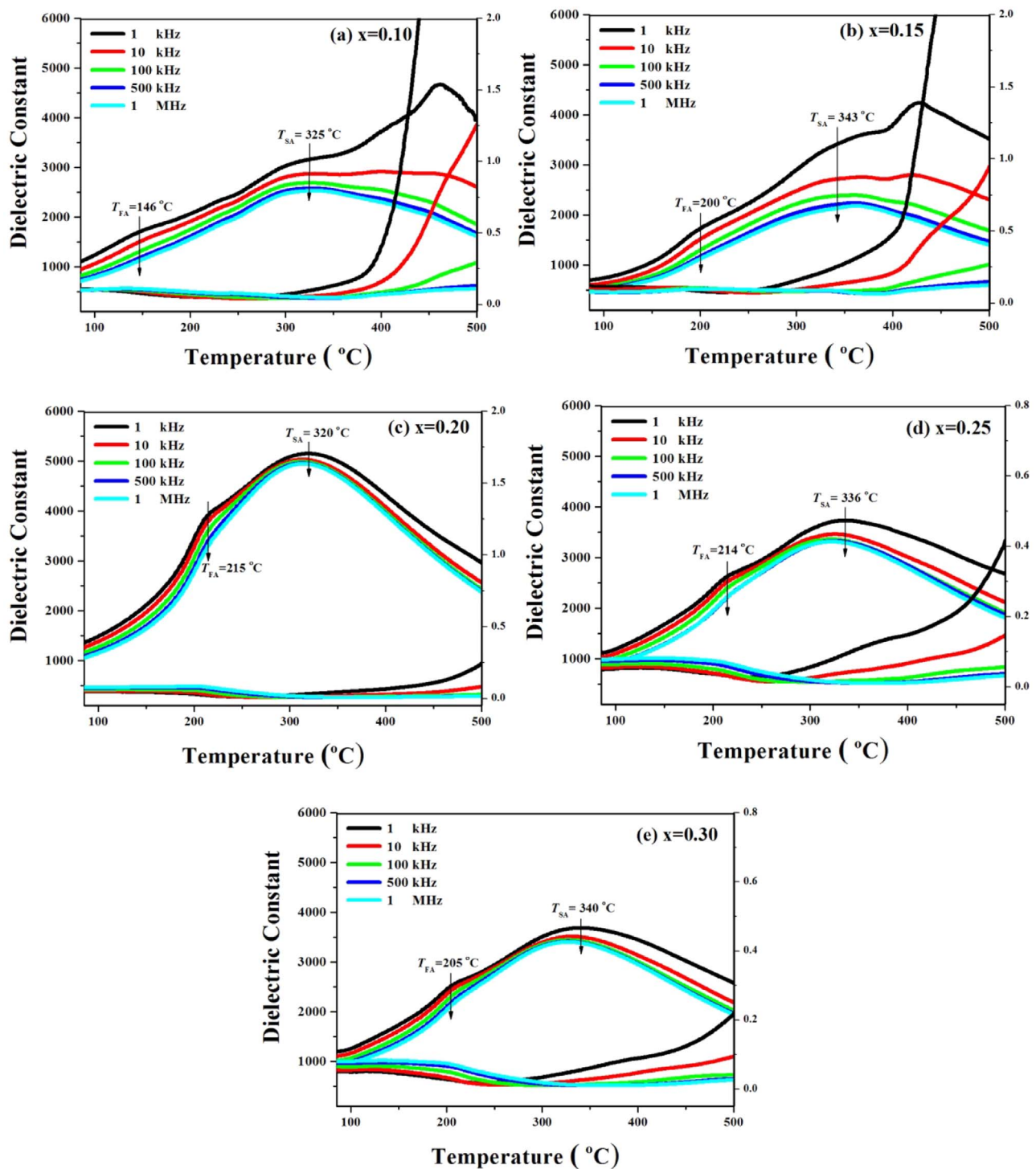


Fig. 6. Temperature dependence of dielectric properties in the BNT-BKT-BZT system: (a) 0.80BNT-0.10BKT-0.10BZT, (b) 0.75BNT-0.15BKT-0.10BZT, (c) 0.70BNT-0.20BKT-0.10BZT, (d) 0.65BNT-0.25BKT-0.10BZT and (e) 0.60BNT-0.30BKT-0.10BZT.

to 0.10, and then decreased with a further increase in y (BZT) content (Table 1). The same trend was observed in the samples of increase x (BKT) contents, which show the maximum value of dielectric constant is 5455 at $x = 0.15$ (Table 1). This behavior can be assigned to substitution of Bi, Na and Ti atoms (with atomic radius: 156 pm, 186 pm and 147 pm respectively) by Ba, Zr and K atoms (with atomic radius: 222 pm, 160 pm and 220 pm respectively) [13,23,24]. The addition of y (BZT) and x (BKT) in the BNT matrix makes the lattice structure incompact which is favorable for domain wall motion, hence the relative permittivity increases. When the y (BZT) and x (BKT)

contents reaches its limit, further addition saturates the BNT lattice matrix and causes the clamping of wall domain [25]. This clamping will restrain the macro-micro domain switching in some degree. This is the reason that the relative permittivity declined at y (BZT) = 0.15 and x (BKT) = 0.20.

The P - E hysteresis loop and the S - E hysteresis loops of 0.80- y BNT-0.20BKT- y BZT and 0.90- x BNT- x BKT-0.10BZT ceramics measured up to an electric field of 50 kV/cm are shown in Fig. 7 and Fig. 8, respectively. Depending on the y (BZT) and x (BKT), the (1- x - y)BNT- x BKT- y BZT solid-solutions are found either in a (ergodic) relaxor state

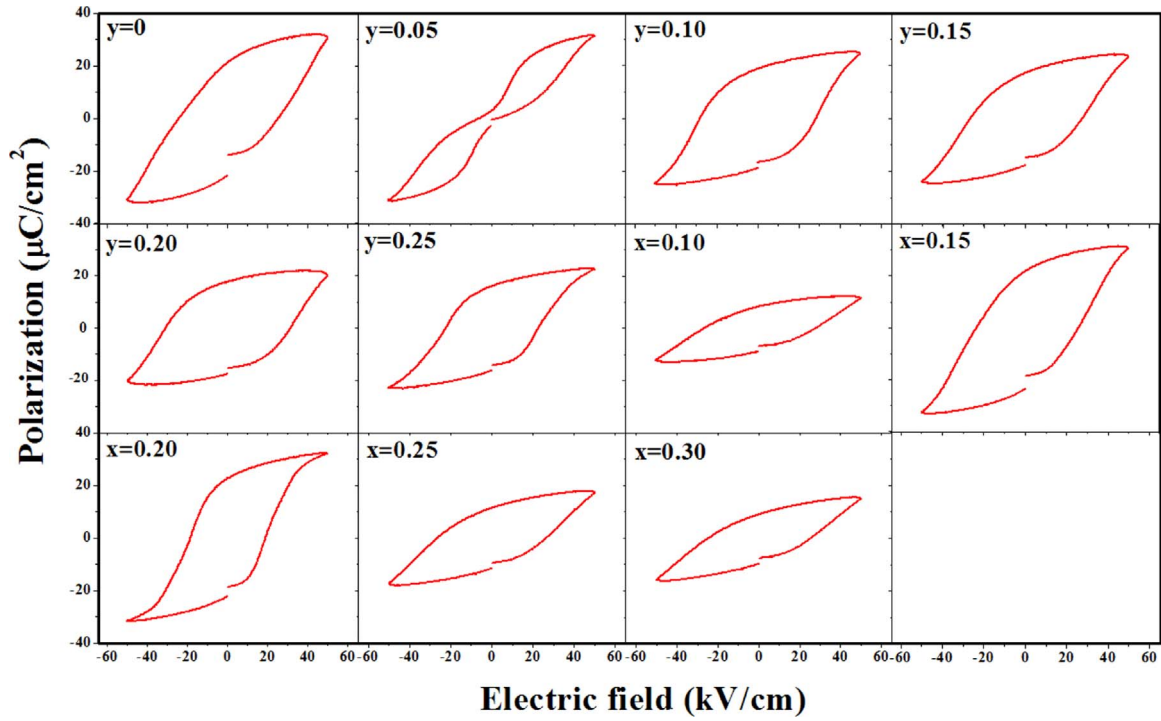


Fig. 7. P - E hysteresis loop of (a) 0.80- y BNT-0.20BKT- y BZT and (b) 0.90- x BNT- x BKT-0.10BZT ceramics measured at 0.1 Hz.

or in a non-ergodic/ferroelectric-like state. The ferroelectric state is characterized by a long-range ordering of electric dipoles. The relaxor state the electric polarization is highly localized and displays short-range coherence only, which mean existence of polar nano-regions (PNRs). Non-ergodic type of relaxor is the one which transforms irreversibly into the ferroelectric state by electric poling and an ergodic does so reversibly [26,27]. At $y=0$, the polarization hysteresis loops displayed a typical ferroelectric-like square loop, typical of non-ergodic relaxor, with maximum values of $P_r \sim 21.6 \mu\text{C}/\text{cm}^2$, $P_{\text{max}} \sim 30.5 \mu\text{C}/\text{cm}^2$, and $E_c \sim 25.2 \text{ kV}/\text{cm}$, which exhibited a typical butterfly-shaped loop with S_{max} of 0.11% and a calculated d_{33}^* of 220 pm/V in bipolar strain electric field (S - E). This is indicative of ferroelectric domain switching at E_c where the largest S_{neg} of -0.02% was observed. When there was an increase of $y = 0.05$, the P_r and E_c both decrease rapidly and P - E hysteresis loops turn to be pinched which is indicative of the development of an ergodic phase at zero fields at room temperature [28]. This also corresponded to a large electric field induced strain of 0.12% with a d_{33}^* value of 240 pm/V along with a drastic reduction in

cm^2 , and $E_c \sim 25.2 \text{ kV}/\text{cm}$, which exhibited a typical butterfly-shaped loop with S_{max} of 0.11% and a calculated d_{33}^* of 220 pm/V in bipolar strain electric field (S - E). This is indicative of ferroelectric domain switching at E_c where the largest S_{neg} of -0.02% was observed. When there was an increase of $y = 0.05$, the P_r and E_c both decrease rapidly and P - E hysteresis loops turn to be pinched which is indicative of the development of an ergodic phase at zero fields at room temperature [28]. This also corresponded to a large electric field induced strain of 0.12% with a d_{33}^* value of 240 pm/V along with a drastic reduction in

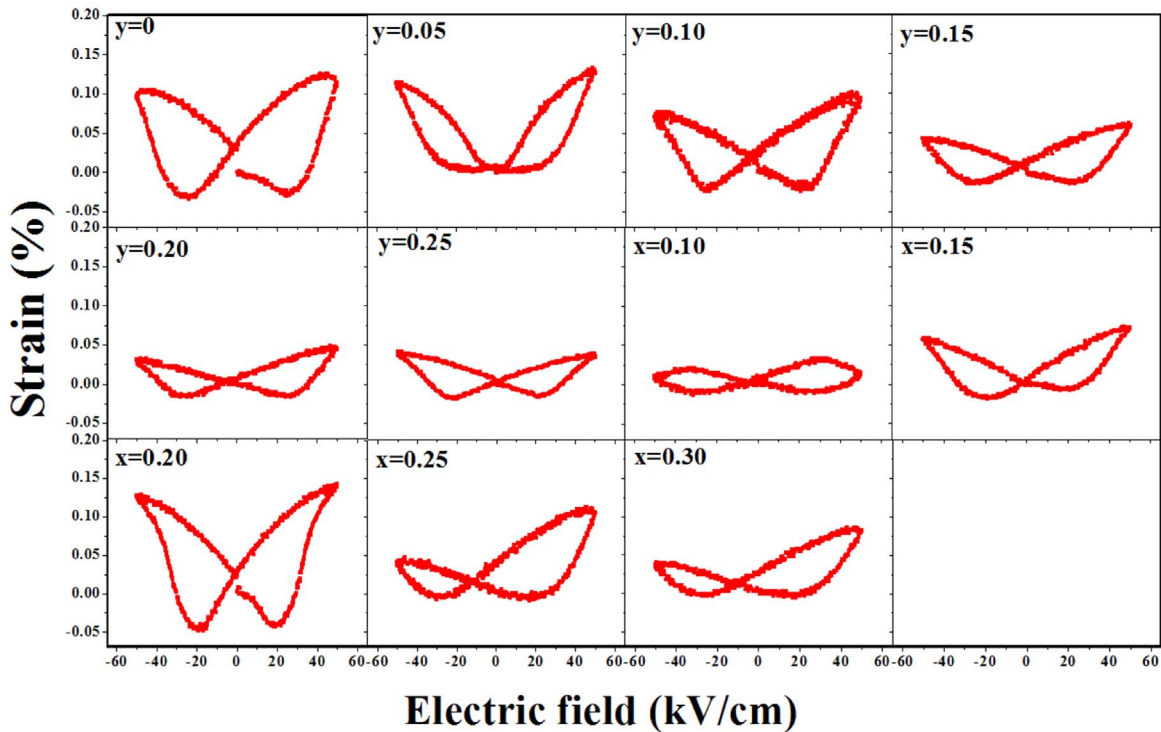


Fig. 8. Strain loop of (a) 0.80- y BNT-0.20BKT- y BZT and (b) 0.90- x BNT- x BKT-0.10BZT measured at 0.1 Hz.

S_{neg} from -0.02% to a minimum value of -0.007% (Table 1). At higher $y(\text{BZT})$ content, where the polarization data transitions from a pinched nature to ferroelectric-like behavior and the P_r and E_c increased considerably as the amount of $y(\text{BZT})$ increased up to 0.25. The P - E hysteresis data turn to typical ferroelectric-like behavior with square loops (Fig. 7), which is indicative of non-ergodic behavior. The bipolar strain electric field (S - E) loops also showed a normal butterfly shape with increased negative strain (Fig. 8). In the case of increase $x(\text{BKT})$ contents, at $x = 0.10$, the P - E loop exhibited a well saturated typical ferroelectric-like behavior with remnant polarization $P_r \sim 7.6 \mu\text{C}/\text{cm}^2$, $P_{\text{max}} \sim 11.3 \mu\text{C}/\text{cm}^2$ and $E_c \sim 30.6 \text{ kV}/\text{cm}$, which exhibited a typical butterfly-shaped loop with S_{max} of 0.01% and a calculated d_{33}^* of 20 pm/V in bipolar strain electric field (S - E). When increased of $x(\text{BKT})$ contents from 0.10 to 0.20, the P - E loop and S - E loops can be improved which showed the largest P_r of $\sim 7.6 \mu\text{C}/\text{cm}^2$, largest P_{max} of $\sim 11.3 \mu\text{C}/\text{cm}^2$, largest S_{max} of 0.14% and largest d_{33}^* of 280 pm/V (see in Table 1). At $x(\text{BKT}) = 0.25$ and $x(\text{BKT}) = 0.30$, the polarization hysteresis loop has becomes very weak and appearance of strain loops has become asymmetric. The asymmetric strain loops, is most likely due to increased tetragonality as certified by XRD analysis [29] and due to presence of internal bias, which is commonly observed in lead-free ceramics, e.g., in $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ -Based [30] $0.76\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ - 0.24SrTiO_3 [31], $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.935+x}\text{Ba}_{0.065}\text{Ti}_{1-x}(\text{Pr}_{0.5}\text{Nb}_{0.5})_x\text{O}_3$ [32], $\text{Bi}_{0.5+x}(\text{Na}_{1-y}\text{K}_y)_{0.5-3x}\text{TiO}_3$ [33]. The internal bias field is believed to be the result of defect dipoles of acceptor ions and oxygen vacancies, which lead to piezoelectric “hardening” effect, by stabilizing and pinning of the domain wall motion [34].

4. Conclusions

$(1-x-y)\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ - $x\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ - $y\text{BaZr}_{0.05}\text{Ti}_{0.95}\text{O}_3$ ($0 \leq y \leq 0.25$ and $0.10 \leq x \leq 0.30$) were prepared by using a solid-state reaction method. The variations of x and y contents directly affect the crystal structure, microstructure, and electrical properties of 0.80 - $y\text{BNT}$ - 0.20BKT - $y\text{BZT}$ and 0.90 - $x\text{BNT}$ - $x\text{BKT}$ - 0.10BZT ceramics. The structure identified the phase transition from rhombohedral and tetragonal symmetry. When increased of $x(\text{BZT})$ content promote grain growth and the addition of $y(\text{BZT})$ suppress grain growth. The dielectric constant show pronounced dependence on frequency. With increased frequency, dielectric constant for all ceramics decrease. The $(1-x-y)\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ - $x\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ - $y\text{BaZr}_{0.05}\text{Ti}_{0.95}\text{O}_3$ solid solutions exhibited diffuse phase transition behavior. The largest S_{max} of 0.14% corresponding to a high-field effective d_{33}^* of 280 pm/V was found in the composition 0.70 - $y\text{BNT}$ - 0.20BKT - 0.10BZT .

Conflict of interest

We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

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