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Electromechanical Properties and Morphotropic Phase Boundary of $Na_{0.5}Bi_{0.5}TiO_3$-$K_{0.5}Bi_{0.5}TiO_3$-$BaTiO_3$ Lead-free Piezoelectric Ceramics

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Abstract. The crystal structure and electromechanical properties of two ternary ceramic $Na_{0.5}Bi_{0.5}TiO_3$-$K_{0.5}Bi_{0.5}TiO_3$-$BaTiO_3$ (NBT-KBT-BT) systems were investigated. A gradual change in crystalline structure and microstructure with the increase of KBT and BT concentrations were observed. It was ascertained that the rhombohedral-tetragonal morphtropic phase boundary (MPB) lies in the range of $0.024 \leq x \leq 0.030$ for $(1–5x)$ NBT-$4x$KBT-xBT system and $0.025 \leq y \leq 0.035$ for $(1 - 3y)$ NBT—$2y$ KBT—y BT system at room temperature. The piezoelectric constant d_{33} and electromechanical coupling factor k_p of the ceramics attain a maximum value of 150 pC/N and 0.298, respectively. The MPB phase diagram of NBT-KBT-BT ternary system was determined by phase analysis of XRD patterns from calcined specimens. The ferroelectric properties of the $(1 - 5x)$ NBT—$4x$ KBT—x BT system have been characterized. The ternary system ceramics have relatively high Curie temperature T_c.

Keywords: $Na_{0.5}Bi_{0.5}TiO_3$, piezoelectric properties, morphtropic phase boundary, perovskite

1. Introduction

At present, lead zirconate titanate (PZT) based ceramics are the most widely applied piezoelectric materials because of their superior electrical properties. However, the evaporation of toxic lead during the fabrication of the ceramics causes an environmental problem. Therefore, there is an increasing interest of investigating lead-free piezoelectric materials to replace PZT based piezoelectric ceramics. Sodium bismuth titanate, $(Na_{0.5}Bi_{0.5})TiO_3$ (NBT), which was found by Smolenskii et al. [1], is a kind of perovskite-type ferroelectric with a relatively large remanent polarization ($P_r = 38\ \mu C/cm^2$) at room temperature and a relatively high Curie temperature ($T_c = 320°C$). For its strong ferroelectricity at room temperature, NBT has been considered to be a promising candidate material for lead-free piezoelectric ceramics. However, it is difficult to pole NBT due to the high coercive field ($E_c = 7.3$ kV/mm), making it difficult to obtain the desirable piezoelectric properties. Therefore, NBT-based solid solutions that can be poled easily have recently been studied [2–8]. Particularly, optimum electromechanical properties are expected for the NBT-based solid solution with a morphotropic phase boundary (MPB).

Among the NBT-based binary lead-free piezoelectric systems, two binary systems of $(Na_{0.5}Bi_{0.5})TiO_3$-$(K_{0.5}Bi_{0.5})TiO_3$ (NBT-KBT) and $(Na_{0.5}Bi_{0.5})TiO_3$-$BaTiO_3$ (NBT-BT) have obtained the most extensive investigation because they have good piezoelectric performance near the MPB. The MPB compositions exist in the range of 0.06–0.07 mol BT with piezoelectric constant $d_{33} = 125$ pC/N and 0.16–0.20 mol KBT with $d_{33} = 100$ pC/N reported by Takenaka et al. [2] and Sasaki et al. [4], respectively. Recently, Nagata et al. [9] reported that the pseudo- three-component ceramic system focusing on MPB of the two binary compositions showed good piezoelectric constant and high Curie temperature. Wang et al. [10] also

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reported that (0.95 − x) NBT—xKBT—0.05BT solid solutions have good electromechanical performance and high depolarization temperature. However, the MPB composition range of the ternary system is still unclear from their investigations. In this paper, the compositional dependence of crystal structure and the piezoelectric properties for two ternary NBT-KBT-BT systems were investigated, and the MPB compositions range for the ternary system was also obtained.

2. Experimental

A conventional ceramic fabrication technique was used to prepare (1 − 5x) NBT—4x KBT—xBT (x = 0, 0.010, 0.020, 0.024, 0.028, 0.030, 0.032) and (1–3y) NBT—2y KBT—y BT (y = 0, 0.010, 0.020, 0.025, 0.030, 0.035, 0.040) ceramics. Reagent grade oxide and carbonate powders of Bi_2O_3, Na_2CO_3, K_2CO_3, $BaCO_3$ and TiO_2 were used as starting raw materials. The oxides and carbonates were mixed in ethanol with agate balls by ball milling for 4 h. After being mixed, the dried powder was calcined at 900–950°C for 2 h. The calcined powder was reground by ball milling for 6 h. The dried powder was mixed with PVA and pressed at 150 MPa into pellets 20 mm in diameter and about 1.5 mm in thickness. The green compacts were sintered at 1150–1200°C for 2 h in air atmosphere. The silver paste was used as electrode on the surfaces of polished specimens and then fired at 800°C for 10 min. The specimens for measurement of piezoelectric properties were poled in silicon oil at 80°C under 3–4 kV/mm for 15 min.

X-ray powder diffraction (XRD) patterns for the unpoled ceramics were taken on a D/MAX-III X-ray diffractometer with Cu K_α radiation (λ = 1.5418 Å) and graphite monochrometer. The microstructure of the specimens was observed by a JEOL JSM-5610LV scanning electron microscope (SEM) using surface sections etched heating at 1100°C for 0.5 h. The piezoelectric constant d_{33} of the samples was measured by means of quasistatic d_{33} meter (ZJ-3A) at 110 Hz based on Berlincourt method. The piezoelectric properties were measured by means of resonance-antiresonance method on the basis of IEEE standards using a precision impedance analyzer (HP4294A). The electromechanical coupling factor k_p was calculated from the resonance and antiresonance frequencies based on the Onoe's formulas[11]. Dielectric properties of samples were determined using the HP4294A impedance analyzer at 1 kHz. Temperature dependence of dielectric constant was measured for determination of Curie temperature, T_c, at 1 kHz using an automated dielectric measurement system with a LCR meter (TH2816). The remanent polarization P_r and coercive field E_c were determined from P-E hysteresis loops obtained by Radiant Precision Workstation ferroelectric testing system.

3. Results and Discussion

Figures 1 and 2 show the X-ray diffraction (XRD) patterns of (1 − 5x) NBT—4xKBT—x BT and (1 − 3y) NBT—2yKBT—y BT ceramics, respectively. A pure

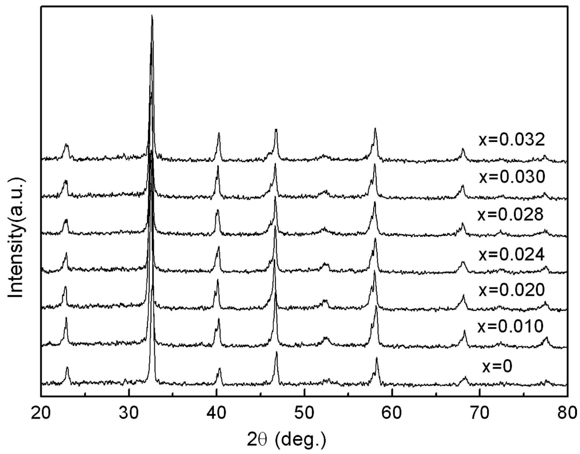

Fig. 1. XRD patterns of (1 − 5x) NBT—4xKBT—x BT system.

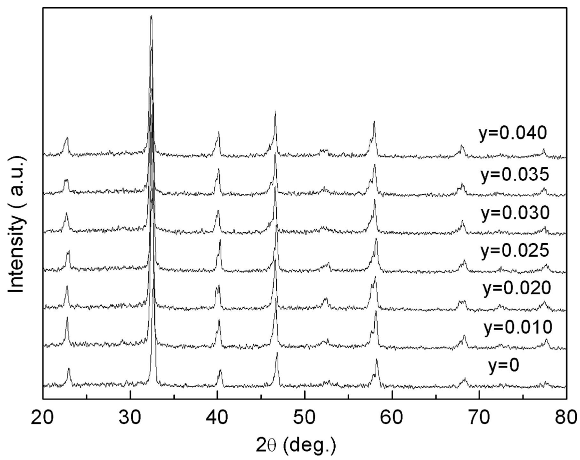

Fig. 2. XRD patterns of (1 − 3y) NBT—2yKBT—y BT system.

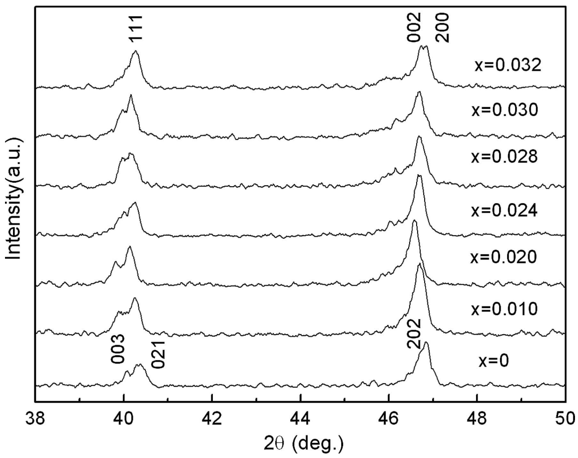

Fig. 3. XRD patterns of $(1 - 5x)$ NBT—$4x$ KBT—x BT system in 2θ range of 38–50°.

perovskite structure without any secondary impurity phases could be confirmed. Figures 3 and 4 show the XRD patterns of the two ternary systems in the 2θ range of 38–50°. The rhombohedral symmetry of NBT at room temperature is characterized by a (0 0 3)/(0 2 1) peak splitting between 39 and 41° and a single peak of (2 0 2) between 46 and 48°. In Fig. 3, the (0 0 3)/(0 2 1) peak splitting is obvious until $x = 0.030$. A distinct (0 0 2)/(2 0 0) peak splitting between 46 and 48° can be seen when $x \geq 0.024$, corresponding to a tetragonal symmetry. Therefore, it can be suggested that the MPB of $(1 - 5x)$ NBT—$4x$KBT—x BT system lies in the composition range of $0.024 \leq x \leq 0.030$ at room temperature, where rhombohedral and tetragonal phases coexist. The MPB range of $(1 - 3y)$ NBT—$2y$KBT—y BT ceramics is different with the range of $(1 - 5x)$ NBT-$4x$KBT-x BT ceramics, but can be ascertained in the range of $0.025 \leq y \leq 0.035$ in Fig. 4.

Figure 5 depicts the MPB phase diagram of the ternary NBT-KBT-BT system based on the XRD results and references [2–5]. The rhombohedral and tetragonal co-existence composition range is in a narrow content which means that a few varied compositions would greatly affect the piezoelectric properties.

Figure 6 shows the SEM micrographs of $(1 - 3y)$ NBT—$2y$KBT—y BT ceramics. It was found that the size of grains become inhomogeneous and the average size of grains decreases with the increasing of KBT and BT concentrations y, which indicate the growth of grains would be depressed with increasing of KBT and BT concentrations corresponding to previously reports [12].

Figure 7 presents the piezoelectric and dielectric properties of $(1 - 5x)$ NBT—$4x$ KBT—x BT ceramics. The piezoelectric constant d_{33} and electromechanical coupling factor k_p display a similar variation, enhancing with the increasing of x through a maximum value in a composition near the MPB and then tending to decrease. The piezoelectric constant d_{33} attains a maximum value of 149 pC/N at $x = 0.030$ and the electromechanical coupling factor k_p reaches to the maximum value of 0.282 at $x = 0.028$. A similar tendency of dielectric constant $\varepsilon_{33}^T/\varepsilon_0$ and dielectric loss

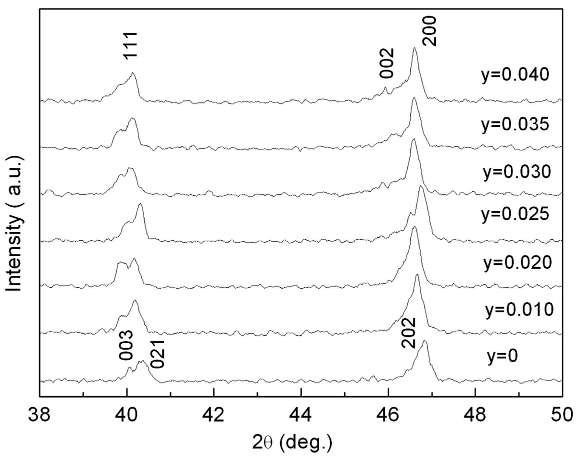

Fig. 4. XRD patterns of $(1–3y)$ NBT-$2y$KBT-yBT system in 2θ range of $38 - -50°$.

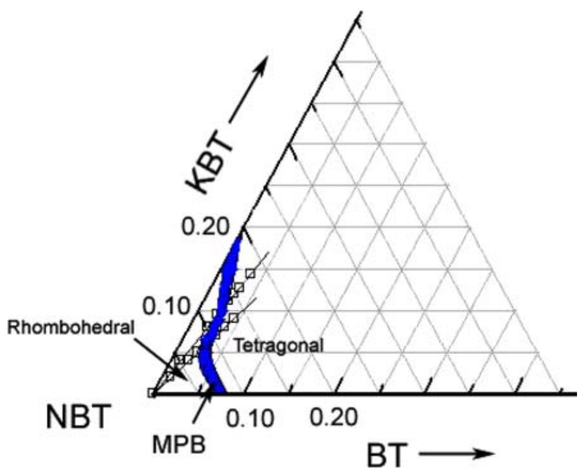

Fig. 5. MPB phase diagram of NBT-KBT-BT ternary system.

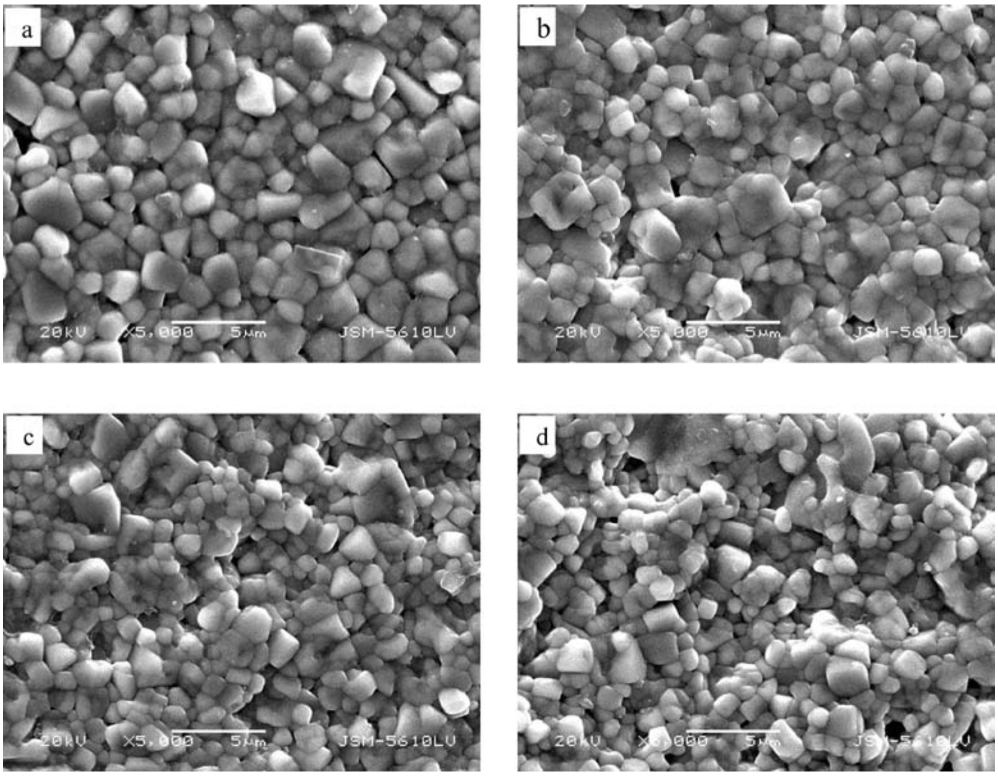

Fig. 6. SEM images of $(1-3y)$ NBT—$2y$ KBT—y BT system (a: 0.010; b: $y = 0.025$; c: $y = 0.035$; d: $y = 0.040$).

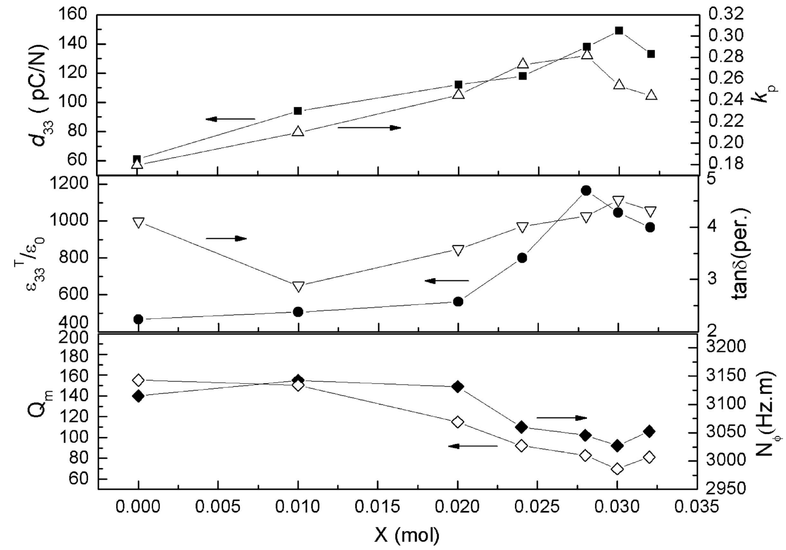

Fig. 7. Piezoelectric and dielectric properties of $(1-5x)$ NBT—$4x$KBT—x BT ceramics as a function of x.

tanδ of the specimens as a function of x reveals that incorporation of KBT and BT into NBT will increase both of them near the MPB compositions. From Fig. 7, it can be seen the mechanical quality factor Q_m of the specimens increases with increasing x amount initially then decreasing, reaches the minimum value at $x = 0.030$ and then shows a slight increase with more x. A tendency of frequency constant N_ϕ of the specimens similar to the Q_m can be seen, which only a different location of the maximum value at $x = 0$.

Figure 8 presents the piezoelectric and dielectric properties of $(1-3y)$ NBT—$2y$ KBT—y BT ceramics. The compositional dependence of dielectric and piezoelectric properties is similar to the $(1-5x)$ NBT—$4x$ KBT—x BT ceramics. The best piezoelectric constant d_{33} is 150 pC/N and electromechanical coupling factor k_p is 0.298 at $y = 0.035$.

From the above electromechanical properties of the two ternary NBT-KBT-BT systems, it can be concluded that the good dielectric and piezoelectric properties lies in near MPB composition range similar to PMN-PT and PZT systems [13, 14]. It is attributed to an increase in the number of possible spontaneous polarization direction for the compositions near the MPB due to the coexistence of rhombohedral and tetragonal phases. This is also explained by having equivalent energy for the coexistence of rhombohedral and tetragonal phases can be transformed each other in poling process, which enhance the piezoelectric and electromechanical activities. In addition, the best piezoelectric constant d_{33} and electromechanical coupling factor k_p are always near the side of tetragonal phase of the MPB. The reason can be interpreted the more domains of the tetragonal crystalline can be transformed applied strong poling electric field [14].

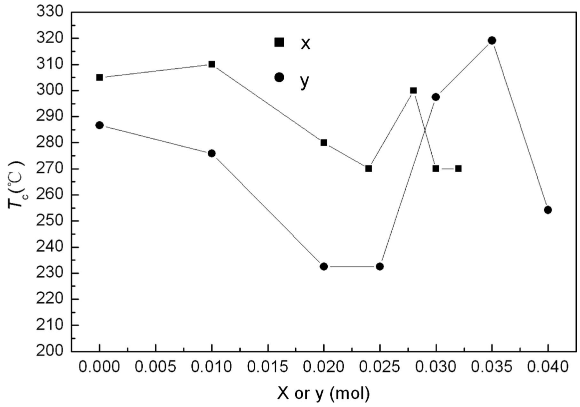

Fig. 9. Curie temperature T_c of (1–5x) NBT - 4xKBT - xBT and (1–3y) NBT - 2yKBT - yBT ceramics as a function of x and y at 1 kHz.

Figure 9 shows the Curie temperature T_c as a function of x and y in $(1-5x)$ NBT—$4x$KBT—x BT and $(1-3y)$ NBT—$2y$KBT—y BT ceramics. The Curie temperature demonstrates an irregular variation tendency with concentration x and y. This variation tendency of Curie temperature is different from the PMN-PZT ternary system [15]. The reason is complex because the

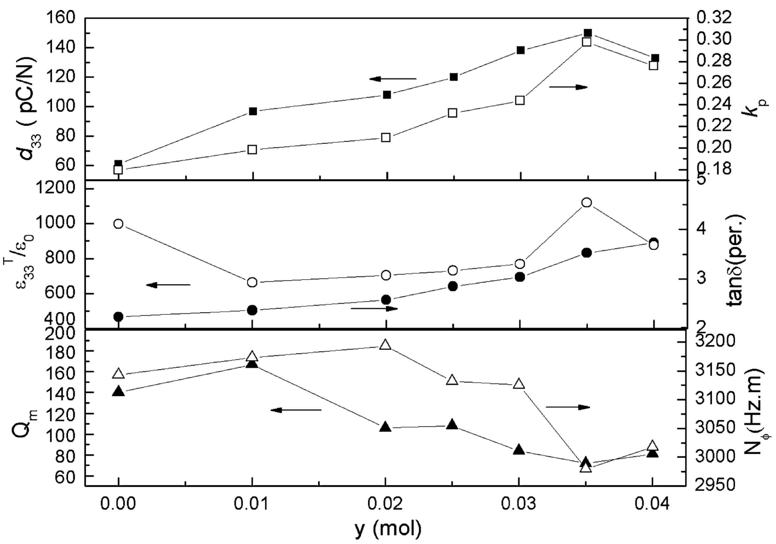

Fig. 8. Piezoelectric and dielectric properties of $(1-3y)$ NBT—$2y$KBT—y BT ceramics as a function of y.

Curie temperature of KBT and BT is 380°C and 120°C, respectively. The cooperation of KBT and BT results in the irregular variation tendency of Curie temperature with concentration x and y. Of cause, more experiments should be done to make clear the reason of the variation tendency. However, the Curie temperature T_c is almost above 270°C, and these compositions may be used in a relatively high temperature.

The measurement of P-E hysteresis loops was conducted to examine the ferroelectric properties of $(1 - 5x)$ NBT—$4x$ KBT—x BT ceramics. Figure 10 shows the saturated P-E hysteresis loops of $(1 - 5x)$ NBT—$4x$ KBT—x BT ceramics with $x = 0$–0.032. It can be seen that both the remanent polarization P_r and coercive field E_c decrease with the increasing concentration of x. However, their decreased degrees with the substituting content x are not the same rate. The pronounced difference is near the MPB compositions range. For $x = 0.030$, the remanent polarization is 31.4 μC/cm^{2}which is slight less than 31.8 μC/cm^2 of pure NBT ceramic, however, the coercive field E_c is 4.13 kV/mm which is distinctly less than 6.17 kV/mm of pure NBT ceramics. For NBT-based solid solutions, decreasing coercive field was usually regarded as a main strategy to modify poling process and improve piezoelectric properties [3, 16, 17]. In present work, the variation tendency of the ferroelectric properties is the same as the trend of piezoelectric properties. It has been proposed that high remanent polarization P_r and low coercive field E_c are presumably responsible for their large piezoelectric properties [10]. On one hand, a high coercive field is disadvantageous to the sufficient reorientation of ferroelectric domains during electrical poling, generating a negative effect on piezoelectric properties. On the other hand, a high remanent polarization indicates a strong ferroelectricity, which enhances piezoelectric properties [18]. Therefore, the piezoelectric properties of the specimens are dependent on the dual contribution of remanent polarization and coercive field.

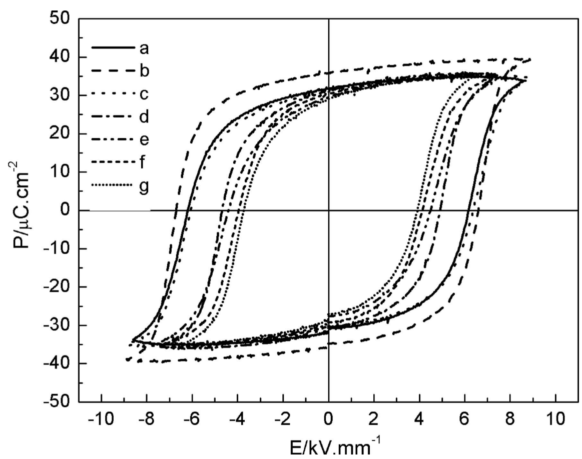

Fig. 10. Saturated P-E hysteresis loops of $(1 - 5x)$ NBT—$4x$KBT—x BT system a: $x = 0$; b: $x = 0.01$; c: $x = 0.02$; d: $x = 0.024$; e: $x = 0.028$; f: $x = 0.030$; g: $x = 0.032$.

4. Conclusions

The crystal structure and electromechanical properties of two ternary NBT-KBT-BT systems have been investigated. A gradual change in crystalline structure and microstructure with KBT and BT concentrations has been observed. The MPB of the ceramics exists in the range of $0.024 \le x \le 0.030$ for $(1 - 5x)$ NBT—$4x$KBT—x BT system and $0.025 \le y \le 0.035$ for $(1 - 3y)$ NBT-$2y$KBT- yBT system at room temperature. The MPB phase diagram of NBT-KBT-BT ternary system has been determined by phase analysis of XRD patterns from calcined samples. The compositions near the MPB exhibit relatively high piezoelectric properties which accompany a relatively high remanent polarization and lower coercive field. The ternary system ceramics have relatively high Curie temperature T_c.

Acknowledgments

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