Composition Range and Electrical Properties of the Morphotropic Phase Boundary in $Bi_{0.5}(Na_{0.80}K_{0.20})_{0.5}TiO_3$-$(Ba_{0.7}Sr_{0.3})TiO_3$ System

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The lead-free piezoelectric ceramic binary system of $(1-x)Bi_{0.5}(Na_{0.80}K_{0.20})_{0.5}TiO_3$-$x(Ba_{0.7}Sr_{0.3})TiO_3$ or $(1-x)$ BNKT-xBST (with x ranging from 0.05 to 0.15 mol fraction) near the morphotropic phase boundary (MPB) has been investigated. The ceramics were synthesized by a conventional mixed-oxide method and sintered at 1125°C for 2 h. All BNKT-BST samples had relative density higher than 98% of their theoretical values. X-ray diffraction patterns showed that all compositions had a pure perovskite structure and BST effectively diffused into the BNKT lattice during sintering to form a solid solution. Crystal structure changed from rhombohedral-rich phase to tetragonal-rich phase with increasing BST content. Because of such MPB-like behavior, the highest dielectric (T_c = 325°C, ε_r = 1827, tan δ = 0.0823) and piezoelectric performances (d_{33} = 225 pC/N) were obtained in the BNKT-0.11BST sample.

Keywords: lead-free, piezoelectric, morphotropic phase boundary, dielectric

1. INTRODUCTION

Although $Pb(Zr, Ti)O_3$ is well recognized for playing a dominant role among other piezoelectric materials, lead is considered to be toxic and causes a crucial environmental problem.[1-3] In recent years, lead-free piezoelectric ceramics have attracted considerable attention because of their outstanding advantages for environmental friendly.[4] $Bi_{0.5}(Na_{1-x}K_x)_{0.5}TiO_3$ (or BNKT) is also known as a candidate lead-free piezoelectric ceramic material. Sasaki *et al.*[5] have reported that a solid solution of BNKT showed improved piezoelectricity in the morphotopic phase boundary (MPB) region at $0.16 \leq x \leq 0.20$. This system's MPB structure possessed relatively high d_{33} = 151 pC/N and d_{31} = 46.9 pC/N. Moreover, BNKT-based ceramics modified with $SrTiO_3$[6] and $Ba(Zr_{0.04}Ti_{0.96})O_3$[7] showed improved piezoelectric properties compared with pure BNKT. Our preliminary research has also indicated that $(Ba_{0.7}Sr_{0.3})TiO_3$ was an effective additive for improving the piezoelectric properties of $Bi_{0.5}(Na_{0.80}K_{0.20})_{0.5}TiO_3$.[8] The results showed that BNKT-0.10BST was found to be an optimum condition that maximized d_{33} value (214 pC/N). In this work, $(Ba_{0.7}Sr_{0.3})TiO_3$ was employed as an additive for $Bi_{0.5}(Na_{0.80}K_{0.20})_{0.5}TiO_3$ ceramic to form $(1-x)Bi_{0.5}(Na_{0.80}K_{0.20})_{0.5}TiO_3$-$x(Ba_{0.7}Sr_{0.3})TiO_3$ or $(1-x)$BNKT-xBST (x = 0.05 - 0.15 mol fraction). This work focused on the MPB composition between BNKT and BST where the best piezoelectricity could be achieved.

2. EXPERIMENTAL PROCEDURE

$Bi_{0.5}(Na_{0.80}K_{0.20})_{0.5}TiO_3$ and $(Ba_{0.7}Sr_{0.3})TiO_3$ powders were prepared by a conventional mixed oxide method. Dried powders were calcined at 900°C for 2 h for BNKT and 1100°C for 2 h for BST. The mixed powders $(1-x)$BNKT-xBST (x = 0.05, 0.07, 0.09, 0.10, 0.11, 0.13 and 0.15 mol fraction) were produced. The pellets were sintered at 1125°C for 2 h. An x-ray diffractometer was used to identify the phase of the ceramics. Bulk density was measured with Archimedes' method. A scanning electron microscope was used to determine microstructure. Dielectric constant as a function of temperature was measured by 4284A LCR-meter. A standard Sawyer-Tower circuit was used to measure hysteresis loop. The samples were poled in silicone oil at 60°C under 5 kV/mm for 15 min. Finally, d_{33} value was recorded using a d_{33}-meter.

3. RESULTS AND DISCUSSION

The addition of BST to the BNKT ceramic caused a slight decrease in sample density. However, the values were rather similar (5.76 - 5.80 g/cm³), corresponding to at least 98% of their theoretical values (see Table 1).

X-ray diffraction patterns of BNKT-BST ceramics at 2θ = 10 - 80° are shown in Fig. 1(a). All the ceramics possessed a perovskite structure and no second phase could be detected.

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Table 1. Physical and electrical properties of (1-*x*)BNKT-*x*BST ceramics.

x	Density (g/cm^3)	*c/a*	Grain size (μm)	T_c (°C)	ε_r [a]	tan δ [a]	P_r (μC/cm^2)	E_c (kV/cm)	R_{sq}	d_{33} (pC/N)
0.05	5.80 ± 0.02	1.0115	0.40 ± 0.04	320	1556	0.0559	13.23	10.18	0.48	170
0.07	5.80 ± 0.01	1.0120	0.40 ± 0.03	320	1734	0.0700	25.29	16.55	0.86	188
0.09	5.79 ± 0.01	1.0122	0.40 ± 0.03	321	1738	0.0698	25.82	19.33	0.95	209
0.10	5.78 ± 0.01	1.0124	0.39 ± 0.04	324	1745	0.0705	25.85	21.74	0.98	214
0.11	5.78 ± 0.01	1.0124	0.41 ± 0.05	325	1827	0.0823	27.42	22.16	1.03	225
0.13	5.76 ± 0.01	1.0145	0.46 ± 0.06	312	1793	0.0774	26.74	23.48	1.01	207
0.15	5.76 ± 0.01	1.0160	0.46 ± 0.07	310	1430	0.0576	24.04	25.27	0.99	205

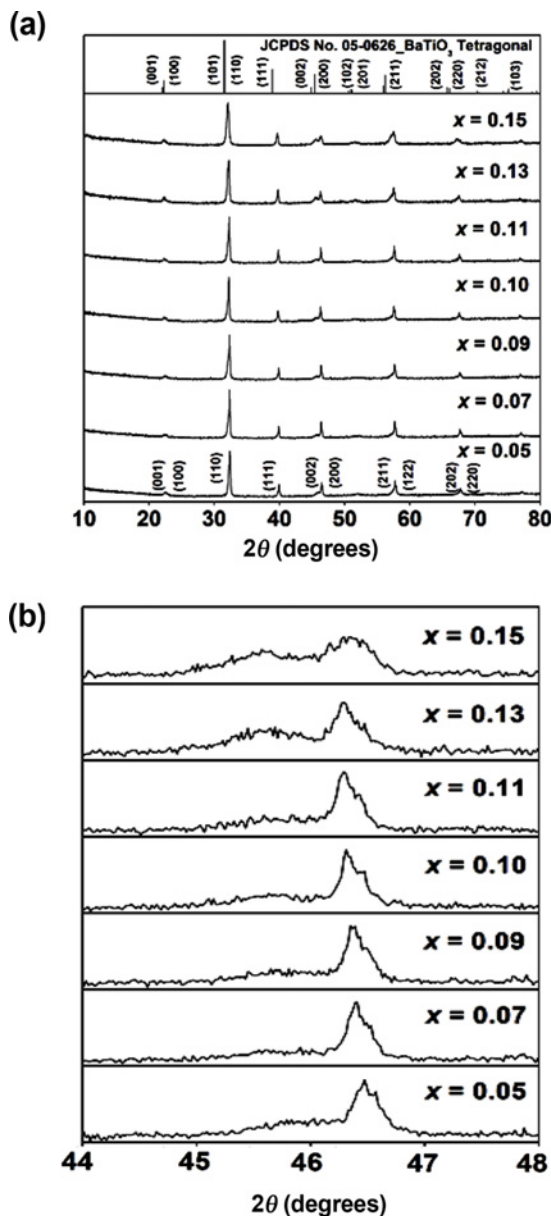[a]Dielectric data obtained at room temperature and at a frequency of 1 kHz.

Fig. 1. X-ray diffraction patterns of BNKT-BST ceramics where (a) $2\theta = 10 - 80°$ and (b) $2\theta = 44 - 48°$.

This suggested that BST had diffused into the BNKT lattice to form a solid solution. Apparently, the positions of peaks slightly shifted towards lower angles. This was attributed to the differences in ionic radii of Bi^{3+} (1.17 Å), Na$^+$ (1.18 Å), K$^+$ (1.33 Å), Ba^{2+} (1.42 Å) and Sr^{2+} (1.26 Å),[9] resulting in an enlargement of unit cell size. A similar enlargement of unit cell size was also observed when (Ba$_{0.7}$Sr$_{0.3}$)TiO$_3$ was added to (Bi$_{0.5}$Na$_{0.5}$)TiO$_3$ ceramic, in a previous study by Lee et al.[10] Detailed scans at $2\theta \approx 44 - 48°$ are shown in Fig. 1(b). BNKT-0.05BST ceramic showed mixed rhombohedral and tetragonal structures with rhombohedral dominating over tetragonal structure. This mixture of phases was maintained even when BST was added to BNKT up to 11 mol. %. It seemed that at $x = 0.11$ it came close to the MPB composition of BNKT-BST systems. When BST content was increased over 11 mol. %, the (002) and (200) peaks were more widely separated which indicated a tetragonal-rich phase, corresponding to an increase in the tetragonality (*c/a*) as shown in Table 1.

SEM micrographs of BNKT-BST ceramics are shown in Fig. 2 and their grain size values are listed in Table 1. High quality and dense ceramics were achieved for all compositions. BNKT-0.05BST contained cubic-like shape with an average length of ~0.4 μm. The addition of higher BST content to BNKT had no significant influence on grain size value. The grain size of all compositions was rather similar (0.39 - 0.46 μm).

The temperature dependence of dielectric constant (ε_m) and dielectric loss (tan δ) for all samples measured at 10 kHz are shown in Fig. 3. Curie temperature (T_c) increased with increasing BST and reached a maximum value of 325°C at $x = 0.11$. With further increase in BST, T_c started to decrease. Room temperature dielectric constant (ε_r) and dielectric loss (tan δ) are also listed in Table 1. The ε_r increased with increasing BST and reached a maximum value of 1827 at $x = 0.11$. It should be noted that the ε_r value of BNKT-0.11BST ceramic in this work was higher than the ε_r value (~949) of the MPB composition of the BNKT-0.06BZT system observed previously by Chen et al.[7] With the increasing

amount of BST, a slight decrease in ε_r was observed. In addition, variation of piezoelectric behavior with increasing BST showed a similar trend to that of the dielectric response.

Fig. 2. SEM micrographs of (1-x)BNKT-xBST ceramics where (a) $x = 0.05$, (b) $x = 0.07$, (c) $x = 0.09$, (d) $x = 0.10$, (e) $x = 0.11$, (f) $x = 0.13$ and (g) $x = 0.15$.

Fig. 3. Plots of temperature dependence on dielectric constant and dielectric loss of BNKT-BST ceramics.

The piezoelectric constant (d_{33}) initially increased reaching a maximum value of 225 pC/N at $x = 0.11$. The d_{33} value was much higher than that observed earlier in the BNT-0.08BST composition by Lee *et al.*[10] who obtained $d_{33} \sim 160$ pC/N. The d_{33} was then decreasing in turn with further increasing BST, indicating that the compositions slightly deviated to the tetragonal-rich phase. The change in crystal structure to be more tetragonal-rich phase may also contribute to the reduction in dielectric and piezoelectric performances of BNKT-BST ceramics similar to the reduction of both ε_r and d_{33} observed in previous work on the BNKT-BZT system.[7] For the MPB-like behavior of this ceramic system, the maximum dielectric ($T_c = 325°C$, $\varepsilon_r = 1827$, tan $\delta = 0.0823$) and piezoelectric performance ($d_{33} = 225$ pC/N) were obtained at a composition of $x = 0.11$.
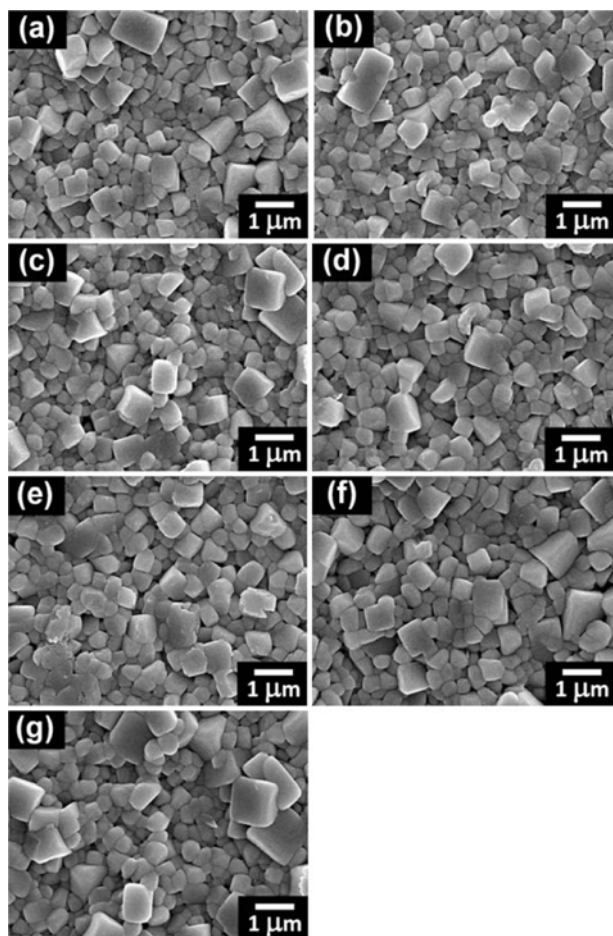

Fig. 4. Plots of polarization as a function of electric field of (1-x) BNKT-xBST ceramics where (a) $x = 0.05$, (b) $x = 0.07$, (c) $x = 0.09$, (d) $x = 0.10$, (e) $x = 0.11$, (f) $x = 0.13$ and (g) $x = 0.15$.
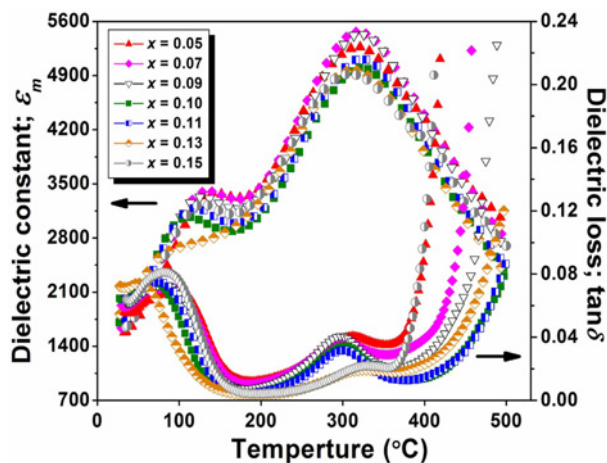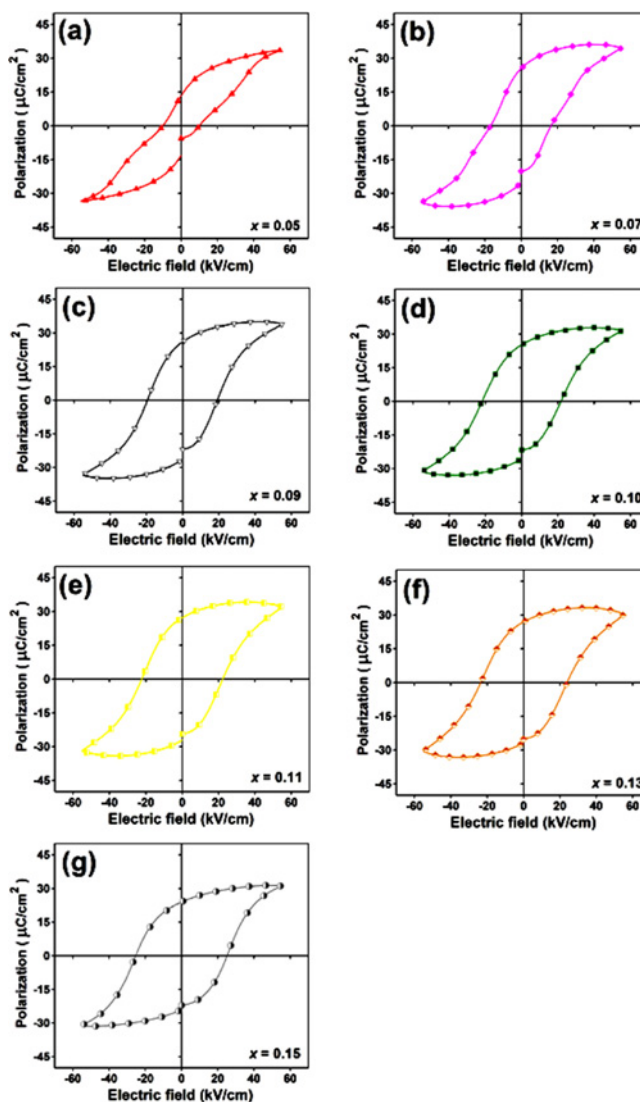
Figure 4 shows *P-E* hysteresis loops of BNKT-BST ceramics obtained at room temperature. Normal *P-E* hysteresis loops were observed for all samples. For more details, the remanent polarization (P_r), coercive field (E_c) and loop squareness (R_{sq}) are also listed in Table 1. P_r and R_{sq} increased with increasing BST and reached the maximum values of 27.42 μC/cm^2 and 1.03, respectively, at $x = 0.11$. However, E_c gradually increased with increasing BST. Because of the MPB-like behavior, improved ferroelectric performances where P_r and R_{sq} were maximized could be achieved for the BNKT-0.11BST composition. This seemed to be the main mechanism governing the observed ferroelectric properties similar to previous work on BNKT-BZT.[7] With increasing BST content, a slight decrease in P_r and R_{sq} was then observed.

4. CONCLUSIONS

Lead-free piezoelectric ceramics (1-*x*)BNKT-*x*BST (when $x = 0.05 - 0.15$ mol fraction) were successfully synthesized by a conventional mixed oxide method. X-ray diffraction patterns revealed that the MPB region with coexisting rhombohedral and tetragonal structures was found to occur at $x = 0.11$. The sample at MPB composition showed an improved dielectric ($T_c = 325$°C, $\varepsilon_r = 1827$, tan $\delta = 0.0823$), ferroelectric ($P_r = 27.42$ μC/cm^2, $R_{sq} = 1.03$) and piezoelectric properties ($d_{33} = 225$ pC/N) compared to the end-members.

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