

## Electromechanical and ferroelectric properties of $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3 - (\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3 - \text{BaTiO}_3$ lead-free piezoelectric ceramics

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Lead-free piezoelectric ceramics  $(0.95-x)(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3 - x(\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3 - 0.05\text{BaTiO}_3$  (abbreviated as BNT-BKT-BT100x, with  $x$  ranged from 0 to 20 mol %) have been studied. Effects of amount of BKT on the electrical properties and crystal structure were examined. BNT-BKT-BT5 ceramics give good performances with piezoelectric constant  $d_{33} = 148$  pC/N, electromechanical coupling factor  $k_p = 34$  %,  $k_t = 49.2$  %, free permittivity  $\epsilon_{33}^T/\epsilon_0 = 700$ , and dissipation factor  $\tan \delta = 2$  % at 1 kHz. Accordingly, the sample shows larger remanent polarization and lower coercive field than 0.95BNT-0.05BT ceramics. X-ray diffraction analysis shows that incorporated BKT diffuses into the BNT-BT lattice to form a solid solution during sintering, but changes the crystal structure from rhombohedral to tetragonal symmetry at higher BKT amounts. © 2004 American Institute Of Physics. [DOI: 10.1063/1.1767592]

Although  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$  ceramics (abbreviated as PZT) are playing a dominant role in piezoelectric materials, waste of products containing Pb causes a crucial environmental problem under ground water. A promising way to solve this problem is to develop lead-free piezoelectric ceramics to replace PZT ceramics to minimize lead pollution. Recently, more and more attention has been paid to the investigation of lead-free piezoelectric ceramics.<sup>1</sup>

$(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$  ceramics (abbreviated as BNT) with a rhombohedral perovskite structure have been considered to be a good candidate for lead-free piezoelectric ceramics because of their strong ferroelectricity at room temperature and high Curie temperature  $T_C$  of 320 °C.<sup>2-4</sup> In addition, it reveals an anomaly of dielectric properties as a result of low temperature phase transition from the ferroelectric to the antiferroelectric phase at about 200 °C, which can be called the depolarization temperature ( $T_d$ ).<sup>5</sup> However, their electromechanical properties are much lower than those of PZT ceramics and there is also some difficulty in poling BNT ceramics. Comparing BNT with PZT in terms of composition and structure, three obvious differences can be seen. First, A site of BNT ceramics is occupied by  $\text{Bi}^{3+}$  and  $\text{Na}^+$  ions. Furthermore, they have relatively small radii ( $\text{Bi}^{3+}$  with 1.14 Å and  $\text{Na}^+$  with 0.94 Å) comparing with  $\text{Pb}^{2+}$  in the A site of PZT which has a large radii of 1.32 Å. Second, unlike PZT ceramics, BNT ceramics has no morphotropic phase boundary (MPB). It is known that the MPB plays a very important role in PZT ceramics because the piezoelectric and dielectric properties show a maximum over a specific compositional range around the MPB. Third, BNT ceramics undergo a low temperature transition from the ferroelectric to the antiferroelectric phase at  $T_d$ , while PZT ceramics have no such transition. Above  $T_d$ , BNT ceramics will be depolarized. Based on the above-noted comparison and analysis, it is considered that besides substituting  $\text{Bi}^{3+}$  or  $\text{Na}^+$  with larger cations, it is very important to make use of the MPB phenomenon in improving the piezoelectric properties of BNT ceramics. In addition, special attention should also be paid to

$T_d$ . It has been reported that BNT-based compositions modified with  $\text{BaTiO}_3$  (BT),<sup>5</sup>  $(\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3$  (BKT),<sup>6</sup>  $\text{NaNbO}_3$ ,<sup>7</sup>  $\text{BaTiO}_3 + \text{CeO}_2$ ,<sup>8</sup> and so on showed improved piezoelectric properties and easier treatment in the poling process compared with pure BNT ceramics. But the electromechanical properties are still too low for practical use or  $T_d$  is reduced significantly. However, it is noted that among them, the BNT-BT system and BNT-BKT system are very interesting as they have rhombohedral ( $F_R$ )-tetragonal ( $F_T$ ) MPB.<sup>5,6</sup> These systems reveal relatively high piezoelectric and dielectric properties at the composition near the MPB, meanwhile they have relatively high  $T_d$ . Thus, it is hopeful that the multicomponent systems like a combination of BNT-BKT-BT is effective in improving the piezoelectric properties further without decreasing  $T_d$  greatly. Recently, Nagata *et al.* reported their work on BNT-BKT-BT system.<sup>9</sup> However, the report was limited to piezoelectric constant and Curie temperature  $T_C$ . It is still indispensable to well understand the features of the BNT-BKT-BT system including  $T_d$ , ferroelectric properties, and so on. The aim of this study is to investigate the piezoelectric and ferroelectric properties of  $(0.95-x)(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3 - x(\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3 - 0.05\text{BaTiO}_3$  ceramics (abbreviated as BNT-BKT-BT100x, with  $x$  ranged from 0 to 20 mol %) and the relationship between its composition and structure. 0.05BT was chosen because 0.95BNT-0.05BT is a composition near the MPB.

Conventional mixed oxide techniques were used to prepare the BNT-BKT-BT100x ceramics. Commercially available chemicals of  $\text{Bi}_2\text{O}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{BaCO}_3$ , and  $\text{TiO}_2$  with purities higher than 99% were used as the starting materials. BNT, BKT, and BT were prepared at first. BNT and BKT were calcined at 800 °C for 1 h and BT was calcined at 1150 °C for 2 h. Then, they were weighted according to the above-noted formula and were milled in alcohol using  $\text{Y}_2\text{O}_3$ -stabilized zirconia balls for 10 h. The mixtures were dried and added with PVA as a binder for granulation. The granulated powders were pressed into discs in diameter of 22 mm and thickness of 2 mm. The compacted discs were sintered at 1170 °C for 2 h in air. Silver paste was applied on both surfaces of the discs and fired at 650 °C as elec-

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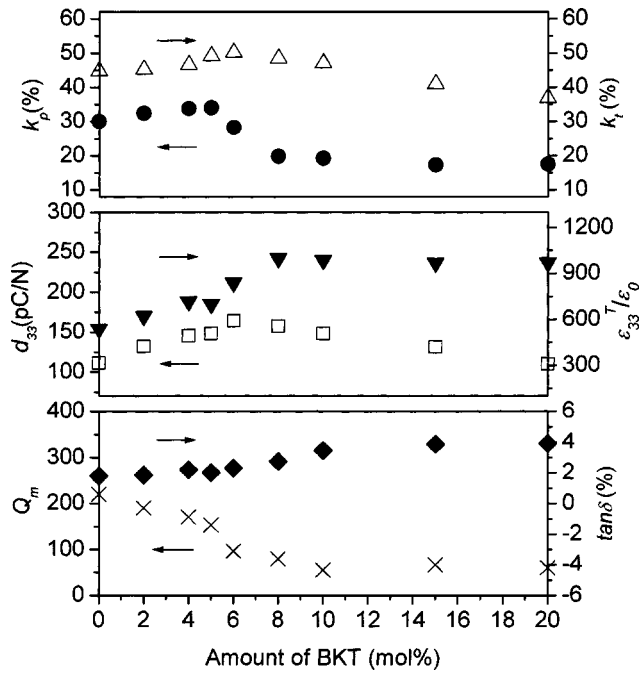


FIG. 1. Piezoelectric and dielectric properties of the BNT-BKT-BT100x ceramics as a function of the amount of BKT.

trodes. The samples for measurement of piezoelectric properties were poled in silicone oil at 80 °C under 4.5 kV/mm for 5 min.

The density of the sintered samples was measured using the Archimedes method. The  $d_{33}$  coefficient of the poled sample was measured at 100 Hz using a  $d_{33}$  meter (ZJ-30 PIEZO  $d_{33}$  METER). The resonance measurements were conducted using an impedance analyzer (Hewlett-Packard 4294A Impedance Analyzer). The electromechanical coupling factors were calculated from the resonance and the antiresonance frequencies according to Onoe's formulas.<sup>10</sup> Dielectric properties of the samples were determined using the HP4294A impedance analyzer at 1 kHz. A standard Sawyer-Tower circuit was used to measure the polarization hysteresis ( $P$ - $E$ ) loop at 100 Hz. The crystal phase of the sample was examined by using an x-ray diffractometer (XRD-Philips Expert System).

Figure 1 shows the piezoelectric and dielectric properties of the BNT-BKT-BT100x ceramics as a function of BKT amount. All ceramic samples have high density around 5.71–5.79 g/cm<sup>3</sup>. Electromechanical coupling factor  $k_p$  increases with the amount of BKT up to 5 mol % and then decreases with further increase in BKT amount. At 5 mol % BKT, the sample shows the optimal  $k_p$  of 34 %. Variation of electromechanical coupling factor  $k_t$  and piezoelectric constant  $d_{33}$  with BKT amount is almost similar to that of  $k_p$ , but their maximum value occurs at 6 mol % of BKT. Free permittivity  $\epsilon_{33}^T/\epsilon_0$  of the samples increases with increasing BKT amount initially, reaches the maximum at 8 mol % of BKT and then shows a slight decrease with more BKT. Incorporation of BKT into BNT-BT system reveals a tendency to increase the dissipation factor  $\tan\delta$  and reduce the mechanical quality factor  $Q_m$ . At BKT amount level lower than 5 mol %, the samples have relatively low  $\tan\delta$  and relatively high  $Q_m$ . The  $d_{33}$  is proportional to the electromechanical coupling factor,  $k_{33}$ , and square of the free permittivity,  $\epsilon_{33}^T$ , and the elastic compliance,  $s_{33}^E$ , as follows

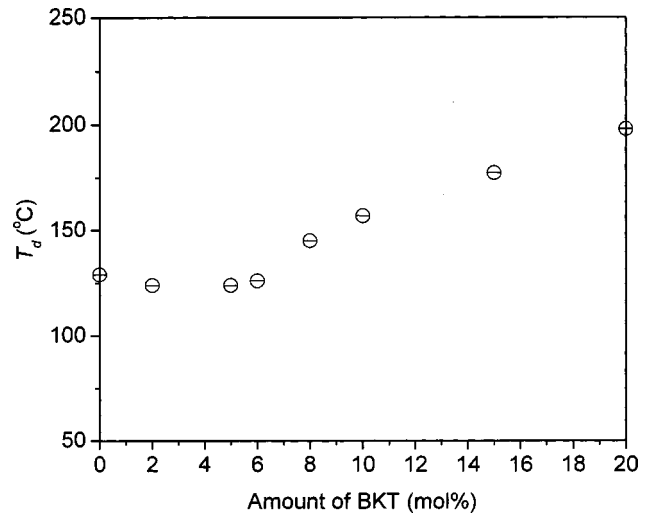


FIG. 2. Depolarization temperature  $T_d$  of the BNT-BKT-BT100x ceramics as a function of the amount of BKT.

$$d_{33} = k_{33} \sqrt{\epsilon_{33}^T \epsilon_{33}^E} \quad (1)$$

Thus, it is easy to explain why BNT-BKT-BT6 ceramics shows maximum  $d_{33}$  other than BNT-BKT-BT5 ceramics. From Fig. 1, it can be seen the BNT-BKT-BT100x ceramics with a proper amount of BKT possesses improved piezoelectric and dielectric properties. Besides this, it is noted that BNT-BKT-BT100x ceramics still keep or increase the depolarization temperature of the BNT-BT system as shown in Fig. 2. It is known that  $T_d$  is an important factor for BNT-based piezoelectric ceramics in view of their practical use. Generally, an obvious improvement on the piezoelectric and dielectric constant of BNT-based ceramics through modification is accompanied by a significant decrease in  $T_d$ .<sup>8,13</sup> That is because the additives in BNT-based composition cause defects such as vacancies, lattice deformation and they facilitate the domain movement leading to higher piezoelectric and dielectric properties but decreasing  $T_d$ . However, BNT-BKT-BT100x multicomponent system not only gives good electrical properties, but also has high  $T_d$ .

The measurement of  $P$ - $E$  hysteresis loops was conducted to examine the ferroelectric properties of BNT-BKT-BT100x ceramics. Figure 3 shows the  $P$ - $E$  hysteresis loops of BNT-BKT-BT100x ceramics with 0, 5, 10, and 20 mol % of BKT obtained at room temperature and 160 °C respectively. It is obvious that incorporation of BKT in BNT-BT composition up to 20 mol % decreases the coercive field, indicating the facilitation of domain movement which may be caused by the larger deformations in the lattice. At room temperature, it can be seen that the BNT-BKT-BT5 ceramics has a remanent polarization  $P_r$  of 35.9  $\mu\text{C}/\text{cm}^2$ , which is significantly larger than 29.1  $\mu\text{C}/\text{cm}^2$  for 0.95BNT-0.05BT ceramics. However, an increased amount of BKT leads to a decrease in the remanent polarization  $P_r$ . At 20 mol % BKT, the remanent polarization  $P_r$  even becomes smaller than that of 0.95BNT-0.05BT ceramics. That is to say, incorporation of a proper amount of BKT in BNT-BT composition enhances the ferroelectric properties significantly. At 160 °C, the  $P$ - $E$  hysteresis loop of all samples became very narrow. However, except for BNT-BKT-BT20 ceramics, all other BNT-BKT-BT100x ceramics with  $T_d$  lower than 160 °C show double-like  $P$ - $E$  hysteresis loops, which may be ascribed to an antiferroelec-

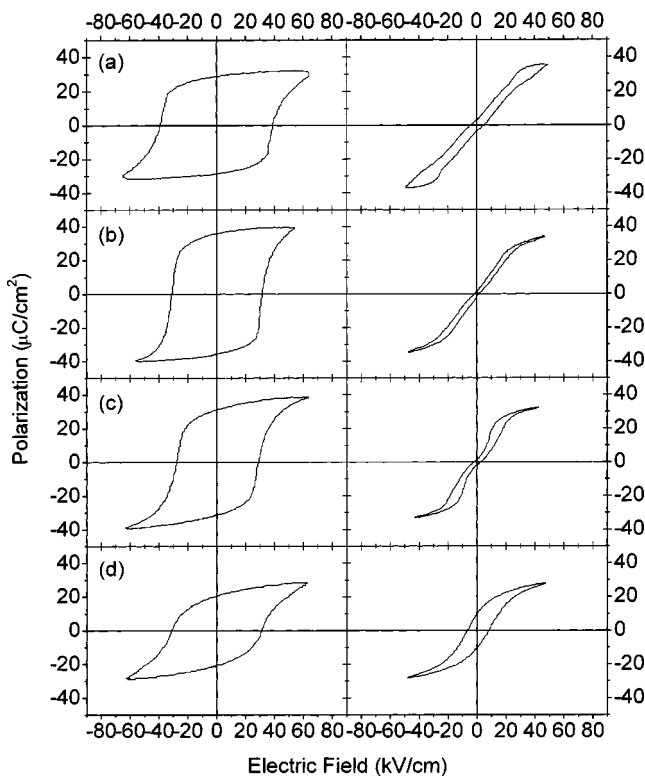


FIG. 3.  $P$ - $E$  hysteresis loops of BNT-BKT-BT100 $x$  ceramics with (a) 0 (top), (b) 5, (c) 10, and (d) 20 mol % of BKT measured at room temperature (left) and at 160°C (right).

tric feature. In contrast, the  $P$ - $E$  hysteresis loops of BNT-BKT-BT20 ceramics with  $T_d$  over 160 °C show a typical ferroelectric feature. It seems that BNT-BKT-BT100 $x$  ceramics undergo a transition from ferroelectric to antiferroelectric phase at  $T_d$ . However, it has not been confirmed by other experimental measurements if an antiferroelectric phase exists in BNT ceramics at temperature between  $T_d$ - $T_C$ .<sup>11,12</sup> Some researchers thought that the presence of  $T_d$  in BNT ceramics could be due to macro-micro domains switching.<sup>13</sup> Thus, the actual mechanism is still not very clear and further investigation will be required.

All of the x-ray diffraction (XRD) patterns of the BNT-BKT-BT100 $x$  ceramics have pure perovskite structure. The XRD patterns of the samples in the  $2\theta$  ranges of 38–48° are shown in Fig. 4. BKT appears to have diffused into the lattice to form a solid solution. It is evident that at room temperature, BNT-BKT-BT0 is in rhombohedral phase and BKT is in tetragonal phase. With the incorporation of 10 mol % of BKT, the crystal structure turns into a tetragonal symmetry featured with splitting of the (200) and (002) peaks at around  $2\theta$  of 46.5°. More BKT leads to the (200) and (002) peaks separated more widely, indicating the increasing tetragonality of the lattice. Hence, it can be inferred that there should exist a rhombohedral-tetragonal morphotropic phase boundary in the BNT-BKT-BT100 $x$  composition. At 5 mol % BKT, no obvious change in the XRD pattern was observed compared with that of BNT-BKT-BT0 ceramics, but the peak at around 46.5° is slightly asymmetrical. As the optimal electromechanical property occurs in this composition, its crystal structure is considered to be a coexistence of rhombohedral and tetragonal phases. That is to

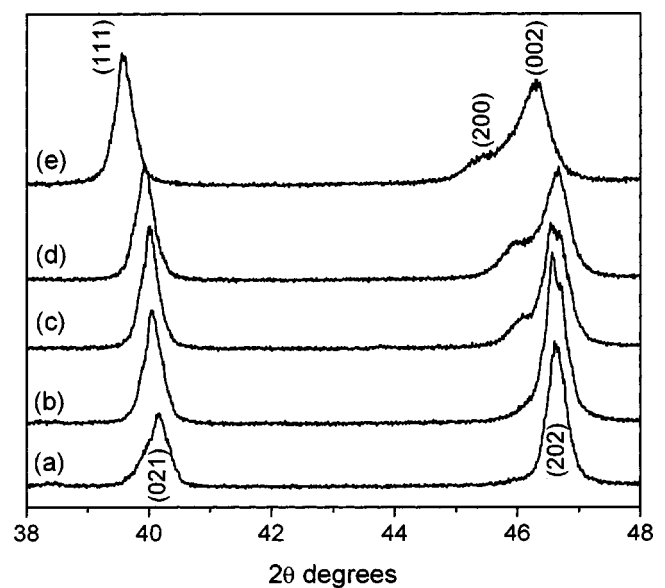


FIG. 4. X-ray diffraction patterns at  $2\theta$  between 38° and 48° of BNT-BKT-BT100 $x$  ceramics with (a) 0, (b) 5, (c) 10, (d) 20 mol % of BKT and (e) BKT ceramics.

say, the morphotropic phase boundary should be near the BNT-BKT-BT5 composition.

In summary,  $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ - $(\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3$ - $\text{BaTiO}_3$  (BNT-BKT-BT) system has been investigated. Variations of the electrical properties and structure with the amount of BKT have been examined. During sintering, the incorporated BKT diffuses into the lattice of BNT-BT-based composition to form a solid solution. The incorporation of a proper amount (~5 mol %) of BKT will enhance the piezoelectric properties significantly. It also increases the remanent polarization and lowers the coercive field, however, it almost does not reduce the depolarization temperature  $T_d$ . At high amount level of BKT, the crystal structure of the samples is changed from a rhombohedral into a tetragonal symmetry.

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