Piezoelectric and Dielectric Properties of $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3\text{-Ba}(\text{Zr}_{0.04}\text{Ti}_{0.96})\text{O}_3$ Lead-Free Piezoelectric Ceramics

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鉛無し圧電セラミックス $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3\text{-Ba}(\text{Zr}_{0.04}\text{Ti}_{0.96})\text{O}_3$ の圧電と誘電特性

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Lead-free piezoelectric ceramics $(1-x)(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3\text{-Ba}(\text{Zr}_{0.04}\text{Ti}_{0.96})\text{O}_3$ (abbreviated as BNT-BZT100x, with x ranged from 2 to 10 mol%) have been investigated. The samples were prepared by a conventional sintering technique. Effect of amount of BZT on the electrical properties and microstructures of BNT-BZT lead-free piezoelectric ceramic were examined. The X-ray diffraction (XRD) patterns shows that incorporated BZT diffuses into the BNT lattice to form a solid solution during sintering, but changes the crystal structure from rhombohedral to tetragonal symmetry at higher BZT amounts. The measurements of piezoelectric properties reveal that BNT-BZT6 ceramics has highest piezoelectric performance: the piezoelectric constant d_{33} reached to 168 pC/N and planar electromechanical coupling factor k_p enhanced to 0.27. The morphotropic phase boundary (MPB) between BNT (rhombohedral) and $\text{Ba}(\text{Zr}_{0.04}\text{Ti}_{0.96})\text{O}_3$ (tetragonal) should be near the BNT-BZT6 composition. [Received August 10, 2006; Accepted September 21, 2006]

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1. Introduction

In recent years, lead-free piezoelectric ceramics have attracted considerable attentions as one of important piezoelectric materials because of its outstanding advantages in free control atmosphere and no lead pollution. $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ composition (abbreviated as BNT) is an important lead-free piezoelectric material with a rhombohedral perovskite structure discovered by Smolenskii et al. in 1960.¹⁾ As $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ composition exhibits a strong ferroelectricity and high Curie temperature $T_c = 320^\circ\text{C}$,²⁾⁻⁴⁾ it has been considered to be a good candidate of lead-free piezoelectric ceramics to replace the widely used lead-based piezoelectric materials. However, this material has a drawback of high conductivity to cause problems in poling process. To improve its properties, some modifications on BNT composition have been performed. It has been reported that BNT-based compositions modified with BaTiO_3 ,⁵⁾ NaNbO_3 ,⁶⁾ BiFeO_3 ,⁷⁾ $(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$ ⁸⁾ or La_2O_3 ⁹⁾ showed improved piezoelectric properties and easier treatment in polling process comparing with pure BNT ceramics. Among them, BaTiO_3 (BT) is well-known lead-free piezoelectric materials with a tetragonal phase. It was reported that MPB compositions exist in the case of $x = 0.06\text{--}0.07$ for $(1-x)(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3\text{-BaTiO}_3$.

$\text{Ba}(\text{Zr}_{0.04}\text{Ti}_{0.96})\text{O}_3$, as well as BaTiO_3 , has an tetragonal symmetry at room temperature. $\text{Ba}(\text{Zr}_{0.04}\text{Ti}_{0.96})\text{O}_3$ (BZT) ceramic are known to have high piezoelectric and dielectric properties.^{10),11)} The solid solution of BNT and BZT seem to have MPB between the tetragonal and rhombohedral phases. It is well known that large piezoelectric properties can be expected at the MPB composition.¹²⁾ However, there have been few studies on the properties of BNT ceramics modified with $\text{Ba}(\text{Zr}_{0.04}\text{Ti}_{0.96})\text{O}_3$.

In the present work, $\text{Ba}(\text{Zr}_{0.04}\text{Ti}_{0.96})\text{O}_3$ was added into BNT ceramics as an additive based on the formula $(1-x)$

$(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3\text{-Ba}(\text{Zr}_{0.04}\text{Ti}_{0.96})\text{O}_3$ (abbreviated as BNT-BZT100x, with x ranged from 2 to 10 mol%), and its effects on the microstructure as well as on the dielectric and piezoelectric properties of the ceramics were investigated. We attempt to determine the existence of MPB and the enhancement of the properties for $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ and $\text{Ba}(\text{Zr}_{0.04}\text{Ti}_{0.96})\text{O}_3$ systems with rhombohedral and tetragonal crystal structures, respectively.

2. Experimental procedure

BNT-BZT100x ceramics were prepared by a conventional mixed-oxide technique using commercially available metal oxides or carbonate powders: Bi_2O_3 , Na_2CO_3 , BaCO_3 , ZrO_2 and TiO_2 . The powders were weighed and mixed well in alcohol with zirconium balls by ball-milling for 10 h. The calcination was then conducted at 800°C for 2 h. The calcined mixture was ball-milled in alcohol again for 6 h. After drying, it was mixed thoroughly with a PVA binder solution and uniaxially pressed into disk samples with a diameter of 20 mm and a thickness of 2 mm. The disk sample was then sintered at 1150°C for 2 h in air. The crystallite structure of the sintered sample was examined using an X-ray diffractometer (XRD, D/Max-3C, Japan) with $\text{Cu K}\alpha$ radiation.

Silver paste was applied to the top and bottom surfaces of the samples as electrodes. The ceramic samples were polarized under a dc field of 7.5 kV/mm at 100°C in a silicon oil bath for 15 min. Piezoelectric constant d_{33} of the samples were measured by means of quasistatic d_{33} meter (ZJ-3A) based on Berlincourt method. Dielectric constant ϵ_{33}/ϵ_0 was obtained by measuring the capacitance at 1 kHz using an impedance analyzer (HP4192A). Resonance measurements were performed using an impedance analyzer (HP 4294A). The electromechanical coupling factors k_p were calculated from the resonance and the anti-resonance frequencies according to Onoe's formulas.¹³⁾

Fig. 1. X-ray diffraction patterns of BNT-BZT100x system (with x ranged from 2 to 1 mol%).

3. Results and discussion

The BNT-BZT100x ceramics were well sintered at 1150°C with a high-density ratio of more than 95% of the theoretical density for 2 h in air. As show in Fig. 1, all of the X-ray diffraction (XRD) patterns of the BNT-BZT100x ceramics have pure perovskite structure. BZT appears to have diffused into the lattice to form a solid solution. In this case, barium can occupy a (Bi, Na) site and $(\text{Zr}_{0.04}\text{Ti}_{0.96})$ can enter a titanium site of BNT.

The XRD patterns of the samples in the 2θ ranges of $45\text{--}51^\circ$ are shown in Fig. 2. It is evident that at room temperature, BNT is in rhombohedral phase and $\text{Ba}(\text{Zr}_{0.04}\text{Ti}_{0.96})\text{O}_3$ is in tetragonal phase. Only the (200) peak is observed in the diffraction patterns for BNT-BZT100x ($x=0.02, 0.04$) which have a rhombohedral structure. On the other hand, (200) and (002) peaks are observed in the diffraction patterns for BNT-BZT100x ($x=0.1$) which have a tetragonal structure. At 6 mol% BZT, no obvious change in the XRD pattern was observed compared with that of BNT-BZT4 ceramics, but the peak at around 47.5° is slightly asymmetrical, featured with slightly splitting of the (200) and (002) peaks. More BZT 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-BZT100x ($x=0.02\text{--}0.1$) composition. Figure 3 shows the lattice parameters of samples of the BNT-BZT100x system. In the region of the tetragonal phase, the lattice parameter a and c increases gradually with an increasing amount of the BZT phase (x). The difference between a and c also increases with increasing x .

The interplanar distance $d_{(h,k,l)}$ of tetragonal phase is expressed as

$$d_{(h,k,l)} = \frac{a}{\sqrt{h^2 + k^2 + \left(\frac{a}{c}\right)^2 l^2}} \quad (1)$$

where a , c are the lattice parameter, h , k , l are indices of crystallographic plane. The Bragg equation is expressed as follows:

$$2d_{(h,k,l)} \sin \theta = \lambda \quad (2)$$

where θ is Bragg angle, λ is wavelength. Combining the Eqs. (1) and (2), $\sin \theta$ can be expressed as

Fig. 2. X-ray diffraction patterns of BNT-BZT100x system in the 2θ range of $44\text{--}52^\circ$.

Fig. 3. Lattice parameter as a function of composition for BNT-BZT100x system.

$$\sin \theta = \frac{\lambda}{2} \sqrt{\frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}} \quad (3)$$

From Eq. (3), we have

$$\theta_{(200)} - \theta_{(002)} = \arcsin \left(\frac{\lambda}{a} \right) - \arcsin \left(\frac{\lambda}{c} \right) \quad (4)$$

where $\theta_{(200)}$ and $\theta_{(002)}$ are Bragg angle for (200) and (002) crystal plane respectively. As the difference between a and c also increases with increasing x , from Eq. (4), it is easy to explain why more BZT leads to the (200) and (002) peaks separated more widely.

Figure 4 shows the dependence of the planar electro-mechanical coupling factor k_p and piezoelectric constant d_{33} on the chemical composition for the synthesized BNT-BZT100x ceramics. Coupling factor K_p increases with the amount of BZT up to 6 mol% and then decreases with further increase in BZT amount. At 6 mol% BZT, the sample shows the optimal k_p of 27%. Variation of the piezoelectric constant d_{33} with BZT amount is almost similar to that of k_p . The optimized BZT amount is also about 6 mol%, giving maximum d_{33} value of 168 pC/N. Figure 5 shows the dependence of the dielectric constant $\epsilon_{33}^T/\epsilon_0$ and dissipation factor $\tan \delta$ on the chemical composition for BNT-BZT100x. Dielectric constant $\epsilon_{33}^T/\epsilon_0$ of the samples increases with increasing BZT

Fig. 4. Piezoelectric constant d_{33} and planar electromechanical coupling factor k_p as a function of composition for BNT-BZT100x system.

Fig. 5. Dielectric constant $\epsilon_{33}^T/\epsilon_0$ and dissipation factor $\tan \delta$ as a function of composition for BNT-BZT100x system.

amount initially, reaches the maximum at 6 mol% ($\epsilon_{33}^T/\epsilon_0 = 950$) of BZT and then decreases with more BZT. Variation of the dissipation factor $\tan \delta$ with BZT amount is similar to that of $\epsilon_{33}^T/\epsilon_0$, and at $x=0.06$, the samples have relatively high $\tan \delta$ ($\tan \delta = 1.37\%$). In summary, it can be seen that the optimal electromechanical property occurs in BNT-BZT6 composition. Combining the result of XRD, it can be concluded that the morphotropic phase boundary (MPB) should be near the BNT-BZT6 composition.

The effect of BZT addition on the properties of BNT ceramics can be attributed to two factors: the chemical modification of the material and the influence on microstructure. At a small amount of BZT, chemical modification caused by dissolution of BZT into the BNT lattice plays a major role on the properties of BNT-BZT ceramics. When the added amounts of BZT are increased to cause change in microstructure, the influence of microstructure on the properties of BNT-BZT ceramics may become dominant. At the MPB composition (6 mol% BZT), the crystal structure of ceramics is considered to be a coexistence of rhombohedral and tetragonal phase.¹⁴⁾ As the free energy of rhombohedral phase is close to that of tetragonal phase, when applied a electric field, these two phase are easy to change each other. It is helpful to promote the

Table 1. Properties of BNT-BZT6, BNT-BZT8 and BNBT6 Lead-Free Piezoelectric Ceramics

Ceramic composition	$d_{33}(\text{pC/N})$	$k_p(\%)$	$\epsilon_{33}^T/\epsilon_0$
BNT-BZT6	168	27	950
BNT-BZT8	163	21	892
BNBT6	125	20.8	580

movement and polarization of ferroelectric active ion at this case, leading to the increase in dielectric constant $\epsilon_{33}^T/\epsilon_0$ and electromechanical coupling factor k_p . The increase in piezoelectric constant d_{33} at MPB composition may be attributed to an increase flexibility in domain wall.⁸⁾ At higher amount of BZT (>6 mol% BZT), chemical modification plays a major role on the properties of BNT-BZT ceramics again.

The dielectric, piezoelectric properties of BNT-BZT6, BNT-BZT8 and a typical lead-free piezoelectric ceramics such as BNT-BT6 are shown in Table 1. Among them, BNT-BZT6 has the highest d_{33} and k_p . It is obvious that BNT-BZT6 is promising candidate for lead-free piezoelectric ceramic and can be used in practical applications.

From the X-ray diffraction patterns and the dependence of the piezoelectric and dielectric properties on the chemical composition, the BNT-BZT system was found to have MPB, similar to PZT, which enhance the piezoelectric properties. From these results, it is certain that piezoelectric performance can be improved by selecting compounds with a different crystal structure and forming a microstructure using their mixtures.

4. Conclusions

BNT-BZT100x ternary system focusing on the MPB between tetragonal and rhombohedral phase has been investigated. These materials can be synthesized by conventional ceramic sintering technique. The crystalline structure, dielectric and piezoelectric properties of these ceramics were studied. Results of X-ray diffraction (XRD) show that the ceramics exhibit pure perovskite structure. The measurements of dielectric and piezoelectric properties reveal that the BNT-BZT6 ceramic provide relatively high piezoelectric constant d_{33} (up to 168pC/N) and high electromechanical coupling factor k_p (up to 27%). It is obvious that this piezoelectric ceramic is promising candidate for lead-free piezoelectric ceramic and can be used in practical applications.

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