Relationship between crystal structure and ferroelectric properties in Bi$_{0.5-0.5x}$Na$_{0.5-0.5x}$Sr$_x$Ti$_{1-x}$Zr$_x$O$_3$ ceramics

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The crystal structure, piezoelectric and ferroelectric properties of the Bi$_{0.5-0.5x}$Na$_{0.5-0.5x}$Sr$_x$Ti$_{1-x}$Zr$_x$O$_3$ (BNSTZ) ceramics were characterized in this study. From the variations in the lattice parameters, the solubility limit of the BNSTZ ceramics was determined to be $x = 0.075$. The crystal structure refinement revealed that the distortion of (Bi, Na and Sr)O$_{12}$ polyhedron decreases with increasing $x$ and such the variation in the distortion exerts an influence on the decrease in remnant polarization from 35 to 28 $\mu$C/cm$^2$. Although the slight shifts of the depolarization temperature ($T_d$) and rhombohedral-tetragonal phase transition temperature ($T_{R,T}$) to lower temperature were recognized, it suggested that the shift of $T_d$ is predominant for the increase in dielectric constant at room temperature which leads to the enhancement of the dielectric constant at room temperature which leads to the enhancement of the ferroelectric properties of the ceramics can be modulated by the formation of solid solutions with Bi$_{0.5}$Na$_{0.5}$TiO$_3$, BaTiO$_3$, K$_{0.5}$Na$_{0.5}$NbO$_3$, etc. Therefore, it is considered to be one of the candidates for lead-free piezoelectric ceramics. However, the BNSTZ ceramic is hard to pole and its piezoelectric properties are not favorable because of its relatively large coercive field ($E_c = 73$ kV/cm). In order to improve the piezoelectric and dielectric properties of the BNSTZ ceramic, various BNT-based solid solutions have been developed. The piezoelectric and dielectric properties of the ceramics can be modified by the formation of solid solutions with Bi$_{0.5}$K$_{0.5}$TiO$_3$, BaTiO$_3$, K$_{0.5}$Na$_{0.5}$NbO$_3$, etc. For example, the BNT–SrTiO$_3$ ceramics lead to the decrease in the depolarization temperature ($T_d$) and rhombohedral-tetragonal phase transition temperature ($T_{R,T}$), leading to the enhancing the piezoelectric constant. Similar results were also reported for the BNT–BaTiO$_3$, BNT–CaZrO$_3$ and BNT–Ba(Ti/Zr)O$_3$ ceramics. Such the formation of solid solutions influences the lattice distortions due to the different sizes of the cations, which can cause a shift in the temperature-dependent polymorphotropic phase transitions, or may trigger the formation of a morphotropic phase boundary (MPB). However, in the case of BNT–SrZrO$_3$ ceramic, the relationship between crystal structure and piezoelectric properties has not been clarified to date. Thus, the (1–$x$)BNT–SrTiO$_3$ ceramics, i.e., Bi$_{0.5-0.5x}$Na$_{0.5-0.5x}$Sr$_x$Ti$_{1-x}$Zr$_x$O$_3$, were synthesized; the characterization of crystal structure and piezoelectric properties was performed in this study.

1. Introduction

PbZr$_{1-x}$Ti$_x$O$_3$ (PZT) and related perovskite ceramics have been typical compositions for high performance actuators and transducers, owing to their superior dielectric, piezoelectric, and electromechanical coupling coefficients. On the other hand, worldwide efforts to eliminate the use of hazardous substances like lead from electronics and their wastes indicate difficulty in the use of piezoelectric ceramics. Bi$_{0.5}$Na$_{0.5}$TiO$_3$ (BNT), which is lead-free piezoelectric material with rhombohedral structure, may be able to replace the PZT-based ceramics. In addition, a relatively large remnant polarization ($P_r = 38 \mu$C/cm$^2$) at room temperature and a high Curie temperature ($T_c = 320^\circ$C) for the BNT ceramic have been reported by Suchaniz et al. Therefore, it is considered to be one of the candidates for lead-free piezoelectric ceramics. However, the BNT ceramic is hard to pole and its piezoelectric properties are not favorable because of its relatively large coercive field ($E_c = 73$ kV/cm). In order to improve the piezoelectric and dielectric properties of the BNT ceramic, various BNT-based solid solutions have been developed. The piezoelectric and dielectric properties of the ceramics can be modified by the formation of solid solutions with Bi$_{0.5}$K$_{0.5}$TiO$_3$, BaTiO$_3$, K$_{0.5}$Na$_{0.5}$NbO$_3$, etc. For example, the BNT–SrTiO$_3$ ceramics lead to the decrease in the depolarization temperature ($T_d$) and rhombohedral-tetragonal phase transition temperature ($T_{R,T}$), leading to the enhancing the piezoelectric constant.

2. Experimental methods

The BNSTZ ceramics were synthesized via a conventional solid-state reaction method using high-purity carbonates and oxides: Bi$_2$O$_3$, Na$_2$CO$_3$, SrCO$_3$, TiO$_2$, and ZrO$_2$ as starting materials. The powders were weighed based on the stoichiometry and mixed with acetone; after drying, the powders obtained were calcined at 800$^\circ$C for 5 h. Subsequently, the calcined powders were reground and polyvinyl alcohol (PVA) was added as a binder. The milled powders were uniaxially pressed into disks at 60 MPa; the disks were sintered at 1000 to 1220$^\circ$C for 2 h. Au electrodes and Pt paste were coated on the top and bottom surfaces of the samples for the dielectric measurements. The samples were poled at 60$^\circ$C for 30 min in a silicone oil bath under a dc electric field of 4 kV/mm. The crystalline phase of the ceramics was identified by X-ray powder diffraction (XRPD, RINT2000) using Cu K$_\alpha$ radiation; crystal structure analysis was performed using the Rietveld method. The bulk density of the samples was estimated by using Archmedes method. The dielectric constant and dielectric loss of poled samples were measured as a function of temperature using a LCR meter at 100 Hz, 1 kHz, 5 kHz, 100 kHz and 1 MHz. The $P$–$E$ hysteresis loop and piezoelectric constant ($d_{33}$) were measured using a TF analyzer 2000 and $d_{31}$ meter, respectively. The planar electromechanical coupling factor $k_p$ was determined with an impedance analyzer by resonance-antiresonance method basis of IEEE standards.

3. Results and discussion

Figure 1 shows the XRPD profiles of the BNSTZ ceramics. It was found that most compositions exhibit a single perovskite structure, except for compositions with $x > 0.1$ for which a small amount of a secondary phase was detectable. Moreover, it was recognized that the diffraction peaks shift to lower diffraction

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Key-words : Bi$_{0.5}$Na$_{0.5}$TiO$_3$, Ferroelectric property, Piezoelectric property, Crystal structure analysis, Lead-free
angles with increasing composition $x$. In order to clarify the effects of Sr and Zr substitutions for (Bi, Na) and Ti on the crystal structure of the BNSTZ ceramics, the structure refinements were performed by the Rietveld method. The crystal structural parameters belonging to the rhombohedral with space group $R3c$ were used as the initial parameters for the crystal structural refinement of the BNSTZ ceramics. The refined lattice parameters and axis angle of BNSTZ with rhombohedral symmetry at $x = 0$ were $a = 5.488(3)\, \text{Å}$, $c = 13.498(6)\, \text{Å}$ and $\alpha_R = 89.836(1)^\circ$, respectively; these values were similar to those of BNT reported by Lee et al. The lattice parameter of pseudo-cubic perovskite, $a_P$, was calculated from equation $a_P = a_R/\sqrt{2}$, where $a_R$ is the lattice parameter of rhombohedral symmetry. The calculated lattice parameter of BNSTZ with pseudo-cubic symmetry is shown in Fig. 2. The lattice parameter, $a_P$, for the BNSTZ ceramics increased up to $x = 0.075$, though the lattice parameters were almost constant above $x = 0.075$. These variations in the lattice parameters for the BNSTZ ceramics may be due to the ionic radii, $r$, of the Sr$^{2+}$ ($r = 1.44\, \text{Å}$, C.N. = 12), Bi$^{3+}$ ($r = 1.39\, \text{Å}$, C.N. = 12), Na$^+$ ($r = 0.87\, \text{Å}$, C.N. = 6) and Ti$^{4+}$ ($r = 0.57\, \text{Å}$, C.N. = 6) cations, where C.N. represents the coordination number. Therefore, the solubility limit for the BNSTZ ceramics was determined to be approximately $x = 0.075$.

Figure 3 shows a schematic diagram of the $BO_6$ octahedra ($B = \text{Ti and Zr}$) and (Bi, Na and Sr)O$_{12}$ polyhedra of the BNSTZ ceramics, respectively; the variations in the cation-oxygen bond lengths in the BNSTZ ceramics are shown in Fig. 4. Significant variations in the $B$-O and (Bi, Na and Sr)-O bond lengths in the...
BO₆ octahedra and (Bi, Na and Sr)O₁₂ polyhedra were recognized by the Sr and Zr substitutions for (Bi, Na) and Ti, respectively. The B–O₁ bond length in the BNSTZ ceramics increased by the Sr and Zr substitutions for (Bi, Na) and Ti, whereas the B–O₂ bond length decreased. The Sr and Zr substitutions for (Bi, Na) and Ti also exert an influence on the (Bi, Na and Sr)–O bond length in the (Bi, Na and Sr)O₁₂ polyhedra as shown in Fig. 4. From the results of the refined cation-oxygen bond lengths, the covalencies of the cation-oxygen bonds were calculated to clarify the relationships between the Sr and Zr substitutions for (Bi, Na) and Ti and the variations in the cation-oxygen bond length. Therefore, the covalencies of the cation-oxygen bond in the BNSTZ ceramics were calculated using the following equations:

\[
x = (R/R_s)^{-N}, \quad (1)
\]

\[
f'c = aM, \quad (2)
\]

Covalency = \(f'_c/s \times 100\%\), \( (3)\)

where \(x, R, R_s, \) and \(N\) represent the bond strength, the refined cation-oxygen bond length, and empirical parameters, respectively. Moreover, \(f'_c, a,\) and \(M\) are the covalence and the empirical parameters which relate to the bond length, respectively. Figure 5 shows the effects of Sr and Zr on the covalencies of the cation-oxygen bonds in the BNSTZ ceramics. As for the covalencies of the (Bi, Na and Sr)–O bonds of the BNSTZ ceramics, the covalencies of the (Bi, Na and Sr)–O₃ and (Bi, Na and Sr)–O₅ bonds decreased with increasing \(x\), whereas the covalencies of the (Bi, Na and Sr)–O₄ and (Bi, Na and Sr)–O₂ bonds increased as a function of the composition \(x\). Zhou et al.\(^{18}\) reported that the covalency of the BNT ceramic along the c-axis is a very important factor, which is one of the main reasons that the BNT has ferroelectric properties. The covalencies of the (Bi, Na and Sr)–O₂ and (Bi, Na and Sr)–O₅ bonds are mainly along the c-axis, as shown in Fig. 3. It is also recognized that the covalencies of the B–O₁ and B–O₂ bonds in the BO₆ octahedra are almost constant. Such variations in the covalencies may influence the ferroelectric properties of the BNSTZ ceramics.

The phase transformation can also be discussed from the structural distortion which is related to \(\alpha_E\) belonging to the angle between axes. Then, the structural distortion, \(\Delta\), is estimated using the following formula:\(^{19}\)

\[
\Delta = \frac{1}{Z} \sum \left( \frac{R - \bar{R}}{R} \right)^2, \quad (4)
\]

where \(Z\) is the coordination number, \(R\) is the individual bond length, and \(\bar{R}\) is the average bond length. Figure 6 shows the compositional dependences of \(\alpha_E\) angle and structural distortions of (Bi, Na, and Sr)O₁₂ polyhedra and BO₆ \((\Bar{B} = \text{Ti and Zr})\) octahedra. The \(\alpha_E\) increased with increasing \(x\) and the structural distortion of (Bi, Na, and Sr)O₁₂ polyhedra decreased, whereas that of BO₆ octahedra is almost constant. A less distorted unit cell usually accompanies lower strain and smaller \(E_c\) during domain alignment.\(^{13}\) It is reported that a smaller \(E_c\) is found when \(\alpha_E\) is closer to 90° in the rhombohedral phase.\(^{13}\) Therefore, variations in \(\alpha_E\) may also influence the ferroelectric properties of the BNSTZ ceramics.

Room temperature measurements of polarization versus electric field were performed on the samples in order to determine the values of \(E_c\) and \(P_t\) for the ferroelectric materials, as shown in Fig. 7. The details on relative density, ferroelectric and piezoelectric properties of BNSTZ ceramics are also summarized in Table I. The BNSTZ ceramics were exposed to a frequency of 50kHz and to an external electric field of 90 kV/cm. When comparative measurements for the hysteresis loops of all the samples are employed, it is recognized that an increase in the compositional fraction \(x\) in the BNSTZ ceramics causes a decrease in \(P_t\)
from 35 μC/cm² for x = 0 to 28 μC/cm² for x = 0.075. A further decrease in the $E_c$ value of the BNSTZ ceramics can be observed with compositional variation, where $E_c$ is 31 kV/cm. Therefore, the Sr and Zr substitutions for (Bi, Na) and Ti is effective to improve the $E_c$ values.

The temperature dependence of the dielectric constant and dielectric loss of the poled BNSTZ ceramics in the frequency range of 100 Hz to 1 MHz were shown in Fig. 8. The dielectric peak of the BNT ceramic was reported to be 320°C, which corresponds to the Curie temperature ($T_c$). The $T_c$ of the BNSTZ ceramics was not changed by the Sr and Zr substitutions for (Bi, Na) and Ti, though the dielectric constant at room temperature increased. The $T_d$ is also an important factor for BNT ceramic for their practical applications because the piezoelectric behavior disappears above $T_d$. The $T_d$ was determined from the high temperature peak of dielectric loss of the poled sample at approximately 180°C. The $T_d$ values of the BNSTZ ceramic slightly shifted to lower temperature from 180 to 145°C as shown in Fig. 8. Moreover, the phase transition temperatures from rhombohedral to tetragonal phases ($T_{R-T}$) are also determined; such the temperature also slightly decreased with an increase in the composition x. On the other hand, in the BNT–SrTiO₃, BNT–BaTiO₃, and BNT–Ba(Zr/Ti)O₃ ceramics, the shift of $T_{R-T}$ of the ceramics to lower temperature was reported, resulting in the formation of MPB which leads to the enhancement of piezoelectric constant and the dielectric constant at the room temperature, though such the remarkable shift of $T_{R-T}$ was not recognized in BNSTZ ceramics as described above. Thus, the slight shift of $T_d$ in the BNSTZ ceramic may be predominant for the enhancement of dielectric constant and piezoelectric properties. Based on the measurements of the XRPD and dielectric properties, no MPB was recognized by the Sr and Zr substitutions for (Bi, Na) and Ti from x = 0 to 0.075. The relationships between dielectric constant of poled sample at the room temper-
The decrease in the structural distortions of BNSTZ ceramics were recognized by the Sr and Zr substitutions for (Bi, Na) and Ti, no remarkable variation in the covalencies of (Bi, Na and Sr)–O2 and (Bi, Na and Sr)–O3 bonds were recognized by the Sr and Zr substitutions for (Bi, Na) and Ti. Moreover, the decrease in the structural distortions of BNSTZ ceramics may relate to the decrease in \( P_T \) of the ceramics. The depolarization temperature and rhombohedral-tetragonal phase transition temperature are slightly decreased to lower temperature; the slight shift of \( T_d \) in the BNSTZ ceramic may be predominant for the enhancement of dielectric constant and piezoelectric properties. As a result, ferroelectric and piezoelectric properties of the BNSTZ ceramic at \( x = 0.075 \) indicated \( P_T = 28 \mu C/cm^2 \), \( E_d = 31 kV/cm \), \( d_{33} = 86 pC/N \) and \( k_p = 18.7\% \), respectively.

**References**