Ferroelectric and piezoelectric properties, and crystal structures of (Bi₅Na)(Ti,M)O₃ (M = Nb, Ta)

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Bi₀.₅Na₀.₅TiO₃-based materials have drawn much attention as a lead-free ferroelectric and piezoelectric materials. We focused on Bi₀.₅Na₀.₅TiO₃–NaNbO₃ and Bi₀.₅Na₀.₅TiO₃–NaTaO₃ solid solutions, which can be denoted as (Bi₀.₅(1–x)Na₀.₅(1+y))(Ti₁–xMₓ)O₃ (M = Nb, Ta; x = 0.025, 0.05), and then investigated their ferroelectric and piezoelectric properties, and crystal structures using quantum beam. It was found that the ferroelectric and piezoelectric properties were deteriorated by the Nb and Ta substitutions with x = 0.05. Since the crystal structure analysis on the as-synthesized samples could not explain the change in the ferroelectric and piezoelectric properties, we analyzed the crystal structure of the samples after a polarization. It was indicated that the tilting angle of adjacent (Ti,M)O₆ increased significantly only in the case of Bi₀.₅Na₀.₅TiO₃, the Nb- and Ta-substituted samples with x = 0.025. It was considered that the crystal structure after the polarization played an important role for the ferroelectric and piezoelectric properties.

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1. Introduction

Lead zirconium titanate-based materials have been applied widely for electromechanical transduction devices since they show excellent ferroelectric and piezoelectric properties at a wide temperature range. Due to high environmental load of lead compounds, however, a replacement of the materials by lead-free oxides has been in progress actively in the last few decades. As the lead-free ferroelectric and piezoelectric materials, Bi₀.₅Na₀.₅TiO₃ (BNT) based solid solutions with a perovskite structure can be regarded as promising because of its large remanent polarization Pᵣ, and thus relatively good ferroelectric and piezoelectric properties.¹⁻¹⁰ Since it was reported that a solid solution of Bi₀.₅Na₀.₅TiO₃–NaNbO₃ could exhibited Pᵣ of 25–33 μC cm⁻²,²⁻³ we have paid special attention to the solid solution and a similar system, Bi₀.₅Na₀.₅TiO₃–NaTaO₃, which can be also denoted as (Bi₀.₅(1–x)Na₀.₅(1+y))(Ti₁–xMₓ)O₃ (M = Nb and Ta). In this work, these BNT-based solid solutions with a perovskite structure were synthesized, and then ferroelectric and piezoelectric properties of the samples were studied. Moreover, their crystal structures were analyzed by a Rietveld analysis using neutron and synchrotron X-ray diffractions. Especially, the structures after a polarization treatment were investigated in detail since the ferroelectric and piezoelectric properties are directly related to the crystal structures of not the pristine samples but the polarized samples. Based on the results, we discussed effects of Nb or Ta substitutions on the ferroelectric, piezoelectric, and structural properties in (Bi₀.₅(1–x)Na₀.₅(1+y))(Ti₁–xMₓ)O₃ (M = Nb and Ta).

2. Experimental

(Bi₀.₅(1–x)Na₀.₅(1+y))(Ti₁–xMₓ)O₃ (M = Nb and Ta; x = 0–0.05) were synthesized by a solid state reaction method. Bi₂O₃, Na₂CO₃, TiO₂ (anatase), Nb₂O₅, and Ta₂O₅ were mixed for 2 h in appropriate proportions, and then calcined at 850 °C in air for 3 h. After pelletizing the calcined powders, the pellets were sintered at 1150 °C in air for 3 h. The sintered samples were identified by laboratorial X-ray diffraction measurements (MiniFlexII, Rigaku), and the metal compositions were evaluated by inductively coupled plasma spectrometry (ICPE-9000, Shimadzu) and atomic absorption spectrometry (AA-6200, Shimadzu). Densities of the pellets were calculated by the Archimedes method, and the morphologies were observed by a scanning electron microscope (SEM; S-2600N, Hitachi High-Tech.). To investigate ferroelectric and piezoelectric properties, we measured E–P hysteresis loops (TF2000FE, aixACCT), k₃₃ (HP4192A, Agilent) and d₃₃ (PM300, Piezo Test). For the piezoelectric-property measurements, polarized samples were prepared by applying 0–8 kV mm⁻¹ at 70 °C to the pellets. We also measured dielectric constants, ϵ,

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and dielectric loss, $\tan \delta$, as a function of temperature (HP4284A, Agilent). To investigate crystal structures, neutron diffraction patterns [HERMES, JRR-3 ($\lambda = 0.1845$ nm); Echidna, ANSTO ($\lambda = 0.1622$ nm)] and synchrotron X-ray diffraction patterns [BL19B2, Spring-8 ($\lambda = 0.05$ nm)] were measured. Both the synthesized materials and the polarized pellets were ground in a mortar, and then the diffraction measurements of the powders were performed with sample spinning to eliminate contribution of preferred orientation. Rietveld refinements using the data were performed with a RIETAN-FP program, and then refined crystal structures were visualized by a VESTA.

### 3. Results and discussion

#### 3.1 Characterization

**Figure 1** shows X-ray diffraction patterns of the as-synthesized samples. It was demonstrated from this figure that all the diffraction peaks could be attributed to a perovskite structure with a space group of $R3c$. To gain deeper understanding crystal structure, we performed a Rietveld analysis in the following subsections. From SEM images of the samples given in Fig. S1, it was confirmed that all the pellets were sufficiently dense, and the densities could be evaluated as 93% or above by the Archimedes method. Table S1 shows metal compositions of the samples, and the result demonstrated that the analytical compositions were almost equal to the nominal values.

#### 3.2 Electric property

**Figures 2(a) and 2(b)** show $P-E$ hysteresis loops at 5 Hz for the samples. We also evaluated remanent polarizations, $P_r$, and coercive fields, $E_c$, as a function of maximum applied field, $E_{\text{max}}$, and the results are presented in Figs. 2(c) and 2(d). In both the Nb- and Ta-substituted samples, the ferroelectric properties were almost independent of the substitution amount up to $x = 0.025$. On the other hand, the properties were changed significantly in the samples with $x = 0.05$; that is, $P_r$ was decreased by the Nb substitution and $E_c$ was decreased by the Ta substitution.

![Fig. 1. X-ray diffraction patterns of (Bi$_{0.5(1-x)}$Na$_{0.5(1+x)}$)- (Ti$_{1-x}$M$_x$)O$_3$. (a) $x = 0$, (b) M = Nb, $x = 0.025$, (c) M = Nb, $x = 0.05$, (d) M = Ta, $y = 0.025$, (e) M = Ta, $y = 0.05$.](image)

**Table 1** lists electromechanical coupling factors, $k_p$, and piezoelectric constants, $d_{13}$ of the samples, although $k_p$ of the Nb-substituted oxide with $x = 0.05$ could not be measured. Both the Nb- and Ta-substituted samples with $x = 0.025$ exhibited better piezoelectric properties than BNT, and such a tendency agreed well with a previous work in the case of Nb-substituted samples. As the substitution amount became $x = 0.05$, however, the piezoelectric properties were deteriorated considerably.

**Figure 3** shows temperature dependencies of dielectric constant and dielectric loss at 1 MHz. In both the solid-solution systems, the dielectric loss could be suppressed by the partial substitution of Nb and Ta. In the Ta-substituted sample with $x = 0.05$, however, a peak appeared around 200°C in the dielectric constant behavior against temperature [Fig. 3(c)]. This implies that a phase-transition temperature from rhombohedral to tetragonal phase became lower by the partial substitution of Ta.

#### 3.3 Crystal structures of as-synthesized samples (neutron diffraction)

Since ferroelectric and piezoelectric properties in BNT-based materials should be related to crystal structures, we investigated effects of the Nb and Ta substitutions on crystal structures of the as-synthesized samples by means of a Rietveld analysis using neutron diffraction patterns. As can be seen in Table S1, some samples had larger $[\text{Ti}] + [\text{M}]$ ($M = \text{Nb}$ or Ta) values than unity. This indicates that Ti, Nb, and/or Ta occupy the A site in the perovskite structure or that Bi and/or Na are deficient in the samples. The latter situation can be considered as likely due to high vapor pressure of Bi and Na at high temperature. Therefore, we renormalized the metal compositions so that sums of $[\text{Ti}] + [\text{M}]$ became unity and then fixed site occupancies of the metals based on the metal compositions. As an example, **Fig. 4** shows a Rietveld refinement pattern of the Nb-substituted sample with $x = 0.025$, and **Table 2** lists refined structure parameters of the hexagonal cell (S. G.: $R3c$). In this case, atomic positions can be expressed by using four parameters, as given in Table S2. In addition, we can define a tilting angle of adjacent (Ti,M)O$_6$ octahedra, $\omega$, and a compressibility along the $c$ axis, $\zeta$, which can be calculated according to following equations:

$$\tan \omega = 4e\sqrt{3}$$

$$\frac{1 + \zeta}{\cos \omega} = \frac{c}{\sqrt{6a}}$$

| Sample | $k_p$/% | $d_{13}$/pCN$^{-1}$ |
|--------|--------|----------------------|
| $x = 0$ | 15.8   | 75                   |
| M = Nb, $x = 0.025$ | 28.3   | 84                   |
| M = Nb, $x = 0.05$ | —      | 36                   |
| M = Ta, $x = 0.025$ | 19.1   | 83                   |
| M = Ta, $x = 0.05$ | 14.8   | 20                   |
As for \( \zeta \), negative and positive values mean that the octahedron is compressed and elongated along the \( c \) axis, respectively.

Table 3 summarizes the refined structure parameters, \( \omega \), \( \zeta \), quadratic elongations, \( \Delta \), and bond angle variances, \( \sigma \), of (Ti,M)O\(_6\) octahedra. By substituting Nb or Ta for Ti, the quadratic elongation and the bond angle variance were increased, indicating larger distortion within (Ti,M)O\(_6\) although the tilting angle were decreased. Moreover, the compressibility along the \( c \) axis were smaller in both the substituted samples, compared with Bi\(_{0.5}\)Na\(_{0.5}\)TiO\(_3\). These results demonstrated that the octahedron was compressed and then was distorted by the Nb or Ta substitution.

Spontaneous polarizations, \( P_s \), calculated by the refined structure parameters, and a contribution of each site to \( P_s \) are shown in Fig. 5. In the Nb and Ta substituted samples, the contributions of (Bi,Na) and (Ti,M) sites to \( P_s \) were smaller and larger, respectively, compared with Bi\(_{0.5}\)Na\(_{0.5}\)TiO\(_3\). As a result, \( P_s \) was almost independent of the metal composition. Such tendencies cannot explain the result that the ferroelectric and piezoelectric properties were deteriorated by Nb or Ta substitution with \( x = 0.05 \). Therefore, we performed the similar structure analysis on the samples after an electric polarization, in a following subsection.

### 3.4 Crystal structures of polarized samples (synchrotron X-ray diffraction)

According to previous works, an electric field induced phase transition was observed in some ferroelectric materials. Taking this result into account, we performed the Rietveld refinement using synchrotron X-ray diffraction for the polarized samples (after the piezoelectric tests), as in the case of the as-synthesized samples. In the experiments, the samples before the polarization were also ground in the same way as that after the polarization to eliminate an effect of the mechanical stress on the structural change. As an example, Fig. 6 shows the refinement pattern of the Nb-substituted sample with \( x = 0.025 \). Fig. 7 also presents a change of X-ray diffraction pattern by the polarization for all the sample. As can be seen in Fig. 7, peak splits after the polarization could be observed only in Bi\(_{0.5}\)Na\(_{0.5}\)TiO\(_3\), the Nb- and Ta-substituted samples with \( x = 0.025 \), which showed better ferroelectric and piezoelectric properties.
than the others. To gain deeper understanding on the crystal structures, the tilting angles of (Ti,M)O₆ and the compressibility along the c axis of the polarized samples are summarized in Table 4. It was found that the compressibilities along the c axis were decreased after the polarization only in the case of Bi₀.₅Na₀.₅TiO₃, the Nb- and Ta-substituted samples with x = 0.025, which showed better ferroelectric and piezoelectric properties. Moreover, the tilting angle, ω, in these samples became larger significantly after the polarization, and then the values were larger than those of the Nb- and Ta-substituted samples with x = 0.05. From the results, it can be concluded that

Table 2. Refined structure parameters of (Bi₀.₅(1−x)Na₀.₅(x+1)) (Ti₁−xMₓ)O₃ (x = 0.025). B are atomic displacement parameters. Numbers in parentheses are estimated standard deviations of last significant digits, and those without a deviation were fixed. R-factors were Rₚ = 7.43 %, Rₑ = 5.60 %, Rₑₑ = 5.40 %, and S = 1.37. Refined lattice parameters were a = 0.55043(6) nm, c = 1.3548(1) nm

| Atom | Site | g  | x  | y  | z  | 10² × B/Å² |
|------|------|----|----|----|----|-------------|
| Bi   | 6a   | 0.469 | 0 | 0 | 0.263(8) | 3.2(1) |
| Na   | 6a   | 0.508 | 0 | 0 | 0.010(1) | 0.2(1) |
| Ti   | 6a   | 0.977 | 0 | 0 | 0.010(1) | 0.2(1) |
| Nb   | 6b   | 0.023 | 0 | 0 | 0.367(1) | 2.01(7) |
| O    | 18b  | 0.99(1) | 0.125(9) | 0.336(1) | 1/12 | 2.01(7) |
the change in the crystal structures, especially the tilting angles, by the polarization might have a positive influence on the piezoelectric properties. In other words, one should investigate crystal structures of Bi$_{0.5}$Na$_{0.5}$TiO$_3$-based materials after a polarization.

4. Conclusions

In this work, we studied ferroelectric and piezoelectric properties of (Bi$_{0.5}$Na$_{0.5}$Ti$_{1-x}$M$_x$)$_3$O$_9$ (M = Nb and Ta, x = 0.025 and 0.05), and then analyzed the crystal structures.

| Table 3. Structural parameters of (Bi$_{0.5}$(1-x)Na$_{0.5}$(1+x))(Ti$_{1-x}$M$_x$)O$_3$ |
|-----------------------------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| x = 0 M = Nb | M = Nb x = 0.05 | M = Ta x = 0.025 | M = Ta x = 0.05 |
| $R_{wp}$/% | 8.62 | 7.43 | 9.47 | 4.87 | 4.57 |
| $R_p$/% | 6.55 | 5.60 | 6.38 | 3.85 | 3.63 |
| $R_f$/% | 6.02 | 5.40 | 5.40 | 4.96 | 5.11 |
| S | 1.43 | 1.37 | 1.48 | 0.99 | 0.89 |
| $a$/nm | 0.54952(5) | 0.55043(6) | 0.54964(7) | 0.54876(6) | 0.54894(6) |
| $c$/nm | 1.3552(1) | 1.3548(1) | 1.3509(2) | 1.3503(1) | 1.3493(2) |
| $\omega$/degree | 8.93(1) | 8.34(1) | 7.99(1) | 8.47(1) | 8.14(1) |
| $\zeta \times 10^4$ | -0.54 | -0.58 | -0.63 | -0.64 | -0.66 |
| $\Delta$ | 1.002 | 1.005 | 1.005 | 1.003 | 1.005 |
| $\sigma^2$/degree$^2$ | 5.51 | 13.9 | 15.7 | 7.3 | 15.5 |

Fig. 5. Spontaneous polarization, $P_s$, and contribution of each ion to $P_s$ of (a) (Bi$_{0.5}$(1-x)Na$_{0.5}$(1+x))(Ti$_{1-x}$Nb$_x$)O$_3$ and (b) (Bi$_{0.5}$(1-x)Na$_{0.5}$(1+x))(Ti$_{1-x}$Ta$_x$)O$_3$. $\triangle$ $\blacktriangle$: Spontaneous polarization, $\circ$ $\bullet$: Contribution of Bi/Na site, $\square$ $\blacksquare$: Contribution of Ti/Nb/Ta site.

Fig. 6. Rietveld refinement pattern of (Bi$_{0.5}$(1-x)Na$_{0.5}$(1+x))(Ti$_{1-x}$Nb$_x$)O$_3$ ($x = 0.025$) after the polarization. Plus marks show observed synchrotron X-ray diffraction intensities, and a solid line represents calculated intensities. Vertical makes below the patterns indicate the positions of allowed Bragg refractions. A curve at the bottom is a difference between the observed and calculated intensities in the same scale.
structures by a Rietveld analysis. Although the ferroelectric and piezoelectric properties were almost independent of the Nb and Ta substitution at least up to $x = 0.025$, these properties were deteriorated in the Nb- and Ta-substituted samples with $x = 0.05$. To discuss such changes from the viewpoint of the crystal structures, we performed the crystal structure analysis on the samples after the polarization. As a result, it was found that the tilting angle of adjacent (Ti,M)O$_6$ became larger only in (Bi$_{0.5(1-x)}$Na$_{0.5(1+x)}$)(Ti$_{1-x}$M$_x$)O$_3$ with $x = 0.025$, and the values were larger than those of the samples with $x = 0.05$. Therefore, it could be concluded that the structure change after the polarization had a significant influence on the ferroelectric and piezoelectric properties.

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References

1) T. Takenaka, K. Maruyama and K. Sakata, *Jpn. J. Appl. Phys.*, 30, 2236–2239 (1991).
2) T. Takenaka, T. Okuda and T. Takegahara, *Ferroelectrics*, 196, 175–178 (1997).
3) C. Xu, D. Lin and K. W. Kwok, *Solid State Sci.*, 10, 934–940 (2008).
4) D. Lin, K. W. Kwok and H. L. W. Chan, *Solid State Ionics*, 178, 1930–1937 (2008).
5) M. Izumi, K. Yamamoto, M. Suzuki, Y. Noguchi and M. Miyayama, *Appl. Phys. Lett.*, 93, 242903 (2008).
6) Y. Hiruma, K. Yoshii, H. Nagata and T. Takenaka, *J. Appl. Phys.*, 103, 084121 (2008).
7) C. Zhou, X. Liu, W. Li and C. Yuan, *Mater. Chem. Phys.*, 114, 832–836 (2009).
8) Y.-J. Dai, S. Zhang, T. R. Shrout and X.-W. Zhang, *J. Am. Ceram. Soc.*, 93, 1108–1113 (2010).
9) Y. Yuan, C. J. Zhao, X. H. Zhou, B. Tang and S. R. Zhang, *J. Electroceram.*, 25, 212–217 (2010).
10) F. Wang, M. Xu, Y. Tang, T. Wang, W. Shi and C. M. Leung, *J. Am. Ceram. Soc.*, 95, 1955–1959 (2012).
11) F. Izumi and K. Momma, *Solid State Phenom.*, 130, 15–20 (2007).
12) K. Momma and F. Izumi, *J. Appl. Crystallogr.*, 44, 1272–1276 (2011).
13) H. D. Megaw and C. N. W. Darlington, *Acta Crystallogr. A*, 31, 161–173 (1975).
14) K. Robinson, G. V. Gibbs and P. H. Ribbe, *Science*, 172, 567–570 (1971).
15) M. K. Durbin, E. W. Jacobs, J. C. Hicks and S.-E. Park, *Appl. Phys. Lett.*, 74, 2848–2850 (1999).
16) T. Iamsasri, G. Tutuncu, C. Uthaisar, S. Wongsaenmai, S. Pojprapai and J. L. Jones, *J. Appl. Phys.*, 112, 042101 (2015).

![Fig. 7. Comparison of synchrotron X-ray diffraction patterns between unpolarized and polarized samples. (a) $x = 0$, (b) M = Nb, $x = 0.025$, (c) M = Nb, $x = 0.05$, (d) M = Ta, $y = 0.025$, (e) M = Ta, $y = 0.05$. Patterns of unpolarized and polarized samples are given in I and II, respectively.](image)

![Table 4. Tilting angles of (Ti,M)O$_6$ and the compressibility along the c axis of (Bi$_{0.5(1-x)}$Na$_{0.5(1+x)}$)(Ti$_{1-x}$M$_x$)O$_3$ before and after the polarization](table)