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Piezoelectric Anisotropies of Bismuth Layer-Structured Ferroelectrics

Hajime Nagata, Takeshi Takahashi and Tadashi Takenaka
Faculty of Science and Technology, Science University of Tokyo, Noda, Chiba-ken, 278-8510, Japan
Fax: 81-471-23-0856, e-mail: nagata@takenaka.ee.noda.sut.ac.jp

Anisotropic characterizations of bismuth layer-structured ferroelectrics (BLSF) are investigated for two series of $Na_{(m-3+x)/2}Bi_{(m+5-x)/2}Ti_{m-x}Nb_xO_{3m+3}$ [NBTN$m(x)$], (m=2, $1 \leqq x \leqq 2$ and $3 \leqq m \leqq 5$, $0 \leqq x \leqq m$) and $Sr_{m-3+x}Bi_{4-x}Ti_{m-x}Ta_xO_{3m+3}$ [SBTT$m(x)$] (m=2, $1 \leqq x \leqq 2$ and $3 \leqq m \leqq 5$, $0 \leqq x \leqq 2$. Curie temperatures, T_c, of SBTTm increase as the Sr concentration decreases and reach the maximum value of 760 ℃ for SBTT2(1.25). In the series of NBTN$m(x)$, NBTN2(1.1) [$Na_{0.05}Bi_{2.95}Ti_{0.9}Nb_{1.1}O_9$] ceramic shows the highest T_c more than 900 ℃ and the largest anisotropy k_{33}/k_{31}(=4.3). It seems that grain-oriented BLSF ceramics of SBTTm and NBTNm series have the large anisotropy in their electrical properties.
Key words : bismuth layer-structured ferroelectrics, BLSF, anisotropy, electromechanical coupling factor, Curie temperature

1. INTRODUCTION

A family of bismuth layer-structured ferroelectrics (BLSF) is attractive from applicational viewpoints for electronic materials such as dielectrics, piezoelectrics and pyroelectrics because BLSF are characterized by their low dielectric constant, ε_s, high Curie temperature, T_c, and large anisotropy, k_t/k_p or k_{33}/k_{31} in electromechanical coupling factors, k. Therefore, the BLSF ceramics are seen as a superior candidate for piezoelectric sensor materials with wide working temperature ranges and anisotropic characteristics, or for pyroelectric sensor materials with a large figure of merit.

The bismuth layer-structured oxide (BLSO) are generally represented by the chemical formula, $A_{m-1}Bi_2B_mO_{3m+3}$, where A is a combination of one or more mono-, di- and trivalent ions and B is a combination of tetra-, penta- and hexavalent ions, and the integer m takes any of the values from 1 to 5. BLSO have BO_6 octahedra like perovskite, pyrochore and tungsten-bronze structures and many of them seem to be ferroelectrics. The condition of electrical neutrality gives the formula $(m-1)N(A)+mN(B)=6m$, where $N(A)=\Sigma N(A)/(m-1)$ and $N(B)=\Sigma N(B)/m$ indicate the mean valences of the A and the B ions. However, BLSO have a great variety of available combinations of A and B ions, respectively.

In this paper, as a part of studies on BLSF compounds, anisotropic characterizations of BLSF are investigated for two series of $Na_{(m-3+x)/2}Bi_{(m+5-x)/2}Ti_{m-x}Nb_xO_{3m+3}$ [NBTN$m(x)$], (m=2, $1 \leqq x \leqq 2$ and $3 \leqq m \leqq 5$, $0 \leqq x \leqq m$) and $Sr_{m-3+x}Bi_{4-x}Ti_{m-x}Ta_xO_{3m+3}$ [SBTT$m(x)$] (m=2, $1 \leqq x \leqq 2$ and $3 \leqq m \leqq 5$, $0 \leqq x \leqq 2$).

2. EXPERIMENTAL

Ceramic samples are prepared by a conventional sintering technique. Reagent-grade oxide or carbonate powders of Na_2CO_3, $SrCO_3$, Bi_2O_3, Nb_2O_5, TiO_2 and Ta_2O_5 with 99+% purity were used as the starting materials. These materials mixed by ball milling were calcined at 800 ℃ for 2 h. After calcining, the ground and ball-milled powders were pressed into disks of 20 mm in diameter and about 1～15 mm in thickness. These disks were sintered at 1100～1200 ℃ for 2 h under an air atmosphere.

The crystalline structure was confirmed by an X-ray diffraction using CuKα radiation through a Ni filter at a scanning speed of 1 deg/min. Electrodes were made with fired-on Ag-Pd or Pt paste for electrical measurements such as dielectric and piezoelectric properties. The temperature dependences of dielectric constant ,ε_s, and dielectric loss tangent, tan δ, were measured at 1 or 10 MHz using an automatic dielectric measurement system with a multifrequency LCR meter (YHP 4275A) in the temperature range from RT to 950 ℃. The D-E hysteresis loop was observed at RT using a standard Sawyer-Tower circuit at 50Hz. Piezoelectric properties were measured by means of the resonance antiresonance method on the basis of IEEE standards using an impedance analyzer (YHP 4192A). The electromechanical coupling factor, k_{33}, were calculated from the resonance and antiresonance frequencies using Onoe's formula. Temperature dependence of resistivity was measured by using a high resistance meter (YHP 4329A).

3. RESULTS AND DISCUSSION

3.1 $Na_{(m-3+x)/2}Bi_{(m+5-x)/2}Ti_{m-x}Nb_xO_{3m+3}$ system

Figure 1 shows the phase relation between well-known bismuth layer-structured ferroelectrics such as Bi_3TiNbO_9 (BTN) (m=2), $Na_{0.5}Bi_{2.5}Nb_2O_9$ (NBN) (m=2), $Bi_4Ti_3O_{12}$ (BIT) (m=3) and $Na_{0.5}Bi_{4.5}Ti_4O_{15}$ (NBT) (m=4) including perovskite compounds $(Bi_{0.5}Na_{0.5})TiO_3$ and $NaNbO_3$. The general formula of the phase relation in Fig.1 is as follows:

$$Na_{(m-3+x)/2}Bi_{(m+5-x)/2}Ti_{m-x}Nb_xO_{3m+3}$$

where x is the number of Nb ions in the layer structure and $1 \leqq x \leqq 2$ for $m=2$ and $0 \leqq x \leqq m$ for $3 \leqq m \leqq 5$. This formula is abbreviated to NBTN$m(x)$. The B-site of the left ($x=0$) or right ($x=m$) longitudinal straight line, that is, $Na_{(m-3)/2}Bi_{(m+5)/2}Ti_mO_{3m+3}$ ($3 \leqq m \leqq 5$) or $Na_{m-1.5}Bi_{2.5}Nb_mO_{3m+3}$ ($2 \leqq m \leqq 5$), is only occupied by Ti^{4+} or Nb^{5+} ion.

X-ray diffraction patterns of NBTN2 at room temperature show the same patterns as BTN ($m=2$). These compounds seem to be BLSO with $m=2$. It was easy to sinter these ceramics with a high measured density ratio than 95% to theoretical density. Figure 2 shows lattice constants, a and b, and a lattice distortion, b/a, for NBTN2 as a function of Nb ions. Lattice constants, a and b, become longer and the lattice distortion, b/a, becomes smaller with increasing the Nb concentration (x).

Figure 3 shows the Curie temperature, T_c, of NBTB2 as a function of Nb concentration (x). The T_c becomes lower with increasing the Nb concentration. In other word, the T_c becomes higher with increasing the Bi concentration. It is considered that Bi ions are strongly influence on the increase of the T_c and the anisotropy, k_t/k_p or k_{33}/k_{31}. NBTN2(1.05) ceramic displays the highest T_c of 905 ℃. The T_c of NBTNm series[4] becomes higher with decreasing the layer-number, m. Therefore, it is clear that NBTN2 have a wide working temperature range for piezoelectric sensor materials.

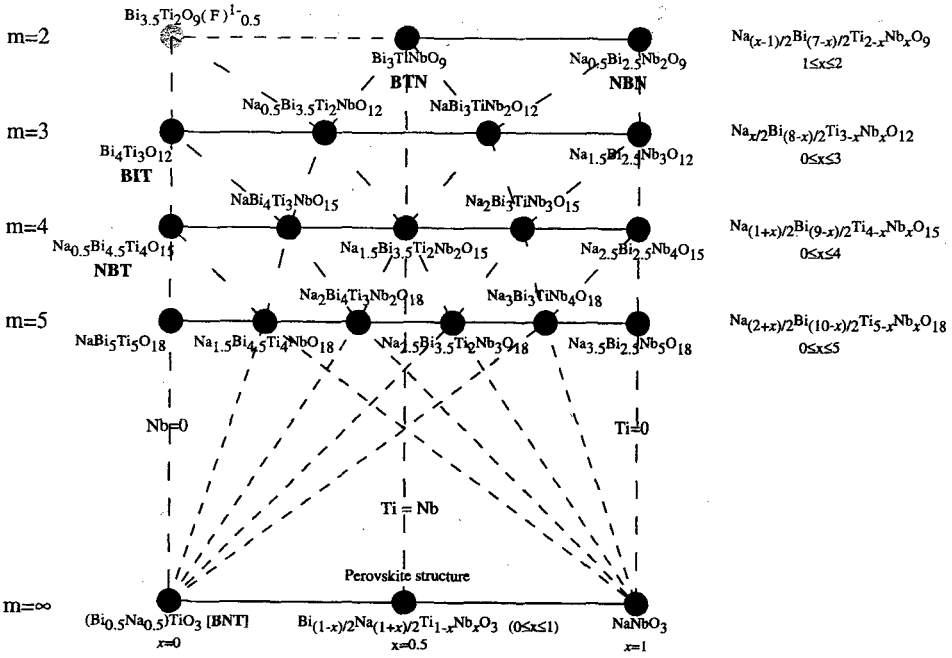

Fig. 1 The phase relation between bismuth layer-structured ferroelectrics such as Bi_3TiNbO_9 (BTN) ($m=2$), $Na_{0.5}Bi_{2.5}Nb_2O_9$ (NBN) ($m=2$), $Bi_4Ti_3O_{12}$ (BIT) ($m=3$) and $Na_{0.5}Bi_{4.5}Ti_4O_{15}$ (NBT) ($m=4$) including perovskite compounds $(Bi_{0.5}Na_{0.5})TiO_3$ and $NaNbO_3$.

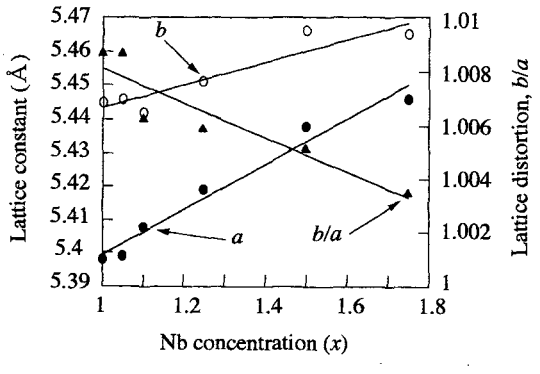

Fig. 2 Lattice constants, a and b, and a lattice distortion, b/a for NBTN2 as a function of Nb concentration (x).

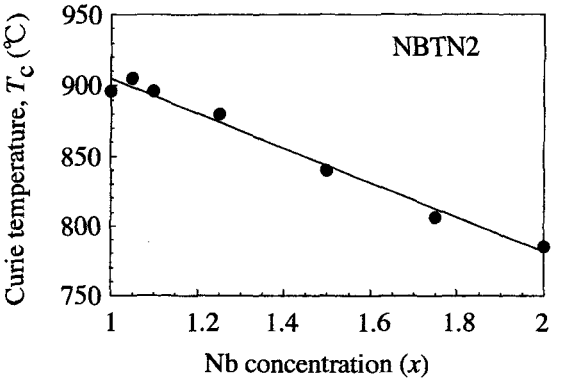

Fig. 3 Curie temperature, Tc, for NBTB2 as a function of Nb concentration (x).

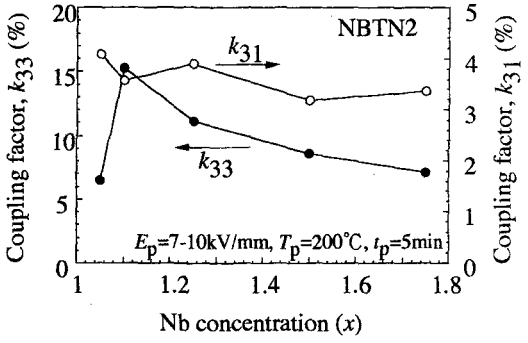

Fig. 4 Electromechanical coupling factors, k_{33} and k_{31}, of NBTN2 as a function of Nb concentration (x).

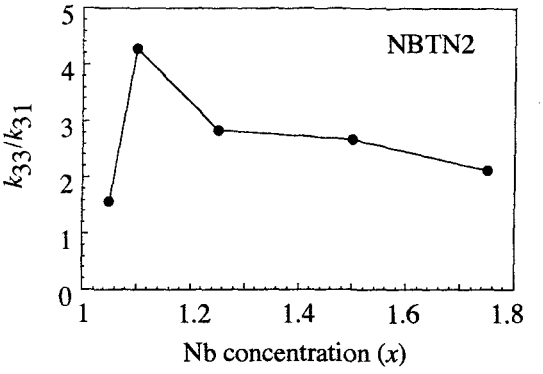

Fig. 5 The anisotropy, k_{33}/k_{31}, in electromechanical coupling factor of NBTN2 as a function of Nb concentration (x).

Figure 4 shows electromechanical coupling factors, k_{33} and k_{31} of NBTN2 as a function of Nb concentration (x). As a poling condition, poling field, E_p=7-10 kV/mm , poling temperature, T_p=200 ℃, and poling time, t_p=5 min were chosen for NBTN2, respectively. The largest value of k_{33} (=0.153) was obtained for the NBTN2(1.1) ceramic. However, the k_{33} of NBTB2(1.0) and NBTN2(1.05) ceramics is relatively smaller than that of NBTN2(1.1) because it was very hard to pole these ceramics. Figure 5 shows the anisotropy, k_{33}/k_{31}, of NBTB2 as a function of Nb concentration (x). The largest anisotropic characteristic of the k_{33}/k_{31} displays at x=1.1, that is, the k_{33}/k_{31}=4.3 for NBTN2(1.1). In the future work, it should be confirmed that grain-oriented NBTN2 ceramics show the larger anisotropies in coupling factors.

Dielectric and piezoelectric properties of NBTN2 ceramics were summarized in Table I. The $\varepsilon_{33}^T/\varepsilon_0$ are lower than those of PZT system. It also seems that NBTN2 ceramics are superior for high frequency applications.

Table I Dielectric and piezoelectric properties for NBTN2(x).

	NBTN2(1.05)	NBTN2(1.1)	NBTN2(1.25)	NBTN2(1.5)	NBTN2(1.75)
ρ [g/cm^3]	7.85	7.76	7.70	7.70	7.44
T_c [℃]	905	896	880	840	785
$\varepsilon_{33}^T/\varepsilon_0$	118	123	117	121	119
k_{33} [%]	6.45	15.3	11.1	8.54	7.11
k_{31} [%]	4.08	3.57	3.91	3.19	3.36
k_{33}/k_{31}	1.58	4.28	2.83	2.67	2.11
d_{33} [pC/N]	5.87	15.0	10.5	8.31	6.81

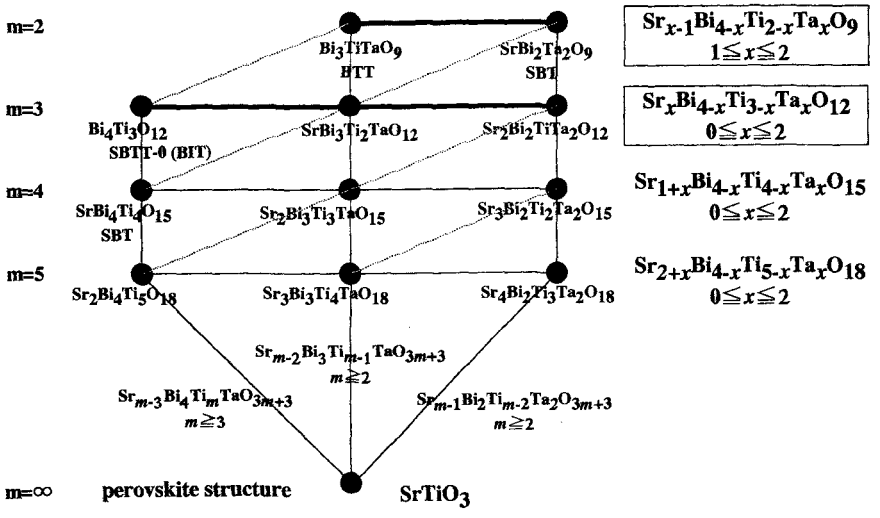

Fig. 6. Phase relation between well-known bismuth layer-structured ferroelectrics such as Bi_3TiTaO_9 (BTT) (m=2), $SrBi_2Ta_2O_9$ (SBT) (m=2), and $Bi_4Ti_3O_{12}$ (BIT) (m=3).

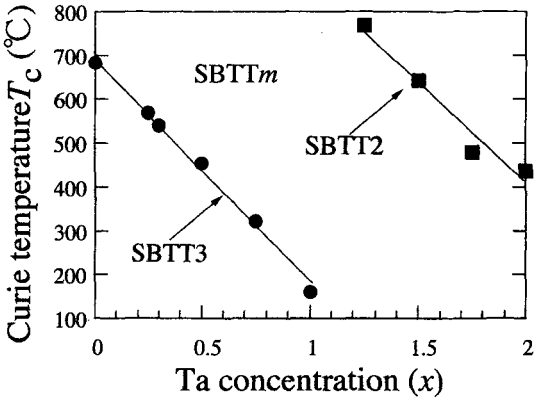

Fig. 7 Curie temperature, T_c, as a function of Sr concentration (x) for SBTT2 and SBTT3.

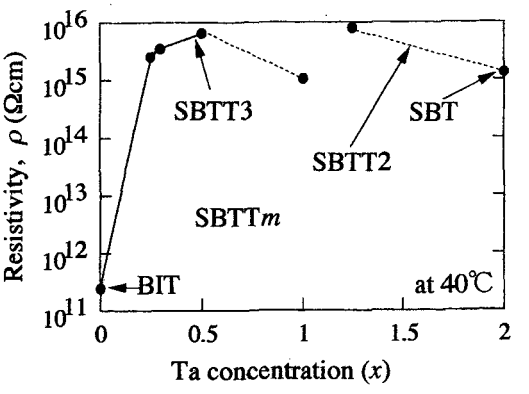

Fig. 8 Resistivity, ρ, as a function of Sr concentration (x) for SBTT2 and SBTT3 at 40 ℃.

3.2 $Sr_{m-3+x}Bi_{4-x}Ti_{m-x}Ta_xO_{3m+3}$ system

Figure 6 shows the phase relation between well-known bismuth layer-structured ferroelectrics such as Bi_3TiTaO_9 (BTT) (m=2), $SrBi_2Ta_2O_9$ (SBT) (m=2) and $Bi_4Ti_3O_{12}$ (BIT) (m=3) including a perovskite compound $SrTiO_3$. The general formula of the phase relation in Fig. 6 is as follows:

$$Sr_{m-3+x}Bi_{4-x}Ti_{m-x}Ta_xO_{3m+3}$$

where x is the number of Ta ions in the layer structure and $1 \leqq x \leqq 2$ for m=2 and $0 \leqq x \leqq 2$ for $3 \leqq m \leqq 5$. Hereafter the formula is abbreviated to SBTTm(x).

X-ray diffraction patterns of SBTTm show the single phase of bismuth layer-structured compounds with an orthorhombic symmetry for m=2 and 3. The ceramic samples of SBTT2 and SBTT3 were easily sintered with a high measured density ratio more than 95% to theoretical density except SBTT2(1).

Figure 7 shows the T_c of SBTT2 and SBTT3 as a function of Sr concentration (x). The T_c is relatively high comparing with those of PZT system. The T_c of the SBTT2 is higher than those of SBTT3. The T_c shifts to lower temperature with increasing Sr concentration (x). The reason why the T_c becomes lower temperature is due to the increase of modified $SrTiO_3$. SBTT2(1.2) ceramic has the highest T_c (=785 ℃) in the prepared samples.

Figure 8 shows a resistivity, ρ, as a function of Sr concentration (x) for SBTT2 and SBTT3 at 40 ℃. SBTT2 and SBTT3 have the high ρ of about 10^{14}-10^{15} Ω·cm except SBTT3(0) (BIT).

4. CONCLUSIONS

Anisotropic piezoelectric characterizations of BLSF are investigated for two series of $Na_{(m-3+x)/2}Bi_{(m+5-x)/2}Ti_{m-x}Nb_xO_{3m+3}$ [NBTNm(x)], (m=2, $1 \leqq x \leqq 2$ and $3 \leqq m \leqq 5$, $0 \leqq x \leqq m$) and $Sr_{m-3+x}Bi_{4-x}Ti_{m-x}Ta_xO_{3m+3}$ [SBTTm(x)] (m=2, $1 \leqq x \leqq 2$ and $3 \leqq m \leqq 5$, $0 \leqq x \leqq 2$). In NBTN2 series, NBTN(1.1) [$Na_{0.05}Bi_{2.95}Ti_{0.9}Nb_{1.1}O_9$] has higher T_c of 896 ℃ and the largest anisotropy, k_{33}/k_{31}(=4.3). It seems that NBTN2 series have the large anisotropy in their electrical properties. In SBTTm series, SBTT2(1.25) ceramic shows the highest T_c of 785 ℃. NBTN2 and SBTT2 ceramics are seen as a superior candidate for piezoelectric sensor materials with high-T_c and large anisotropic characteristics.

5. ACKNOWLEDGMENT

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