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Temperature dependence of piezoelectric properties on Nd and V co-substituted $Bi_4Ti_3O_{12}$ ceramics for ceramic resonator applications

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Abstract

The temperature dependences of the piezoelectric properties of $(Bi_{4-y}Nd_y)_{1-(x/12)}(Ti_{3-x}V_x)O_{12}$ [BNTV-x, y ($x = 0.01$, $y = 0.00$–1.00)] were investigated for environmentally friendly lead-free piezoelectric ceramic resonators with low-temperature coefficients of resonance frequency, *TC-f*. The |*TC-f*| in the (33) mode improved with increasing concentration of modified Nd ions, y, and exhibited the smallest |*TC-f*| value of 77.4 ppm/°C at $y = 0.75$ (BNTV-0.75). The |*TC-f*| in the other vibration mode (t), was also investigated for the BNTV-0.75 ceramic, and a smaller value of 42 ppm/°C was obtained. The (t) mode of the BNTV-0.75 ceramic showed excellent piezoelectric properties: $Q_m = 4200$, $Q_{e\ max} = 31$ and *TC-f* = −49.8 ppm/°C. These properties are very similar to those of commercialized hard PZT ceramics for resonator applications. The BNTV-0.75 ceramic seems to be a superior candidate material for lead-free piezoelectric applications of ceramic resonators.

Keywords: A. Grain growth; A. Sintering; C. Piezoelectric properties

1. Introduction

Piezoelectric ceramics have been widely used for several applications, such as those in filters for mobile communications, resonators for microprocessors, actuators for inkjet printers, transformers for back light inverters of liquid crystal displays and sensors for detecting shock in hard disk drives (HDDs). The materials used for these applications are currently based on lead titanate ($PbTiO_3$) and lead zirconate titanate (PZT), which are utilized with several compositional modifications.

The family of bismuth layer-structured ferroelectrics (BLSFs) [1–4] is one of the attractive lead-free materials from the viewpoint of their application to electronic functional devices such as resonators and high temperature sensors [5–8]. In the case of resonator applications, piezoelectric elements are used as inductors, thus, it is necessary that they have a high electrical quality factor, $Q_{e\ max}$, and a high mechanical quality factor, Q_m, rather than a large electromechanical coupling factor, k. BLSFs are characterized by their high quality factors, Q_m [9–12], and $Q_{e\ max}$ [13], and low-temperature coefficient of resonance frequency, *TC-f* [14–16]. Therefore, we have studied BLSF materials as an excellent candidate for lead-free materials for ceramic resonator applications. Furthermore, BLSFs generally have higher Curie temperatures, T_c, than PZT based materials. In addition, because of their small coupling factor, they can also have higher frequency accuracy with fine tolerance [17].

The chemical formula of BLSF is generally represented by $(Bi_2O_2)^{2+}(A_{m-1}B_mO_{3m+1})^{2-}$, where A is a combination of one or more mono-, di-, or trivalent ions, or a mixture of them, B is a combination of tetra-, penta-, and hexavalent ions, and m is an integer corresponding to the number of BO_6 octahedra in pseudo perovskite blocks. In the crystal structure, perovskite blocks $(A_{m-1}B_mO_{3m+1})^{2-}$, are interleaved with $(Bi_2O_2)^{2+}$ layers along the c-axis, and ferroelectricity arises mainly in the perovskite blocks.

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Recently, bismuth titanate, $Bi_4Ti_3O_{12}$ (BIT, $m = 3$), has been studied widely and actively due to its large spontaneous polarization [2]. Furthermore, Nd substituted BIT (BNT) and V co-substituted BNT (BNTV) have received a great deal of attention because these substitutions lead to larger remanent polarization, P_r [17–20]. In addition, the defect formation mechanism of these systems has been extensively explored and it is recognized that their defect structure is closely related to the polarization properties [21–24]. From our previous studies, the piezoelectric properties of $(Bi_{4-y}Nd_y)_{1-(x/12)}(Ti_{3-x}V_x)O_{12}$ [BNTV-x, y ($x = 0$–0.03, $y = 0.00$–1.00)] ceramics were reported by focusing on Q_m and $Q_{e\ max}$ [25]. The excellent piezoelectric properties of both high Q_m ($\sim$4200) and $Q_{e\ max}$ ($\sim$51) were obtained in the BNTV-0.01, 0.75 ceramic by suppressing the formation of oxygen vacancies and promoting domain switching during the poling process. These values are excellent for the ceramic resonator application with higher frequency accuracy and fine tolerance. However, the *TC-f* behaviors for this system have not been reported yet. *TC-f* is very important for the practical use of resonator applications. In the practical level, the $|TC\text{-}f|$ value of 0 ppm/°C is ideal but at least 50 ppm/°C is required. In this study, the temperature dependences of piezoelectric properties were investigated for BNTV ceramics in the (33) and (t) modes.

2. Experimental procedure

Ceramic samples of $(Bi_{4-y}Nd_y)_{1-(x/12)}(Ti_{3-x}V_x)O_{12}$ [BNTV-y ($x = 0.01$, $y = 0.00$–1.00)] and $Bi_{4-y}Nd_yTi_3O_{12}$ [BIT-Nd ($x = 0.00$, $y = 0.75$)] were prepared by a conventional sintering technique. Reagent-grade oxide and hydroxide powders of Bi_2O_3, TiO_2 V_2O_5 and $Nd(OH)_3$ of more than 99.9% purity were used as the starting materials. These materials were mixed by ball milling and calcined at 600 °C for 1 h and 850 °C for 2 h. After calcining, the ground and ball-milled powders were pressed into disks 20 mm in diameter and about 10 mm in thickness. These disks were sintered at 1070–1150 °C for 2 h in air.

The crystal structure was confirmed by X-ray diffraction analysis using Cu Kα radiation. Samples were polished and thermally etched for microstructural examination by scanning electron microscopy (SEM, HITACHI S-2400). The temperature dependences of dielectric constant, ε_r, and dielectric loss tangent, tan δ, were measured at 1 MHz using an automatic dielectric measurement system with a multifrequency LCR meter (HP 4275A) in the temperature range from room temperature to 750 °C. Specimens for piezoelectric measurements were polarized in a stirred silicone oil bath at applied fields of $E_p = 3$–12 kV/mm, temperatures of $T_p = 100$–200 °C, and time durations of $t_p = 7$–15 min. Piezoelectric properties were measured by a resonance–antiresonance method on the basis of IEEE standards, using an impedance analyzer (HP 4294A). Longitudinal vibrations of the (33) and (t) modes were measured using a rectangular specimen of 4 mm × 2 mm × 2 mm and a plate specimen of Ø16 mm × 1.5 mm. The electromechanical coupling factor, k_{33}, was calculated from the resonance and antiresonance frequencies. $Q_{e\ max}$ is defined as the tangent of the maximum phase, θ_{max}, in the inductance frequency region between resonance and anti-resonance frequency. The temperature dependence of f_r was measured in the range from −25 to 125 °C using a temperature controller, TABAI-ESPEC SU-240. The temperature coefficient, $TC\text{-}f_r$, is defined as follows:

$$TC\text{-}f_r = \frac{f_{r[125\,^\circ C]} - f_{r[-25\,^\circ C]}}{f_{r[20\,^\circ C]} \times T} \tag{1}$$

where f_r [−25 °C] and f_r [125 °C] are the resonance frequencies at −25 and 125 °C, respectively, and T is the measurement temperature range (150 °C).

3. Results and discussion

X-ray diffraction patterns for BNTV and BIT-Nd ceramics show a single phase of bismuth layer structured compounds with the layer number $m = 3$. In BNTV-y ($y = 0.0$–1.0) ceramics, the lattice distortion ratio of a- and b-lattice parameters, a/b, decreased to $a/b \approx 1$ with increasing amount of Nd. This tendency was in good agreement with the examination of rare-earth-substituted bismuth titanates reported by Wolfe and Newnham [19]. Prepared samples have high relative density ratios of more than 95% relative to the theoretical density.

Table 1 shows the sintering temperatures and resistivities, ρ, of BIT, BIT-Nd and BNTV-0.75 ceramics. The ρ value of BIT-Nd, BIT-V and BNTV ceramics were about 10^{13} to 10^{14} Ω cm at room temperature. It is thought that the cause of the low resistivity of the BIT ceramic is the Bi vaporization during sintering at a high temperature of 1100 °C. As V substitution has an effect of lowering the sintering temperature, it is expected to suppress the Bi vaporization [24]. On the other hand, the sintering temperature of the Nd-substituted BIT (BIT-Nd) was 1150 °C. However, the BIT-Nd ceramic maintains high resistivity (about 10^{13} Ω cm). This result implies that Nd ions preferentially substitute unstable Bi ions, which easily vaporize from the perovskite block. The optimum charge neutralities were observed for the composition ratios of $x = 0.01$ and $y = 0.75$ (BNTV-0.75).

Fig. 1 shows the frequency dependence of impedance, Z (magnitude, $|Z|$, and phase, θ) for BNTV-0, 0.25 and 0.75

Table 1
Sintering temperatures and resistivities of BIT, BIT-Nd and BNTV-0.75 ceramics

	BIT	BIT-Nd ($y = 0.75$)	BIT-V ($x = 0.01$)	BNTV-0.75
Sintering temperature (°C)	1100	1150	1010	1090
Resistivity, ρ (Ω cm)	1.67×10^{10}	1.83×10^{13}	4.57×10^{13}	8.32×10^{13}

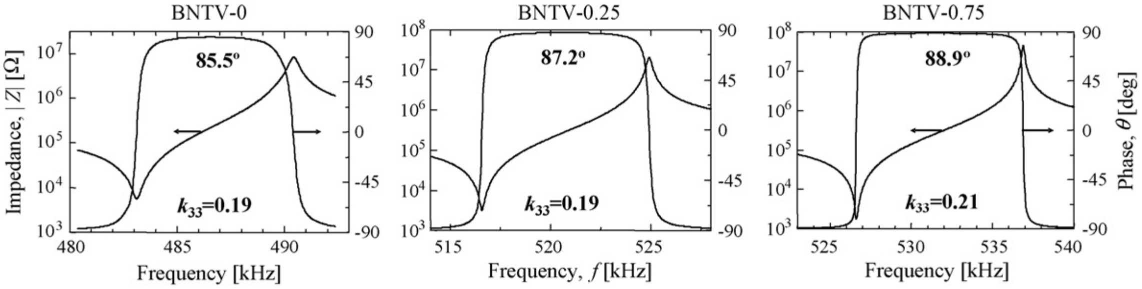

Fig. 1. Frequency dependence of impedance, Z (magnitude, $|Z|$, and phase, θ) for BNTV-0, 0.25 and 0.75 ceramics.

ceramics. The k_{33} of BNTV ceramics increased with increasing concentration of Nd ions. The largest k_{33} of the BNTV-y ceramic was 0.21 at $y = 0.75$, which is one of the highest k_{33} values of BLSF ceramics. Furthermore, the maximum θ in the frequency dependence of impedance is one of the standard parameters for indicating the degree of full poling. The maximum θ value of BNTV-0, 0.25 and 0.75 ceramics were 85.5°, 87.2° and 88.9°, respectively. The BNTV-0.75 ceramic was easier to pole sufficiently than other ceramics. These results also contribute to the Q_e and Q_m values. The highest Q_e and Q_m values of 51 and 4200 were obtained at BNTV-0.75 by suppressing the formation of oxygen vacancies and promoting domain switching during the poling process.

Fig. 2 shows the temperature dependences of the resonance frequencies in the longitudinal (33) mode of BIT-Nd, BIT-V, BNTV-0.25 and 0.75. Each curve has a negative linear slope. The $|TC\text{-}f_r|$ values were 70–80 ppm/°C and decreased with increasing concentration of Nd ions. In the case of the longitudinal (33) mode, antiresonance frequency, f_a, can be expressed by

$$f_a = \frac{1}{2x}\sqrt{\frac{1}{\rho \times s_{33}^{D}}} \tag{2}$$

$$s_{33}^{E} = \frac{s_{33}^{D}}{1 - k_{33}^{2}} \tag{3}$$

where x, ρ and s_{33}^{D} are the vibration length of the (33) mode specimen, the observed density and the elastic compliance, respectively. Each parameter is supposed to have a temperature dependent. The thermal expansion coefficients, α, of general piezoelectric ceramics are known to be 0.5–5 ppm/°C. Here, the changes in vibration length and density were calculated using the largest value, $\alpha = 5$ ppm/°C. Finally, the frequency change from −25 to 125 °C due to the thermal expansion of the sample was estimated to be 2.47 ppm/°C. The contribution from the thermal expansion terms is small enough to be ignored. However, because this value is only a rough estimate, additional work and discussion are required. Table 2 summarizes the piezoelectric properties of BNTV-0, 0.25 and 0.75 ceramics. s_{33}^{E} decreased with increasing concentration of Nd ion, which means that the BNTV ceramics became harder with increasing concentration of Nd ion. $|TC\text{-}f|$ improved as BNTV ceramics became harder.

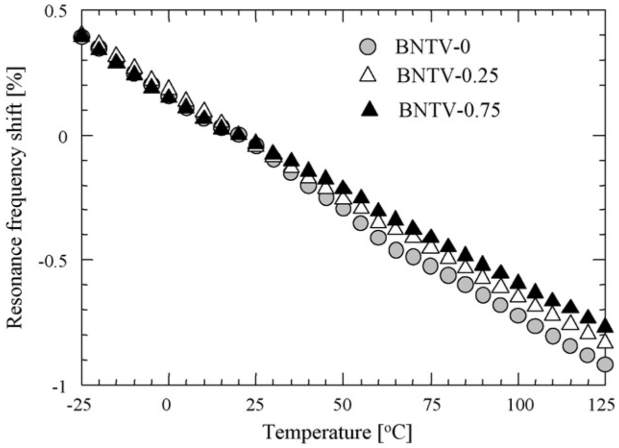

Fig. 2. Temperature dependences of the resonance frequencies in the longitudinal (33) mode of BIT-Nd, BIT-V, BNTV-0.25 and BNTV-0.75.

Table 2
Piezoelectric properties of BNTV-0, 0.25 and 0.75 ceramics

	BNTV-0.00	BNTV-0.25	BNTV-0.75
k_{33} (%)	19.0	19.0	21.5
$Q_{e\ max}$	12.8	21.1	50.9
Q_m	1500	2900	4200
$TC\text{-}f_r$ (ppm/°C)	−87.3	−82.3	−77.4
s_{33}^{E} (pm^2/N)	8.64	7.60	7.55

Fig. 3 shows the frequency dependence of impedance, Z (magnitude, $|Z|$, and phase, θ) for BNTV-0.75 ceramics in the (t) mode. BNTV-0.75 ceramic shows good $Q_{e\ max}$ and Q_m values of 31 and 4200, respectively. Therefore, the (t) mode of BNTV-0.75 is a good candidate for resonator applications. Fig. 4 shows the temperature dependences of the resonance frequency shift in the (33) and (t) modes of BNTV-0.75. A $|TC\text{-}f|$ value of 49.8 ppm/°C was achieved in the (t) mode, which is smaller than that in the (33) mode. At present, we are unable to find an appropriate reason why the (t) mode has a smaller $|TC\text{-}f|$ value than the (33) mode. However, the elastic compliance may be related to this difference in $TC\text{-}f$ between the (33) and (t) modes. In the case of the (t) mode, antiresonance frequency, f_a can be expressed by

$$f_a = \frac{1}{2t}\sqrt{\frac{c_{33}^{D}}{\rho}} \tag{4}$$

$$c_{33}^{E} = c_{33}^{D}(1 - k_t^2) \tag{5}$$

where x, ρ and c_{33} are the vibration length of the (t) mode specimen, the observed density and the elastic stiffness,

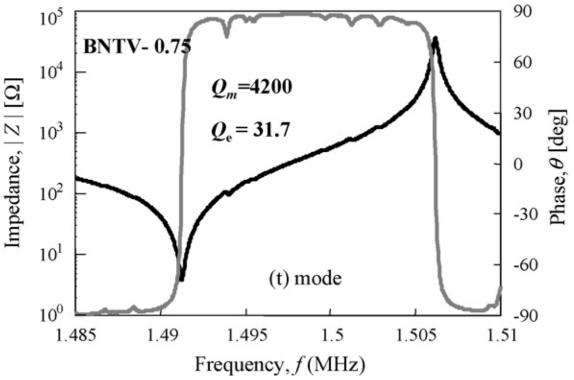

Fig. 3. Frequency dependence of impedance, Z (magnitude, $|Z|$, and phase, θ) for BNTV-0.75 ceramic in the (t) mode.

respectively. Then, c_{33}^{E} can be transformed to elastic compliance, s, using the following equation:

$$c_{33}^{\mathrm{E}} = \frac{s_{11}^{\mathrm{E}} + s_{12}^{\mathrm{E}}}{s_{33}^{\mathrm{E}}(s_{11}^{\mathrm{E}} + s_{12}^{\mathrm{E}}) - 2(s_{13}^{\mathrm{E}})^2} = \frac{1}{s_t^{\mathrm{E}}} \tag{6}$$

Here, the inverse of c_{33}^{E} is defined as an apparent elastic compliance, s_t^{E}, of the (t) mode. The relationship between s_{33}^{E} and s_t^{E} can be expressed by

$$s_t^{\mathrm{E}} = s_{33}^{\mathrm{E}} - \frac{2(s_{13}^{\mathrm{E}})^2}{s_{11}^{\mathrm{E}} + s_{12}^{\mathrm{E}}} = s_{33}^{\mathrm{E}} - \frac{2(s_{13}^{\mathrm{E}})^2}{s_{11}^{\mathrm{E}}(1 - \sigma^{\mathrm{E}})} \tag{7}$$

where σ is the Poisson's ratio. From Eq. (7), s_t^{E} should be smaller than s_{33}^{E}, theoretically. Table 3 shows the TC-f and s_*^{E} of the BNTV-0.75 ceramic in the (33) and (t) modes. For comparison, the corresponding values for other BLSF ceramics, $SrBi_2Nb_{1.95}V_{0.05}O_9$ (SBNV) and $Sr_{1.4}Ca_{0.6}Bi_4Ti_5O_{18}$ (SCBT), were listed in Table 3. The apparent s_t^{E} value of the BNTV ceramic is smaller than s_{33}^{E}. Also in both SBNV and SCBT ceramics, the same tendency was observed between s_t^{E} and s_{33}^{E}. From the experimental and theoretical results, the apparent s_t^{E} in the (t) mode is smaller than s_{33}^{E} in the (33) mode. At the same time, the $|TC\text{-}f|$ of the (t) mode is smaller than that of the (33) mode for BNTV, SBNV and SCBT ceramics. From both results, the vibration mode with a smaller s value ((t) mode) also has a smaller $|TC\text{-}f|$ value. As regards the compositional dependences of s_{33}^{E} and $|TC\text{-}f|$ for BNTV ceramics in Table 2, the $|TC\text{-}f|$ improved for the composition with smaller s_{33}^{E}. Therefore, a smaller $|TC\text{-}f|$ value can be achieved probably when the value is smaller, which means that a stiffer vibration mode is more stable against changes in temperature. From these speculations, it can be concluded that the (t) mode is a better vibration mode for bringing about a smaller $|TC\text{-}f|$. The (t) mode has one more advantage: it gives a higher resonance frequency than the (33) mode, because the vibration length of the (t) mode is shorter. Finally, the (t) mode of the BNTV-0.75 ceramic showed excellent piezoelectric properties: $Q_{\mathrm{m}} = 4200$, $Q_{\mathrm{e\ max}} = 31$ and $TC\text{-}f = -49.8$ ppm/°C. These properties are very similar to commercialized hard PZT ceramics for resonator applications. The BNTV-0.75 ceramic seems to be a superior candidate material for lead-free piezoelectric applications of ceramic resonators.

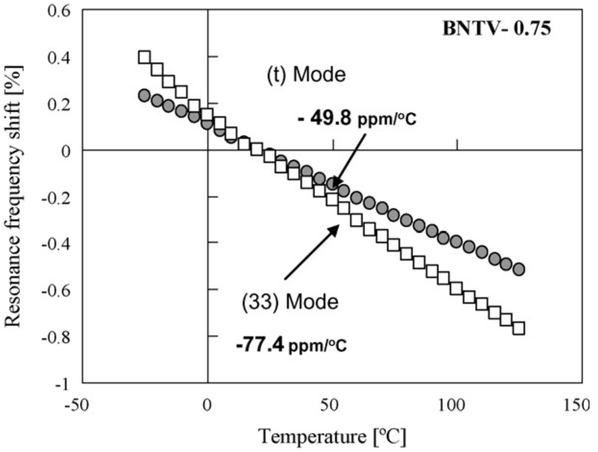

Fig. 4. Temperature dependences of the resonance frequencies in the (33) and (t) modes of BNTV-0.75.

Table 3
Temperature dependences of resonance frequency, TC-f, and s_*^{E} of BNTV-0.75, $SrBi_2Nb_{1.95}V_{0.05}O_9$ (SBNV) and $Sr_{1.4}Ca_{0.6}Bi_4Ti_5O_{18}$ (SCBT) ceramics in (33) and (t) modes

	TC-f (ppm/°C)	Elastic compliance, s_*^{E} (pm^2/N)
$(Bi_{4-y}Nd_y)_{1-(x/12)}(Ti_3V_x)_{12}$ ($m = 3$, $y = 0.75$, $x = 0.01$, BNTV-y)		
(33)	−77.4	7.55
(t)	−49.8	6.72
$SrBi_2Nb_{2-x}V_xO_9$ ($m = 2$, $x = 0.05$, SBNV-x)		
(33)	−42.1	8.44
(t)	−25.2	7.00
$(Sr_{1-x}Ca_x)_2Bi_4Ti_5O_{18}$ ($m = 5$, $x = 0.3$, SCBT-x)		
(33)	−65.4	8.30
(t)	−28.2	6.79

4. Conclusions

Temperature dependences of piezoelectric properties in the (33) and (t) modes of $(Bi_{4-y},Nd_y)_{1-(x/12)}(Ti_{3-x},V_x)O_{12}$ [BNTV-y ($x = 0.01$, $y = 0.00$–1.00)] were investigated as environmentally friendly lead-free piezoelectric ceramics for ceramic resonator applications with low-temperature coefficients of resonance frequency, TC-f. The following results were obtained. First, the $|TC\text{-}f|$ in the (33) mode improved with increasing concentration of modified Nd ions, y, and displayed the smallest $|TC\text{-}f|$ value of 77.4 ppm/°C at $y = 0.75$ (BNTV-0.75). Second, the (t) mode of the BNTV-0.75 ceramic showed excellent piezoelectric properties: $Q_{\mathrm{m}} = 4200$, $Q_{\mathrm{e\ max}} = 31$ and $|TC\text{-}f| = 49.8$ ppm/°C. And the last, the (t) mode is a better vibration mode for obtaining a smaller $|TC\text{-}f|$ than the (33) mode because the apparent elastic compliance, s_t^{E}, is smaller than s_{33}^{E}. From these results, the BNTV ceramic seems to be a superior candidate for a lead-free piezoelectric ceramic for resonator applications.

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