$(Bi_{1/2}Na_{1/2})TiO_3$-$BaTiO_3$ System for Lead-Free Piezoelectric Ceramics

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$(Bi_{1/2}Na_{1/2})TiO_3$–$BaTiO_3$ System for Lead-Free Piezoelectric Ceramics

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One of the $(Bi_{1/2}Na_{1/2})TiO_3$ (BNT)-based solid solutions, Ba-modified bismuth sodium titanate, $(Bi_{1/2}Na_{1/2})_{1-x}Ba_xTiO_3$ (BNBT), is studied for its dielectric and piezoelectric properties as a new group of lead-free piezoelectric ceramics. A rhombohedral (F_α)-tetragonal (F_β) morphotropic phase boundary (MPB) is shown to exist at $x=0.06\sim0.07$ by X-ray data, and dielectric and piezoelectric properties. BNBT ceramics with the MPB composition are superior as piezoelectric ceramics in high-frequency ultrasonic applications or as piezoelectric actuator materials because of a lower free permittivity, $\varepsilon_{33}^{T}/\varepsilon_0$, and a high electromechanical coupling factor, k_t or k_{33}, along with high mechanical strength.

KEYWORDS: piezoelectric ceramics, lead-free, relaxor, bismuth sodium titanate, $(Bi_{1/2}Na_{1/2})TiO_3$-based, mechanical strength

§1. Introduction

Lead-free or low-lead-content piezoelectric and/or pyroelectric ceramics have recently attracted interest in the control-free atmosphere and pollution-free sintering process with suppression of PbO evaporation.

Bismuth sodium titanate, $(Bi_{1/2}Na_{1/2})TiO_3$ (abbreviated as BNT),[1-4] is considered to be an excellent candidate as a key material of lead-free piezoelectric and/or pyroelectric ceramics because BNT is strongly ferroelectric and has the Curie temperature $T_c=320$°C, remanent polarization $P_r=38\ \mu C/cm^2$, and coercive field $E_c=73$ kV/cm at room temperature. Also, the dielectric properties display a very interesting anomaly wherein the low-temperature phase transition at $T=200$°C marks the transition from the ferroelectric to the antiferroelectric phase.[5] However, data on the piezoelectric and the pyroelectric properties of BNT ceramics are scarce due to the unsuccessful poling process. A rhombohedral symmetry of BNT at room temperature predicates that the solid solution[6-10] with tetragonal perovskite has a rhombohedral (F_α)-tetragonal (F_β) morphotropic phase boundary (MPB). Recent results of BNT-based solid-solution ceramics with the MPB indicate that they are very useful as lead-free or low-lead-content piezoelectric and/or pyroelectric ceramic materials, in addition to being superior as piezoceramics in high-frequency ultrasonic applications, with a low free permittivity, $\varepsilon_{33}^{T}/\varepsilon_0$, and a high electromechanical coupling factor, k_t or k_{33}, along with high mechanical strength, because the poling process of ferroelectric ceramics with MPB compositions seems to be remarkably effective in promoting piezoelectric and pyroelectric activities by electrical poling as it has a high chance of success compared with nonmodified BNT ceramics.

In this paper, dielectric, piezoelectric and ferroelectric properties of a BNT-based solid solution, $(Bi_{1/2}Na_{1/2})_{1-x}Ba_xTiO_3$ (abbreviated as "BNBT-100x"), are studied from the viewpoint of a new group of lead-free piezoelectric ceramics with a rhombohedral (F_α)-tetragonal (F_β) MPB.

§2. Experimental

The conventional ceramic fabrication technique was used to prepare BNBT ceramics. Reagent-grade metal oxide or carbonate powders with 99%+purity of Bi_2O_3, $NaCO_3$, $BaCO_3$, and TiO_2 were used as the starting raw materials. The oxides mixed by ball-milling were calcined at 800°C for one hour. After calcining, the ceramic powders were ground and ball-milled until the peak distribution of average particle size reached about 1 μm, and were pressed into discs 20 mm in diameter and about 1 mm in thickness. The pressed-disc samples were sintered at 1200°C for two hours in an air atmosphere.

Fired-on silver paste was used as the electrodes for the dielectric, piezoelectric and electrostrictive measurements. Temperature dependence of the dielectric constant, ε_S, and loss tangent, $\tan\delta$, of unpoled samples were measured for the determination of the Curie temperature, T_c, at 1 MHz and the free dielectric constant, $\varepsilon_{33}^{T}/\varepsilon_0$, of poled samples at 10 kHz by means of an automated dielectric measurement system with a multifrequency LCR meter (YHP 4275A). D-E hysteresis loops were observed by a standard Sawyer-Tower circuit at 50 Hz.

Specimens for piezoelectric measurements were poled at 60°C in a stirred silicone oil bath by applying a dc electric field of 3 kV/mm for 5 minutes. 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 factors, k_{33} and k_{31}, were calculated from the resonance and the antiresonance frequencies using Onoe's formula.

Mechanical properties were measured to obtain the bending strength by the three-point bending strength test method against unpoled and poled samples.

§3. Results and Discussion

The atmosphere was not controlled during the sintering process because the small evaporation of PbO leads to the easy sintering of the ceramics with a high measured density to theoretical density ratio, which is different from conventional PZT or PZT-based ceramics. Lattice constants at room temperature obtained from X-ray diffraction data show that the rhombohedral (F_α)-tetragonal (F_β) MPB exists at the compositions of $x=0.06\sim0.07$.

Figure 1 shows the dielectric constant, ε_S, of unpoled and $\varepsilon_{33}^T/\varepsilon_0$, of poled BNBT-100$x$ as a funcfion of the amount (x) of modified Ba ions. The $\varepsilon_{33}^T/\varepsilon_0$ after poling is smaller than ε_S before poling, which is a favorable case for high-frequency applications owing to lower dielectric constant. The ε_S-temperature curves display a broad shape near the Curie point, T_c, and may be a result of the diffuse phase transition because the BNBT system is a typical example of a relaxor ferroelectric with A-site complex ions. Figure 2 shows the temperature dependence of ε_S and loss tangent, tan δ, of BNBT-5 near the MPB composition. The three phases of ferroelectric, antiferroelectric and paraelectric, which exist in a wide temperature range, can be recognized by anomalies of the dielectric constant and loss tangent. D-E hysteresis loops of the BNBT ceramics were easily observed over a wide composition range with a relatively large remanent polarization, P_r, of about 20 $\mu C/cm^2$ near the MPB composition. Figure 3 shows the D-E hysteresis loops of BNBT-5 at (a) room temperature and (b) at 160°C, which correspond with reasonable agreement to the ferroelectric and antifetroelectric phases, shown in Fig. 2, respectively.

Figure 4 shows the phase relationship among $(Bi_{1/2}Na_{1/2})TiO_3$ [BNT] and $BaTiO_3$ [BT] in the $(Bi_{1/2}Na_{1/2})_{1-x}Ba_xTiO_3$ [BNBT] system obtained from the combination of all data on X-ray diffraction patterns and dielectric and ferroelectric properties. An MPB exists near the composition of $x=0.06$ (BNBT-6). On the other hand, the $(Bi_{1/2}Na_{1/2})_{1-x}Pb_xTiO_3$ case[11] requires the value of $x=0.12\sim0.13$ to achieve an MPB due to the smaller ionic radius of Pb as compared to that of the Ba

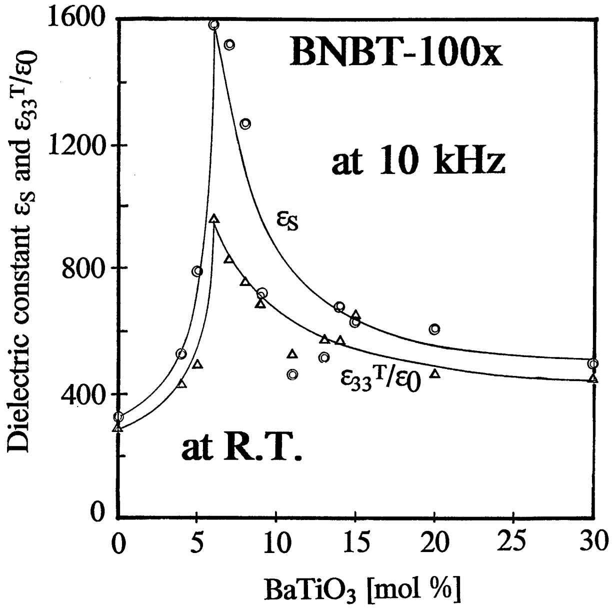

Fig. 1. Dielectric constant, ε_S, of unpoled and $\varepsilon_{33}^T/\varepsilon_0$ of poled BNBT-100x at room temperature as a function of the amount (x) of modified Ba ions.

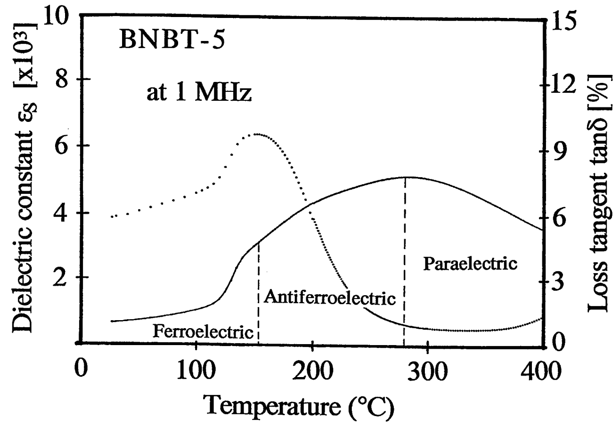

Fig. 2. Temperature dependence of dielectric constant, ε_S, and loss tangent, tan δ, of BNBT-5 with the three phases of ferroelectric, antiferroelectric and paraelectric in the temperature range.

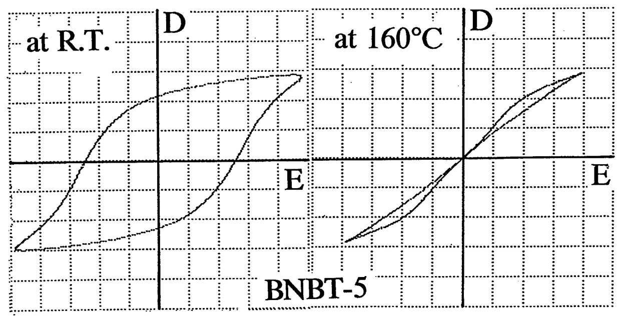

Fig. 3. D-E hysteresis loops of BNBT-5 near MPB composition at (a) room temperature and (b) at 160°C, corresponding to ferroelectric and antiferroelectric phases, respectively.

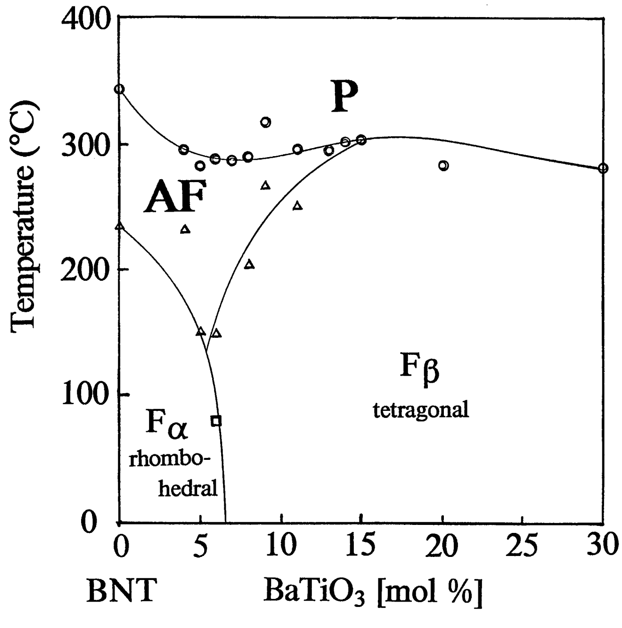

Fig. 4. Phase relationship among $(Bi_{1/2}Na_{1/2})TiO_3$ and $BaTiO_3$ in the $(Bi_{1/2}Na_{1/2})_{1-x}Ba_xTiO_3$ [BNBT-100x] system. (F_α: ferroelectric rhombohedral phase, F_β: ferroelectric tetragonal phase, AF: antiferroelectric phase, P: paraelectric phase).

ion. The value of the modified ions necessary to form the MPB seems to depend on the ionic radii of A-site ions, as shown in Fig. 5.

Figures 6 and 7, respectively, show electromechanical coupling factors, k_t, k_p, k_{33} and k_{31}, and frequency constants, N_t, N_p, N_{33} and N_{31}, of BNBT-100x as a function of the amount (x) of modified Ba ions. The coupling factor, k_{33}, in the longitudinal mode is higher than 50% at the MPB. On the other hand, the coupling factor, k_{31}, in the transverse mode shows a lower value. The k_t values of $BaTiO_3$-rich compositions are falsely higher than those of the k_{33} because it is rather difficult to determine the resonance and antiresonance frequencies due to much spurious resonance. The frequency constant, N_p, displays over 3000 Hz·m because of its mechanical hardness, as mentioned below.

Figure 8 shows Weibull plots of the 3-point bending strength, σ, and fracture probability, F $(=1-S)$, in BNBT-6 before and after poling. The mechanical strength of the poling direction parallel to the applied pressure in the test, $\sigma[/\!/]$, seems to be higher than that of the perpendicular poling direction, $\sigma[\perp]$. The σ[unpoled] of unpoled samples usually lies[12] midway between $\sigma[/\!/]$ and $\sigma[\perp]$. However, $\sigma[\perp]$ in this case was only slightly higher than σ[unpoled]. The reason seems to be that the perpendicular poling direction to the bending pressure in BNBT-6 is the wide direction of the rectangular plate, which is not the same case as that of the length direction in PZT.[12] The pressure in the former is applied parallel to the polarization; on the other hand, the pressure in the latter is perpendicular to the polarization. The mechanical properties of the BNBT ceramics indicate it to be very hard with a high bending strength of

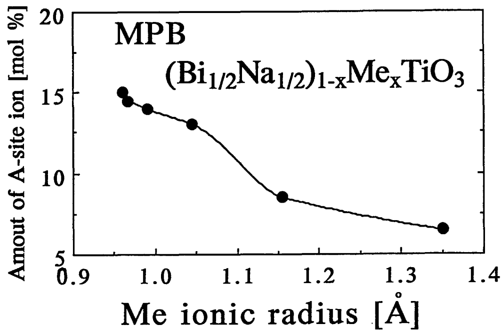

Fig. 5. Amount in mol% of the A-site ion needed to form the MPB as a function of the ionic radii of A-site ions.

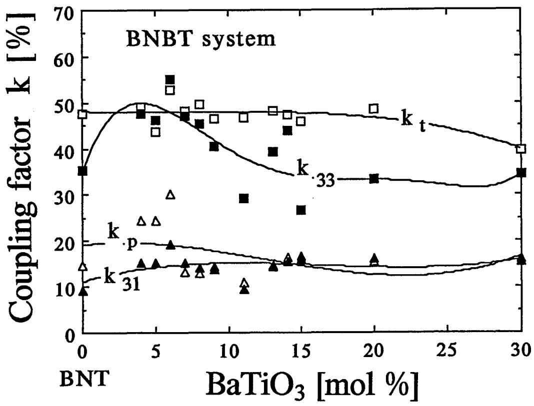

Fig. 6. Electromechanical coupling factors, k_t, k_p, k_{33} and k_{31}, of BNBT ceramics as a function of the amount (x) of modified Ba ions.

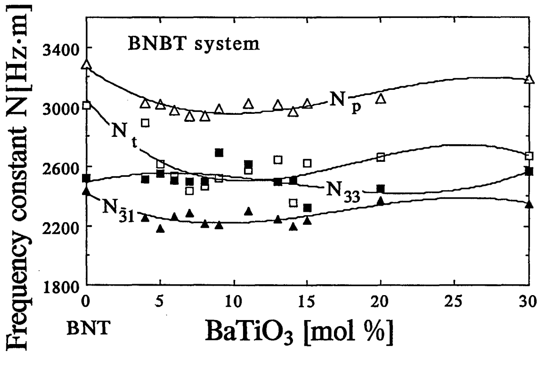

Fig. 7. Frequency constants, N_t, N_p, N_{33} and N_{31}, of BNBT ceramics as a function of the amount (x) of modified Ba ions.

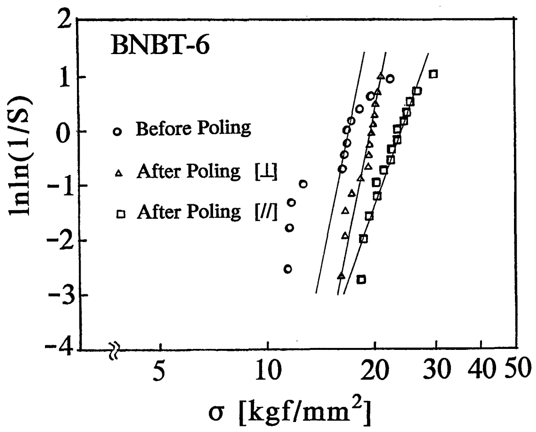

Fig. 8. Weibull plots of the 3-point bending strength, σ, and the fracture probability, $F\,(=1-S)$ in BNBT-6 ceramic before and after poling. [$\perp$] and [$/\!/$] indicate the poling directions relative to the applied pressure in the test.

Table I. Piezoelectric properties of $(Bi_{1/2}Na_{1/2})_{0.94}Ba_{0.06}TiO_3$ [BNBT-6].

Dielectric constant		Piezoelectric constant	
$\varepsilon^T_{33}/\varepsilon_0$	580	d_{33}	125
$\varepsilon^T_{11}/\varepsilon_0$	733	d_{31} (10^{-12} C/N)	40
		d_{15}	194
Loss tangent			
tan δ (%)	1.3	Elastic constant	
		s_{33}	10.0
Coupling factor		s_{11} (10^{-12} m^2/N)	8.59
k_{33}	55.0	s_{55}	23.3
k_{31} (%)	19.2		
k_{15}	49.8	Bending strength	
		σ (MPa)	200
Frequency constant			
N_p	2975	Curie temperature	
N_{33} (Hz·m)	2507	T_c (°C)	288
N_{31}	2264		
N_{15}	1586		

about 20 kgf/mm^2 (~200 MPa), which is the same case as with another BNT-based solid solution.[10] This value is two or three times larger than those of conventional piezoelectric ceramics such as PZT or PZT-based ceramics. The BNBT ceramics may be superior for piezoelectric actuator devices. we should study why BNT-based ceramics have a higher mechanical strength.

Table I summarizes the dielectric, piezoelectric, elastic and mechanical properties of BNBT-6 with the MPB. BNBT ceramics are superior for piezoelectric applications, having a relatively low free permittivity, $\varepsilon_{33}^{T}/\varepsilon_0$, a high electromechanical coupling factor, k_{33} (>50%), and a high-frequency constant, N_p ($\cong$3000 Hz·m), along with a high mechanical strength (σ=200 MPa).

§4. Conclusions

Dielectric, piezoelectric, and mechanical properties of $(Bi_{1/2}Na_{1/2})TiO_3$ (BNT)-$BaTiO_3$ (BT) solid solution, $(B_{1/2}Na_{1/2})_{1-x}Ba_xTiO_3$ (BNBT-100x), were studied, as these are superior candidate materials for lead-free piezoelectric ceramics.

X-ray diffraction data show that a rhombohedral (F_α)-tetragonal (F_β) morphotropic phase boundary (MPB) exists at x=0.06~0.07 with agreements of dielectric and piezoelectric properties. Well-sintered ceramics, with measured density ratios over 90%, were obtained in an uncontrolled atmosphere during the sintering process because of lead-free compositions.

BNBT ceramics, with a relatively low free permittivity, $\varepsilon_{33}^{T}/\varepsilon_0$, and a high electromechanical coupling factor, k_{33}, along with high mechanical strength, appear effective for high-frequency ultrasonic uses or piezoelectric actuator applications.

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