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2003 Jpn. J. Appl. Phys. 42 7401

(http://iopscience.iop.org/1347-4065/42/12R/7401)

Jpn. J. Appl. Phys. Vol. 42 (2003) pp. 7401–7403
Part 1, No. 12, December 2003

Large Piezoelectric Constant and High Curie Temperature of Lead-Free Piezoelectric Ceramic Ternary System Based on Bismuth Sodium Titanate-Bismuth Potassium Titanate-Barium Titanate near the Morphotropic Phase Boundary

Hajime NAGATA, Masaki YOSHIDA, Yoichi MAKIUCHI and Tadashi TAKENAKA

Faculty of Science and Technology, Tokyo University of Science, Yamazaki 2641 Noda, Chiba-ken 278-8510, Japan

(Received May 29, 2003; accepted August 13, 2003; published December 10, 2003)

A lead-free piezoelectric ceramic ternary system based on bismuth sodium titanate, $(Bi_{1/2}Na_{1/2})TiO_3$ (BNT) - bismuth potassium titanate $(Bi_{1/2}K_{1/2})TiO_3$ (BKT) - barium titanate $BaTiO_3$ (BT) near the morphotropic phase boundary (MPB) between the tetragonal and rhombohedral phases has been investigated. In the case of $a(Bi_{1/2}Na_{1/2})TiO_3$–$bBaTiO_3$–$c(Bi_{1/2}K_{1/2})TiO_3$ [BNBK(100a/100b/100c)] solid solution ceramics, the highest piezoelectric constant $d_{33} = 191$ pC/N, Curie temperature, $T_c = 301$°C, electromechanical coupling factor, $k_{33} = 0.56$ and dielectric constant, $\varepsilon_{33}{}^{T}/\varepsilon_0 = 1141$ are observed for the BNBK(85.2/2.8/12) composition which has a tetragonal phase near the MPB. The d_{33} value is the highest so far reported for all lead-free piezoelectric ceramics with $T_c > 300$°C. The BNT-BKT-BT ternary ceramics system sintered at 1200°C for 2 h in air has a pure perovskite structure and a high density more than 95% of the theoretical density.
[DOI: 10.1143/JJAP.42.7401]

KEYWORDS: lead-free, piezoelectric ceramics, morphotropic phase boundary, Curie temperature, dielectric constant, piezoelectric constant, bismuth sodium titanate, barium titanate, bismuth potassium titanate

1. Introduction

The piezoelectric property plays an important role for electric materials. The most widely used piezoelectric materials are $PbTiO_3$-$PbZrO_3$ three component ceramics (PZT system).[1,2] However, it is desired that lead-free materials be used for environmental protection. Thus, it is necessary to search for lead-free piezoelectric materials that have excellent properties such as those found in the PZT system.

Bismuth sodium titanate, $(Bi_{1/2}Na_{1/2})TiO_3$ (BNT),[3–5] is considered to be an excellent candidate key material of lead-free piezoelectric ceramics. The BNT ceramic exhibits a large remanent polarization, P_r=38 μC/cm^2, a Curie temperature T_c=320°C and a phase transition point from ferroelectric to antiferroelectric T_p=200°C. However, data on piezoelectric properties of the BNT ceramic are scarce because it is difficult to pole this ceramic due to its large coercive field, E_c(=73 kV/cm). Therefore, BNT-based solid solutions that can be poled easily have recently been studied.[6–9] Particularly, a large piezoelectricity is expected for the BNT-based solid solutions with a morphotropic phase boundary (MPB).

Barium titanate, $BaTiO_3$ and bismuth potassium titanate, $(Bi_{1/2}K_{1/2})TiO_3$, are well-known lead-free piezoelectric materials with a tetragonal phase. Figure 1 shows the phase relationship between $(Bi_{1/2}Na_{1/2})TiO_3$ (rhombohedral), $(Bi_{1/2}K_{1/2})TiO_3$ (tetragonal) and $BaTiO_3$ (Tetragonal). (1-x)$(Bi_{1/2}Na_{1/2})TiO_3$–$x$$BaTiO_3$ (BNBT-100x) and (1-y)-$(Bi_{1/2}Na_{1/2})TiO_3$–$y$$(Bi_{1/2}K_{1/2})TiO_3$ (BNKT-100y) solid solution systems already have been reported by Takenaka *et al.*[10] and Sasaki *et al.*,[11] respectively. It was reported that MPB compositions exist in the case of $x = 0.06$-0.07 for BNBT-100x and $y = 0.16$-0.20 for BNKT-100y.

In this study, the dielectric and piezoelectric properties of the solid solutions of the pseudo-three-component ceramic system, $(Bi_{1/2}Na_{1/2})TiO_3$–$BaTiO_3$–$(Bi_{1/2}K_{1/2})TiO_3$ (BNBK), were investigated, focusing on MPB compositions. Figure 2 shows the phase relationship of BNBK around the MPB. Both BNBT-6 and BNKT-16 exist on the rhombohedral side, and both BNBT-7 and BNKT-20 exist on the tetragonal side around the MPB region. Compositions prepared in this experiment are expressed as

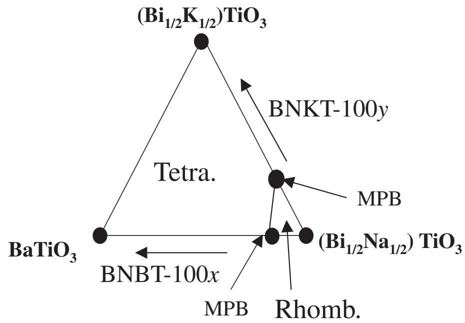

Fig. 1. Phase relationship between $(Bi_{1/2}Na_{1/2})TiO_3$ (rhombohedral), $(Bi_{1/2}K_{1/2})TiO_3$ (tetragonal) and $BaTiO_3$ (tetragonal).

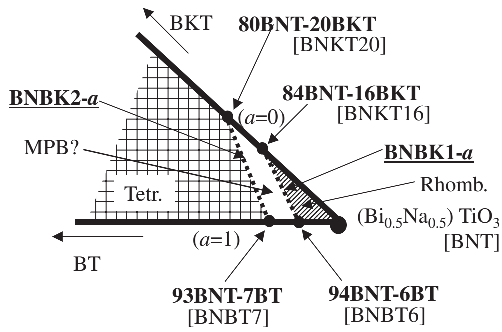

Fig. 2. Phase relationship of the $(Bi_{1/2}Na_{1/2})TiO_3$–$BaTiO_3$–$(Bi_{1/2}K_{1/2})TiO_3$ (BNBK) system around the MPB.

a(BNBT6)–(1-a)(BNKT16)

(BNBK1-a, $a = 0, 0.2, 0.4, 0.6, 0.8, 1$)

a(BNBT7)–(1-a)(BNKT20)

(BNBK2-a, $a = 0, 0.2, 0.4, 0.6, 0.8, 1$).

2. Experimental

A conventional ceramic fabrication technique was used to prepare BNBK. Reagent-grade metal oxide or carbonate powders were used as starting raw materials. These oxide or carbonate powders were mixed in ethanol with zirconium balls by ball-milling for 10 h. After calcining, the ground and ball-milled ceramic powders were pressed into sample discs and were sintered at 1200°C for 2 h in air. The crystal phase of the sintered ceramics was checked using an X-ray diffractometer (XRD, Rigaku RINT-2000).

Fire-on silver paste was used as the electrode for electrical measurements such as dielectric and piezoelectric measurements. The temperature dependences of dielectric constant, ε_r, and loss tangent, $\tan\delta$, were measured for the determination of Curie temperature, T_c, at 1 MHz using an automated dielectric measurement system with a multi-frequency LCR meter (YHP 4275A). Specimens for piezoelectric measurements were poled at room temperature in a silicone oil bath by applying a dc electric field of 5–9 kV/mm for 10 min. Piezoelectric properties were measured by a resonance-antiresonance method on the basis of EMAS-6100 standards using an impedance analyzer (YHP 4192A). The longitudinal vibration of the (33)-mode was measured using a rectangular specimen of $2 \times 2 \times 5$ mm. Free permittivity, $\varepsilon_{33}{}^{T}$, was obtained by measuring the capacitance at 1 kHz using an impedance analyzer (YHP 4192A).

3. Results and Discussion

The X-ray diffraction patterns of BNBK1-a and BNBK2-a ($a = 0$, 0.2, 0.4, 0.6, 0.8 and 1) show a single-phase perovskite structure with rhombohedral (F_α) and tetragonal (F_β) symmetries. The difference between the two structures (F_α and F_β) can be seen clearly in the X-ray diffraction patterns in the 2θ range of 94° to 97°. Figure 3 shows the X-ray diffraction patterns for BNBK1-a and BNBK-2a ($a = 0$, 0.2, 0.4, 0.6, 0.8 and 1) in the 2θ range of 94° to 97°. All the XRD patterns of BNBK2 have a splitting (400) reflection of (400, 040) and (004) with tetragonal symmetry. On the other hand, the XRD patterns of BNKT1-0, -0.2, -0.4 and -0.6 have a single reflection (400) with rhombohedral symmetry. These results confirm that the MPB exists almost between the two systems of BNBK1 and BNBK2. These ceramics were very easy to sinter with a fine body and a high measured density ratio of more than 95% of the theoretical density.

Figure 4 shows Curie temperature, T_c, as a function of a

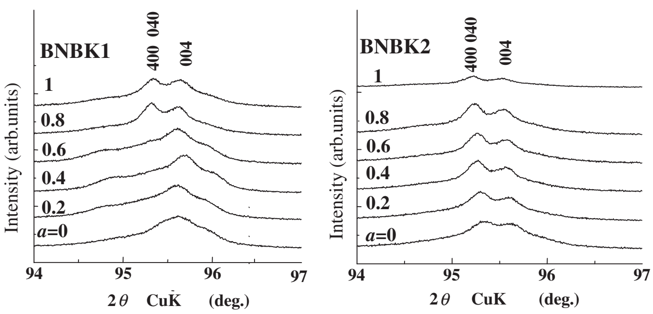

Fig. 3. X-ray diffraction patterns of BNBK1-a and BNBK-2a ($a = 0$, 0.2, 0.4, 0.6, 0.8 and 1) in the 2θ range of 94° to 97°.

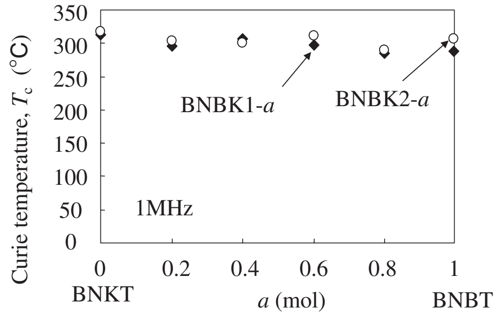

Fig. 4. Curie temperature, T_c, as a function of a value for BNBK1-a and BNBK2-a.

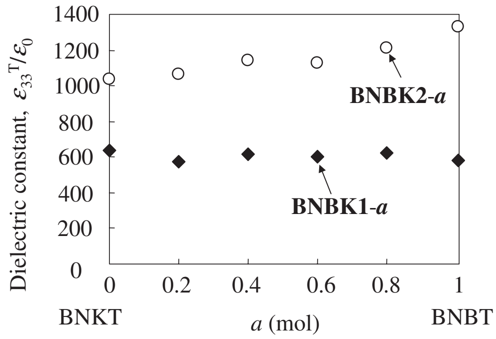

Fig. 5. Compositional dependence of electromechanical coupling factor, k_{33}, for BNBK1 and BNBK2.

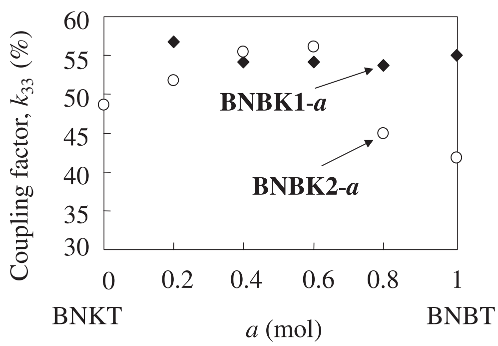

Fig. 6. Compositional dependence of the dielectric constant, $\varepsilon_{33}{}^{T}/\varepsilon_0$ (after poling), for BNBK1 and BNBK2.

value for BNBK1-a and BNBK2-a. The T_c values of BNBK1 and BNBK2 are almost constant at approximately 300°C.

Figure 5 shows the compositional dependence of electromechanical coupling factor, k_{33}, for BNBK1 and BNBK2 ceramics. For BNBK1, the k_{33} is almost constant at approximately 0.55, which is relatively large for lead-free piezoelectric ceramics. While, BNBT2-0.4 and -0.6 have a large k_{33} of more than 0.55.

Figure 6 shows the compositional dependence of dielectric constant, $\varepsilon_{33}{}^{T}/\varepsilon_0$ (after poling), for BNBK1 and BNBK2. The $\varepsilon_{33}{}^{T}/\varepsilon_0$ of BNBK2 with the tetragonal phase is relatively high at approximately 1000 or more, while that of BNBK1 with the rhombohedral phase is approximately 600. On the other hand, the dielectric constants, ε_r (before poling), at room temperature is almost constant at approx-

Table I. Dielectric, piezoelectric, elastic and mechanical properties of typical lead-free piezoelectric ceramics such as BNBK(85.2/2.8/12), BNBT-6, BNKT-20, $BaTiO_3$ and $(K_{0.5}Na_{0.5})NbO_3$.

	BNBK (85.2/2.8/12)	BNBT-6	BNKT-20	$BaTiO_3$	$(K_{0.5}Na_{0.5})NbO_3$ (Hot Press)
Curie temperature, T_c (°C)	301	288	317	135	420
Density, ρ_0 (g/cm^3)	5.82	5.83	5.76	5.70	4.25
Dielectric constant, $\varepsilon_{33}{}^{T}/\varepsilon_0$	1141	580	1030	1420	420
Coupling factor, k_{33}	0.56	0.55	0.49	0.49	0.53
Coupling factor, k_p	0.33	—	27.0	0.35	0.45
Mechanical quality factor, Q_m	84	81	109	—	240
Frequency constant, N_{33} (Hz·m)	2300	2507	2313	—	—
Frequency constant, N_p (Hz·m)	2960	—	—	—	1700
Elastic constant, $s_{33}{}^{E}$ (pm^2/N)	11.7	10.0	10.6	8.93	—
Piezoelectric constant, d_{33} (pC/N)	191	125	151	191	160

imately 1200 for BNBK1 and BNBK2. ε_r is sensitive to poling treatment and $\varepsilon_{33}{}^{T}/\varepsilon_0$ after the poling depends on the crystal structure. The $\varepsilon_{33}{}^{T}/\varepsilon_0$ of BNBK2 with the tetragonal phase is almost the same as ε_r, while that of BNBK1 with the rhombohedral phase decreases by approximately one-half of ε_r. This tendency is similar to that of the PZT system.[2)]

Elastic compliance, $s_{33}{}^{E}$, was obtained from vibration length, x, density, ρ, anti-resonance frequency, f_a, and k_{33}, on the basis of EMAS-6100 standards. The $s_{33}{}^{E}$ values are almost the same at approximately $10 \times 10^{-12}\,m^2/N$ for BNBK1 and BNBK2. Piezoelectric constant, d_{33}, is calculated using

$$d_{33} = k_{33}\sqrt{\varepsilon_{33}{}^{T} \cdot s_{33}{}^{E}}. \quad (1)$$

From the results of $s_{33}{}^{E}$, k_{33} and $\varepsilon_{33}{}^{T}/\varepsilon_0$ shown in Fig. 5 and 6, it is thought that a large d_{33} is obtained in BNBK2-0.4 and -0.6 due to a large k_{33} and $\varepsilon_{33}{}^{T}/\varepsilon_0$. Figure 7 shows the compositional dependence of piezoelectric constant, d_{33}, for BNBK1 and BNBK2. All of the d_{33} values of BNBK2 are larger than those of BNBK1. This result is attributed to the difference in $\varepsilon_{33}{}^{T}$ shown in Fig. 6. For BNBK2, the maximum d_{33} was 191 pC/N for the BNBK2-0.4 composition which has a tetragonal phase near the MPB. That is, this composition of BNBK2-0.4 is the same as that of BNBK(85.2/2.8/12) for $a(Bi_{1/2}Na_{1/2})TiO_3 - bBaTiO_3 - c(Bi_{1/2}K_{1/2})TiO_3$ [BNBK(100a/100b/100c)]. Table I summarizes the dielectric, piezoelectric, elastic and mechanical properties of typical lead-free piezoelectric ceramics such as BNBK(85.2/2.8/12), BNBT-6, BNKT-20, $BaTiO_3$ and $(K_{0.5}Na_{0.5})NbO_3$. Among them, BNBK(85.2/2.8/12) has the largest d_{33} with a high T_c (> 300°C). It is thought that BNBK2-0.4 is a candidate material for lead-free piezoelectrics with a relatively large d_{33} (=191 pC/N) and a high T_c (=301 °C).

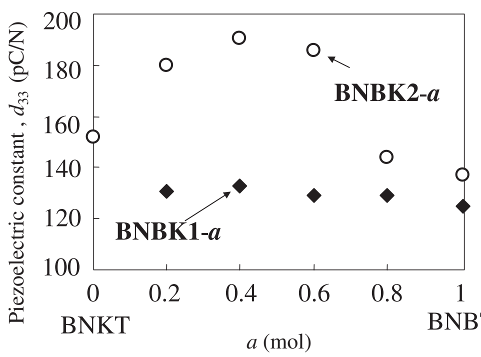

Fig. 7. Compositional dependence of the piezoelectric constant, d_{33}, for BNBK1 and BNBK2.

4. Conclusion

The dielectric and piezoelectric properties of solid solutions of the ternary system, $(Bi_{1/2}Na_{1/2})TiO_3$ (BNT), $(Bi_{1/2}K_{1/2})TiO_3$ (BKT) and $BaTiO_3$ (BT), $a(Bi_{1/2}Na_{1/2})TiO_3$–$bBaTiO_3$–$c(Bi_{1/2}K_{1/2})TiO_3$ [BNBK(100a/100b/100c)], were investigated, focusing on the MPB the between tetragonal and rhombohedral phases. The main results are as follows:

1) The maximum piezoelectric constant, d_{33} (=191 pC/N), was obtained for BNBK(85.2/2.8/12) (BNBK2-0.4) with the tetragonal phase around the MPB region.
2) The Curie temperature, T_c, electromechanical coupling factor, k_{33}, and dielectric constant, $\varepsilon_{33}{}^{T}/\varepsilon_0$ of BNBK-(85.2/2.8/12) are 301°C, 0.56 and 1141, respectively.
3) It is thought that BNBK(85.2/2.8/12) is a candidate material for lead-free actuator applications due to its relatively large d_{33} and high T_c.

Acknowledgement

This work was partially supported by a Grant-in-Aid for Scientific Research (B) (No. 13555176) from the Japan Society for the Promotion of Science.

1) E. Sawaguchi: J. Phys. Soc. Jpn. **8** (1953) 615.
2) T. Yamamoto: Jpn. J. Appl. Phys. **35** (1996) 5104.
3) G. A. Smolensky, V. A. Isupov, A. I. Agranovskaya and N. N. Krainic: Sov. Phys. Solid State **2** (1961) 2651.
4) C. F. Buhrer: J. Chem. Phys. **36** (1962) 798.
5) J. Suchanicz, K. Roleder, A. Kania and J. Handerek: Ferroelectrics **77** (1988) 107.
6) H. Nagata and T. Takenaka: Jpn. J. Appl. Phys. **36** (1997) 6055.
7) T. Takenaka, A. Hozumi, T. Hata and K. Sakata: *Silicates Industries — Ceramic Science and Technology* **58** (1993) 136.
8) K. Sakata and Y. Masuda: Ferroelectrics **7** (1974) 347.
9) H. Nagata and T. Takenaka: Jpn. J. Appl. Phys. **37** (1998) 5311.
10) T. Takenaka, K. Maruyama and K. Sakata: Jpn. J. Appl. Phys. **30** (1991) 2236.
11) A. Sasaki, T. Chiba, Y. Mamiya and E. Otsuki: Jpn. J. Appl. Phys. **38** (1999) 5564.