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Lead-free piezoelectric ceramics of $(Bi_{1/2}Na_{1/2})TiO_3$–$(Bi_{1/2}K_{1/2})TiO_3$–$(Bi_{1/2}Ag_{1/2})TiO_3$ system

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Abstract The ternary lead-free piezoelectric ceramics system of $0.90[x(Bi_{1/2}Na_{1/2})TiO_3–(1-x)(Bi_{1/2}K_{1/2})TiO_3]–0.10(Bi_{1/2}Ag_{1/2})TiO_3$ (x=0.77, 0.79, 0.81, 0.83, 0.85) were successfully synthesized by conventional ceramic sintering technique. The samples were studied by X-ray diffraction, dielectric, ferroelectric and piezoelectric measurements. The MPB composition of the system appears to be near BNKA-79 according to the results of the X-ray diffraction and ferroelectric properties. The sample with x=0.79 showed the highest piezoelectric constant d_{33}=160 pC/N. The maximum electromechanical coupling factors, k_p and k_t, are 0.30 for BNKA-79 and 0.42 for BNKA-85, respectively.

Keywords Lead-free piezoelectric ceramic · Bismuth sodium titanate · Bismuth potassium titanate · Bismuth silver titanate · Morphotropic phase boundary

1 Introduction

Piezoelectric ceramics have been widely used for various applications such as ultrasonic generators, actuators, filters and other electronic devices. Most of these materials are lead zirconate titanate (PZT) ceramics. Due to the environmental concerns, manufactures are more and more constrained to reduce and ultimately eliminate the lead content of their products. Thus, it is necessary to search for new lead-free piezoelectric materials to replace widely used PZT piezoelectric ceramics.

Bismuth sodium titanate, $(Bi_{1/2}Na_{1/2})TiO_3$ (BNT), is considered to be a good candidate of lead-free piezoelectric ceramics because BNT exhibits a strong ferroelectricity and high Curie temperature [1–3]. BNT-based solid solution ceramics, such as BNT–$(Bi_{1/2}K_{1/2})TiO_3$ (BNT–BKT) [4, 5], BNT–$BaTiO_3$ [6, 7], BNT–$NaNbO_3$ [8, 9], have been extensively studied. It has been reported that these ceramics showed improved piezoelectric properties and easier treatment in polling process comparing with pure BNT ceramics. Particularly, the dielectric and piezoelectric properties of the BNT-based solid solutions show a maximum over a specific compositional range around the morphotropic phase boundary (MPB).

Since the large ferroelectricity of BNT-based solid solutions is attributed to Bi^{3+} ions at the A-site in the perovskite structure (ABO_3), a logical approach is to replace Na^+ with alternative cations. The similarity of Na^+ and Ag^+ in terms of their ionic radii and A-site coordination geometry suggests that Ag^+ would be a reasonable substitute for Na^+. $(Bi_{1/2}Ag_{1/2})TiO_3$ (BAT) was reported to be ferroelectric with cubic symmetry [10]. However, there is little information on the dielectric or piezoelectric properties of BAT and other perovskites containing Ag^+ on the A-site. The reason is thought to be that the poor thermal stability of Ag_2O prevents synthesis via a conventional solid-state reaction process [11].

In this study, the binary system BNT–BKT modified with 10 mol% of BAT is reported for the first time. The investigations of BNT–BKT modified with different contents of BAT are undertaking and the results will be published elsewhere. The ternary system BNT–BKT–BAT

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solid solution was successfully synthesized by conventional ceramic sintering technique. The compositions prepared in this experiment are expressed as $0.90[x(Bi_{1/2}Na_{1/2})TiO_3–(1-x)(Bi_{1/2}K_{1/2})TiO_3]–0.10(Bi_{1/2}Ag_{1/2})TiO_3$ (abbreviated to BNKA-100x), x=0.77, 0.79, 0.81, 0.83, 0.85. Here the Na/K mole ratio ranges from 77/23 to 85/15, which is near the MPB of BNT–BKT system. The dielectric, ferroelectric and piezoelectric properties of the ternary system were investigated.

2 Experimental procedures

A conventional ceramic fabrication technique was used to prepare the BNKA ceramics. Reagent-grade Na_2CO_3, K_2CO_3, Bi_2O_3, Ag_2O and TiO_2 were used as the starting materials. These powders were weighed according to the stoichiometric proportions and were mixed in ethanol with Y_2O_3-stabilized zirconia balls by ball-milling for 4 h. Then, the dried powders were calcined at 950 °C for 3 h under a constant oxygen flow rate of 1 L/min. After calcination, the ground and ball-milled powders were mixed with polyvinyl alcohol and pressed with a pressure of 1,500 kg/cm^2 into discs of 15 mm in diameter and about 1.5 mm in thickness. The compacted discs were finally sintered at 1,140–1,160 °C for 3 h in air. Silver paste was fired on both sides of the discs as electrodes for electrical measurements. The specimens for measurement of piezoelectric properties were poled at 80 °C in a silicone oil bath by applying a DC electric field of 4.0 kV/mm for 15 min.

The crystal structure of the samples was determined by X-ray diffraction (XRD) analysis with a Rigaku D/Max 2550V X-ray diffractometer using Cu-K_α radiation. The temperature dependence of dielectric constant and dissipation factor were examined with an HP 4284A precision LCR meter at several frequencies from 100 Hz to 1 MHz. The *P–E* hysteresis loops were observed using a TF Analyzer 2000 FE-Module ferroelectric tester at room temperature. The piezoelectric constant d_{33} was measured by the direct piezoelectric method using a quasi-static d_{33} meter (Model ZJ-3A, Institute of Acoustics, Chinese Academy of Sciences, Beijing). The electromechanical coupling factors, k_p of planar mode and k_t of thickness mode, were determined by the resonance and anti-resonance method on the basis of IEEE standards using HP 4294A precision impedance analyzer.

3 Results and discussion

Figure 1 shows the X-ray diffraction patterns of the BNKA ceramics. All the patterns show the single phase of a perovskite structure and no detectable impurity Ag phase appears. Figure 2 shows the X-ray diffraction patterns in the 2θ range of 44–49°. In the diffraction pattern for BNKA-77, (200) and (002) peaks are observed, which has a tetragonal symmetry. On the other hand, BNKA-85 shows a single peak (202) with rhombohedral symmetry. Mixtures of those peaks are observed in the diffraction pattern for x between 0.79 and 0.83. Therefore, MPB of BNKA systems should exist near x=0.79–0.83. At room temperature, BNT is a rhombohedral symmetry and BKT is a tetragonal symmetry. There is a rhombohedral–tetragonal MPB in their solid solution near 0.81BNT–0.19BKT composition [4]. Thus, it can be concluded that addition of BAT in BNT–BKT system does not lead to an obvious change in the phase structure.

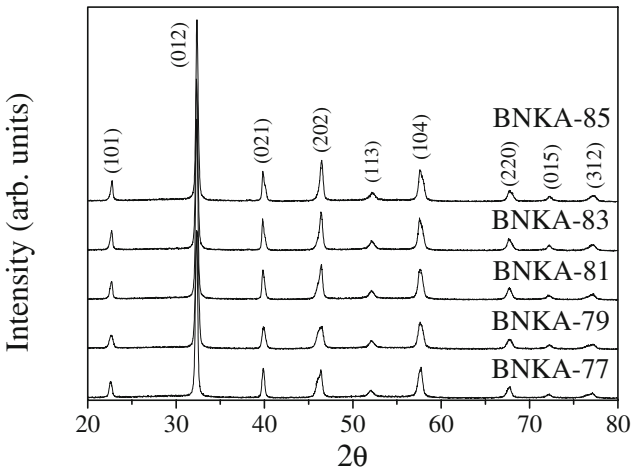

Fig. 1 X-ray diffraction patterns of BNKA ceramics

Figure 3 shows the dependence of the dielectric constant and dissipation factor of unpoled and poled BNKA ceramics on the chemical composition. The dielectric constant, $\varepsilon_{33}^{T}/\varepsilon_0$ (after polling), decreases from 1,300 to 700 while x value increases from 0.77 to 0.85. The $\varepsilon_{33}^{T}/\varepsilon_0$

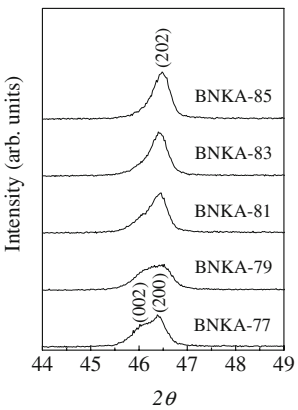

Fig. 2 X-ray diffraction patterns at 2θ between 44 and 49° of BNKA ceramics

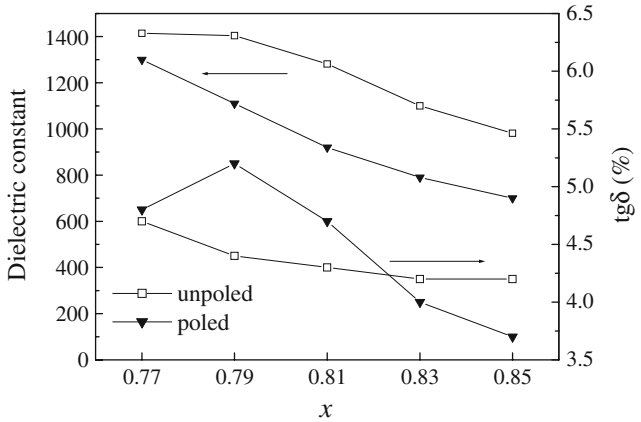

Fig. 3 Dielectric constant and dissipation factor of unpoled and poled samples as a function of composition for BNKA ceramics at 1 kHz and room temperature

values are larger than those of the BNT–BKT ceramics with the same Na/K ratio [4]. The dissipation factor, tanδ, of poled samples increases with increasing x up to x=0.79, then decreases monotonously. The tan δ shows a minimum of 3.7% for the poled sample at x=0.85.

Figure 4 shows the temperature dependence of dielectric constant and dissipation factor of BNKA-77 and BNKA-85 at different frequencies. The temperature corresponding to maximum value of dielectric constant is called as maximum temperature (T_m). There is another low temperature transition near 100 °C, the temperature is named as depolarization temperature (T_d). Above T_d, BNKA ceramics will be depolarized. Consequently, T_d is an important factor in the view of practical uses. Some researchers thought that T_d of BNT-based ceramics corresponding to the transition between ferroelectric phase and anti-ferroelectric phase [6, 7]. However, it has not been confirmed by other experimental results such as X-ray diffraction [12] and time dependence of electric permittivity [13]. The actual mechanism of the phase transition has not been clear yet and still needs further investigation.

From Fig. 4, it can be found that the dielectric constant, dissipation factor and transition temperature (T_m and T_d) of BNKA ceramics are strongly measuring-frequency dependent. The maximum of the dielectric constant decreases as the measuring frequency increases and its temperature (T_m) is shifted towards low temperature as well. The depolarization temperature (T_d) is shifted towards high temperature with increasing measuring frequency. All the curves display a broad shape near T_m, similar to those observed for other BNT-base solid solutions [4, 7, 8]. This could be a result of the diffuse phase transition and indicates that the BNKA system is a relaxor ferroelectric with A-site complex cations.

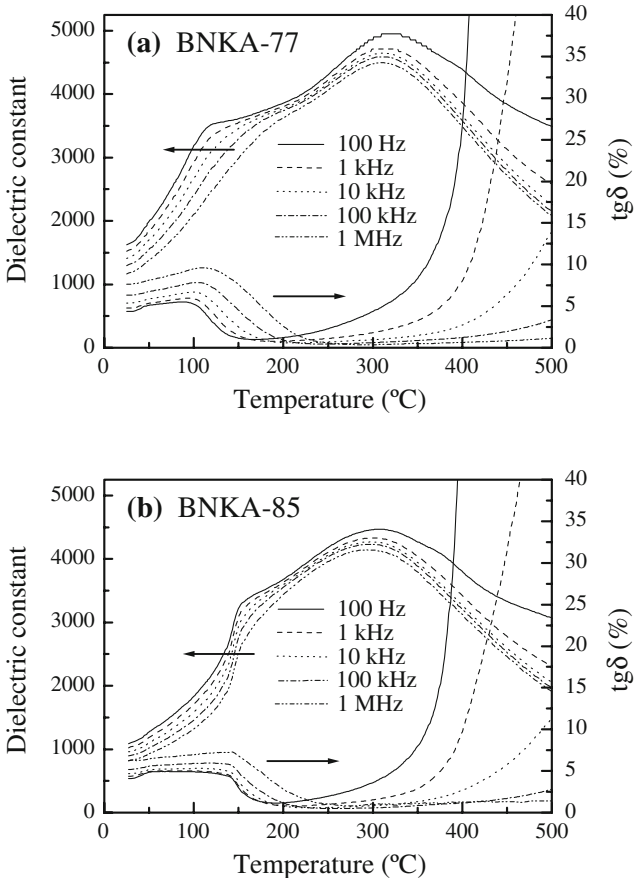

Fig. 4 Dielectric constant and dissipation factor as a function of temperature and frequency for (**a**) BNKA-77 and (**b**) BNKA-85

Figure 5 shows T_m and T_d at 1 kHz of BNKA-100x ceramics as a function of x value. The T_m of the BNKA ceramics with x more than 0.81 is almost constant at approximately 300 °C. On the other hand, the T_d shifts to

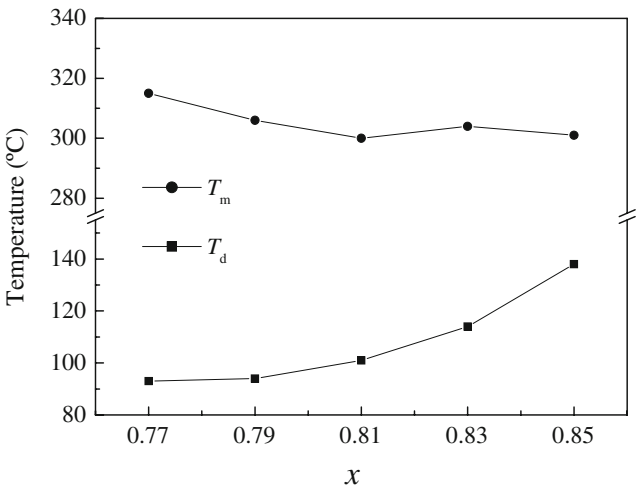

Fig. 5 Phase transition temperature T_m and T_d as a function of composition for BNKA ceramics at 1 kHz

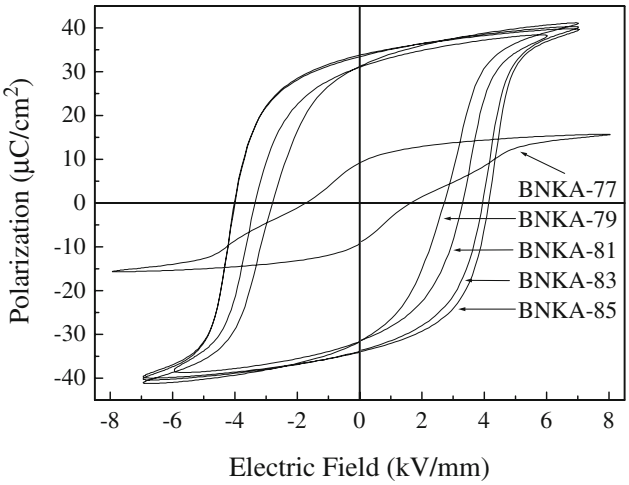

Fig. 6 *P–E* hysteresis loops for BNKA ceramics at room temperature

higher temperature with increasing the amount of BNT, remarkably in the compositional range of $x>0.83$.

Figure 6 shows the *P–E* hysteresis curves of BNKA ceramics at room temperature. Large loops which indicate high ferroelectricity are observed for $x\geq0.79$. The remanent polarization P_r and coercive field E_c increase with increasing the amount of BNT. The maximum P_r and E_c are determined to be 32.3 μC/cm^2 and 4.14 kV/mm respectively, at $x=0.85$. These values are comparable with the previously reported data for the BNT–BKT system [4]. For the sample of BNKA-77, *P–E* hysteresis loop reveals a little anti-ferroelectric feature for the narrow loop near zero point, which could not be observed in the BNT–BKT system. This reason may be due to the different crystal structure of BNKA-77 comparing with other compositions.

The detailed electrical properties of BNKA ceramics are summarized in Table 1. It can be found that d_{33} and k_p decrease, while k_t increases a little when the amount of BNT improves. The k_t of BNKA-79 is lower than that of BNKA-85, this may be due to the large dissipation factor, tan δ, of BNKA-79. The sample with $x=0.79$ has the highest piezoelectric constant $d_{33}=160$ pC/N. The maximum electromechanical coupling factors, k_p and k_t, are 0.30 for BNKA-79 and 0.42 for BNKA-85, respectively.

The MPB compositions appear to be near $x=0.79$–0.83 according to the results of the X-ray diffraction. The d_{33} and k_p show maximum at $x=0.79$ and the hysteresis loop of BNKA-77 shows a little anti-ferroelectricity. Based on all these results, the MPB composition should be near BNKA-79. From the viewpoint of piezoelectric applications, BNKA-85 would be a potential candidate lead-free material, with a relatively low dielectric constant, high piezoelectric constant and electromechanical coupling factors, along with a relatively high depolarization temperature.

4 Conclusions

$0.90[x(Bi_{1/2}Na_{1/2})TiO_3–(1-x)(Bi_{1/2}K_{1/2})TiO_3]–0.10(Bi_{1/2}Ag_{1/2})TiO_3$ solid solution ceramics were successfully synthesized by a conventional ceramic fabrication technique. The crystal structure, dielectric, piezoelectric properties and *P–E* hysteresis loops were investigated. As a result, the MPB composition of the BNKA-100*x* system exists near that of BNKA-79. The maximum d_{33} value of 160 pC/N was observed at $x=0.79$. The maximum electromechanical coupling factors, k_p and k_t, are 0.30 for BNKA-79 and 0.42 for BNKA-85, respectively. BNKA-85 seems to be the promising candidate as lead-free piezoelectric ceramics.

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Table 1 Electrical properties of BNKA ceramics.

Sample		BNKA-77	BNKA-79	BNKA-81	BNKA-83	BNKA-85
Dielectric constant	$\varepsilon_{33}^T/\varepsilon_0$	1,300	1,110	920	790	700
Dissipation factor	tan δ	4.8	5.2	4.7	4.0	3.7
Piezoelectric constant (pC/N)	d_{33}	25	160	143	130	119
Coupling factor	k_t	–	0.38	0.39	0.41	0.42
	k_p	–	0.30	0.29	0.28	0.26
Frequency constant (Hz·m)	N_t	–	2,417	2,414	2,474	2,459
	N_p	–	2,893	2,914	2,980	3,018
Remanent polarization (μC/cm^2)	P_r	5.14	28.8	29.4	32.1	32.3
Coercive field (kV/mm)	E_c	1.72	2.72	3.31	4.02	4.14
Depolarization temperature (°C)	T_d	93	94	101	114	138

References

1. G.A. Smolenskii, V.A. Isupov, A.I. Agranovskaya, N.N. Krainik, Sov. Phys., Solid State **2**, 2651 (1961)
2. J. Suchanicz, K. Roleder, A. Kania, J. Handerek, Ferroelectrics **77**, 107 (1988)
3. C.F. Buhrer, J. Chem. Phys. **36**, 798 (1962)
4. T.B. Wang, L.E. Wang, Y.K. Lu, D.P. Zhou, J. Chin. Ceram. Soc. **14**, 14 (1986)
5. A. Sasaki, T. Chiba, Y. Mamiya, E. Otsuki, Jpn. J. Appl. Phys. **38**, 5564 (1999)
6. T. Takenaka, K. Maruyama, K. Sakata, Jpn. J. Appl. Phys. **30**, 2236 (1991)
7. X.X. Wang, H.L.W. Chan, C.L. Choy, Solid State Commun. **125**, 395 (2003)
8. T. Takenaka, T. Okuda, K. Takegahara, Ferroelectrics **196**, 175 (1997)
9. T. Wada, K. Toyoike, Y. Imanaka, Y. Matsuo, Jpn. J. Appl. Phys. **40**, 5703 (2001)
10. Y. Inaguma, T. Katsumata, R. Wang, K. Kobashi, M. Itoh, Y.-J. Shan, T. Nakamura, Ferroelectrics **264**, 127 (2001)
11. J.H. Park, P.M. Woodward, J.B. Parise, R.J. Reeder, I. Lubomirsky, O. Stafsudd, Chem. Mater. **11**, 177 (1999)
12. J.A. Zvirgzds, P.P. Kapostins, J.V. Zvirgde, T.V. Kruzina, Ferroelectrics **40**, 75 (1982)
13. K. Roleder, J. Suchanicz, A. Kania, Ferroelectrics **89**, 1 (1989)