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Electrical properties of $Na_{1/2}Bi_{1/2}TiO_3$–$BaTiO_3$ ceramics

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Abstract

Lead-free $Na_{1/2}Bi_{1/2}TiO_3$–$BaTiO_3$ piezoelectric ceramics with perovskite structure were studied. The piezoelectric properties of $(1-x)Na_{1/2}Bi_{1/2}TiO_3$–$xBaTiO_3$ ($x=0.02$, 0.04, 0.06, 0.08, 0.10) ceramics were reported and their piezoelectric properties reach extreme values near the MPB (about $x=0.06$). Influences of nonstoichiometry and doping on the structures and piezoelectric properties of $(Na_{1/2}Bi_{1/2})_{0.92}Ba_{0.08}TiO_3$ ceramics were further studied. The relationship between piezoelectric constant and depolarization temperature of nonstoichiometric and doped ceramics was also investigated. It was found that in most of $Na_{1/2}Bi_{1/2}TiO_3$–$BaTiO_3$ ceramics studied, their depolarization temperatures were much lower than maximum temperatures of dielectric constant–temperature curves; the origin of this phenomenon was discussed.

Keywords: Doping; Electrical properties; (Na,Bi)TiO_3–$BaTiO_3$; Nonstoichiometry; Piezoelectric properties

1. Introduction

Ever since the discovery of piezoelectric effect, piezoelectric materials have been rapidly developed and widely used. At present, the most widely-used piezoelectric materials are Pb(Zr,Ti)O_3(PZT)-based ceramics because of their superior piezoelectric properties. However, because the evaporation of harmful lead oxides during the preparation of Pb-contained ceramics has detrimental influence on environment, lead-free piezoelectric materials such as $Na_{1/2}Bi_{1/2}TiO_3$-based oxides, bismuth layer structure oxides and tungsten bronze-type oxides have been studied in order to replace PZT-based ceramics.

Sodium bismuth titanate, $Na_{1/2}Bi_{1/2}TiO_3$, is a kind of perovskite ferroelectric discovered by Smolenskii et al. in 1960.[1] At room temperature, $Na_{1/2}Bi_{1/2}TiO_3$ is strongly ferroelectric with a relatively large remnant polarization, $P_r=38$ μC/cm^2, and a relatively large coercive field, $E_c=73$ kV/cm.[1] Because of its large coercive field and relatively large conductivity, pure $Na_{1/2}Bi_{1/2}TiO_3$ is hard to be poled and its piezoelectric properties is not desirable. Therefore $Na_{1/2}Bi_{1/2}TiO_3$-based solid solutions were studied to improve piezoelectric properties. $Na_{1/2}Bi_{1/2}TiO_3$-based ceramics are considered to be one group of promising lead-free or low-lead piezoelectric ceramics.[2–8] $Na_{1/2}Bi_{1/2}TiO_3$–$BaTiO_3$ ceramics were studied by several researchers.[2,7] The morphotropic phase boundary (MPB) of this solid solution system is near $x=0.06$. Takenaka reported that the composition of $(Na_{1/2}Bi_{1/2})_{0.94}Ba_{0.06}TiO_3$, which is near the MPB, has relatively good piezoelectric properties. The coupling factor and piezoelectric constant of the composition are $k_{33}=0.55$, $k_{31}=0.19$, $d_{33}=125$ pC/N and $d_{31}=40$ pC/N, respectively.[2]

In this paper, the piezoelectric properties of $Na_{1/2}Bi_{1/2}TiO_3$–$BaTiO_3$ ceramics near the morphotropic phase boundary (MPB) were studied. Influences of nonstoichiometry and doping on piezoelectric properties and structure of $(Na_{1/2}Bi_{1/2})_{0.92}Ba_{0.08}TiO_3$ ceramics were further studied.

2. Experimental procedures

The conventional mixed oxides method was used to prepare $Na_{1/2}Bi_{1/2}TiO_3$–$BaTiO_3$ ceramics according to formulas of $(1-x)$ $Na_{1/2}Bi_{1/2}TiO_3$–$xBaTiO_3$ ($x=0.02$, 0.04, 0.06, 0.08, 0.10) (abbreviated as NBBTX, $X=2$, 4, 6, 8, 10), $(Na_{1/2}Bi_{1/2})_{0.92-x}Ba_{0.08}TiO_3$ (abbreviated as NBBT81), $(Na_{1/2}Bi_{1/2})_{0.92+x}Ba_{0.08}TiO_3$ (abbreviated as NBBT82), $(Na_{1/2}Bi_{1/2})_{0.92}Ba_{0.08}TiO_3+xNb_2O_5$ (abbreviated as NBBT83) and $(Na_{1/2}Bi_{1/2})_{0.92}Ba_{0.08}$ TiO_3

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$+xCo_2O_3$ (abbreviated as NBBT84) ($x \leqslant 0.01$). The starting raw materials were reagent-grade Bi_2O_3, Na_2CO_3, TiO_2, $BaCO_3$, Nb_2O_5 and Co_2O_3. The oxides were mixed and then calcinated at 800–900 °C for 2 h. After calcination, the ground and ball milled ceramic powder was pressed into discs of 15 mm in diameter and 1 mm in thickness. The pressed discs were sintered at 1160–1180 °C for 1 h. The preparation procedure can be seen in Fig. 1. The crystal structures of sintered ceramics were determined by X-ray diffraction (model D/Mas-rB, Japan).

The sintered pellets were polished and electroded with silver paste. The specimens were poled in a silicone oil bath at 80 °C under a d.c. field of 3–4 kV/mm for 20 min.

The resonance and anti-resonance frequencies were measured using HP4192A impedance analyzer. The thickness and planar frequency constant (N_t, N_p respectively) were calculated. The thickness and planar coupling coefficient (k_t, k_p respectively) were calculated based on the Onoe's formulas.[9] The capacitance and dielectric loss $tg\delta$ were measured by CY2611 capacitance-meter (home made) and dielectric constant ε_{33}^T was calculated. The measurement frequency was 1 kHz. The piezoelectric constant d_{33} was measured by ZJ-3A quasistatic d_{33}-meter (home made) based on Berlincourt method. The coercive field E_c and remnant polarization P_r were determined from D–E loops obtained by Sawyer–Tower circuit. The temperature dependence of depolarization current of poled specimens was measured using the same electric circuit as in Ref. 10. The heating rate was 6 °C/min. The depolarization temperatures of spontaneous polarization T_d of the samples were obtained. The temperature dependence of dielectric constant of unpoled specimens at 1 kHz was measured using a system composed of furnace, capacitance bridge and X–Y recorder (model LM-15, home made). The heating rate was 2 °C/min. T_m, where the temperature dependence of dielectric constant curve reaches maximum, was determined.

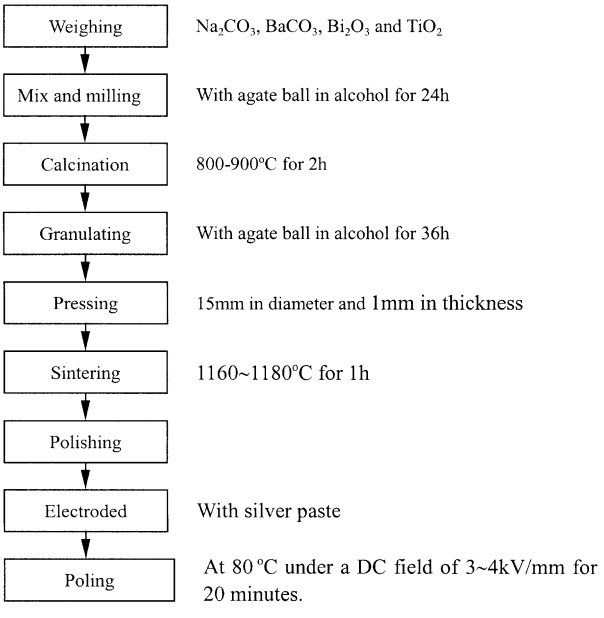

Fig. 1. Flowchart of sample preparation.

3. Results and discussion

3.1. The X-ray diffraction patterns of (1−x) $Na_{1/2}Bi_{1/2}TiO_3$–x$BaTiO_3$ ceramics

The X-ray diffraction patterns of $(1-x)$ $Na_{1/2}Bi_{1/2}TiO_3$–$xBaTiO_3$ ($x = 0.02$, 0.04, 0.06, 0.08, 0.10) ceramics are shown in Fig. 2. The NBBTX ceramics were all pure perovskite structure. At room temperature, the symmetry of $Na_{1/2}Bi_{1/2}TiO_3$ is rhombohedral and $BaTiO_3$ is tetragonal. Their solid solutions have rhombohedral-tetragonal morphotropic phase boundary (MPB). X-ray diffraction revealed that NBBT2 and NBBT4 ceramics were rhombohedral symmetry. With the increasing component of $BaTiO_3$, the structures of NBBT8 and NBBT10 ceramics turned into tetragonal symmetry with the (003) and (021) peaks combining into one peak and (202) peak splitting. The NBBT6 ceramics have the features of both rhombohedral and tetragonal symmetry. Therefore the MPB of $Na_{1/2}Bi_{1/2}TiO_3$–$BaTiO_3$ system is near $x = 0.06$ and this result coincides with Refs.2 and 7.

3.2. The electrical properties of (1−x) $Na_{1/2}Bi_{1/2}TiO_3$–x $BaTiO_3$ ceramics

The detailed electrical properties of NBBTX ceramics are shown in Table 1. The NBBTX ceramics possess the properties of relatively large ratio of k_t/k_p, low dielectric constant and high frequency contant. Those characters make them suitable for ultrasound applications. They all have relatively large remnant polarization P_r and large coercive field E_c, obtained from D–E hysteresis loops. The relatively small d_{33} (~100 pC/N) and large loss tangent (~0.02) are other features of the ceramics of this system.

Similar to PZT-based ceramics, the piezoelectric properties of $(1-x)Na_{1/2}Bi_{1/2}TiO_3$–$xBaTiO_3$ system, such as electromechanical coupling coefficient k, piezoelectric constant d_{33} and dielectric constant ε etc. vary with the component fraction of $BaTiO_3$ and reach extreme values near the MPB, as shown in Fig. 3.

3.3. Relationship between depolarization temperature and maximum temperature of ε–T curves

Figs. 4 and 5 show the temperature dependence of depolarization current curves and dielectric constant–temperature (ϵ–T) curves of NBBTX ceramics. For

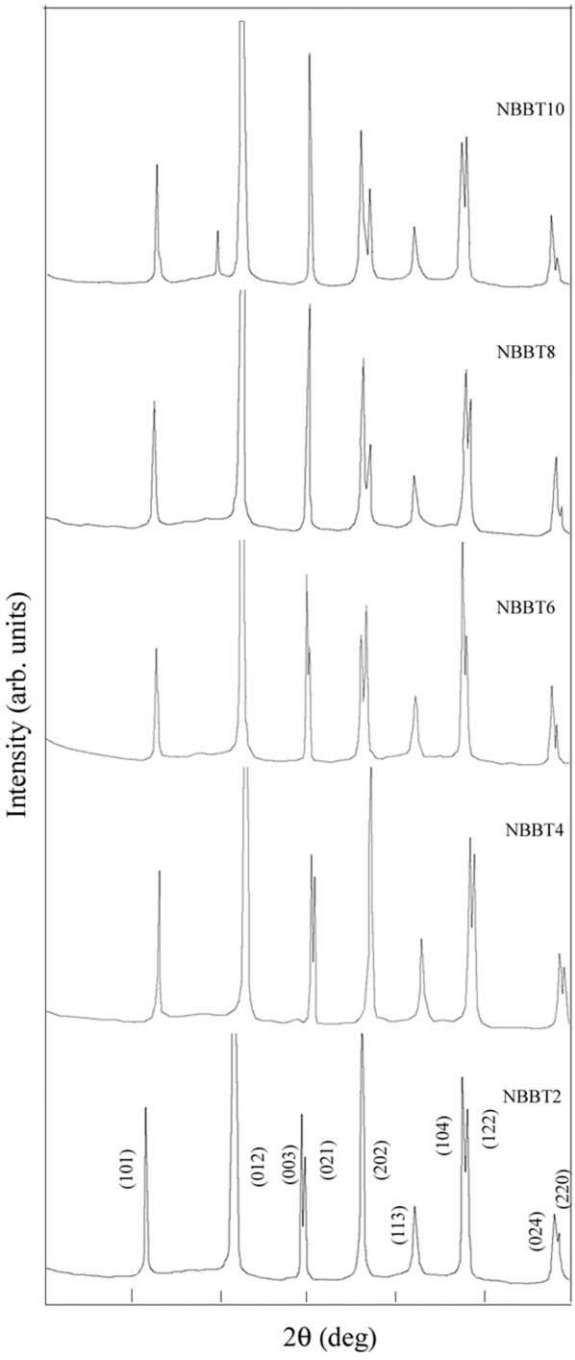

Fig. 2. X-ray diffraction patterns of $(1-x)Na_{1/2}Bi_{1/2}TiO_3$–$xBaTiO_3$ ceramics.

normal ferroelectrics, depolarization temperature (T_d) and maximum temperature (T_m) of ε–T curves should coincide with each other, which can named as Curie temperature (T_c). The existence of T_c is due to the phase transition between ferroelectric phase and paraelectric phase. However, it is not the case for NBBTX ceramics. It can be noted that except NBBT10 ceramic, T_d of NBBTX ceramics is much lower than T_m. The differences between T_m and T_d were about 85, 65, 125, and 110 °C for NBBT2, NBBT4, NBBT6 and NBBT8 ceramics, respectively. When NBBTX ceramics were heated to the temperature above T_d, d_{33} of the samples became zero. Based on these experiment results, it is obvious that T_m could not be seen as Curie point and it is not the temperature where phase transition between ferroelectric phase and paraelectric phase takes place. One possible origination of this phenomenon is the occurrence of ferroelectric-anti-ferroelectric phase transition. Some authors thought that in pure $Na_{1/2}Bi_{1/2}TiO_3$, antiferroelectric phase existed.[11] However, experimental results such as X-ray diffraction,[12] Roman and neutron scattering,[13,14] pyroelectric measurement and time dependence of electric permittivity[15] did not confirm this opinion. Therefore the existence of antiferroelectric in NBBTX ceramics is of little possibility and if it does exist, it should appear gradually with the increasing addition of $BaTiO_3$ in $Na_{1/2}Bi_{1/2}TiO_3$. Similar phenomenon takes place in $Pb(Fe_{1/2}Nb_{1/2})O_3$ and PLZT relaxor ferroelectric ceramics and it was discussed based on macro–micro domains switching.[16,17] We proposed that this phenomenon also originate from macro–micro domains switching. This problem need more investigation and is still open to discuss.

3.4. Influence of nonstoichiometry and doping on the structures and piezoelectric properties of $Na_{1/2}Bi_{1/2}TiO_3$–$BaTiO_3$ ceramics

Seen from Table 1, NBBT8 ceramic has favorable piezoelectric properties such as high ratio of k_t/k_p, relatively large d_{33} etc. Hence we carried out further experiments on NBBT8 ceramics to study influence of nonstoichiometry and doping on the structure and piezoelectric properties. Specimens of nonstoichiometry (NBBT81 and NBBT82 ceramics) and doping in B-site (NBBT83 and NBBT84 ceramics) were prepared and studied.

Fig. 6 shows the X-ray patterns of NBBT81–NBBT84 ceramics. Compared with NBBT8 ceramics, nonstoichiometry and doping in B-site do not alter the tetragonal symmetry of NBBT8 ceramics. It should be noted that the first peak of NBBT84 ceramic splits, which means doping Co^{3+} in B-site improves deformation and distortion of structure. For ceramics with tetragonal structure, the relationship of their structure parameters can be described as follows:

$$1/d^2 = (h^2 + k^2)/a^2 + 1^2/c^2$$

Because axis a and c are not equal, the first diffraction peak is in fact the combination of (100) and (001) peaks. In NBBT81, NBBT82 and NBBT83 ceramics, the difference between axes a and c is small, hence we cannot observe the splitting of first peak. In NBBT84 ceramic, doping Co^{3+} in B-site can yield oxygen vacancy, which

Table 1
Electrical properties of $(1-x)Na_{1/2}Bi_{1/2}TiO_3$–$xBaTiO_3$ ceramics

Property		Materials				
		NBBT2	NBBT4	NBBT6	NBBT8	NBBT10
Coupling factor	k_t	0.46	0.45	0.40	0.42	0.41
	k_p	0.20	0.21	0.29	0.13	0.14
Piezoelectric constant	d_{33}	78	87	122	112	94
Dielectric constant	ϵ_{33}^T	402	445	601	841	764
Frequency constant (Hz m)	N_p	3190	3000	3000	2950	2980
	N_t	2680	2570	2522	2375	2418
Poisson ratio	σ	0.26	0.25	0.25	0.25	0.24
Dielectric loss	$tg\delta$	0.0173	0.0207	0.0179	0.0204	0.0239
Maximum temperature of ε (°C)	T_m	265	230	225	250	180
Depolarization temperature (°C)	T_d	180	165	100	140	170
Remnant polarization ($\mu C/cm^2$)	P_r	37	–	40	36	22.5
Coercive field (V/mm)	E_c	4700	–	2880	3200	2880

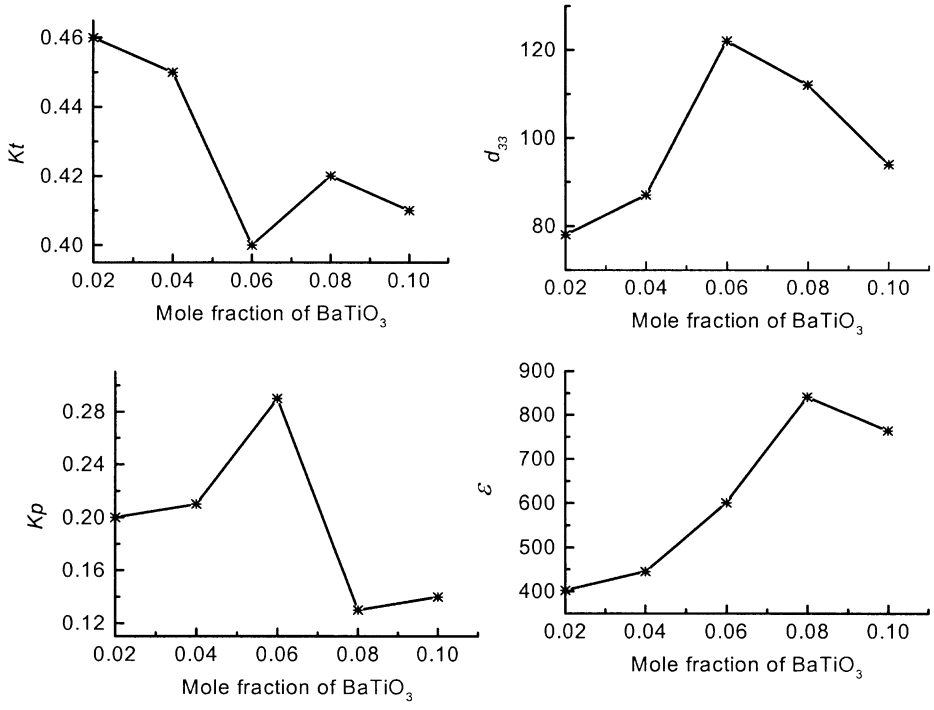

Fig. 3. Dependence of electrical properties of $(1-x)Na_{1/2}Bi_{1/2}TiO_3$–$xBaTiO_3$ ceramics on mole fraction of $BaTiO_3$.

results in the more distortion and deformation of structure, and the first peak splits.

The piezoelectric properties of NBBT81–NBBT84 ceramics are shown in Table 2.

Compared with pure NBBT8, the piezoelectric properties of NBBT81, NBBT82 and NBBT83 are enhanced. Their d_{33} increase from 112 to 140, 125, 149 pC/N respectively. Addition and lack of $(Na_{1/2}Bi_{1/2})^{2+}$ in A-site all can improve piezoelectric constant, which provide methods to improve the piezoelectric properties of $Na_{1/2}Bi_{1/2}TiO_3$-based ceramics. d_{33} Of NBBT83 (doping Nb^{5+} in B-site) is 149 pC/N and may be the largest of $Na_{1/2}Bi_{1/2}TiO_3$-based ceramics at present. Unfortunately its depolarization temperature decreases from 140 °C (for NBBT8 ceramic) to 70 °C.

For piezoelectric ceramics with tetragonal symmetry, sufficient reorientation of 90° domains (strain-producing domains on switching) when specimens are poled can improve their piezoelectric properties. In NBBT81 ceramics, lack of $(Na_{1/2}Bi_{1/2})^{2+}$ yields A-site vacancies that can relax the strain caused by reorientation of 90° domains. Therefore 90° domains in NBBT81 ceramics can be more sufficiently reoriented and piezoelectric properties are improved. For NBBT82 ceramics, B-site vacancies caused by addition of $(Na_{1/2}Bi_{1/2})^{2+}$ in A-site can also relax the strain and improve the piezoelectric

properties; but at same time, because the spontaneous polarization mainly originates from the displacement of B-site cations, B-site vacancies have detrimental effect on piezoelectric properties. In our experiment, the first effect is the main factor and the piezoelectric properties of NBBT82 are improved.

Influences of doping in B-site on the electrical properties of NBBT8 ceramics resemble the corresponding rules of PZT-based ceramics. From Table 2, it can be found that after doping off-valence donors such as Nb^{5+} in B-site, d_{33}, ε and large loss tangent increase, which is opposite the corresponding experimental results of doping acceptors such as Co^{3+} in B-site. Similar to PZT-based ceramics, Nb^{5+} can be seen as soft additive which leads to the enhancement of piezoelectric constant, dielectric constant and dielectric loss etc and Co^{3+} as hard additive.

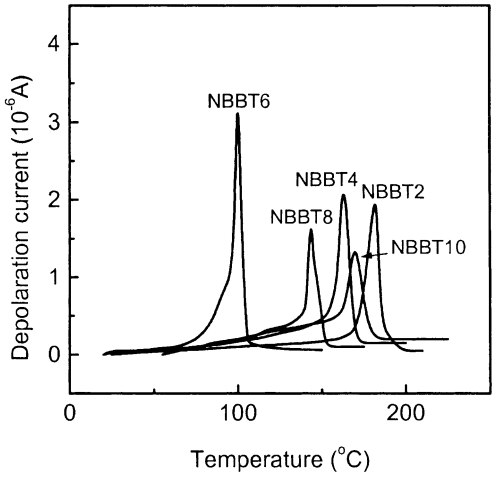

Fig. 4. Temperature dependence of depolarization current of $(1-x)Na_{1/2}Bi_{1/2}TiO_3$–$xBaTiO_3$ ceramics.

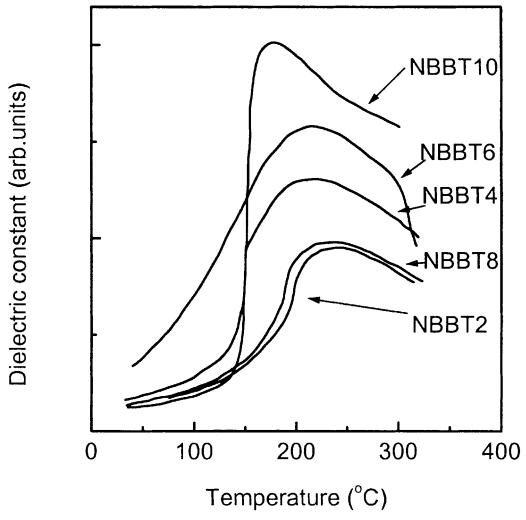

Fig. 5. Temperature dependence of dielectric constant of $(1-x)Na_{1/2}Bi_{1/2}TiO_3$–$xBaTiO_3$ ceramics.

From Table 2, it can also be found that the lower are the depolarization temperatures, the higher are the piezoelectric constants of the ceramics, as shown in Fig. 7.

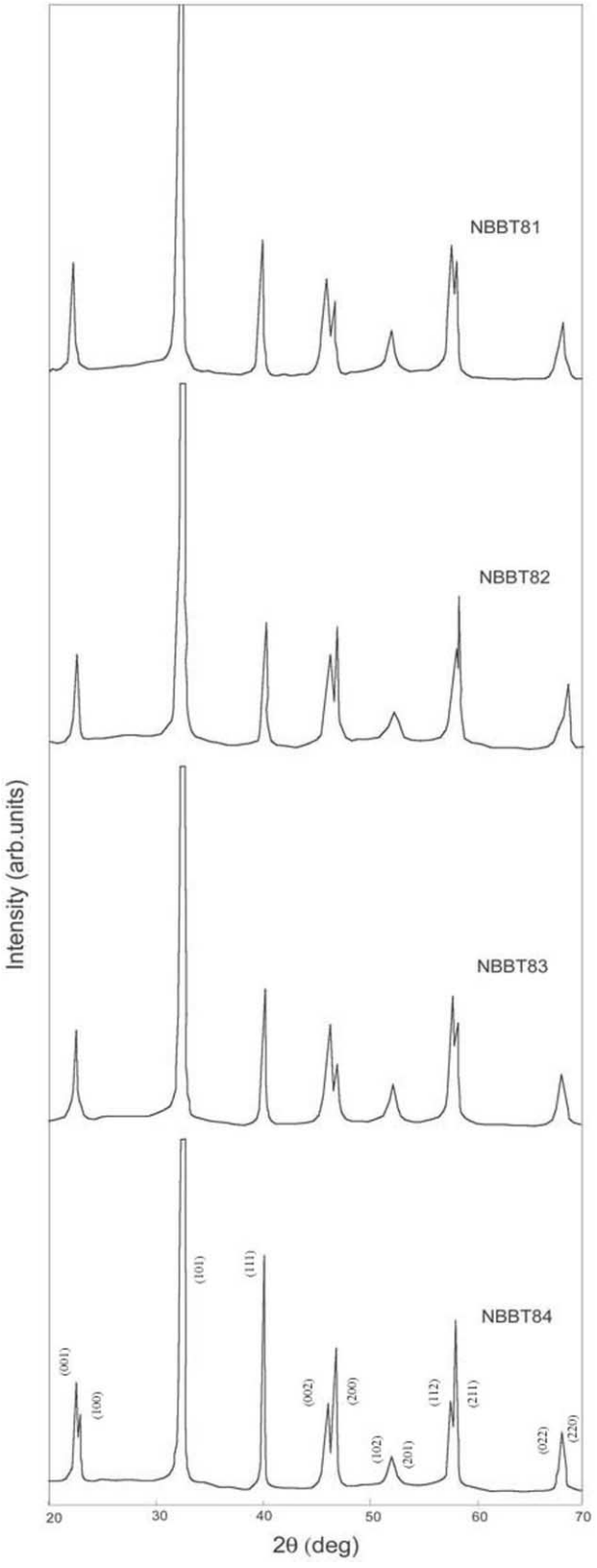

Fig. 6. X-ray diffraction patterns of $Na_{1/2}Bi_{1/2}TiO_3$–$BaTiO_3$ ceramics.

Table 2
Electrical properties of $Na_{1/2}Bi_{1/2}TiO_3$–$BaTiO_3$ ceramics

		NBBT8	NBBT81	NBBT82	NBBT83	NBBT84
Piezoelectric constant (pC/N)	d_{33}	112	140	125	149	108
Dielectric constant	ε_{33}^T	841	870	740	1230	450
Dielectric loss	$Tg\delta$	0.0204	0.0281	0.0212	0.0390	0.0150
Maximum temperature of ε (°C)	T_m	250	210	215	250	About 245
Depolarization temperature (°C)	T_d	140	125	135	70	155

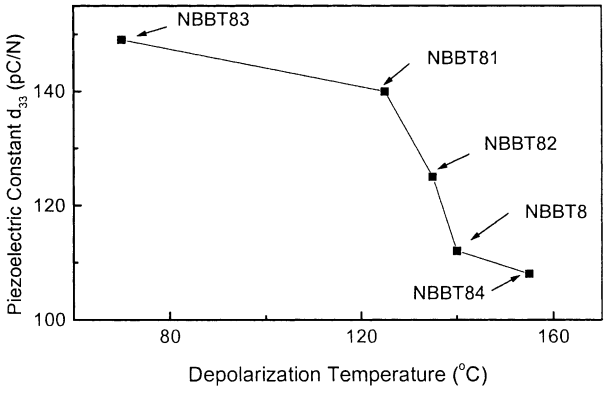

Fig. 7. Relationship between piezoelectric constant and depolarization temperature of $Na_{1/2}Bi_{/12}TiO_3$–$BaTiO_3$ ceramics.

T_d of those ceramics are also lower than T_m of ε–T curves, which is similar to NBBTX ceramics. As mentioned above, it was thought that at depolarization temperature T_d, macro-micro domains switching takes place, therefore depolarization temperature can be seen as the indication of stability of ferroelectric domains. Ferroelectric domains with lower depolarization temperature are less stable, which make it easy for reorientation of 90° domains. Piezoelectric properties are improved with the sufficient reorientation of 90° domains. From the viewpoint of application, depolarization temperature and piezoelectric constant are two important properties for piezoelectric materials. For specimens of nonstoichiometry and doping, the two properties are of correlative dependence. Improvement of piezoelectric properties is at the expense of decrease of depolarization temperature.

4. Conclusion

Piezoelectric properties of $Na_{1/2}Bi_{1/2}TiO_3$–$BaTiO_3$ ceramics system with perovskite structures were studies. The main electrical properties of $(1-x)Na_{1/2}Bi_{1/2}TiO_3$–$xBaTiO_3$ ceramics reach extreme values near the MPB. $Na_{1/2}Bi_{1/2}TiO_3$–$BaTiO_3$ ceramics possess the properties of large ratios of k_t/k_p, low dielectric constant and high frequency content, which are suitable for ultrasonic applications. Influences of nonstoichiometry and doping on the structure and piezoelectric properties of $(Na_{1/2}Bi_{1/2})_{0.92}Ba_{0.08}TiO_3$ were further studied. Addition and lack of $(Na_{1/2}Bi_{1/2})^{2+}$ in A-site can improve piezoelectric properties of $(Na_{1/2}Bi_{1/2})_{0.92}Ba_{0.08}TiO_3$ ceramics. Influence of doping in B-site on piezoelectric properties resembles corresponding rules of PZT-based ceramics. High-valence cations can be seen as soft additive and low-valence cations as hard additive. For ceramics of nonstoichiometry and doping, the lower are the depolarization temperatures, the higher are the piezoelectric constants of the ceramics. The depolarization temperatures of all ceramics studied except NBBT10 are much lower than maximum temperatures of ε–T curves.

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