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Depolarization temperature and piezoelectric properties of $Na_{1/2}Bi_{1/2}TiO_3$–$Na_{1/2}Bi_{1/2}(Zn_{1/3}Nb_{2/3})O_3$ ceramics by two-stage calcination method

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Abstract. **A new group of NBT-based lead-free piezoelectric ceramics, $Na_{1/2}Bi_{1/2}TiO_3$–$Na_{1/2}Bi_{1/2}(Zn_{1/3}Nb_{2/3})O_3$, was synthesized using the two-stage calcination method and depolarization temperatures and piezoelectric properties were also investigated. The XRD analysis showed that the ceramics system had a morphotropic phase boundary (MPB) between the rhombohedral and the tetragonal structure. The highest piezoelectric properties of $d_{33} = 97$ pC/N and $k_t = 0·46$ were obtained near MPB compositions. Furthermore, the depolarization temperatures near MPB compositions were slightly decreased and the lowest T_d was maintained at 210°C.**

Keywords. **Lead-free piezoelectric ceramics; depolarization temperature; perovskite structure; piezoelectric properties.**

1. Introduction

Increasing interest concerning the environmental problems of $Pb(Zr, Ti)O_3$(PZT)-based ceramics has led to the demand of lead-free ferroelectric ceramics in electronic applications (Shieh *et al* 2007). Therefore, potassium bismuth titanate ($K_{1/2}Bi_{1/2}TiO_3$, KBT) (Yoshii *et al* 2006), sodium bismuth titanate ($Na_{1/2}Bi_{1/2}TiO_3$, NBT) (Smolenski *et al* 1961) and barium titanate ($BaTiO_3$, BT) (Takenaka 1989) based solid solution with perovskite structures have been extensively studied. Recently, it has been found that ceramics based on $Na_{1/2}Bi_{1/2}TiO_3$ are good candidates for lead-free piezoelectric materials as NBT based ceramics show a strong ferroelectricity and high Curie temperature (Smolenski *et al* 1961). However, the piezoelectric properties of NBT based ceramics are not enough for most practical uses.

At present, two methods can be used to improve the piezoelectric properties of NBT based ceramics: one is to find new compositions and the other is to use new processing method to improve the piezoelectric properties (Cho *et al* 2003). In PZT based ceramics, the B-site complex piezoelectric ceramics such as $Pb(Zn_{1/3}Nb_{2/3})O_3$–$Pb(Zr,Ti)O_3$ (Vittayakorn *et al* 2004), $Pb(Mg_{1/3}Nb_{2/3})O_3$–$Pb(Zr,Ti)O_3$ (Abe *et al* 1999), $Pb(Ni_{1/3}Nb_{2/3})O_3$–$Pb(Zr,Ti)O_3$ (Yeongho *et al* 2007) have excellent piezoelectric properties and two-stage calcination method was formerly used to prepare the B-site complex ceramics to avoid the existence of pyrochlore phase in perovskite phase (Cho *et al* 2003). Therefore, we adopt the strategy in NBT ceramics in the present work, the B-site substitution of Ti^{4+} by complex ions of $(Zn_{1/3}Nb_{2/3})^{4+}$ and two-stage calcination method were first used to improve the piezoelectric properties of NBT ceramics. In addition, NBT ceramics undergo a low temperature phase transition from ferroelectric to antiferroelectric phase at T_d (Hiruma *et al* 2006). Special attention should also be paid to T_d for practical use because NBT ceramics will be depolarized above T_d. Therefore, $(1-x)Na_{1/2}Bi_{1/2}TiO_3$–$xNa_{1/2}Bi_{1/2}(Zn_{1/3}Nb_{2/3})O_3$ (abbreviated as NBT–NBZNx) ceramics were synthesized by two-stage calcination method and depolarization temperature and piezoelectric properties were investigated in the present study.

2. Experimental

High purity Bi_2O_3, Na_2CO_3, TiO_2, ZnO and Nb_2O_5 (purity over 99·5%) powders were used as starting materials. Our preliminary experiments found that NBT–NBZNx ceramics were not well synthesized by mixing and calcinating all these above powders as used in the conventional oxide mixing process. Therefore, the NBT–NBZNx ceramics were prepared by two-stage calcination method, in which ZnO and Nb_2O_5 powders were first calcined at 1100°C for 4 h which formed $ZnNb_2O_6$, then $ZnNb_2O_6$ was blended with other powders and was calcined at 900°C for 2 h.

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After calcinations, the mixture was ball-milled for 24 h, dried and granulated with PVA as a binder. The granulated powders were then pressed into a disc having a diameter of 18 mm and thickness of 1·2 mm. The compacted discs were sintered at 1190°C for 2 h in air. Silver paste was fired on both faces of the disc at 650°C for 30 min as electrodes. The specimens for measurement of piezoelectric properties were poled in silicon oil at 80°C under 4 kV/mm for 15 min. After 24 h, piezoelectric properties were measured using an impedance analyser (Agilent 4294A) by resonant and anti-resonant method, microstructure and crystal structure were measured by SEM (JSM-5610LV) and X-ray diffractometer (Bruker D8-Advance), respectively. Piezoelectric constant, d_{33}, was measured with a d_{33} meter (ZJ-3A).

X-ray diffraction patterns shown in figure 1 indicate that a single phase of $ZnNb_2O_6$ and a pure perovskite structure solid solution of NBT–NBZN*x* ceramics are synthesized.

3. Results and discussion

Figure 2 shows the XRD patterns of NBT–NBZN*x* ceramics in the 2θ range of 39–48°. The XRD pattern of NBT–NBZN0 has a single reflection {200} owing to its rhombohedral symmetry. On the other hand, the XRD pattern of NBT–NBZN0·05 has a splitting {200} reflection of (200) and (002), indicating its tetragonal symmetry. More NBZN addition leads to wider separation of (200) and (002) peaks, which suggests the tetragonality of the increased lattice. These results reveal that a morphotropic phase boundary (MPB) between rhombohedral and tetragonal structure exists in the NBT–NBZN*x* system.

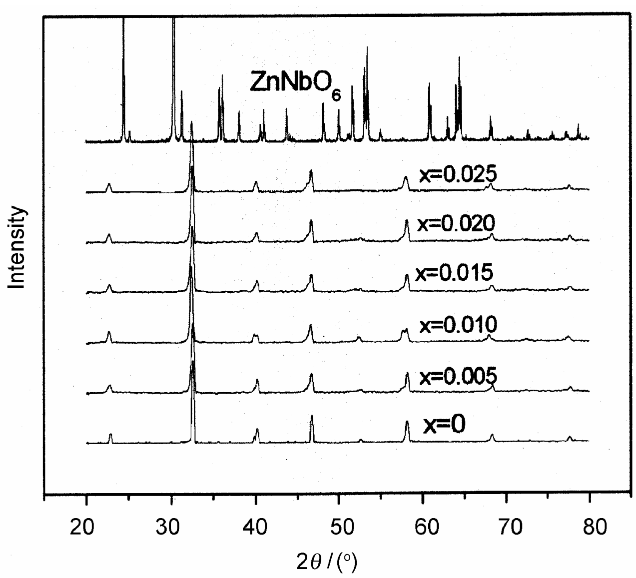

Figure 1. The XRD patterns of $ZnNb_2O_6$ powder and NBT–NBZN*x* ceramics.

Figure 3 shows a typical microstructure of NBT–NBZN*x* ceramics. The SEM observation confirms that the NBT–NBZN*x* ceramics are densely sintered. Furthermore, all NBT–NBZN*x* samples have high density varying from 5·60 g/cm^3–5·76 g/cm^3, which is more than 93% of the theoretical density. In preliminary experiments, we found that the samples were not well-sintered if NBT–NBZN*x* powder was fabricated by direct blending with all the corresponding oxides or carbonates. Therefore, dense NBT–NBZN*x* ceramics were obtained through a modified preparation process using a two-stage calcination method.

Figure 4 shows the piezoelectric constant, d_{33} and the thickness electromechanical coupling factor, k_t, of the NBT–NBZN*x* ceramics as a function of *x*. The piezoelectric

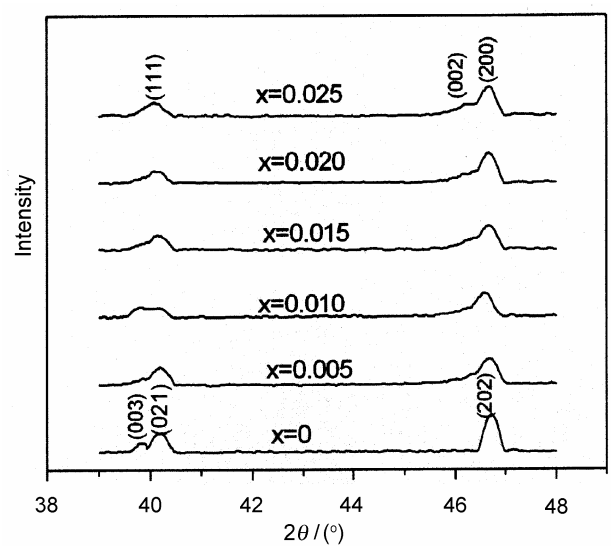

Figure 2. XRD patterns of NBT–NBZN*x* ceramics in 2θ range of 39–48°.

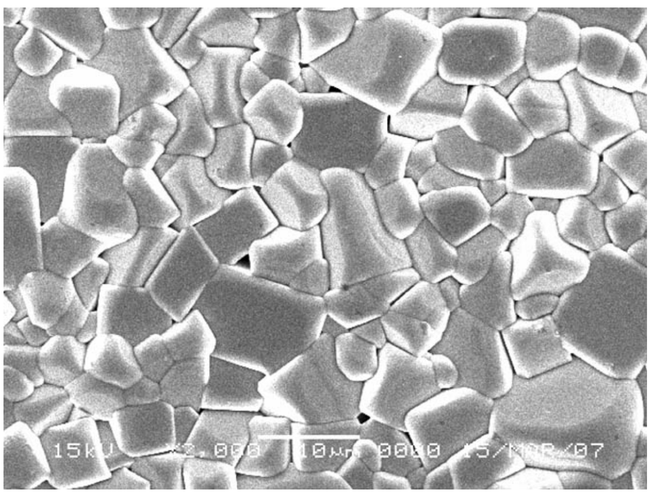

Figure 3. SEM micrograph of NBT–NBZN0·015 ceramic sintered at 1190°C for 2 h.

constant, d_{33} and the thickness electromechanical coupling factor, k_t, first increased, then decreased as x increased, and showed a maximum value of d_{33} = 97 pC/N and k_t = 0·46 at x = 0·010 and 0·020, respectively.

The above piezoelectric properties change of the NBT–NBZNx ceramics demonstrate that the compositions near the MPB have relatively high piezoelectric and electromechanical activities. These high piezoelectric and electromechanical activities can be attributed to an increase in the number of possible spontaneous polarization directions for the compositions near MPB due to the coexistence of rhombohedral and tetragonal phases.

Figure 5 shows the temperature dependence of piezoelectric constants, d_{33}, of NBT–NBZNx ceramics. The depolarization temperatures, T_d, of the MPB compositions were slightly decreased and the lowest T_d maintained at 210°C. The results were not consistent with that of NBT–BT (Bao-Jin 2002) and NBT–KBT (Yoshii 2006) system of lead-free piezoelectric ceramics, whose depolarization temperature, T_d, rapidly dropped near MPB compositions. This is in favour of their possible application as lead-free piezoelectric ceramics.

Figure 6 shows the depolarization temperature, T_d and the Curie temperature, T_C, as a function of x in NBT–NBZNx ceramics. It can be found that both T_d and T_C were slightly decreased near MPB compositions.

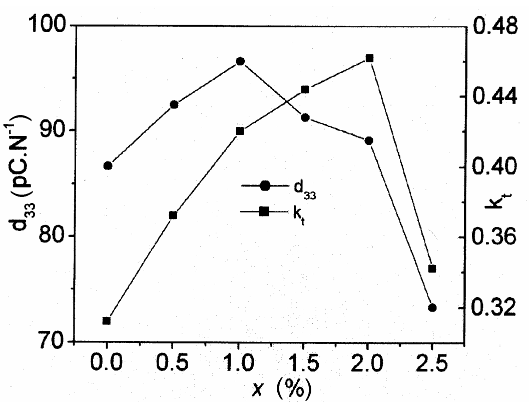

Figure 4. Piezoelectric constant, d_{33} and thickness electromechanical coupling factor, k_t, of NBT–NBZNx ceramics as a function of x.

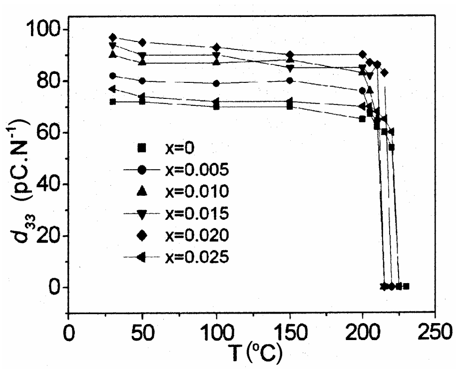

Figure 5. Temperature dependence of piezoelectric constant, d_{33}, of NBT–NBZNx ceramics.

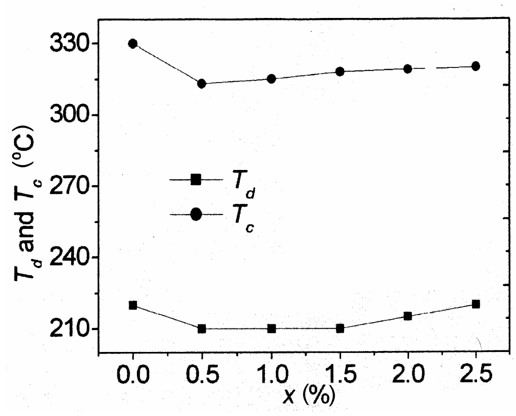

Figure 6. Depolarization temperature, T_d, and Curie temperature, T_c, of NBT–NBZNx ceramics as a function of x.

4. Conclusions

Lead-free piezoelectric ceramics $(1-x)Na_{1/2}Bi_{1/2}TiO_3$–$xNa_{1/2}Bi_{1/2}(Zn_{1/3}Nb_{2/3})O_3$ have been successfully fabricated by the two-stage calcination method. X-ray diffraction showed that NBT–NBZNx ceramics system had a morphotropic phase boundary (MPB) between the rhombohedral and the tetragonal structure. The compositions near the MPB showed excellent piezoelectric properties. The maximum value of the piezoelectric constant, d_{33} = 97 pC/N and the thickness electromechanical coupling factor, k_t = 0·46, were obtained at x = 0·010 and 0·020, respectively. The depolarization temperatures near the MPB compositions were slightly decreased and the lowest T_d maintained at 210°C. This is in favour of their possible application as lead-free piezoelectric ceramics.

References

Abe Y, Yanagisawa T, Kakegawa K and Sasaki Y 1999 *Solid State Commun.* **113** 331

Bao-Jin C, Da-Ren C, Guo-Rong L and Qing-Rui Y 2002 *J. Eur. Ceram. Soc.* **22** 2115

Cho J H, Lee Y H, Chu B J and Kim B I 2003 *Mater. Sci. Forum* **439** 259

Hiruma Y, Nagata H and Takenaka T 2006 *Jpn J. Appl. Phys.* **45** 7409

Shieh J, Wu K C and Chen C S 2007 *Acta Mater.* **55** 3081

Smolenski G A, Isupov V A and Aganovskaya A I 1961 *J. Sov. Phys. Solid State* **2** 2651

Takenaka T 1989 *Ferroelectrics* **230** 389

Yeongho J, Juhyun Y, Sangho L and Jaeil H 2007 *Sens. & Actuators A Phys.* **135** 215

Yoshii K, Nagata H and Takenaka T 2006 *Jpn J. Appl. Phys.* **45** 4493

Vittayakorn N, Rujijanagul G and Tunkasiri T 2004 *Mater. Sci. Eng.* **B108** 258