JOURNAL OF MATERIALS SCIENCE **34** (1999) 3341–3343

Piezoelectric and dielectric properties of PZN-BT-PZT solid solutions

FENG XIA, XI YAO
Electronic Materials Research Laboratory (EMRL), Xi'an Jiaotong University,
Xian 710049, People's Republic of China
E-mail: xiafeng@263.net

$Pb(Zn_{1/3}Nb_{2/3})O_3$ ceramics with the perovskite structure can be stabilized by substituting 6–7 mol % $BaTiO_3$ (BT). Piezoelectric and dielectric properties of the pseudo-binary system $(1-x)(0.94PZN\text{-}0.06BT)\text{-}xPb(Zr_{(1-y)}Ti_y)O_3$ were studied, and the effects of Zr/Ti ratios and thermal annealing process on the piezoelectric and dielectric properties were also discussed. The results show that the piezoelectric properties of this ceramic system are very good when x is about 0.50 and y is about 0.47 with $K_p = 70\%$, $d_{33} = 560$ pC/N, $\varepsilon_m \approx 23{,}000$. These ceramics are favorable to piezoelectric actuators. *© 1999 Kluwer Academic Publishers*

1. Introduction

Lead zinc niobate (PZN) is a typical ferroelectric, which is well-known to exhibit a diffuse phase transition, a high dielectric constant and excellent electrostrictive properties [1]. The solid solution between PZN with rhombohedral symmetry and $PbTiO_3$ (PT) with tetragonal symmetry has a morphotropic phase boundary (MPB) near 9 mol % PT. Single crystals with compositions near the MPB show extremely large dielectric constant ($\varepsilon > 22\,000$) and piezoelectric coefficients, much larger than those of $Pb(Zr_{(1-y)}Ti_y)O_3$ (PZT) ceramics. The planar coupling coefficient K_p is about 92%, the piezoelectric constant d_{33} is up to 1500 pC/N [2]. However, it is very difficult to obtain PZN ceramics with the perovskite structure close to the MPB. Although PZN ceramics with almost a single perovskite phase have been synthesized by hot isostatic processing (HIP), their piezoelectric properties are rather lower than expected [3]. Perovskite-structured PZN ceramics can be obtained by using additives such as $BaTiO_3$, $KNbO_3$ (KN), and $SrTiO_3$, etc. Takennaka *et al.* have reported the piezoelectric properties of PZN-KN-PZT ceramics [4]. In their work, $K_{33} = 70.1\%$, $d_{33} = 377$ pC/N were achieved.

In present work, the PZN ceramics were stabilized by the adding 6 mol % BT. The solid solution 0.94PZN-0.06BT, abbreviated as PZNBT, was used as one composition, and $Pb(Zr_{(1-y)}Ti_y)O_3$ ($y = 0.45 - 0.47$), which also has good piezoelectric properties, was used as another composition to form a pseudo-binary system $(1-x)(0.94PZN\text{-}0.06BT)\text{-}xPb(Zr_{(1-y)}Ti_y)O_3$ (PZNBT-PZT). The piezoelectric and dielectric properties of this pseudo-binary system were studied, and the effects of Zr/Ti ratios on the piezoelectric properties and the effects of thermal annealing processing on the dielectric and piezoelectric properties were also discussed.

2. Experimental

The compositions $(1-x)(0.94PZN\text{-}0.06BT)\text{-}xPb(Zr_{(1-y)}Ti_y)O_3$, where $x = 0.30 - 0.80$, $y = 0.45-0.47$, were prepared by a conventional ceramic processing. Reagent grade PbO, ZnO, Nb_2O_5, $BaCO_3$, TiO_2, and ZrO_2 were used as starting materials. After ball-milling, the mixed oxides were calcined at 1123 K for 2 h. After calcining, the ground and ball-milled powders were pressed into discs with a diameter of 12 mm and a thickness of 1 mm at a pressure of 100 MPa. The specimens were sintered at 1473 K for 2 h. $PbZrO_3$ powder was used to inhibit the vaporation of PbO. After sintering, some of the samples were annealed at 1123 K for 4 h.

The phase structure of the powders was analyzed by Rigaku D/Max-2400 diffractormeter using CuK_α radiation. Silver paste was fired on both sides of the samples at 823 K for 10 min as the electrodes for the dielectric and piezoelectric measurements. The dielectric constants were measured with a HP4274 LCR meter, at a heating rate of 2–3 K/min. Then the samples were poled by applying a DC field of 3–4 kV/mm at 100 °C for 30 min. The piezoelectric planar coupling coefficient (K_p) was determined by the resonance-antiresonance method, using a HP4192A complex impedance analyzer. The values of the piezoelectric constant d_{33} were determined by using a d_{33}-meter.

3. Results and discussion

3.1. Piezoelectric properties of PZNBT-PZT ceramics

Single phase PZN ceramic with perovskite structure is very difficult to produce until other additives are used to stabilize the material. BT is a possible stabilizer requiring only 5–6 mol % to be added. But BT has one disadvantage, it causes the temperature of maximum

0022–2461

TABLE I Effects of Zr/Ti ratio and thermal annealing on the piezoelectric properties of PZNBT-PZT

Sample		AX62	AX60	AX63	AX66
x		0.50	0.50	0.50	0.55
y		0.45	0.47	0.49	0.47
Before annealing	K_p (%)	61.9	66.9	67.6	69.0
	Q_m	100.6	82.2	76.2	85.3
	d_{33} (pC/N)	381	464	527	460
After annealing	K_p (%)	63.9	70.8	70.0	69.6
	Q_m	95.5	78.6	70.63	81.8
	d_{33} (pC/N)	384	501	560	473

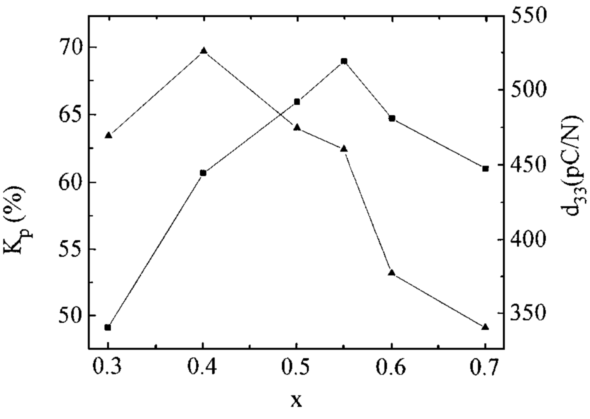

Figure 1 K_p (■) and d_{33} (▲) of PZNBT-PZT ceramics.

dielectric constant T_m to lower rapidly [5], and this effect is detrimental to piezoelectricity. Xiaoli and Xi have attributed this phenomenon to the forming of paramicrovolumes of $Ba(Zn_{1/3}Nb_{2/3})O_3$ [6]. In order to improve the piezoelectric properties of PZN stabilized by BT, it is necessary to add other component to shift T_c to higher temperature, and this additive must also have good piezoelectric properties. Under these conditions, PZT is a very good candidate.

Fig. 1 shows piezoelectric coefficients, K_p and d_{33} of PZNBT-PZT ceramics, where $x = 0.30 - 0.70$, $y = 0.47$. The peak value of K_p is 69%, which appears at $x = 0.55$, while that of d_{33} is 525 pC/N, which occurs at $x = 0.40$.

The Zr/Ti ratio also has an effect on the piezoelectric properties of PZNBT-PZT ceramics. Table I shows the piezoelectric properties of the compositions with different Zr/Ti ratios. When y increases from 0.45 to 0.49, K_p increases from 62 to 67%, and of greater attention is the increase in d_{33} from 381 to 527 pC/N. After annealing at 1123 K for 4 h, there is a increase in the piezoelectric properties of the PZNBT-PZT system (also shown in Table I). For instance, in the composition 0.5PZNBT-0.5PZT ($y = 0.49$), the K_p and d_{33} are increased from 67% and 527 pC/N to 70% and 560 pC/N. The best piezoelectric properties are obtained in 0.5PZNBT-0.5PZT ($y = 0.49$).

For further study, we can define the PZNBT-PZT as follows: m(0.86PZN-0.05BT-0.09PT)-nPb($Zr_{0.53}Ti_{0.47}$)O_3, where $m + n \sim 1$, $n = 0.3$–0.7. The two compositions, (0.86PZN-0.05BT-0.09PT) and $Pb(Zr_{0.53}Ti_{0.47})O_3$ are all lying near a MPB [7, 8], each has very good piezoelectric properties. In 0.86PZN-0.05BT-0.09PT ceramic, d_{33} is about 624 pC/N [9], and in $Pb(Zr_{0.53}Ti_{0.47})O_3$, d_{33} is about 400 pC/N. After forming a new system, the piezoelectric properties are very good: d_{33} is about 560 pC/N, K_p is up to 70%. This helps to explain why the piezoelectric properties of PZNBT-PZT solid solutions were so good, and why increasing the value of y, in other words increasing the content of PT, will improve the piezoelectric properties.

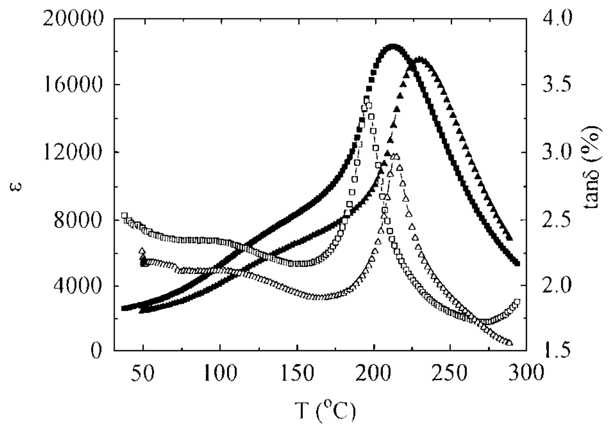

Figure 2 Temperature dependence of the dielectric constant ε (solid), and dissipation factor tan δ (hollow) at 1 kHz of AX60 (■) and AX66 (▲).

3.2. Dielectric properties

In Fig. 2, the temperature dependence of the dielectric constant and dissipation factor at 1 kHz of samples AX60 and AX66 are shown. T_m increases as the amount of PZT increases, while its dielectric constant decreases. Addition of PZT has shifted T_m up to about 493 K, making it suitable for use in actuators applications.

Figs 3 and 4 show dielectric constant and dissipation factor of sample AX60 after annealed at 1123 K for 4 h. The dielectric constant and dissipation factor have apparently increased after annealing, and the Curie peak sharpened. The diffusive factor, δ, can be calculated from the quadratic formula of the following:

$$\frac{1}{\varepsilon} = \frac{1}{\varepsilon_m} + \frac{1}{2\varepsilon_m \delta^2}(T - T_m)^2$$

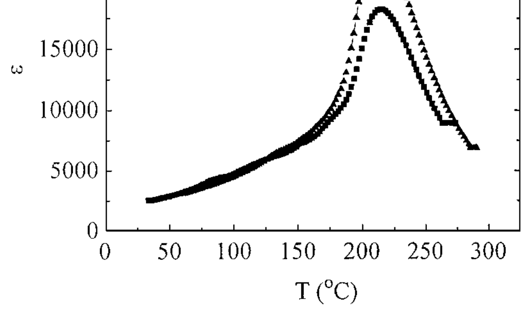

Figure 3 Temperature dependence of dielectric constant, ε, at 1 kHz of sample AX60 reference to annealing.

TABLE II Dielectric parameters of samples AX60 and AX66 reference to annealing

	Before annealing			After annealing		
	T_m (°C)	δ (°C)	ε_m	T_m (°C)	δ (°C)	ε_m
AX60	211.9	39.0	18,200	212.6	32.4	23,860
AX66	229.4	34.8	17,450	228.6	30.7	22,430

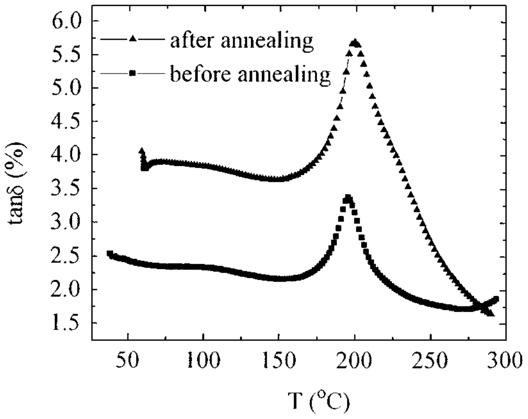

Figure 4 Temperature dependence of dissipation factor, tan δ, at 1 kHz of sample AX60 reference to annealing.

where ε_m is the maximum dielectric constant. T_m is the temperature of maximum dielectric constant measured at 1 kHz. The dielectric parameter are shown in Table II. After annealing, ε_m increases about 31%, and δ decreases.

Jang and Kyu-Mann have ever studied the effects of annealing on PZN-PMN-PT solid solutions, and they attributed the observed dielectric and piezoelectric changes to the elimination of low permittivity intergranular layers [10]. Considering the effects of intergranular layers, the above formula can be rewritten as following:

$$\frac{1}{\varepsilon} = \left(\frac{1}{\varepsilon_m} + \frac{1}{R\varepsilon_{gb}}\right) + \frac{(T - T_m)^2}{2\varepsilon_m\delta^2}$$

where ε_{gb} is the dielectric constant of the intergranular layers, which is about 20. R is the ratio of the thickness of the grains to the thickness of intergranular layers. This formula suggests that the dielectric constant will increased with the same ratio over a wide temperature range, and this phenomena has been approved in H. M. Tang's work. But in our previous [9] and present works, we observed different phenomena: the dielectric constant only apparently increases at the region where $T \approx T_m$, and the dissipation factor also increases abruptly. So the elimination of intergranular layer is not the main reason in our works.

PZN, like $Pb(Mg_{1/3}Nb_{2/3})O_3$(PMN), is a relaxor ferroelectric, which has a diffuse phase transition. The diffuse phase transition characteristics of relaxor ferroelectrics were first explained by Smolenskii [11] on the basis of local compositional fluctuations, it is believed that the polar (ferroelectric) and nonpolar (paraelectric) microregions coexisted over a broad temperature interval. The volume fraction of the microregions was conjectured to vary strongly with temperature, resulting in a broading of the temperature-dependent macroscopic characteristics. Later, Cross [12] proposed a superparaelectric model which was based on the concept of the presence of small polar clusters which underwent coherent thermally driven polarization reversals between crystallographically equivalent orientations. The annealing can't change the ordering degree in the ferroelectrics such as PZN and PMN. But annealing can changes the composition and distributions of the subregions, and eliminates the clamping of motion of microdomian walls and thermally driven polarization reversals of small nano-scale polar clusters caused by inner stress and defects. After annealing, the size of the micropolar regions become small, resulting in the decrease of the diffusive factor. As a result, the motions of microdomain walls and polarization reversals of small polar clusters is easy to undergo in annealed samples when the temperature is near T_m. Their contributions to dielectric constant will account for the increase in dielectric constant in PZN-based ceramics in the temperature range near T_m and that in dissipation factor. The easy reversals of polarization under DC bias after annealing will contributed to the increase in piezoelectric properties. Lead vacancies, resulting from the loss of Pb during annealing, will also help to explain the increase in the dissipation factors.

4. Conclusions

Piezoelectric properties of the pseudo-binary system PZNBT-PZT are very good when x is about 0.50 and y is about 0.49. After thermal annealed, a large increase in the piezoelectric and dielectric properties was observed. In this work, $K_p = 70\%$, $d_{33} = 560$ pC/N, $\varepsilon_m \approx$ 23,000 were achieved.

References

1. A. HALLIYAL and A. SAFARI, *Ferroelectrics* **158** (1994) 295.
2. J. KUWATA, K. UCHINO and S. NOMURA, *Jpn. J. Appl. Phys.* **21** (1982) 1298.
3. T. FUJIU, A. TANAKA and T. TAKENAKA, *ibid.* **30** (1991) L298.
4. T. TAKENNAKA, M. SATOU, K. NAKATA and K. SAKATA, *Ferroelectrics* **128** (1992) 67.
5. A. HALLIYAL, U. KUMAR, R. E. NEWNHAM and L. E. CROSS, *Amer. Ceram. Soc. Bull.* **66** (1987) 671.
6. W. XIAOLI and Y. XI, *Ferroelectrics* **145** (1993) 143.
7. A. HALLIYAL, U. KUMAR, R. E. NEWNHAM and L. E. CROSS, *J. Amer. Ceram. Soc.* **70** (1987) 119.
8. J. JAFFE, W. R. COOK and H. JAFFE, "Piezoelectric Ceramics" (Academic Press, London, 1971) p. 137.
9. FENG XIA, XI YAO and XIAOLI WANG, *J Mater. Sci. Lett.* **17** (1998) 861.
10. HYUN M. JANG and LEE KYU-MANN, *J. Mater. Res.* **10** (1995) 3185.
11. G. A. SMOLENSKII and A. I. AGRANOVSKAYA, *Sov. Phys.-Tech. Phy.* **3** (1958) 1380.
12. L. E. CROSS, *Ferroelectrics* **76** (1987) 241.

Received 23 October 1998
and accepted 27 January 1999