Structure, electrical properties and temperature stability of PIN-PZN-PT piezoelectric ceramics with morphotropic phase boundary compositions

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A series of $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3$ - $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 (PIN-PZN-PT) ternary piezoelectric ceramics with compositions at the morphotropic phase boundary (MPB) were prepared. The phase structure, microstructure, electrical properties and temperature stability of PIN-PZN-PT ceramics were investigated systematically. The structural analysis indicated that an MPB phase consisting of rhombohedral and tetragonal phases was formed in all ceramics. For the selected compositions, dielectric measurements demonstrated that the Curie temperature T_C changed from 237°C to 295°C and showed a strong trend of compositional dependence. All the samples showed good piezoelectric properties. Particularly, the 0.35PIN-0.40PZN-0.25PT sample has the optimum piezoelectric properties, the piezoelectric coefficient d_{33} is 589 pC/N, the electromechanical coupling factors k_p and k_t are 59% and 49%, respectively. Compared with PZN-PT and PMN-PT ferroelectric crystals, the superior limit of usage temperature of PIN-PZN-PT ceramics was achieved around 230°C by thermal depoling method. These results make PIN-PZN-PT ceramics a promising material to meet the practical demands of higher temperature and larger electric field operating ranges.

Keywords: PIN-PZN-PT piezoelectric ceramics; temperature stability; performance-composition maps.

1. Introduction

$\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 (PZN-PT) and $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 (PMN-PT) relaxor ferroelectric single crystals with extraordinary large piezoelectric and electromechanical responses have aroused considerable interest in the industrial and scientific fields.^{1,2} These excellent properties also have caused revolutionary changes in actuators, medical ultrasonic imaging, sensors and other electromechanical devices.^{3,4} However, the relatively low Curie temperature ($T_C \sim 130$ – 170°C) and rhombohedral-tetragonal phase transition temperature ($T_{R-T} \sim 60$ – 95°C) of PZN-PT and PMN-PT ferroelectric crystals make the piezoelectric properties depolarize easily. In addition, the coercive field E_C of about 2.5 kV/cm is not high enough for high-drive applications.^{5,6} Thus, it is highly desirable to develop new high-performance ferroelectric systems with higher T_C/T_{R-T} and larger E_C , which would allow for a wider temperature and electric field usage range and thus greater flexibility of device design. In order to expand the temperature and electric field usage range, numerous compositional systems have been studied. So far, the ternary $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3$ - $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 (PIN-PMN-PT) system has attracted much attention.^{7–12} It is reported that the PIN-PMN-PT single crystals near MPB possess a T_C higher than 170°C and a T_{R-T} higher than 120°C without losing the superior piezoelectric and

electromechanical activity of the binary PMN-PT or PZN-PT crystals. Furthermore, the E_C also increases to about 5 kV/cm, providing much better temperature and field stability.^{13–15}

Recently, a high-performance ternary ferroelectric system $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3$ - $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 (PIN-PZN-PT) with high T_C/T_{R-T} and large E_C has been investigated. Based on the reported results, the PIN-PZN-PT ceramics near MPB possess much higher phase transition temperatures ($T_C > 210^\circ\text{C}$ and $T_{R-T} > 150^\circ\text{C}$) and larger coercive field ($E_C > 10$ kV/cm) compared to PIN-PMN-PT system.^{16–18} The extended temperature and electric field usage range is very attractive for growing large-sized ferroelectric single crystals to satisfy the practical device requirements. The area near the straight line connecting the two MPBs of PZN-0.09PT¹⁹ and PIN-0.37PT²⁰ is the MPB region of the PIN-PZN-PT system. However, there is quite few researches on the PIN-PZN-PT system.^{16–18} In addition, from the perspective of applications, it is very meaningful to completely establish the corresponding performance-composition maps of PIN-PZN-PT system, which is crucial for the design and applications of new piezoelectric materials.

In this work, as an extension of the study on the PIN-PZN-PT system, the phase structure, microstructure, electrical properties and temperature stability of ternary

Fig. 1. Schematic ternary phase diagram and selected sample compositions in the PIN-PZN-PT system.

PIN-PZN-PT ceramics with MPB compositions were studied. These results would be conducive to the development of new piezoelectric materials with wider temperature and larger electric field operating ranges.

2. Experimental Procedure

Ternary PIN-PZN-PT ceramic specimens with MPB compositions were prepared. The schematic ternary phase diagram and selected sample compositions 1#–7# are shown in Fig. 1. In_2O_3 (99.9%), Nb_2O_5 (99.5%), ZnO (99.0%), PbO (99.0%) and TiO_2 (98.0%) powders were used as raw materials. First, In_2O_3 and ZnO with Nb_2O_5 were used to prepare the precursors of InNbO_4 and ZnNb_2O_6 at 1100°C and 1000°C for 6 h, respectively. Then, PbO , ZnNb_2O_6 , InNbO_4 and TiO_2 powders were mixed and wet-milled with ethanol for 24 h. After drying, the mixed powders were calcined at 800°C for 4 h and remilled again. The dried powders were then reground with 5 wt.% PVA and pressed into disks. After burning out the binder at 550°C for 2 h, these pellets were sintered at $1050\text{--}1200^\circ\text{C}$ for 2 h in a sealed Al_2O_3 crucible in a PbZrO_3 atmosphere.

The crystal structure was subsequently detected using X-ray diffraction (XRD, D/MAX-2400, Rigaku, Japan) and the microstructure was investigated by scanning electron microscope (SEM, FEI Quanta FEG250; JEOL, Japan). The mean grain size of the sample was estimated by the linear intercept method. To characterize the electrical properties, the sintered pellets were polished and then electroded with silver paste, fired at 600°C for 20 min. The sample sizes are about 1 mm in thickness and 8.4–8.8 mm in diameter. Temperature-dependent dielectric properties were taken using an LCR meter (E4980A, Agilent) and a temperature controller system. The polarization hysteresis curves were measured at a frequency of 1 Hz by TF analyzer 2000 (aixACCT Systems, Germany). Before the piezoelectric properties test, the ceramic specimens were poled in silicone oil at 130°C for 10 min under an applied field of 30 kV/cm. The piezoelectric coefficient d_{33} was measured using a d_{33} meter (ZJ-3A). The electromechanical coupling factors k_p , k_t and mechanical quality factor Q_m were calculated by the resonance and antiresonance techniques using an impedance analyzer (HP4294A). Thermal depoling experiments were carried out by holding the poled specimens at a variety of temperatures for 10 h with Ag electrodes and then cooling to room temperature, measuring their respective piezoelectric properties and repeating the process.

3. Results and Discussion

3.1. Phase structure and microstructure

Figure 2(a) shows the X-ray diffraction patterns of the PIN-PZN-PT ceramics sintered at their optimum sintering temperatures. Obviously, the typical perovskite-structured phase is evident for all samples and the pyrochlore phase or other impurities are not traced. Moreover, the small splitting or broadening of the (200) reflection peak and the absence of (111) reflection peak splitting indicate that all samples are in the MPB region. Further fine scanning XRD test near 45°

Fig. 2. X-ray diffraction patterns of the PIN-PZN-PT specimens sintered at optimum temperatures.

Fig. 3. SEM micrographs of the fresh surfaces of PIN-PZN-PT specimens: (a) 1#, (b) 2#, (c) 3#, (d) 4#, (e) 5#, (f) 6#, (g) 7#.

was also carried out to judge the phase structure. As shown in Fig. 2(b), the peaks were separated by a single-peak fitting of the (200) reflection peak using a Lorentz function. Three maxima were determined in all XRD patterns, indicating the coexistence of rhombohedral and tetragonal phases, and the tetragonal phase content (TP) was estimated using Eq. (1)²¹:

$$\text{TP}(\%) = \frac{I_{(002)T} + I_{(200)T}}{I_{(002)T} + I_{(200)T} + I_{(200)R}} \times 100\%, \quad (1)$$

where $I_{(200)R}$ is the integral intensity of the rhombohedral (200) reflection peak and $I_{(002)T}$ and $I_{(200)T}$ are the integral intensities of the tetragonal (002) and (200) reflection peaks, respectively. For the 1#, 2#, 3#, 4#, 5#, 6# and 7# specimens, the results of the TP calculation using Eq. (1) were 62%, 59%, 57%, 56%, 44%, 42% and 42%, respectively. It is no doubt that all specimens locate at MPB.²²

Microstructures of the PIN-PZN-PT ceramics sintered at their optimum sintering temperatures are displayed in Fig. 3. It is clear that all samples display a dense microstructure. The mean grain size is on the order of 2.58 μm, 3.60 μm, 2.93 μm, 2.67 μm, 2.29 μm, 4.28 μm and 1.93 μm for 1#, 2#, 3#, 4#, 5#, 6# and 7# samples, respectively.

3.2. Dielectric properties

The dielectric properties versus temperature curves for poled PIN-PZN-PT specimens at 1 kHz are shown in Fig. 4. For the selected compositions, the Curie temperature T_C continuously increased from 237°C to 295°C with an increase in PT content, being associated with the high T_C of PT (490°C), and showed a strong trend of compositional dependence, which means that the T_C in ternary PIN-PZN-PT system within the MPB region is adjustable. Apart from T_C , another

Fig. 4. Dielectric permittivity and dielectric loss versus temperature curves for poled PIN-PZN-PT ceramics with MPB compositions.

dielectric anomaly in the range of 125–170°C prior to T_C could also be observed, which corresponds to the rhombohedral–tetragonal phase transition temperature T_{R-T} . The highest T_{R-T} on the order of 170°C was obtained in the 0.50PIN–0.205PZN–0.295PT ceramic. It is worth noting that the relatively high T_C and T_{R-T} of ternary PIN-PZN-PT system has broad prospects for device applications over a wide temperature range. Table 1 shows the dielectric permittivity ϵ_r and dielectric loss $\tan\delta$ of poled PIN-PZN-PT ceramic samples, the maximum $\epsilon_r = 3372$ is found in 0.40PIN–0.33PZN–0.27PT ceramic, while 0.45PIN–0.26PZN–0.29PT ceramic obtains the minimum $\tan\delta = 1.3\%$.

3.3. Ferroelectric and piezoelectric properties

Figure 5 depicts the P–E hysteresis loops of PIN-PZN-PT ceramics with MPB compositions. All samples exhibit

Fig. 5. P-E hysteresis loops for PIN-PZN-PT ceramics with MPB compositions.

well-shaped loops with saturation. It can be seen that the coercive field E_C in our choosing samples is in the range of 8.7–11.1 kV/cm. Compared with PMN-PT, PZN-PT, and PIN-PMN-PT single crystals,^{3,4} the E_C of PIN-PZN-PT ceramics is significantly improved, preventing the depolarization of the polarized state and facilitating the high excitation signal device applications. Moreover, the remanent polarization P_r values of the samples were greater than $20 \mu\text{C}/\text{cm}^2$, showing good ferroelectricity. It could be ascribed to the enhanced polarization owing to the phases coexistence within the MPB region.²³

Figure 6 shows the piezoelectric coefficient d_{33} and electromechanical coupling factors k_p , k_t as a function of T_C for ternary PIN-PZN-PT ceramics. All samples showed good piezoelectric and electromechanical properties due to the rhombohedral and tetragonal phases coexistence. The piezoelectric coefficient d_{33} and electromechanical coupling factor k_p are in the range of 474–589 pC/N and 48–59%, respectively. The d_{33} , k_p and k_t increased first, reaching the maximum at $T_C = 245^\circ\text{C}$, and then decreased with increasing T_C . The maximum $d_{33} = 589 \text{ pC/N}$, $k_t = 49\%$ and

Fig. 6. The piezoelectric constant d_{33} and electromechanical coupling factors k_p , k_t measured at room temperature versus T_C curves in PIN-PZN-PT ternary ceramics.

$k_p = 59\%$ are presented at the composition 0.35PIN–0.40PZN–0.25PT. Furthermore, considering its relatively higher T_C (245°C), this composition is preferred for high temperature piezoelectric applications. However, the mechanical quality factor Q_m of 0.35PIN–0.40PZN–0.25PT ceramic is only 70, which is too low to be used in certain high power devices, such as transformers or actuators. In these applications, a high Q_m value is very significant due to the important role of mechanical vibration in resonance frequency. The mechanical quality factor Q_m could be improved by means of doping or modification, which will be studied in the future works. The detailed electrical properties of PIN-PZN-PT ceramics with MPB compositions are listed in Table 1.

3.4. Thermal stability of piezoelectric properties

Figure 7 shows the effect of thermal depoling on the piezoelectric coefficients d_{33} of PIN-PZN-PT ceramics with MPB compositions. To quantify the thermal stability of piezoelectric coefficient, the $\Delta d_{33}/d_{33}$ represents the relative change rate of piezoelectric coefficient at high temperature compared with the room temperature value. That is, $\Delta d_{33}/d_{33}$ is defined as

$$\Delta d_{33}/d_{33} = \frac{d_{33}(T) - d_{33}(25^\circ\text{C})}{d_{33}(25^\circ\text{C})}. \quad (2)$$

It shows that the values of $\Delta d_{33}/d_{33}$ in the PIN-PZN-PT ceramics increase slightly with increasing the temperature initially, and then tend to decrease with rising up the temperature. For the 1#, 2#, 3#, 4#, 5#, 6# and 7# specimens, the depoling temperatures determined from the thermal depoling measurements were 110°C , 150°C , 230°C , 210°C , 150°C , 130°C and 130°C , respectively. As shown, the $\Delta d_{33}/d_{33}$ values of 1#, 5#, 6# and 7# specimens exhibit a stronger temperature dependence than the 2#, 3# and 4# ceramics, the $\Delta d_{33}/d_{33}$ values of 1#, 5#, 6# and 7# specimens decrease slightly below T_{R-T} , while the depolarization temperatures presumed from the thermal depoling curves for 2# and 4# ceramics are higher than their T_{R-T} . For example, the $\Delta d_{33}/d_{33}$ of 5# sample begins to sharply decrease near 150°C (below $T_{R-T} \sim 170^\circ\text{C}$), while for the 3# specimen, it decreases sharply only above 150°C (above $T_{R-T} \sim 130^\circ\text{C}$).

As for the difference in temperature stability of the piezoelectric coefficient of the samples, in this study, since all ceramic samples achieved a higher relative density ($> 95\%$), the difference in phase content is mainly considered. Due to the difference in the degree of non- 180° domain reorientation, the d_{33} values of tetragonal-phase composition own better thermal stability than the rhombohedral-structured one.²⁴ As discussed in 3.1, for the 1#, 2#, 3#, 4#, 5#, 6# and 7# specimens, the tetragonal phase contents are 62%, 59%, 57%, 56%, 44%, 42% and 42%, respectively. Since the 5#, 6# and 7# samples have relatively lower tetragonal phase contents, their piezoelectric properties have poor temperature

Table 1. The electrical properties of poled PIN–PZN–PT ceramics with MPB compositions.

Sample	Composition	T_C (°C)	T_{R-T} (°C)	ε_r (RT)	$\tan\delta$ (%) (RT)	d_{33} (pC/N)	k_p (%)	k_t (%)	Q_m	P_r ($\mu\text{C}/\text{cm}^2$)	E_C (kV/cm)	$\Delta d_{33}/d_{33}$ (230°C)
1#	0.30PIN–0.47PZN–0.23PT	237	125	2026	1.7	480	48	47	94	30	9.1	–0.32
2#	0.35PIN–0.40PZN–0.25PT	245	130	2143	1.9	589	59	49	70	35	10.4	–0.26
3#	0.40PIN–0.33PZN–0.27PT	255	—	3372	2.6	523	55	48	84	33	11.1	0.00
4#	0.45PIN–0.26PZN–0.29PT	268	125	1718	1.3	520	50	48	87	24	9.0	–0.03
5#	0.50PIN–0.205PZN–0.295PT	276	170	1936	2.5	504	49	47	110	36	9.9	–0.23
6#	0.55PIN–0.14PZN–0.31PT	278	140	1238	1.8	490	49	47	95	20	8.7	–0.23
7#	0.60PIN–0.07PZN–0.33PT	295	142	1269	2.2	474	48	46	97	27	11.0	–0.16

stability. In addition, the grain size may also have some effect. Samples with larger grain sizes have better temperature stability of piezoelectric properties, it can be attributed to the lower stresses in ceramics with larger grain size.²⁵ Although the 1# sample has the highest tetragonal phase content, its smaller grain size may affect its temperature stability. In addition, its sample composition is closer to the pyrochlore region and may also have a certain effect on its temperature stability. For the 2#, 3# and 4# ceramics, because of their

relatively higher tetragonal phase content and larger grain size, the thermal stability of piezoelectric properties is superior.

Particularly, the highest use temperature was raised to 230°C for 3# specimen, the upper limit of use was almost three times compared with the PZN–PT and PMN–PT crystals. In addition, it was found that the $\Delta d_{33}/d_{33}$ values were rapidly decreased by 20% when the temperatures are higher than 190°C for all samples. The improved usage temperature

Fig. 7. Effect of thermal depoling on the piezoelectric coefficient d_{33} of PIN–PZN–PT ceramics.

Fig. 7. (Continued)

range makes the PIN–PZN–PT a very attractive candidate for high-temperature applications.

4. Conclusion

The phase structure, electrical properties and thermal stability of a sets of PIN–PZN–PT ceramics with compositions at the MPB have been studied for high-temperature piezoelectric applications. For the selected compositions, dielectric measurements demonstrated that the Curie temperature T_C increased from 237°C to 295°C continuously and showed a strong trend of compositional dependence. All samples exhibited excellent piezoelectric properties as a result of the rhombohedral and tetragonal phases coexistence. The optimum properties were found for 0.35PIN–0.40PZN–0.25PT ceramics with ϵ_r of 2143, $\tan\delta$ of 1.9%, T_C of 245°C, d_{33} of 589 pC/N, k_p of 59%, P_r of 35 $\mu\text{C}/\text{cm}^2$ and E_c of 10 kV/cm. Moreover, the ternary PIN–PZN–PT system achieved an increased operating temperature range, which

exhibits very promising applications in high-temperature environment.

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