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Characterization and piezoelectric thermal stability of PIN–PMN–PT ternary ceramics near the morphotropic phase boundary

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ABSTRACT

The phase structure and piezo/dielectric properties of $x\mathrm{Pb(In_{1/2}Nb_{1/2})O_3}$–$y\mathrm{Pb(Mg_{1/3}Nb_{2/3})O_3}$–$z\mathrm{PbTiO_3}$ (PIN–PMN–PT $x/y/z$) ternary ceramics with morphotropic phase boundary (MPB) composition were investigated. It was found that Curie temperatures of choosing composition changed from 165 °C to 293 °C and the piezoelectric properties are almost the same at room temperature in PIN–PMN–PT system near MPB. The piezoelectric coefficient d_{33} and electromechanical coupling factor k_p are higher than 440 pC/N and 60%, respectively. Temperautre and dc bias dependence of piezoelectric response for PIN–PMN–PT ceramics were measured. The usage temperature range was found to be improved, compared with PMN–PT single crystal near MPB.

1. Introduction

Relaxor-based ferroelectric crystals $\mathrm{Pb(Mg_{1/3}Nb_{2/3})O_3}$–$\mathrm{PbTiO_3}$ (PMN–PT) and $\mathrm{Pb(Zn_{1/3}Nb_{2/3})O_3}$–$\mathrm{PbTiO_3}$(PZN–PT) with morphotropic phase boundary (MPB) composition have been extensively studied due to their extraordinary large electromechanical coupling coefficient and piezoelectric coefficient [1] and [2]. The outstanding properties have stimulated the application research in transducers, sensors and actuators [3–5]. The low Curie temperature (T_c = 130–160 °C) of PMN–xPT (x = 30–35) limits their applications in high temperature environment [6–8]. Moreover, the usage temperature range of PMN–xPT ferroelectric material is also restricted by the rhombohedral to tetragonal phase transformation temperature (i.e., T_{R-T}), which is usually lower than 100 °C. Thus, it is important to improve piezoelectric thermal stability of PMN–PT crystals. The PIN–PMN–PT ternary system with relatively high T_c appears to be a promising candidate and has attracted many investigations [9–13].

Hosono et al. [8] found that the MPB composition in $\mathrm{Pb(In_{1/2}Nb_{1/2})O_3}$–$\mathrm{Pb(Mg_{1/3}Nb_{2/3})O_3}$–$\mathrm{PbTiO_3}$ (PIN–PMN–PT) ternary system is an almost linear between the MPBs of PMN–32PT and PIN–37PT. The Curie temperatures of PIN–PMN–PT near MPB are changed from 160 °C to 320 °C by adjusting the composition. It is intensity to study the piezo/dielectric properties of PIN–PMN–PT ceramics. From applied viewpoint, thermal stability of piezoelectric properties and dc bias dependence of piezoelectric response are also expected to be investigated. In this work, the phase structure and electrical properties as well as their thermal stability of PIN–PMN–PT ternary ceramics near MPB were studied. The influence of dc bias dependence of piezoelectric response was investigated. These results would be helpful for developing high temperature piezoelectric materials.

2. Experimental procedure

PIN–PMN–PT ternary ceramic with MPB composition, as shown in Fig. 1, were synthesized using two steps columbite precursor method [14]. The raw materials were oxide powders with purities better than 99.9%. The $\mathrm{MgNb_2O_6}$ and $\mathrm{InNbO_4}$ powder were synthesized at 1000 °C and 1100 °C, respectively for 6 h. The PbO, $\mathrm{MgNb_2O_6}$, $\mathrm{InNbO_4}$ and $\mathrm{TiO_2}$ powders were wet mixed by ball milling with $\mathrm{ZrO_2}$ ball for 5 h and then the mixed powder were calcined at 850 °C for 4 h. Upon milling, the various powders were pressed using PVA binder to form pellets 12 mm in diameter and about 1.2 mm in thickness. After burning out the PVA binder at 550 °C for 4 h, the samples were sintered at 1220 °C for 6 h. To compensate for PbO loss from the pellets, a PbO-rich atmosphere was maintained by placing an equimolar mixture of PbO and $\mathrm{ZrO_2}$ inside the crucible.

The structure of the sintered samples was subsequently examined by X-ray diffraction (XRD RIGAKU D/MAX-2400). Silver paste was fired on both sides of the samples at 600 °C for 10 min. The temperature dependence of dielectric properties was measured by an HP 4284 LCR meter in conjunction with a furnace. The hysteresis loop was measured by TF analyzer 2000. Before piezoelectric experiments, the PIN–PMN–PT samples were poled at 40 kV/cm dc field at 130 °C for 10 min in silicon oil. The d_{33} value was measured using a piezo-d_{33} meter (ZJ-3A). The measurement of temperature and dc bias dependent-piezoelectric coefficient d_{33} is particular described in Ref. [15]. The temperature dependence of piezoelectric coefficient k_p was measured by an HP 4294 LCR meter in conjunction with a furnace.

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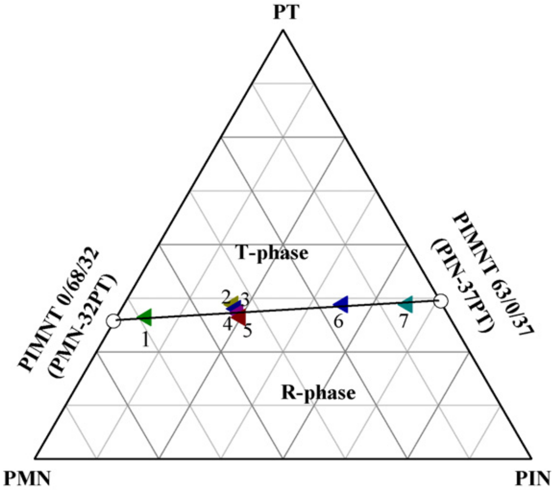

Fig. 1. Composition of samples in PIN–PMN–PT ceramic system.

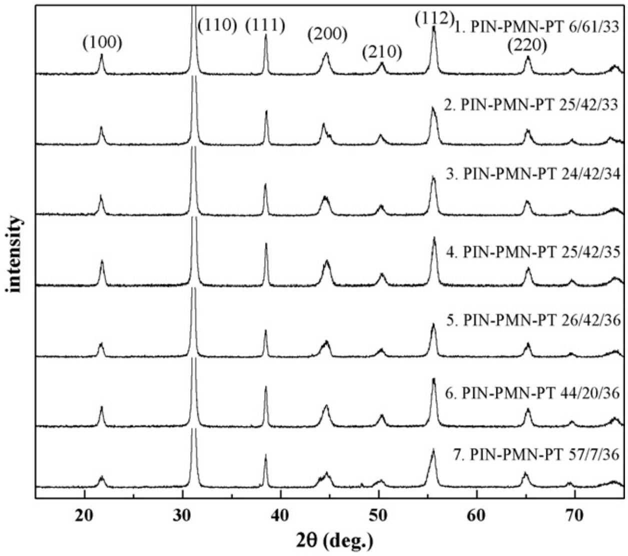

Fig. 2. XRD pattern of PIN–PMN–PT ceramics near MPB.

3. Results and discussion

XRD patterns of the PIN–PMN–PT ceramics with MPB compositions at room temperature are shown in Fig. 2 All of the patterns present pure perovskite phase without any trace of pyrochlore structure. The diffraction peak (2 0 0) shows a broden and no splitting peak, which indicates that the samples are in the MPB region. In addition, the micro-structure transitions of PIN–PMN–PT are induced from rhombohedral to tetragonal phase within the MPB region with increasing PT content.

Fig. 3 displays the SEM micrographs of the fracture surfaces of PIN–PMN–PT ceramics: (a) PIN–PMN–PT 25/42/33, (b) PIN–PMN–PT 24/42/34, (c) PIN–PMN–PT 23/42/35 and (d) PIN–PMN–PT 22/42/36. As shown in the figure, there is no presence of a second phase within the grains or at the grain boundaries. It is clearly evident that all samples are highly dense and their average grain size is about 1–3 μm.

The temperature dependence of the dielectric constant for PIN–PMN–PT ternary ceramics at 1 kHz is shown in Fig. 4. The Curie temperature varies from 165 °C to 293 °C in our choosing composition. As expected the phase transition temperatures ($T_{\max}$) values show a strong compositional dependence within the MPB region. It suggests that $T_{\max}$ of the samples near MPB composition in PIN–PMN–PT ternary system can be adjusted. The detailed

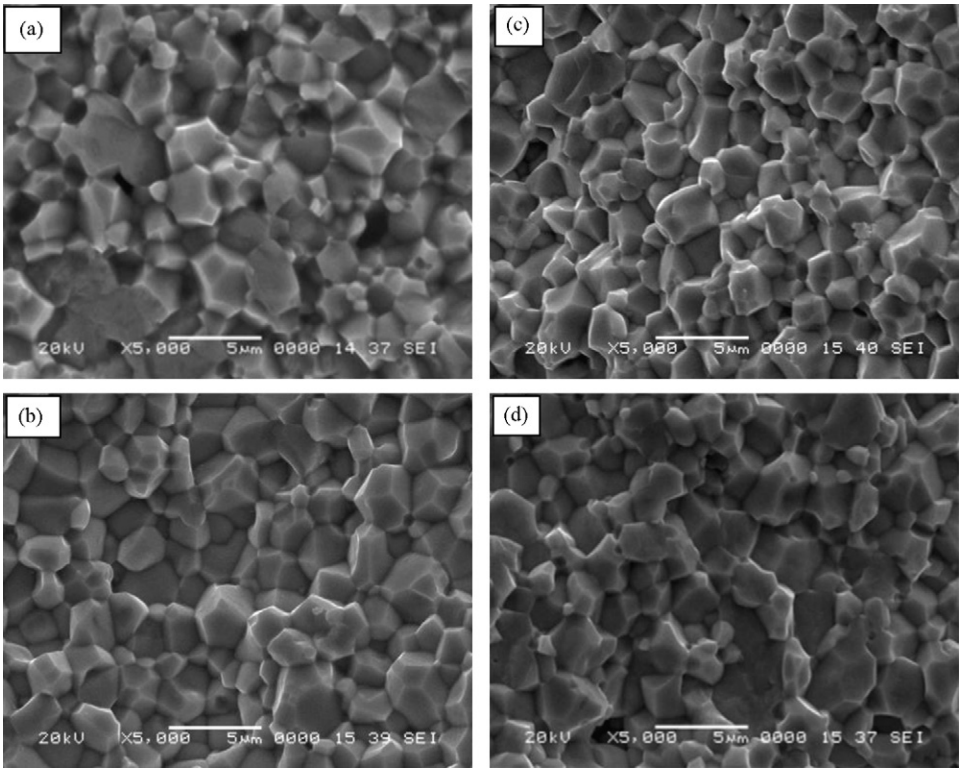

Fig. 3. Scanning electron micrographs of PIN–PMN–PT ceramics near MPB: (a) PIN–PMN–PT 25/42/33, (b) PIN–PMN–PT 24/42/34, (c) PIN–PMN–PT 23/42/35 and (d) PIN–PMN–PT 22/42/36.

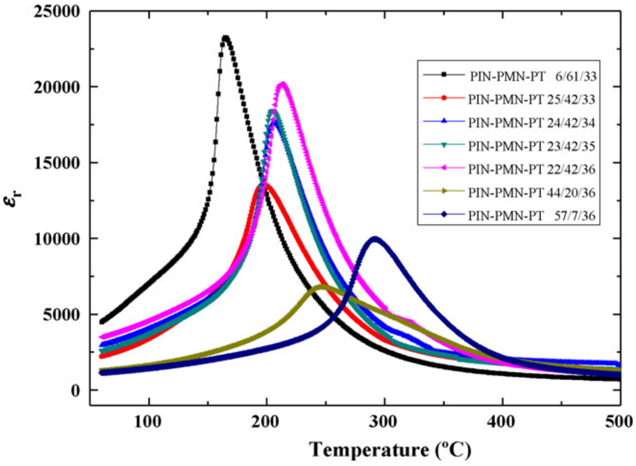

Fig. 4. Temperature dependence of dielectric constants in PIN–PMN–PT ceramics.

Table 1
Dielectric and piezoelectric properties of PIN–PMN–PT ceramics near MPB at room temperature.

Sample	Composition (PIN/PMN/PT)	T_{max} (°C)	ε_{max}	tan δ (%)	d_{33} (pC/N)	k_p (%)	k_t (%)
1	6/61/33	165	23600	3.0	560	62.3	49.5
2	25/42/33	198	13601	3.4	487	60.1	48.5
3	24/42/34	205	18340	3.0	505	64.3	49.1
4	23/42/35	207	17532	3.0	497	61.3	49.0
5	22/42/36	213	20133	3.0	489	62.3	48.7
6	44/20/36	245	8841	2.5	490	62.1	48.2
7	57/7/36	293	9776	2.7	440	60.3	47.3

dielectric and piezoelectric properties of PIN–PMN–PT ceramics are summarized in Table 1. The maximum $k_p = 64.3\%$ and $d_{33} = 560$ pC/N for PIN–PMN–PT 24/42/34 and PIN–PMN–PT 6/61/33 ceramics are presented, respectively. Taking into consideration of the relatively high T_{max}, PIN–PMN–PT 24/42/34 ($T_{max} = 205$ °C) is one of the optimal compositions for high temperature application. As shown in Table 1, the piezoelectric properties show a strong compositional dependence for PIN–PMN–PT ternary ceramic system near the MPB region. Fig. 5 shows the values of d_{33} and k_p as a function of T_{max} in the PIN–PMN–PT ternary ceramic near MPB. The largest value of $d_{33} = 560$ pC/N was observed in PIN–PMN–PT 6/61/33, which has the lowest $T_{max} = 165$ °C. Reversely, the PIN–PMN–PT 57/7/36 has the highest of $T_{max} = 293$ °C and the minimum of $d_{33} = 440$ pC/N in our choosing composition.

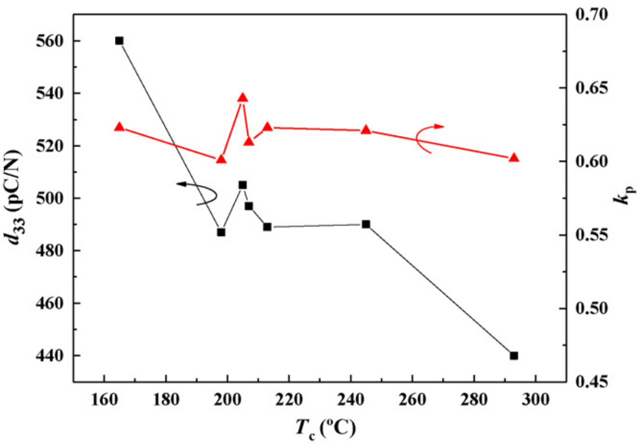

Fig. 5. The piezoelectric constant d_{33} and electromechanical coupling factor k_p as a function of T_{max} in PIN–PMN–PT ceramics.

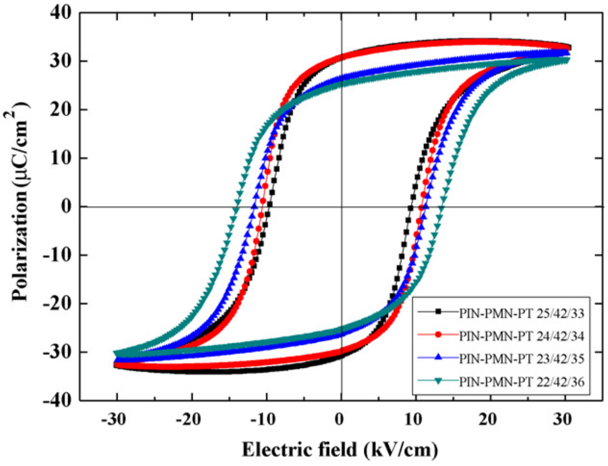

Fig. 6. Hysteresis loops of PIN–PMN–PT ceramics at room temperature.

Fig. 6 displays the hysteresis loops for PIN–PMN–PT ceramics. It shows that the residual polarization (P_r) value decreases with increasing PT content, while the coercive electric field (E_c) value increases, implying that PIN–PMN–PT ceramics become harder. For the MPB composition, the domain wall easily moves because of the coexistence of the rhombohedral and tetragonal phases. The increasing of E_c can be explained by the augment of tetragonal

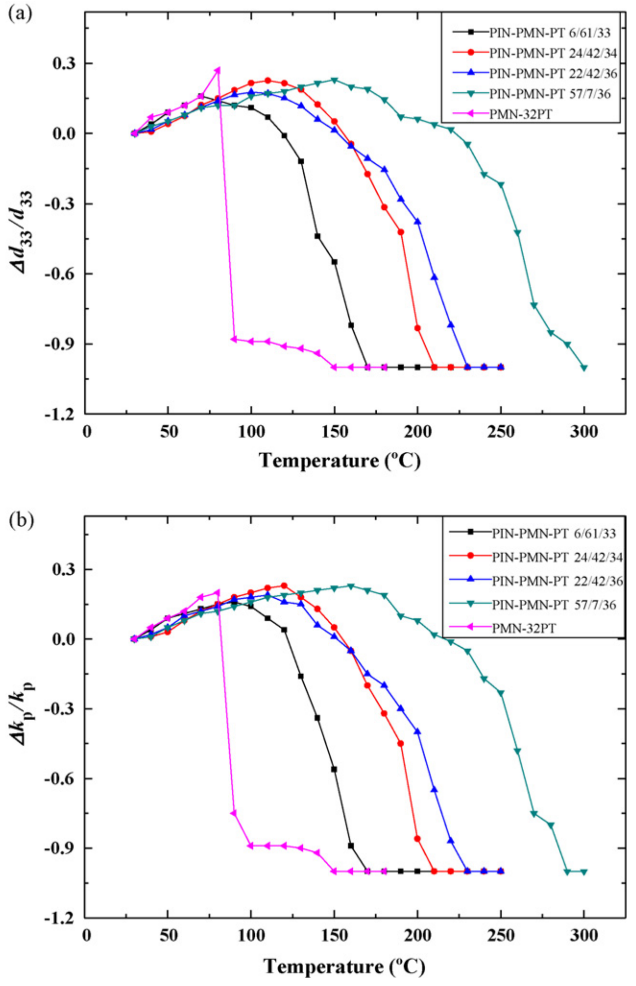

Fig. 7. Temperature-dependent (a) piezoelectric coefficient d_{33} and (b) electromechanical coupling factor k_p of PIN–PMN–PT ceramics.

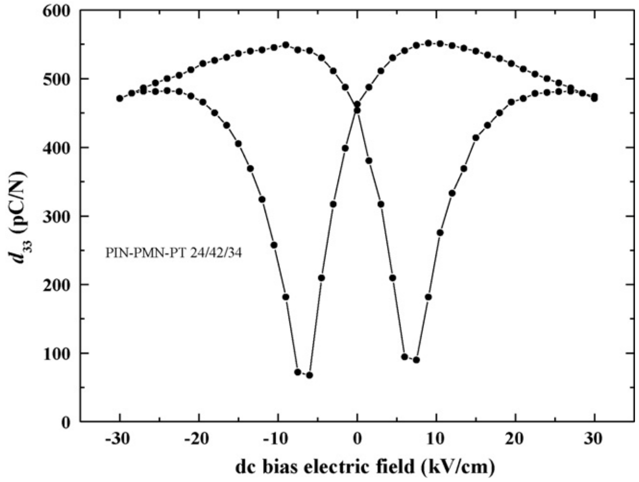

Fig. 8. Dc bias field-dependent-piezoelectric coefficient d_{33} of PIN–PMN–PT 24/42/34 ceramics at room temperature.

phase induced by the increasing of PT, which makes the domain switching more difficult. In general, a high P_r and a low E_c are presumed to be responsible for good piezoelectric properties. The piezoelectric coefficient d_{33} and electromechanical coupling factor k_p for these ceramics are also given in Table 1.

Temperature dependence of piezoelectric coefficient d_{33} and k_p for PIN–PMN–PT ceramics is shown in Fig. 7. For comparing, the result of PMN-32PT single crystals is also shown in Fig. 7. The $\Delta d_{33}/d_{33}$ represents the variation of the piezoelectric coefficient at high temperature compared with the room temperature value, meanwhile $\Delta k_\mathrm{p}/k_\mathrm{p}$ exhibits the variation of the electromechanical coupling factor. The values of d_{33} and k_p in PIN–PMN–PT ceramics increase firstly with the maximum increase of 20%, and then decreases with rising up the temperature. It is found that the d_{33} and k_p values rapidly decrease at the temperature higher than 130 °C, 170 °C, 180 °C and 230 °C for PIN–PMN–PT 6/61/33, PIN–PMN–PT 24/42/34, PIN–PMN–PT 22/42/36 and PIN–PMN–PT 57/7/36, respectively. Although PIN–PMN–PT 57/7/36 has relatively low d_{33} value than that of PIN–PMN–PT 24/42/34 at room temperature, the depolarization temperature approaches 230 °C. Meanwhile the piezoelectric properties at 230 °C are almost the same as that at room temperature. The upper usage temperature limit is nearly double, compared to PIN–PMN–PT 24/42/34 ceramic. As shown in Fig. 7, the depolarization temperature is lower about 60 °C than T_max. The d_{33} and k_p values for PMN-32PT single crystal kept constants to 80 °C, close to its $T_{\mathrm{R-T},}$ and then the constants rapidly decreased. The highest use temperature was rised to 230 °C and the usage temperature range was largely improved, compared with PMN-32PT single crystals. In addition, the $T_\mathrm{R-T}$ of PIN–PMN–PT with MPB composition is 60 °C lower than T_max, which is presumed from temperature dependence of piezoelectric properties. However, there is no evidence to determine the $T_\mathrm{R-T}$ from temperature dependence of dielectric properties.

Fig. 8 shows the dc bias field dependence of piezoelectric coefficient d_{33} for PIN-PMN-PT 24/42/34 ceramic. Under negative bias field the coefficient d_{33} is found to decrease with increasing dc bias, since some domains could be reversed for minimizing the free energy as the temperature increases. On the other hand, under positive bias field a decrease of coefficient d_{33} is observed at highly positive bias field. This decrease can be attributed to the clamping effect of positive dc bias field. The similar response is also reported in soft PZT ceramics [16]. Compared with soft PZT ceramics, the piezoelectric coefficient d_{33} of PIN–PMN–PT ceramics is rather stable under positive bias field.

4. Conclusions

The PIN–PMN–PT ternary ceramic near MPB exhibits excellent piezoelectric properties due to the ease of multi-domains reversal and polarization switching arising from the coexistence of the rhombohedral and tetragonal phases. The depolarization temperature is lower about 60 °C than the phase transition temperatures (T_max). The results of temperature-dependent-piezoelectric effects in PIN–PMN–PT ceramics indicate that this ternary ceramics system within the MPB region show better temperature stability and increased the usage temperature range compared with PMN–32PT single crystals. The better temperature stability and positive bias field stability could provide a basis for piezoelectric device design.

Acknowledgments

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