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Crystal structure and piezoelectric properties of xPb($Mn_{1/3}Nb_{2/3}$)O_3–(0.2 − x)Pb($Zn_{1/3}Nb_{2/3}$)O_3–0.8Pb($Zr_{0.52}Ti_{0.48}$)O_3 ceramics

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Abstract

Pb($Mn_{1/3}Nb_{2/3}$)O_3–Pb($Zn_{1/3}Nb_{2/3}$)O_3–Pb($Zr_{0.52}Ti_{0.48}$)O_3 (designated as PMnN–PZN–PZT) piezoelectric ceramics were prepared and the effects of PMnN content on the crystal structure and electrical properties were investigated. The results show that the pure perovskite phase forms in these ceramics. The crystal structure changes from tetragonal to rhombohedral and the lattice constant decreases with increase of PMnN content. The morphotropic phase boundary (MPB) of xPMnN–(0.2 − x)PZN–0.8PZT ceramics occurs where the content of PMnN, x, lies between 0.05 and 0.085 mol. The dielectric constant (ε), piezoelectric constant (d_{33}) and Curie temperature (T_c) decrease, while the mechanical quality factor (Q_m) increases with the increase of PMnN content. The ceramic with composition 0.075PMnN–0.125PZN–0.8PZT has the optimal piezoelectric properties, ε is 842, d_{33} is 215 pC/N, T_c is 320 °C, k_p is 0.57 and Q_m amounts to 1020, which makes it a promising material for high power piezoelectric devices.

Keywords: C. Electrical properties; Piezoelectric ceramic; Lattice structure; Curie temperature

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1. Introduction

Lead zirconate titanate Pb(Zr,Ti)O_3 (PZT) ceramics are the important piezoelectric materials applied and are widely used in electronic sensors, actuators, resonators and filters [1,2]. To improve their piezoelectric properties, lead-based complex perovskite structure compounds are dissolved into PZT ceramics [3–5]. Compared to the PZT ceramics, multiple compounds have many merits such as low sintering temperature and excellent electrical properties. Moreover, because of the addition of the third and the fourth components, the piezoelectric properties can be adjusted over a wide range.

Pb($Zn_{1/3}Nb_{2/3}$)O_3 (designated as PZN) and Pb($Mn_{1/3}Nb_{2/3}$)O_3 (designated as PMnN) are typical relaxor ferroelectrics with high dielectric constants and relatively low sintering temperatures [6–8]. Fan and Kim investigated Pb($Zn_{1/3}Nb_{2/3}$)O_3–Pb($Zr_{0.47}Ti_{0.53}$)O_3 ceramics [9] with compositions close to the morphotropic phase boundary (MPB) and pointed out that these ceramics have large electromechanical coupling factors k_p. However, the small mechanical quality factor Q_m constrained their use to high power piezoelectric devices such as multilayer piezoelectric transformers and piezoelectric motors. It is necessary to optimize the piezoelectric properties of PZN–PZT ceramics for high power device applications.

The structure and piezoelectric properties of PZN–PZT ceramics combined with PMnN have not been reported. It is expected that PZN–PZT piezoelectric ceramics with additions of PMnN may have excellent piezoelectric properties with higher mechanical quality factors. In this paper, PMnN and PZN were added to PZT ceramics to form solid solutions, and the effects of different amounts of PMnN on the microstructure and electrical properties of the PZN–PZT ceramics were investigated.

2. Experimental procedure

The general formula of the material studied was xPb($Mn_{1/3}$-$Nb_{2/3}$)O_3–(0.2 − x)Pb($Zn_{1/3}Nb_{2/3}$)O_3–0.8Pb($Zr_{0.52}Ti_{0.48}$)O_3 (designated as PMnN–PZN–PZT), where x is 0.025, 0.05, 0.06, 0.075, 0.085, 0.125. Reagent pure Pb_3O_4, ZnO, MnO_2, Nb_2O_5, ZrO_2, and TiO_2 were used as starting materials. Firstly, equal moles of ZnO and Nb_2O_5 were ball-milled for 12 h. The

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mixture was calcined at 1000 °C for 4 h to synthesize $ZnNb_2O_6$. Secondly, $ZnNb_2O_6$, Pb_3O_4, MnO_2, TiO_2, and ZrO_2 were weighed stoichiometrically and ball-milled for 12 h. The powders were calcined at 900 °C for 2 h. After milling for a second time, the powder was pressed into disks 12.0 mm in diameter at 120 MPa, and then sintered at 1200 °C for 2 h. The packing material $PbO{\cdot}ZrO_2$ was put on to a platinum sheet, and covered with an Al_2O_3 crucible to prevent PbO volatilization. The sintered discs were polished and pasted with silver on both surfaces. Samples were poled at 130 °C for 30 min under an electric field of 3 kV/mm in silicone oil. The piezoelectric properties were measured after 24 h aging at room temperature.

The content of the perovskite phase and the lattice constants were examined by X-ray diffraction (XRD, DMX-IIIC, MAC Science, Tokyo, Japan). The microstructure was observed by scanning electron microscopy (SEM, Model Hitachi S-570, Japan). The dielectric constant (ε) and dielectric loss ($\tan\delta$) were measured with a LCR precision electric bridge (Model HP4284, Hewlett-Packard). The piezoelectric constant (d_{33}) was measured with a quasistatic piezoelectric d_{33}-meter (Model ZJ-3D, Institute of Acoustics Academic Sinica, China). The electromechanical coupling factor (k_p) and the electromechanical quality factor (Q_m) were determined by the resonance and anti-resonance technique using a precise impedance analyzer (Model HP4294A, Hewlett-Packard, CA).

3. Results and discussion

Fig. 1 shows the XRD patterns of the PMnN–PZN–PZT ceramics. It is observed that a pure perovskite phase is obtained, with no pyrochlore phase. The sharp peaks indicate good crystallization. The tetragonal and rhombohedral structures can be determined from the double peaks at $2\theta \approx 44.5^\circ$. Fig. 2 shows the XRD peaks at $2\theta \approx 44.5^\circ$ in the PMnN–PZN–PZT ceramics. When the content of PMnN is 0.025 mol, there are double peaks in the XRD pattern, which indicates tetragonal phase formation. The intensity of $(0\,0\,2)_T$ decreases with the increase of PMnN content. When the content of PMnN is greater than 0.075 mol, the $(0\,0\,2)_T$ and $(2\,0\,0)_T$ peaks disappear, and only the single $(2\,0\,0)_R$ peak remains. This supports the phase transition from tetragonal to rhombohedral. The addition of PMnN can lead to lattice distortion and cause the phase change. When the content of PMnN is 0.06 mol, the $(2\,0\,0)_T$ and $(2\,0\,0)_R$ peaks observed in the XRD patterns show that the tetragonal and rhombohedral phases coexist, demonstrating that the ceramic with composition 0.06PMnN–0.14PZN–0.8PZT lies at the morphotropic phase boundary (MPB).

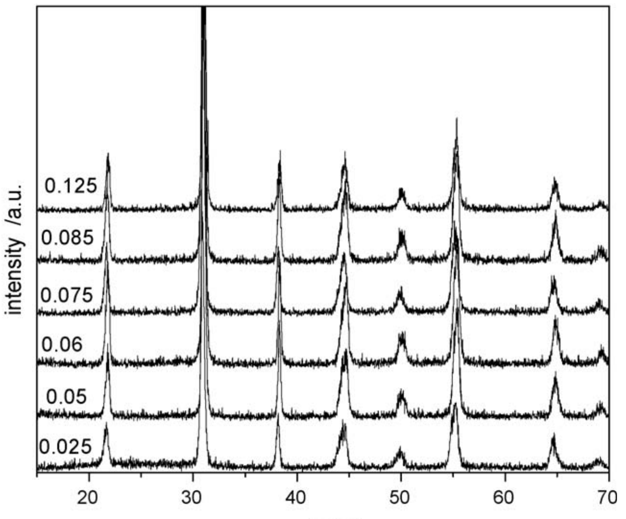


Fig. 1. XRD patterns of PMnN–PZN–PZT ceramics with different amounts of PMnN.

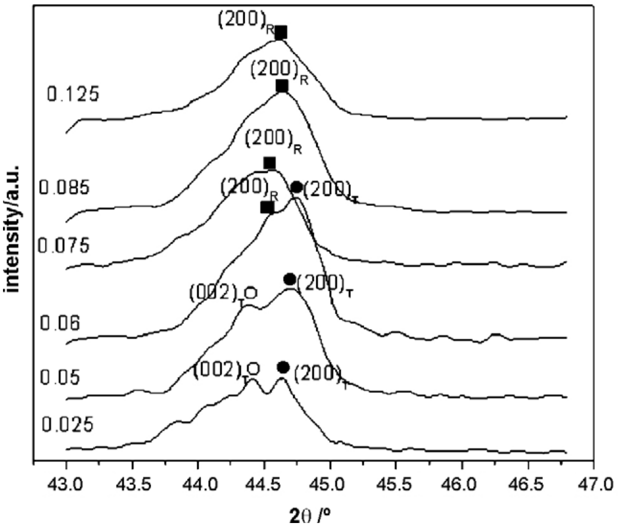


Fig. 2. XRD patterns of PMnN–PZN–PZT ceramics with different amounts of PMnN.

The lattice constants of the ceramics were calculated by a least squares method. Fig. 3 shows the variation of lattice constant with increasing PMnN content. It is observed that the lattice structure changed from tetragonal to rhombohedral with increasing PMnN content. In the rhombohedral region ($x > 0.075$ mol), the lattice constant shows little change with increasing PMnN content.

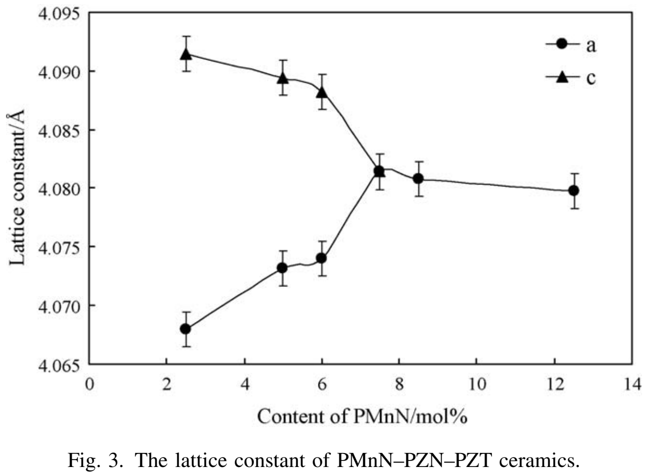
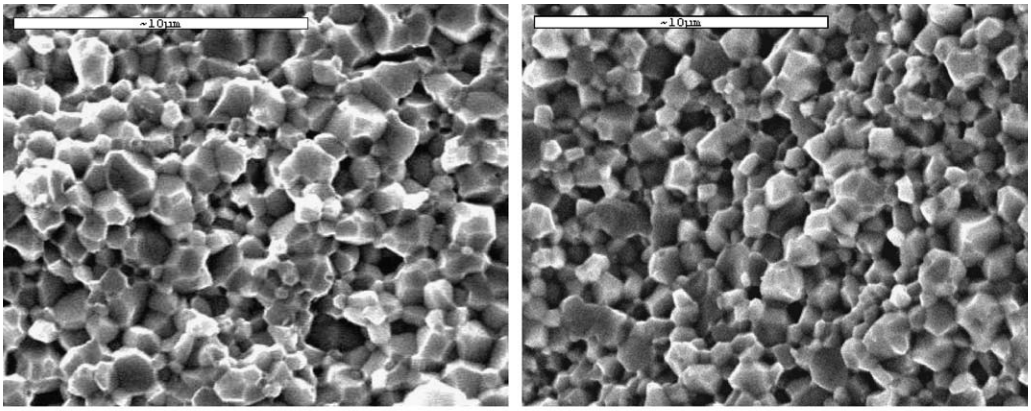
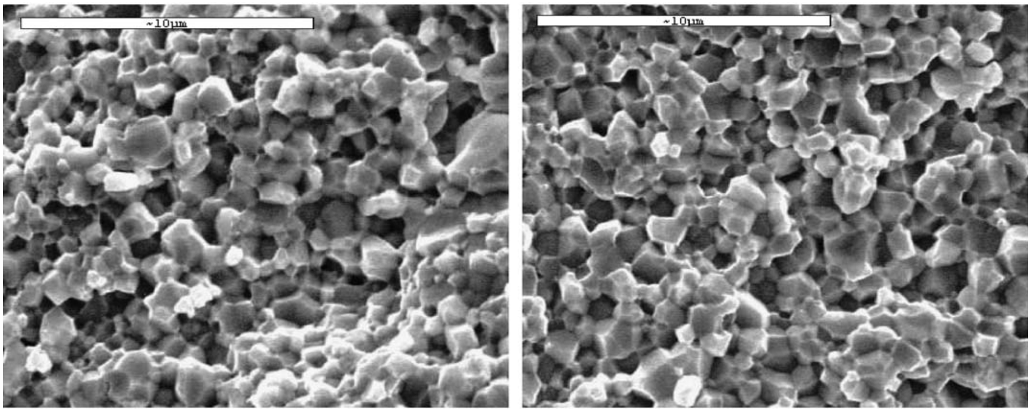


Fig. 3. The lattice constant of PMnN–PZN–PZT ceramics.



(a) 0.025mol (b) 0.05mol



(c) 0.075mol (d) 0.125mol

Fig. 4. SEM photographs of PMnN–PZN–PZT ceramics with different amounts of PMnN.

Fig. 4 shows the microstructure of PMnN–PZN–PZT ceramics with different amounts of PMnN. It is apparent that the sintered specimen is homogeneous and the fracture is intergranular. As PbO has a low melting point (890 °C), it tends to evaporate at high sintering temperature. When the atmospheric material $PbO\cdot ZrO_2$ is used, the evaporation of PbO is suppressed. This is attributed to the equilibrium of PbO vapor pressure established between the compact PMnN–PZN–PZT and the $PbO\cdot ZrO_2$ atmospheric material. The results show that all the ceramic samples are well sintered with grain sizes of ~1 μm. The grain boundaries are clear with few pores. The grain size did not change noticeably with increasing PMnN content.

Fig. 5 shows the dielectric constants of PMnN–PZN–PZT ceramics with different amounts of PMnN. The dielectric constants of both poled and unpoled ceramics decrease with increasing PMnN content. When the content of PMnN is 0.025 mol, the dielectric constant of the poled ceramic is higher than that of the unpoled ceramic. But this observation is completely reversed with increasing PMnN content. For poled piezoelectric ceramics, a virtually complete 180° domain reorientation along the poling direction leads to the elimination of the clamping effect of 180° domains which induced the increase of dielectric constant. On the other hand, the anisotropy resulted in the decrease of the dielectric constant.

It is well known that the dielectric constant is connected to the phase structure and the domain alignment. The dielectric constant of the poled ceramics with tetragonal structure is greater than that of unpoled ceramics because the removal of the clamping effect of 180° domains dominated the anisotropy.

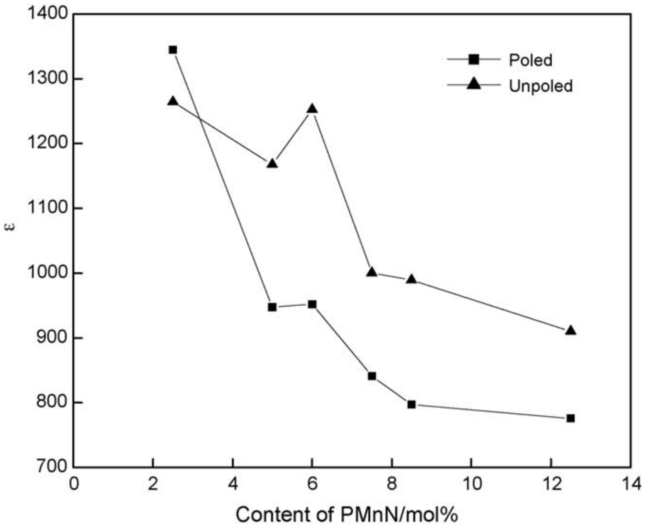


Fig. 5. The dielectric constants of PMnN–PZN–PZT ceramics.

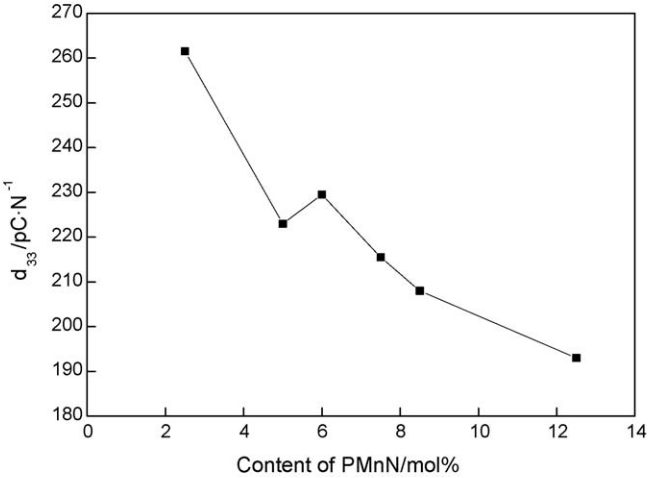


Fig. 6. The piezoelectric constant of PMnN–PZN–PZT ceramics.

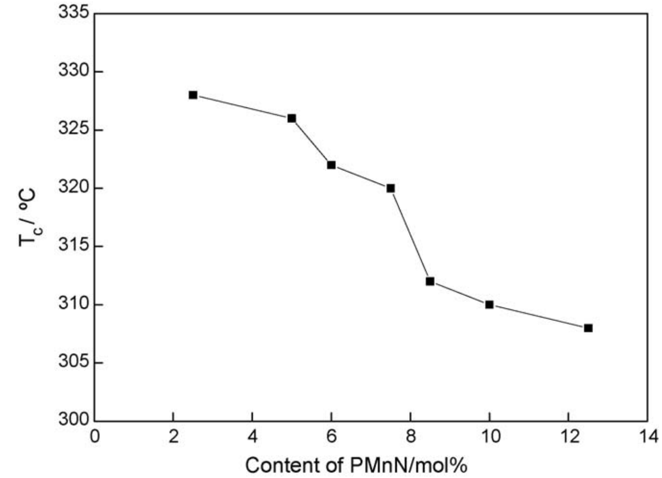


Fig. 8. Curie temperature of PMnN–PZN–PZT ceramics with different amounts of PMnN.

When the material has a rhombohedral structure, the dielectric constant of the unpoled ceramics is higher than that of the poled ceramics because the anisotropy dominates the removal of the clamping effect. These results demonstrate that the phase structure changes from tetragonal to rhombohedral with increasing PMnN content.

Fig. 6 shows the piezoelectric constant d_{33} of PMnN–PZN–PZT ceramics. The piezoelectric constant d_{33} decreases from 262 to 193 pC/N with increasing PMnN content. Fig. 7 shows the relationship between the electromechanical coupling factor (k_p) and the mechanical quality factor (Q_m) as a function of PMnN content. k_p and Q_m change the opposite sense with different amounts of PMnN. Firstly k_p increases when the content of PMnN increases. The maximum value of 0.58 appears at $x = 0.06$ mol. After that, k_p decreases with increasing PMnN content. In contrast, Q_m first decreases with the minimum value of 73.2 obtained at the same value of x, then Q_m increases with increasing PMnN content. The maximum value of Q_m amounts to 1580 at $x = 0.125$ mol.

It can be deduced that the MPB lies in the composition range $x = 0.05$–0.085 mol. All of the piezoelectric properties have an inflexion at $x = 0.06$ mol. It can be deduced that PMnN–PZN–PZT ceramics with compositions near the MPB comprise two coexisting phases, rhombohedral and tetragonal. The direction of spontaneous polarization for the rhombohedral phase is eight while that for the tetragonal phase is six. This means that the spontaneous polarization of the tetragonal phase can be oriented in any one of six crystallographic directions and the rhombohedral phase in any one of eight crystallographic directions. For the two phases coexisting at the MPB, the spontaneous polarization can be oriented along any one of these fourteen directions and the activation energy for domain motion is so low that very weak electric fields can cause changes of the spontaneous polarization. This structural transition means that compositions near the MPB possess the maximum values of dielectric constant and piezoelectric constant.

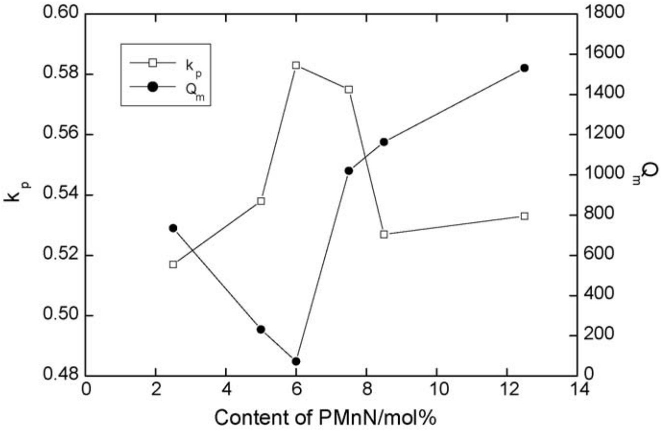


Fig. 7. k_p and Q_m of PMnN–PZN–PZT ceramics with different amounts of PMnN.

Fig. 8 shows the Curie temperature (T_c) of the PMnN–PZN–PZT ceramics. It shows that T_c decreases with increasing PMnN content. Because the ferroelectricity of $Pb(B_1^{2+}{}_{1/3}B_2^{5+}{}_{2/3})O_3$ results from the spontaneous excursion of the B_1^{2+} into the center of the oxygen octahedral, the high T_c means that a large thermodynamic movement energy is needed to destroy the ferroelectricity. The melting points of MnO, ZnO, and ZrO_2 are 1650, 1975, and 2677 °C, respectively. It means that the cohesion energy of the Mn–O bond is lower than that of the Zn–O bond and Zr–O bonds. So it can be deduced that the Curie temperature of PMnN is lower than that of $Pb(Zn_{1/3}Nb_{2/3})O_3$ and $PbZrO_3$. Eitel [10] reported the Curie temperature data for MPB solid solutions with $PbTiO_3$, the Curie temperature of PMnN–$PbTiO_3$ at the MPB is 187 °C, which is lower than $Pb(Zn_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (190 °C) and $PbZrO_3$–$PbTiO_3$ (385 °C) at the MPB. Therefore, the T_c of PMnN–PZN–PZT ceramics falls with increasing PMnN content.

To summarize, the ceramics with composition 0.075PMnN–0.125PZN–0.8PZT show optimal electrical properties: $T_c = 320$ °C, $\varepsilon = 842$, $\tan\delta = 0.0036$, and $d_{33} = 215$ pC/N. Moreover, high Q_m (1020) and k_p (0.57) can be obtained simultaneously, which can meet the needs of high power piezoelectric devices.

4. Conclusion

xPb($Mn_{1/3}Nb_{2/3}$)O_3–(0.2 − x)Pb($Zn_{1/3}Nb_{2/3}$)O_3–0.8Pb($Zr_{0.52}$-$Ti_{0.48}$)O_3 piezoelectric ceramics were prepared by the traditional solid-state method. The results show that PMnN–PZN–PZT ceramics have a pure perovskite phase. The lattice structure changed from tetragonal to rhombohedral with increasing PMnN content, and the MPB lies in the range of PMnN content from 0.05 to 0.085 mol. When the content of PMnN is higher than 0.06 mol, the lattice constant of the rhombohedral phase first increases and then decreases with increasing PMnN content. The maximum value of the lattice constant appears at $x = 0.075$. The dielectric constant ε, electromechanical coupling factor k_p, and dielectric loss tan δ have their maximum values while Q_m has its minimum value when the content of PMnN is 0.06 mol. The Curie temperature T_c of the PMnN–PZN–PZT ceramics decreases with increasing PMnN content. The ceramic with composition 0.075PMnN–0.125PZN–0.8PZT shows the optimum electrical properties: $T_c = 320$ °C, $\varepsilon = 842$, tan $\delta = 0.0036$, $d_{33} = 215$ pC/N, $k_p = 0.57$, $Q_m = 1020$, and is therefore a promising candidate material used in high power piezoelectric devices.

Acknowledgments

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