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Effects of ZnO/Li_2O codoping on microstructure and piezoelectric properties of low-temperature sintered PMN–PNN–PZT ceramics

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Abstract

$Pb(Mg_{1/3}Nb_{2/3})O_3$–$Pb(Ni_{1/3}Nb_{2/3})O_3$–$Pb(Zr_{1/2}Ti_{1/2})O_3$ (designated as PMNT) piezoelectric ceramics codoping with Zn^{2+}/Li^{+} were prepared and the effects of ZnO/Li_2O (Z/L) additive on microstructure, piezoelectric and dielectric properties were investigated. The results show that the pure perovskite phase is formed and the phase structure changes from tetragonal to rhombohedral with different Z/L weight ratios. The Curie temperature T_c, dielectric constant ε, electromechanical coupling factor k_p and piezoelectric constant d_{33} decrease, whereas mechanical quality factor Q_m increases with Z/L weight ratio changing from 1:1 to 1:8. The optimized Z/L weight ratio is 1:1. It is revealed that k_p and d_{33} first increase then decrease, whereas Q_m changes opposite with increasing content of Z/L additive. The PMNT ceramic with Z/L ratio 1:1 and the amount of 1 wt% has excellent piezoelectric properties: $k_p = 0.60$, $d_{33} = 397$ pC/N, $T_c = 251$ °C, $Q_m = 150$, $\varepsilon = 2628$ and tan $\delta = 0.0296$, when sintered at 960 °C. Finally, multilayer piezoelectric actuator is prepared using optimal composition by tape casting. The actuator shows the displacement characteristics of 3.3 μm under electric field 100 V/mm.

Keywords: C. Dielectric properties; C. Piezoelectric properties; Microstructure; Additive; Weight ratio

1. Introduction

Recently, smart materials are used in the aviation technology, especially in smart skins to improve speed, reduce the noise and keep stealth. Smart skins are adaptive complex structures, which are composed of electronic sensors, piezoelectric actuators and circuit feedback systems [1–3]. So it is important to investigate piezoelectric materials used as sensors and actuators in the smart skin. For the piezoelectric ceramics used as sensors and actuators, it is desirable to combine large electromechanical coupling factor (k_p) and low dielectric loss (tan δ), as well as high piezoelectric constant (d_{33}).

$Pb(Zr,Ti)O_3$ (PZT) piezoelectric ceramics have received special attention because of excellent physical properties. It has typical ABO_3 perovskite structure. The materials have been developed and studied for several decades and many works have been done on the doping of PZT ceramics. As a matter of fact, cation dopants are added into PZT ceramics or substitute onto A (Pb^{2+}) or B (Zr^{4+}/Ti^{4+}) sites to improve piezoelectric properties [4–6]. Since the sintering temperature of $Pb(Zr,Ti)O_3$-based piezoelectric ceramics is generally higher than 1200 °C, the multilayer piezoelectric sensors, actuators and transformers are not only submitted over the sintering temperature of 1200 °C but also co-fired with the internal electrode including palladium mole fraction of around 30%. To enhance the economic competitiveness of the piezoelectric devices, the Pd portion among the Ag/Pd electrode should be lowered down to 10% [6]. For the target level of the internal electrode, the co-firing temperature is clearly less than 980 °C. So a number of polynary piezoelectric ceramic systems have been developed [7–9]. And some sintering aids such as Li_2CO_3, CuO and Bi_2O_3 were added to develop the low temperature sintering ceramics [9–11].

However, it is found that the additives such as ZnO and Li_2O codoping on microstructure and properties of PZT-based ceramics were seldom reported. In this paper, $0.03Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.03Pb(Ni_{1/3}Nb_{2/3})O_3$–$0.94Pb(Zr_{1/2}Ti_{1/2})O_3$ (designated as PMNT) ceramics codoping with ZnO/Li_2O (hereafter, Z/L) at different weight ratio were prepared by traditional ceramics process. The effects of Z/L weight ratio and the

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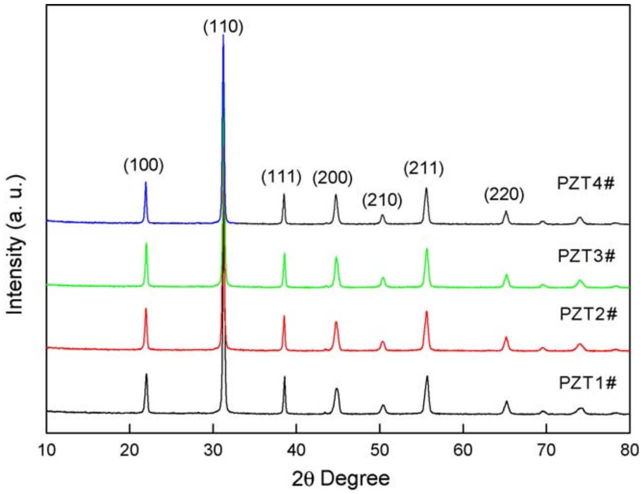


Fig. 1. XRD patterns of PMNT ceramics with different ZnO/Li_2O weight ratios.

content of additive on microstructure and piezoelectric properties were investigated. Finally, the multiplayer piezoelectric actuator was prepared by optimized composition and the displacement was measured.

2. Experimental procedure

The ceramics with compositions of $0.03Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.03Pb(Ni_{1/3}Nb_{2/3})O_3$–$0.94Pb(Zr_{1/2}Ti_{1/2})O_3 + x$ZnO/$Li_2O$ were prepared by a conventional mixed-oxide process, where x is 0.5 wt%, 1 wt%, 1.5 wt%, 2 wt% and 4 wt%. The specimens were fabricated with ZnO/Li_2O at different weight ratios, as shown in Table 1. The samples were numbered as PZT1–8#. The reagent-grade Pb_3O_4, ZrO_2, TiO_2, ZnO, Li_2O, Nb_2O_5, $Ni(CH_3COO)_2{\cdot}4H_2O$ and $Mg(OH)_2{\cdot}4MgCO_3{\cdot}6H_2O$ powders were acetone milled for 12 h with zirconia ball and then calcined at 800 °C for 1 h. The calcined powder was ground, ball-milled again and pressed into disks using PVA as a binder. After burning off PVA, the pellets were sintered at 960 °C for 1 h. The specimens were polished and silver paste was fired on both sides of the samples at 500 °C for 15 min as the electrodes. The samples were poled in 120 °C silicon oil bath by applying a DC electric field of 3 kV/mm for 20 min. The piezoelectric properties were measured after 24 h of aging at room temperature.

The bulk density was measured using the Archimedes method. The phase structure of the sintered ceramics was analyzed by X-ray diffraction analysis (XRD, X'pert MPD

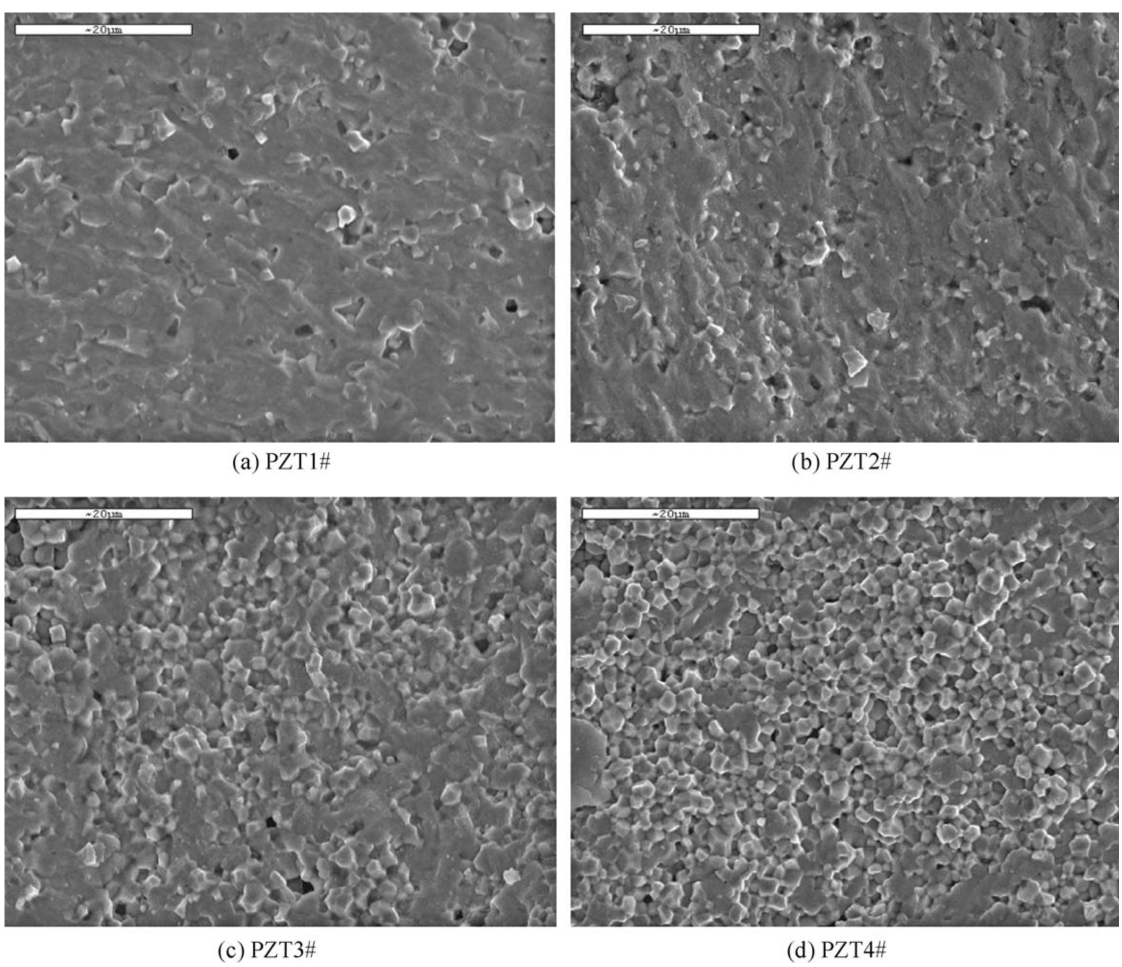


Fig. 2. SEM micrographs of PMNT ceramics with different ZnO/Li_2O weight ratios (2000×).

Table 1
Weight ratio and the content of ZnO/Li_2O additive in PMNT ceramics.

Specimens	PZT1#	PZT2#	PZT3#	PZT4#	PZT5#	PZT6#	PZT7#	PZT8#
ZnO/Li_2O weight ratio	1:1	1:2	1:4	1:8	1:1	1:1	1:1	1:1
Content of ZnO/Li_2O	1.5 wt%	1.5 wt%	1.5 wt%	1.5 wt%	0.5 wt%	1 wt%	2 wt%	4 wt%

PRO, Holland). The fractured surfaces were examined by scanning electron microscopy (SEM, JEM5800). The dielectric properties were measured at the frequency of 1 kHz using an automatic LCR meter (Model HP4284, Hewlett-Packard) at a temperature range from 25 °C to 300 °C. The piezoelectric constant d_{33} was measured using a quasi-static d_{33} meter (Model ZJ-3, Institute of Acoustics Academic Sinica). The electromechanical coupling factor k_p and the electromechanical quality factor Q_m were calculated from the resonance and anti-resonance frequencies using precise impedance analyzer (Model HP4294A, Hewlett-Packard). The ferroelectric hysteresis loops were observed at room temperature by Radiant's RT6000 precision workstation ferroelectric testing system. The displacement of actuator was tested by inductive displacement meter (Model DGS-6A, China).

3. Results and discussion

3.1. Microstructure and piezoelectric properties of PMNT ceramics with different ZnO/Li_2O weight ratios

The XRD patterns of PZT1–4# ceramics sintered at 960 °C are shown in Fig. 1. The results show that all of the samples have pure perovskite structure. No second phase such as pyrochlore phase can be found. Fig. 2 shows the microstructure of fractured surface of PMNT specimens doped with different ZnO/Li_2O (abbreviate as Z/L) weight ratios. It can be seen from Fig. 2(a) that the grain boundaries are not clear and few pores exist. The grain size and density decrease while the grain boundary becomes clearer with the Z/L weight ratio changing from 1:1 to 1:8, which resulted from the high content of Li^+. When the Z/L weight ratio is 1:1 (Fig. 2(a)), the density has the maximum value (relative density >96%). Then density decreases from 7.814 g/cm^3 to 7.762 g/cm^3 with Z/L weight ratio changing from 1:1 to 1:8. The results indicate that increasing the ratio of Li^+ will decrease the density and change microstructure.

The dielectric constant ε and dielectric loss tan δ of PMNT ceramics with different Z/L weight ratios are shown in Fig. 3. It is obvious that the dielectric constants of poled and unpoled ceramics both decrease while the dielectric loss increase with the Z/L weight ratio changing from 1:1 to 1:8. And the dielectric constant of poled ceramic is higher than that of unpoled ceramic. But the difference of ε between the poled ceramic and unpoled ceramic becomes smaller and smaller. When the Z/L weight ratio is 1:8, the dielectric constant of

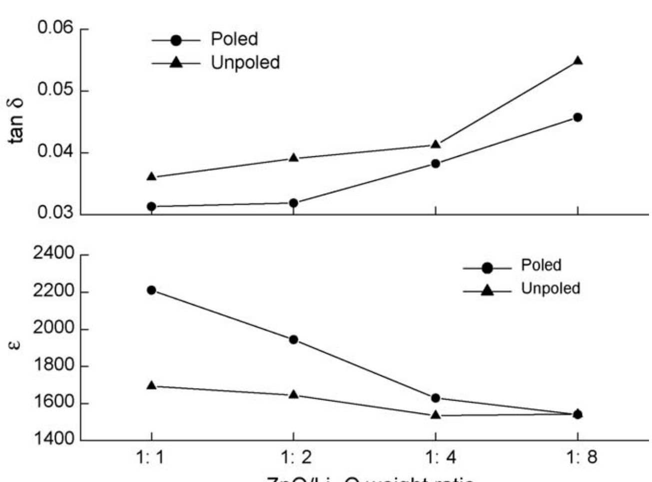


Fig. 3. The dielectric properties of PMNT ceramics with different ZnO/Li_2O weight ratios at 1 kHz.

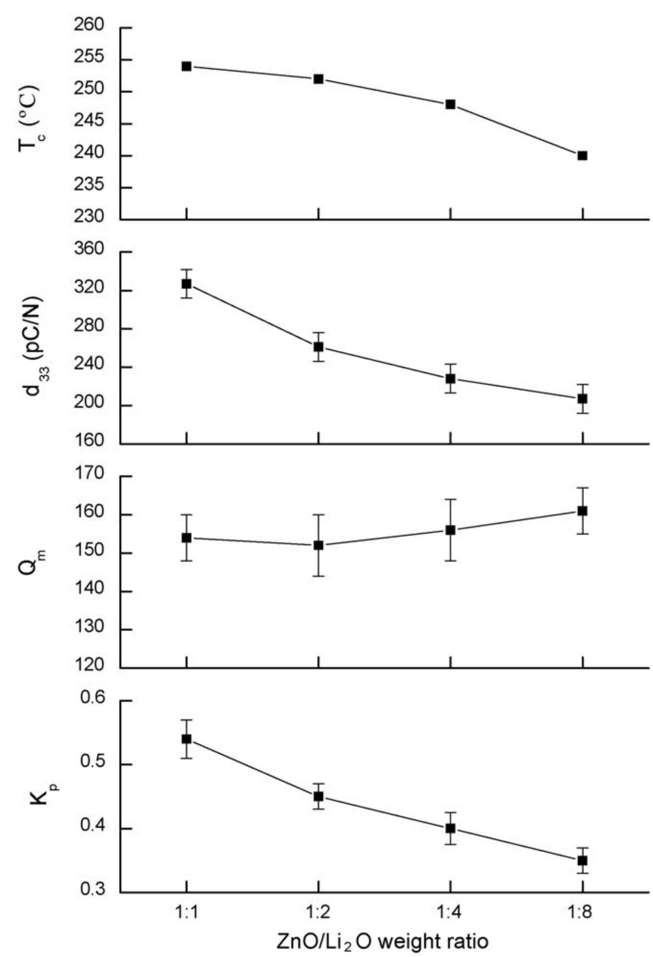


Fig. 4. Piezoelectric properties of PMNT ceramics with different ZnO/Li_2O weight ratios.

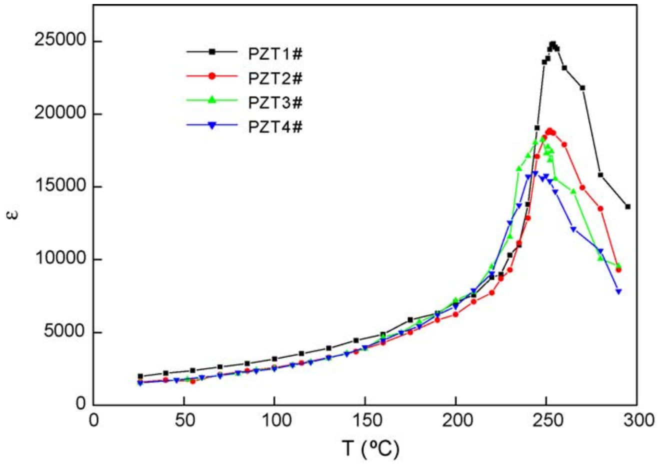


Fig. 5. Dielectric constant as a function of temperature for the PMNT ceramics at 1 kHz.

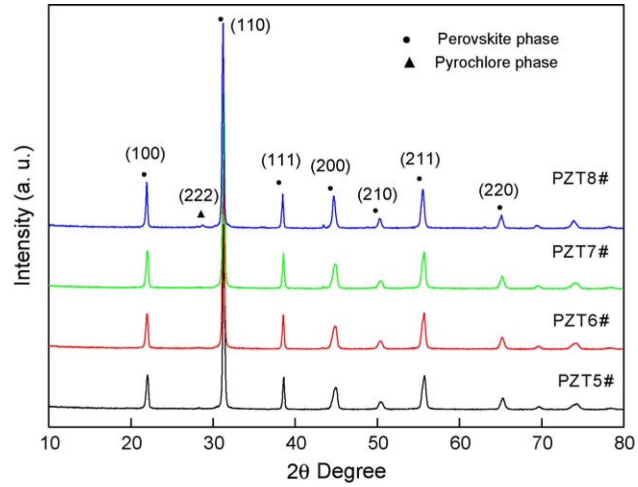
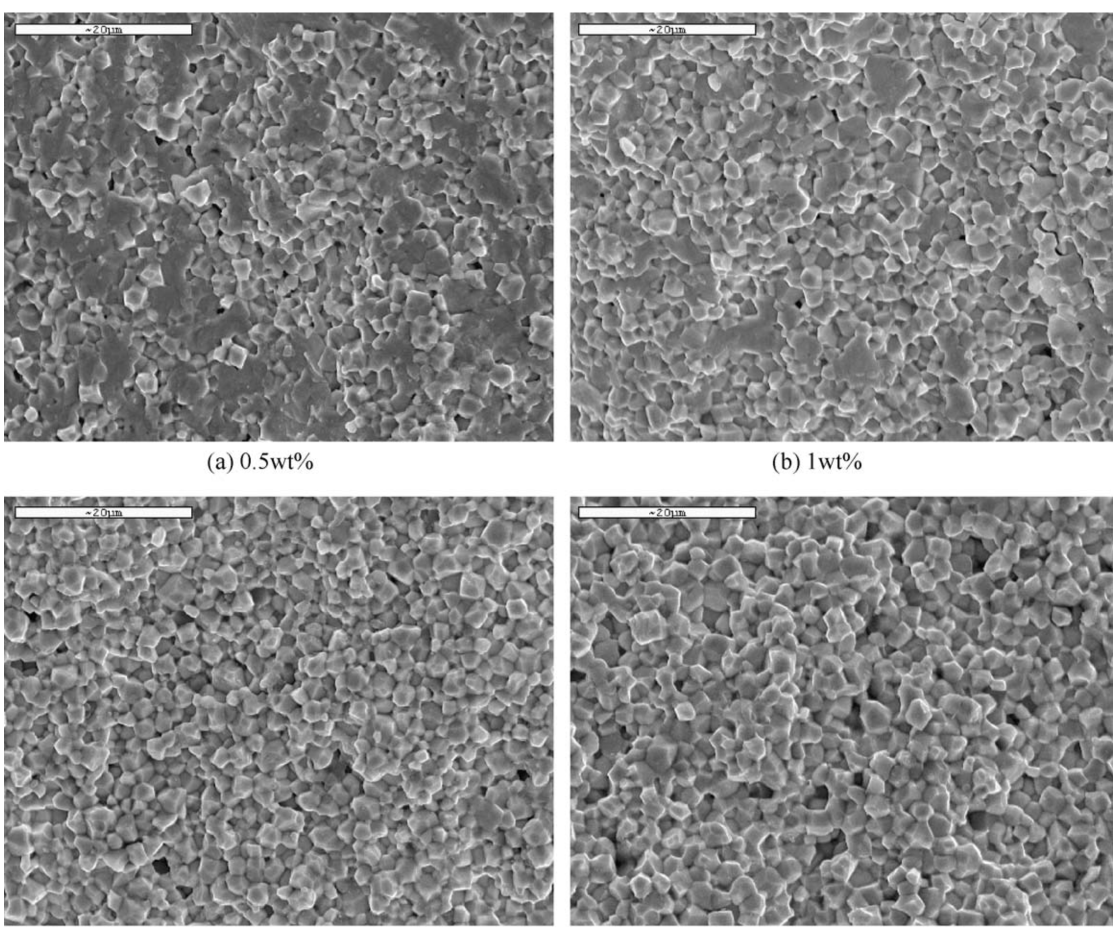


Fig. 6. XRD patterns of PMNT ceramics with different contents of ZnO/Li_2O.

poled ceramic is 1543 that is almost the same as that of unpoled ceramic (1540).

For poled piezoelectric ceramics, the virtually complete 180° domain reorientation along the poling direction led 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 dielectric constant. It is well known that the dielectric constant is connected with phase structure and the domain alignment. ε of poled ceramics with tetragonal structure is higher than that of unpoled ceramics because the removal of the clamping effect of 180° domains dominated the anisotropy. When the material has rhombohedral



(a) 0.5wt% (b) 1wt%

(c) 2wt% (d) 4wt%

Fig. 7. SEM micrographs of PMNT ceramics with different contents of ZnO/Li_2O (2000×).

structure, it is revealed that the dielectric constant of unpoled ceramics is higher than that of poled ceramics because of the anisotropy dominating the removal of the clamping effect. The above results demonstrate that the phase structure changes from tetragonal to rhombohedral with the Z/L weight ratio changing from 1:1 to 1:8. From the analysis for the lattice structure of PMNT ceramics, Li^+ occupied the B-site of perovskite structure and reduced the tetragonality, so the oxygen octahedron distorted because of the ‘‘volume effect’’ and the dielectric loss increases.

Fig. 4 shows the variation of electromechanical coupling factor k_p, mechanical quality factor Q_m, piezoelectric constant d_{33} and Curie temperature T_c of the ceramics with different Z/L weight ratios. It can be observed that T_c, k_p and d_{33} decrease while Q_m increases with the Z/L weight ratio changing from 1:1 to 1:8. The maximum k_p and d_{33} values are 0.54 pc/N and 327 pc/N when the Z/L weight ratio is 1:1.

Fig. 5 shows dielectric constant ε vs. temperature plots of the ceramics. It is obvious that a dielectric constant peak appears in the plot. And the temperature corresponding to the maximum value of dielectric constant is Curie temperature T_c where the phase transition occurs from ferroelectric to paraelectric phase. The Curie temperature decreases from 253 °C to 240 °C with the Z/L weight ratio changing from 1:1 to 1:8. What is more, the maximum value of dielectric constant decreases from 24,831 to 15,709. From above results, it is concluded that the optimized Z/L weight ratio is 1:1.

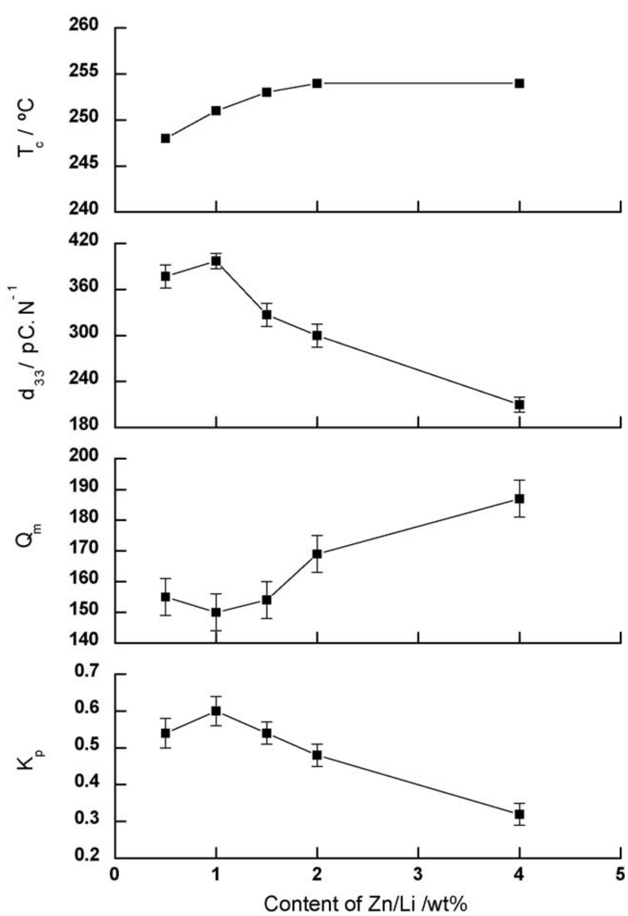


Fig. 8. Piezoelectric properties of the PMNT ceramics with different contents of ZnO/Li_2O.

3.2. Microstructure and piezoelectric properties of PMNT ceramics with different contents of ZnO/Li_2O

In order to find the optimized content of ZnO/Li_2O when weight ratio is 1:1, the specimens were fabricated by adding ZnO/Li_2O as a whole weight of 0.5 wt%, 1 wt%, 2 wt% and 4 wt%, and numbered as PZT5#, PZT6#, PZT7# and PZT8#, respectively. Fig. 6 shows the X-ray diffraction patterns of PZT5–8# specimens as a function of Z/L weight. It can be seen that PZT5–7# have pure perovskite phase structure, but there is a little pyrochlore phase in PZT8# sample. Because PMNT is ABO_3-typed perovskite structure, the ionic radius of Zn^{2+} (74 pm) is similar to Ni^{2+} (69 pm) and Mg^{2+} (72 pm) and Zn^{2+} is much smaller than A-site ion Pb^{2+} (149 pm) [12]. Moreover, Zn^{2+} has the same valence to Ni^{2+} and Mg^{2+} at B-site ion, thus Zn^{2+} may easily enter B-site and replace Ni^{2+} and Mg^{2+} ions in B-site to form $Pb(Zn_{1/3}Nb_{2/3})O_3$. As to $Pb(Zn_{1/3}Nb_{2/3})O_3$ ceramics, it is difficult to synthesize pure perovskite phase and always accompany with $Pb_3Nb_4O_{13}$ pyrochlore phase. The results show that little weight of Z/L cannot change the phase structure of PMNT ceramics. But when the content of Z/L is higher than 2 wt%, it is easy to form pyrochlore phase, which can deteriorate the electrical properties of the ceramics seriously.

Fig. 7 shows the SEM micrographs of PMNT ceramics doped with different contents of Z/L. It can be seen the grain boundary becomes clearer and clearer with increasing Z/L. The result indicates that increasing the content of Z/L will affect the microstructure of PMNT ceramics. Fig. 8 shows the plots of electromechanical coupling factor k_p, mechanical quality factor Q_m, piezoelectric constant d_{33} and Curie temperature T_c of the ceramics with different contents of Z/L. It can be observed that Curie temperature T_c increases, k_p and d_{33} first increase then decrease with the increasing content of Z/L. Q_m shows the opposite change comparing to k_p and d_{33}. The maximum k_p and

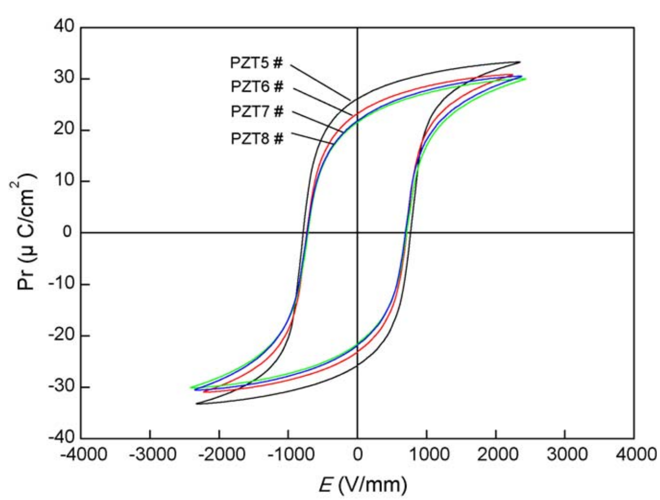


Fig. 9. Hysteresis loops of the PMNT ceramics with different contents of ZnO/Li_2O.

Table 2
Piezoelectric and dielectric properties of PMNT ceramics codoped with ZnO/Li_2O.

Samples	PZT1#	PZT2#	PZT3#	PZT4#	PZT5#	PZT6#	PZT7#	PZT8#
d_{33} (pc/N)	327	261	228	207	377	397	300	210
k_p	0.54	0.45	0.40	0.35	0.54	0.60	0.48	0.32
Q_m	154	152	156	161	155	150	169	187
ε_{max}	24,831	18,884	18,238	15,709	19,396	22,069	19,851	12,957
T_c (°C)	253	252	248	240	248	251	254	254
P_r (μC/cm^2)	23.28	23.54	21.89	22.01	25.95	23.21	21.82	21.81
E_c (V/mm)	735	734	732	732	778	733	712	708

d_{33} values are 0.60 and 397 pc/N when the content of Z/L is 1 wt%. The piezoelectric and dielectric properties of PMNT ceramics are shown in Table 2.

Fig. 9 shows the hysteresis loops of ceramics. The shape of hysteresis loop changes regularly. The remnant polarization P_r and the coercive field E_c decrease obviously with the increasing amount of Z/L. As Table 2 shows, for PZT5# ceramics, E_c is 778 V/mm, P_r is 25.95 μC/cm^2. But for the ceramics doped with 4 wt% Z/L, E_c and P_r decrease to 708 V/mm and 21.81 μC/cm^2 respectively. The results should be attributed that the occupation of Zn^{2+} and Li^+ on the B-site of perovskite structure will bring double effect including the ''volume effect'' and ''charge effect''. On one hand, Zn^{2+} and Li^+ can narrow the vibrating space of the B-site ions in the oxygen octahedron of perovskite structure. On the other hand, Zn^{2+} and Li^+ decrease the space charge and the internal offset electric field, which result in decreasing remnant polarization and coercive field.

Generally, $Pb(Mg_{1/3}Nb_{2/3})O_3$–$Pb(Ni_{1/3}Nb_{2/3})O_3$–$Pb(Zr_{1/2}Ti_{1/2})O_3$ ceramics with high density and excellent piezoelectric properties can be obtained under the sintering temperature of 960 °C by adding 1 wt% ZnO/Li_2O addition with weight ratio 1:1 (PZT6#). The electromechanical coupling factor k_p is 0.60, the Curie temperature T_c is 251 °C, the piezoelectric constant d_{33} is 397 pC/N and the mechanical quality factor Q_m is 150.

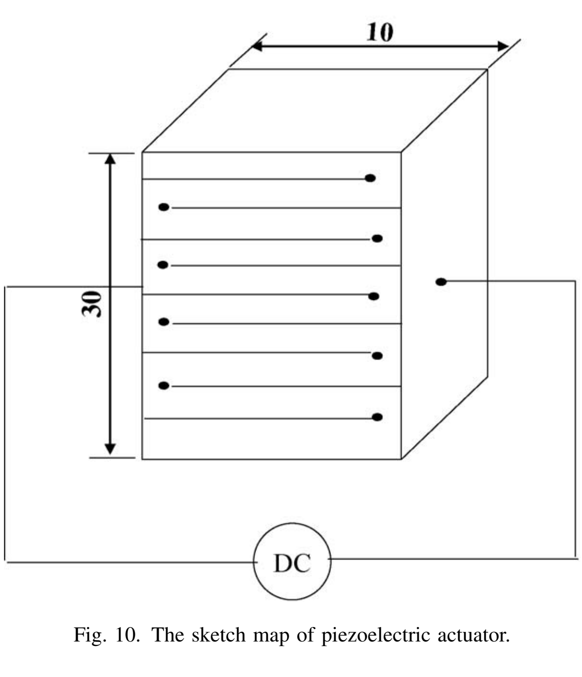


Fig. 10. The sketch map of piezoelectric actuator.

3.3. Fabrication of multilayer piezoelectric actuator

Multilayer piezoelectric actuator (hereafter, MPA) was fabricated using the composition of PZT6# by tape casting. The solvents were ethanol and xylene. The binder and plasticizer were polyvinyl alcohol (PVA) and glycerin, respectively. After completion of the ball-milling process for the slurry, the slurry was degassed under vacuum and tape cast on a plated steel surface. The thickness of green tape is 200 μm. Then the green tapes printed with 90 Ag/10Pd paste were alternatively laminated into 140 layers. The internally electroded and stacked sample was placed between two cover sheets consisting of stacking 10 green sheets. Green bars were fabricated using a laminator by applying a pressure of 4000 psi at 70 °C for 15 min. After the laminated samples were cut into 12 mm × 12 mm square, the binder and plasticizer were burned out at 500 °C for 2 h. The sintered MPA was 10 mm (L) × 10 mm (W) × 30 mm (H) in size. Ag pastes as external electrodes were then printed. Fig. 10 shows the sketch map of the MPA. Fig. 11 shows the displacement changeable as a function of the voltage. The displacement is almost liner increase with increasing voltage. The MPA exhibits a typical shape for piezoelectric ceramics and maximum strain of 25 μm at 150 V. The MPA prepared in this study shows the

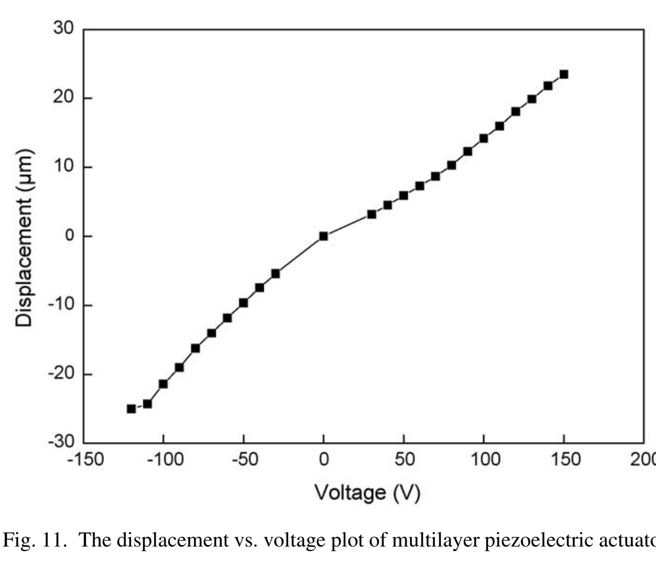


Fig. 11. The displacement vs. voltage plot of multilayer piezoelectric actuator.

displacement characteristics of 3.3 μm under electric field 100 V/mm and will be promising to be used as actuator in smart skins of the aviation technology.

4. Conclusions

$Pb(Mg_{1/3}Nb_{2/3})O_3$–$Pb(Ni_{1/3}Nb_{2/3})O_3$–$Pb(Zr_{1/2}Ti_{1/2})O_3$ (designated as PMNT) piezoelectric ceramics codoped with ZnO/Li_2O were prepared under low sintering temperature 960 °C. The ceramics have the pure perovskite phase and the phase structure changes from tetragonal to rhombohedral with different ZnO/Li_2O weight ratios. The Curie temperature T_c, dielectric constant ε_r, electromechanical coupling factor k_p and piezoelectric constant d_{33} decrease, whereas mechanical quality factor Q_m increases with ZnO/Li_2O weight ratio changing from 1:1 to 1:8. The optimized Z/L weight ratio is 1:1. The results also show that k_p and d_{33} increase first, then decrease with increasing content of ZnO/Li_2O additive. The PMNT ceramic with ZnO/Li_2O ratio 1:1 and the amount of 1 wt% has the best piezoelectric properties. Finally, multilayer piezoelectric actuator was fabricated with 140 layers and 200 μm thickness by tape-casting technology. The actuator shows the displacement characteristics of 3.3 μm under electric field 100 V/mm and will be a promising device used in the aviation technology.

Acknowledgements

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