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Effect of tungsten on the structure and piezoelectric properties of PZN–PZT ceramics

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Abstract

0.2PZN–0.8PZT ceramics with pure perovskite structure were prepared by the two-step method with the addition of 0–1.5 wt.% WO_3 and their piezoelectric properties were investigated. The WO_3 addition influences the lattice structure and W^{6+} will replace B-site ions of perovskite, which will lead to the decrease of the lattice constant. Compared to the increase of the dielectric constant (ε) and mechanical quality factor (Q_m), the values of coercive electric field (E_c), remnant polarization (P_r), electromechanical coupling factor (K_p), and piezoelectric constant (d_{33}) decrease with increasing WO_3 addition. The composition with 1.0 wt.% of WO_3 addition on 0.2PZN–0.8PZT ceramics exhibits excellent piezoelectric properties, showing great promise as practical materials for high power piezoelectric devices.

Keywords: C. Piezoelectric properties; Tungsten doping; Lattice structure; Hysteresis loop

1. Introduction

$Pb(ZrTi)O_3$ (designated as PZT) binary piezoelectric material has been most widely used for device applications [1,2]. However, there are some problems such as high sintering temperature (1300–1350 °C). $Pb(Zn_{1/3}Nb_{2/3})$ (designated as PZN) is a typical relaxor ferroelectric with high dielectric constant and relatively low sintering temperature [3]. The ternary piezoelectric ceramic PZN–PZT will be obtained by adding PZN into PZT since both have similar perovskite lattice structure.

Fan and Kim [4] investigated $Pb(Zn_{1/3}Nb_{2/3})_{0.5}(Zr_{0.47}Ti_{0.53})_{0.5}O_3$ ceramics with composition close to the morphotropic phase boundary (MPB) and clarified that the ceramics has large electromechanical coupling factor K_p. But the mechanical quality factor Q_m is too low to permit their use as high power piezoelectric devices. To meet the special demands of multilayer piezoelectric transformers and actuators, such as high d_{33}, high K_p and Q_m, it is necessary to add some dopants on PZN–PZT ternary ceramics to optimize the piezoelectric properties for device applications. The influence of various substitutions on the B-site of $Pb(ZrTi)O_3$ perovskite has been widely investigated to optimize the piezoelectric properties [5–7]. WO_3 is a dopant used for ABO_3-type relaxor ferroelectrics to lower sintering temperature and promote dielectric properties [8,9]. However, the study of WO_3 doping on the structure and properties of PZN–PZT ceramics has not been reported yet.

In this paper, 0.2PZN–0.8PZT (designated as PZNT) is the chosen composition and the effects of WO_3 on lattice structure and piezoelectric properties of PZNT ceramics were studied. The purpose of the investigation was to obtain ceramics with high mechanical quality factors and high electromechanical coupling factors.

2. Experimental procedure

The general formula of the materials studied was $0.2Pb(Zn_{1/3}Nb_{2/3})O_3$–$0.8Pb(Zr_{0.5}Ti_{0.5})O_3 + xWO_3$, where x is 0 wt.%, 0.5 wt.%, 1.0 wt.%, and 1.5 wt.%, here designated as P1#, P2#, P3#, and P4#, respectively. The samples were prepared by the two-step method to acquire pure perovskite phase [10]. Reagent-grade oxide powders, Pb_3O_4, ZnO, Nb_2O_5, ZrO_2, TiO_2, and WO_3, were used as raw materials. In the first stage, a powder of columbite precursor, $ZnNb_2O_6$, was prepared by calcinations of ZnO with Nb_2O_5 at 1100 °C for 4 h. In the

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second stage, the above precursor with Pb_3O_4, ZrO_2, TiO_2, and WO_3 was weighed and mixed through use of polyethylene jar and ZrO_2 milling media. The mixture was dried and calcined at 850 °C for 2 h. After remilled, the powder was pressed into disks 12.0 mm in diameter at around 120 MPa, and then sintered at 1100 °C for 2 h. The sintered discs were polished and pasted with silver on both surface. The 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 of aging at room temperature.

The content of perovskite phase and the lattice constants were examined by X-ray diffraction (XRD; Model DMX-IIC, Japan). Microstructure evolution of fractured face was observed using a scanning electron microscopy (SEM; Model Hitachi S-570, Japan). The dielectric constant (ε) and dielectric loss (tan δ) were measured by LCR precision electric bridge (Model HP4284, Hewlett-Packard). The piezoelectric constant (d_{33}) was measured with a quasistatic piezoelectric d_{33}-meter (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 precise impedance analyzer (Model HP4294A, Hewlett-Packard, CA). The insulation resistance was tested with insulation testing meter (Model TH2683, China). The ferroelectric hysteresis loops were observed at room temperature by radiant precision workstation ferroelectric testing system. The samples were submerged in silicone oil to prevent arcing during testing.

3. Results and discussions

The XRD patterns of PZNT ceramics with the addition of 0–1.5 wt.% WO_3 are shown in Fig. 1. In these patterns, no second phase (pyrochlore phase, $Pb_3Nb_4O_{13}$) can be found. The results show that all of the samples have pure perovskite structure exhibiting tetragonal symmetry.

As to PZN ceramics, it is difficult to synthesize pure perovskite phase by traditional method. It is reported that some amounts of simple perovskite compounds such as $BaTiO_3$, $PbTiO_3$, and $PbZrO_3$ owning large tolerance factor can stabilize the perovskite phase in PZN ceramics effectively. It is believed that the percentage of $Pb(Zr_{0.5}Ti_{0.5})O_3$ is high enough to form solid solutions with PZN and stabilize the perovskite phase effectively.

The tetragonal lattice constants of PZNT ceramics are calculated by the method of least squares. It was found that the lattice constants a and c decrease with the increasing content of WO_3. For example, parameter a will decrease from 4.0727 Å to 4.0581 Å and parameter c will decrease from 4.1778 Å to 4.0930 Å as the addition of WO_3 increases to 1.5 wt.%. Besides this, the ratio c/a also decreases with increasing WO_3 content, as shown in Fig. 2. When the addition of WO_3 is 1.5 wt.%, the ratio c/a is 1.0086.

After WO_3 was added in PZNT ceramics, W^{6+} would shift into $A(B_1B_2)O_3$-type complex perovskite structure. The ionic radius of W^{6+} (60 pm) [11] is much smaller than A-site ion, Pb^{2+} (149 pm), and the valence of W^{6+} is much higher than that of Pb^{2+}, thus W^{6+} may easily enter B-site and replace the ions in B-site. The radius of B-site ions such as Zn^{2+}, Nb^{2+}, Ti^{2+}, and Zr^{2+} are all larger than that of W^{6+}, as listed in Table 1, which will lead to the distortion of lattice and contribute to the decrease of the lattice constant a and c.

The microstructure of fractured surface of the sintered samples with different amounts of WO_3 is shown in Fig. 3. It can be seen from Fig. 3(a) that the grain boundaries are not clearly seen and some pores exist for undoped specimens. The result indicates that the sample was not well sintered. With the increasing amount of WO_3, the porosity decreases. Comparatively, the microstructure of specimens doped with 1.0–1.5 wt.% WO_3 are more uniform as seen in Fig. 3(c and d), respectively. It can be found that the ceramics are sintered effectively with well-developed grain. An average grain size of ~2 μm is observed.

The sintering temperature of pure PZT ceramic is as high as 1300 °C and that of PZN is over 1200 °C, so undoped specimen is not sintered effectively and has lower density under the sintering temperature of 1100 °C. For the ceramics doped with WO_3, because WO_3 can react with PbO at ~870 °C and form a low melting compound $PbWO_4$. $PbWO_4$ will act as liquid phase at temperature higher than 870 °C, which is beneficial for the particles to dissolve, rearrange and diffuse into perovskite structure in the first stage of sintering. Finally, the liquid phase

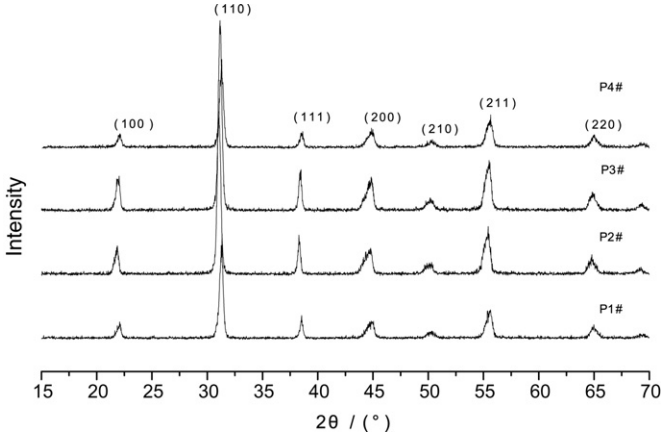

Fig. 1. XRD patterns of WO_3 doped PZNT piezoelectric ceramics.

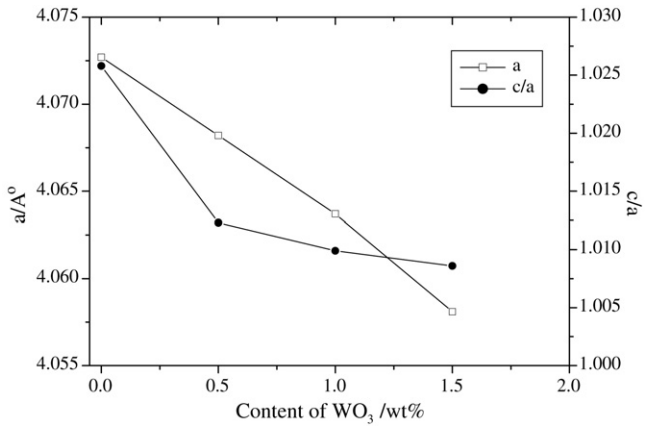

Fig. 2. Lattice constant of WO_3 doped PZNT piezoelectric ceramics.

Table 1
The radius of different ions in PZNT piezoelectric ceramics [11]

	Ions					
	Pb^{2+}	Zn^{2+}	Nb^{5+}	Ti^{4+}	Zr^{4+}	W^{6+}
Ionic size (pm)	149	74	64	60.5	74	60

is absorbed into the crystal, W^{6+} replaced the B-site ions and gave rise to the distortion of the lattice and the unbalance charge of ions. The lead vacancies are generated to charge balancing, which can promote diffusion and beneficial for densification of ceramics. Therefore, the PZNT ceramics doped with WO_3 are more densified than the ceramics without WO_3 under the same sintering condition.

The dielectric constant ε and dielectric loss tan δ of ceramics are shown in Fig. 4. It is obvious that the dielectric constant ε almost increased linearly with the increasing content of WO_3 and the dielectric loss increases subsequently. From the last analysis for the lattice structure of PZNT ceramics, W^{6+} 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. From Fig. 4, when the content of WO_3 is 0.5 wt.%, tan δ has the minimal

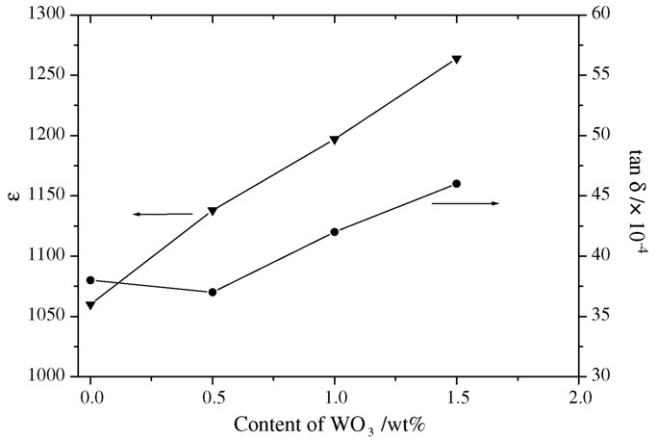

Fig. 4. Dielectric constant ε and dissipation factor tan δ of WO_3 doped PZNT ceramics.

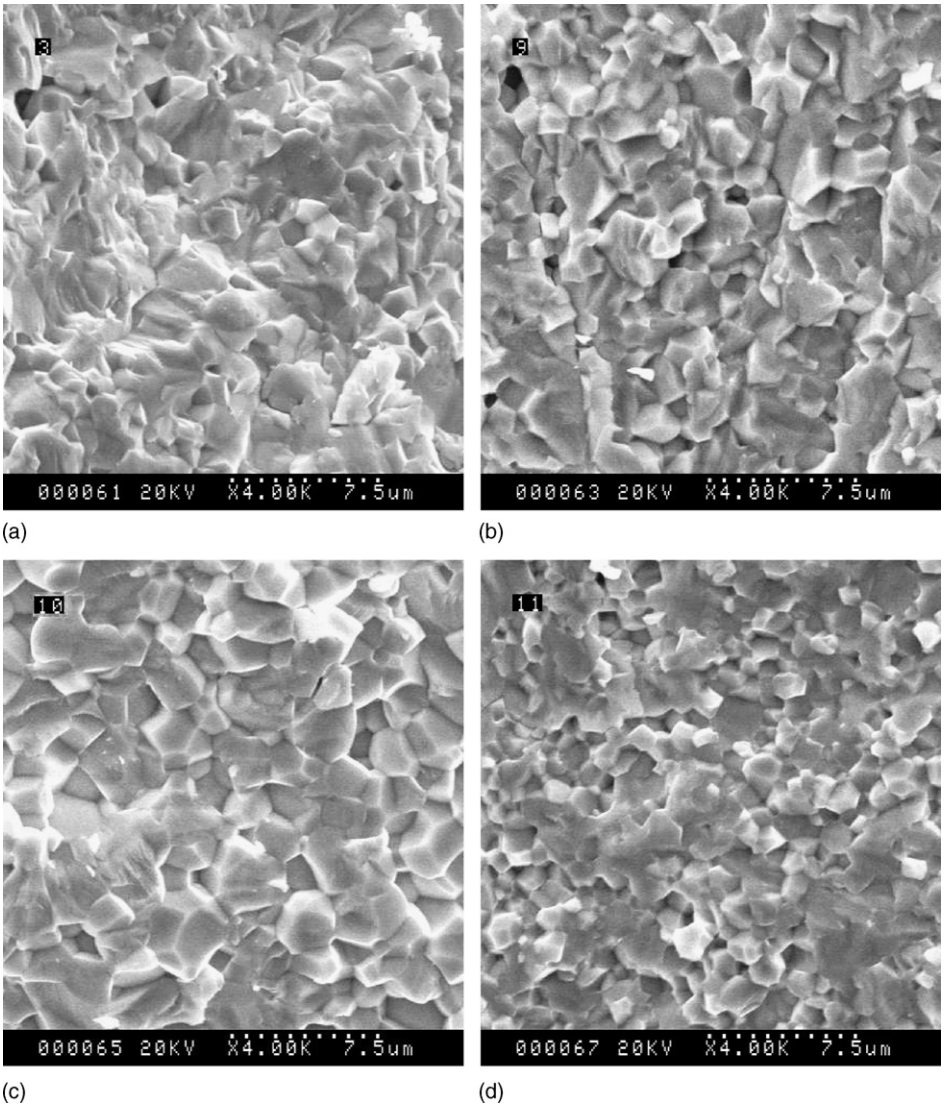

Fig. 3. Microstructure of WO_3 doped PZNT ceramics: (a) 0 wt.%, (b) 0.5 wt.%, (c) 1.0 wt.%, and (d) 1.5 wt.%.

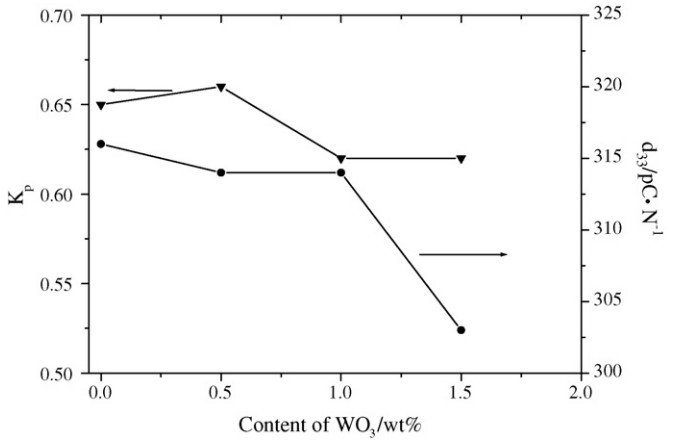

Fig. 5. Electromechanical coupling factor K_p and piezoelectric constant d_{33} of WO_3 doped PZNT ceramics.

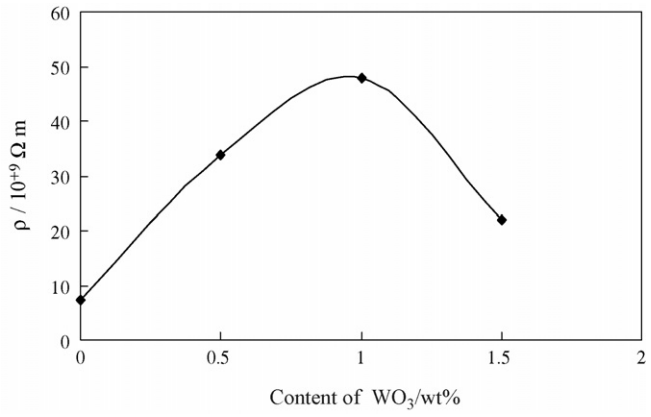

Fig. 7. Insulation resistivity of WO_3 doped PZNT ceramics.

value. And tan δ increases with the further increase of WO_3. When the content of WO_3 is 1.5 wt.%, tan δ is 0.0046.

Fig. 5 shows the variation of electromechanical coupling factor k_p and piezoelectric constant d_{33} as a function of the content of WO_3. It can be found that k_p increases little with small content of WO_3 and then decreases from 0.66 to 0.62 with increasing amount of WO_3. As can be seen, d_{33} shows a small variation as the content of WO_3 is lower than 1.0 wt.%. When the content of WO_3 is higher than 1.0 wt.%, d_{33} decreased rapidly. It is well known that the substitutions of $(Ti, Zr)^{4+}$ by W^{6+} will lead to the creation of Pb^{2+} vacancies, which promote the densification of ceramics. Because the grain size of P4# sample is smaller than that of P3# sample, as shown in Fig. 3, much more grain boundaries are generated, which results in a decrease of d_{33}. The optimized values for K_p of 0.62 and d_{33} of 314 pC/N are obtained for 1.0 wt.% WO_3 content.

For ceramics used for the high power piezoelectric devices, high mechanical quality factor Q_m is required. Fig. 6 shows Q_m of the ceramics. It can be observed that the mechanical quality factor increases from 702 to 1209 with the increasing amount of WO_3, which should be attributed that the addition of WO_3 promotes the densification of PZNT ceramics. Under the sintering temperature of 1100 °C, undoped PZNT ceramics is not sintered effectively, but the PZNT ceramics doped with WO_3 is well sintered and high density were obtained. So doping WO_3 can contribute to decrease sintering temperature and increase the mechanical quality factor.

The insulation resistivity of ceramics is shown in Fig. 7. It can be concluded that all the insulation resistivity are larger than 10^9 Ω m. Besides, the insulation resistivity of ceramics doped with WO_3 is much higher than that of undoped ceramics, as shown in Fig. 7. When the content of WO_3 increases from 0 to 1.0 wt.%, the insulation resisitivity increases, however, when the amount of WO_3 is over 1.0 wt.%, the insulation resistivity decreases. It should be explained that PbO will evaporate at temperature higher than 889 °C, which results in the Pb^{2+} vacancies and contributes to the formation of the divalent negative electricity center in the lattice. It is considered that the lead-based perovskite ceramics without dopant have the characteristics of p-type electric conductance [12]. Having entered the B-site of perovskite structure, W^{6+} will bring excessive electrons and compensate for the shortage of electron caused by Pb^{2+} vacancies, which leads to the disappearance of the p-type electric conductance and the significant increase of the insulation resisitivity. However, the introduction of the excessive electrons will lead to not only the disappearance of p-type electric conductance but also generation of n-type

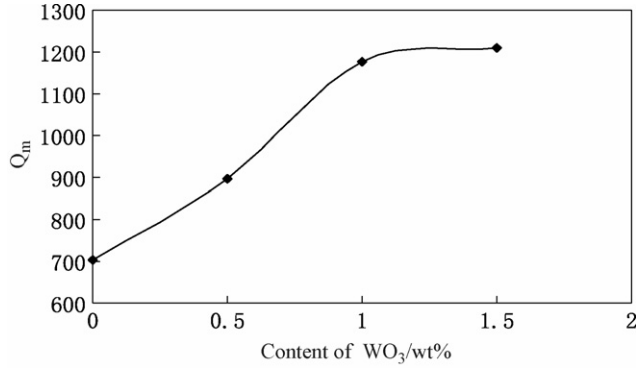

Fig. 6. Mechanical quality factor Q_m of WO_3 doped PZNT ceramics.

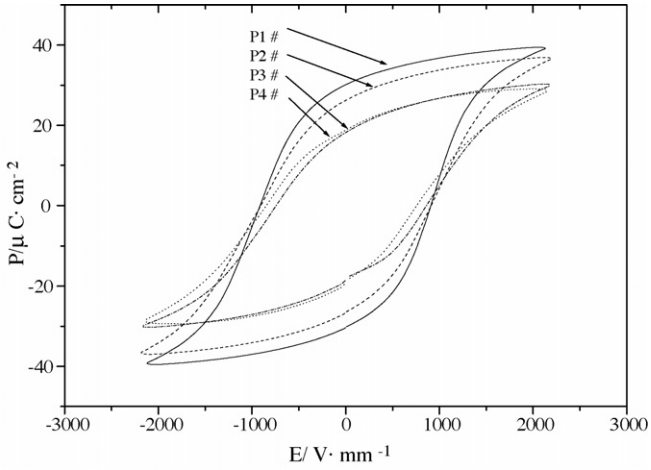

Fig. 8. Hysteresis loop of WO_3 doped PZNT ceramics.

Table 2
The polarization of WO_3 doped PZNT ceramics

Samples	E_c (V/mm)	P_r ($\mu C/cm^2$)	P_s ($\mu C/cm^2$)
P1#	918	30.09	37.98
P2#	909	26.21	35.02
P3#	812	18.78	28.73
P4#	802	18.19	27.91

electric conductance and decrease the insulation resisitivity. Therefore, the optimum content of WO_3 should be 1.0 wt.%.

Fig. 8 shows the hysteresis loop 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 WO_3. As Table 2 shows, for the undoped PZNT ceramics, E_c is 918 V/mm, and P_s and P_r are 37.98 $\mu C/cm^2$ and 30.09 $\mu C/cm^2$, respectively. But for the ceramics doped with 1.5 wt.% WO_3, E_c, P_s, and P_r decrease to 802 V/mm, 27.91 $\mu C/cm^2$, and 18.19 $\mu C/cm^2$, respectively. As above analysis, the occupation of W^{6+} on the B-site of perovskite structure will bring double effect including the ''volume effect'' and ''charge effect''. On one hand, the decrease of the lattice constant a and c narrows the vibrating space of the B-site ions in the oxygen octahedron of perovskite structure. On the other hand, W^{6+} decreases the space charge and the internal offset electric field, which result in decreasing remnant polarization and coercive field.

Generally, the PZNT ceramics with high density can be obtained under the sintering temperature of 1100 °C by adding 1.0 wt.% WO_3 addition. The electromechanical coupling factor k_p is 0.62, the insulation resisitivity ρ is 4.8×10^{10} Ω m, piezoelectric constant d_{33} is 314 pC/N and mechanical quality factor Q_m is 1178, respectively, which is promising material for high power piezoelectric devices.

4. Conclusions

0.2PZN–0.8PZT ceramics with pure perovskite structure were prepared by the two-step method with the addition of WO_3. WO_3 will promote the densification of PZNT ceramics. PZNT ceramics with high density can be obtained at 1100 °C. The addition of WO_3 leads to lattice distortion. W^{6+} will replace B-site ions of the perovskite structure. The lattice constants a, c, and the ratio c/a will decrease with increasing content of WO_3. Compared to the increase of the dielectric constant ε and mechanical quality factor Q_m, the values of coercive electric field E_c, remnant polarization P_r, electromechanical coupling factor K_p, and piezoelectric constant d_{33} will decrease with increasing WO_3 addition. With 1.0 wt.% WO_3 addition, the following optimum properties have been reached: $k_p = 0.62$, $d_{33} = 314$ pC/N, and $Q_m = 1178$; these are promising features for high power piezoelectric devices.

Acknowledgements

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References

[1] M. Kenji, D. Mabuchi, K. Takahiro, et al., Effects of adding various metal oxides on low-temperature sintered Pb(Zr, Ti)O_3 ceramics, Jpn. J. Appl. Phys. 35 (9B) (1996) 5188–5191.
[2] L.L. Tu, W.T. Deng, J.H. Chai, et al., Lead zirconate titanate ceramics and monolithic piezoelectric transformer of low firing temperature, Ferroelectrics 101 (1990) 193–200.
[3] A. Halliyal, A. Safari, Synthesis and properties of lead zinc niobate: $Pb(Zn_{1/3}Nb_{2/3})O_3$-based relaxor ferroelectrics, Ferroelectrics 158 (1994) 295–300.
[4] H.Q. Fan, H.E. Kim, Effect of lead content on the structure and electrical properties of $Pb((Zn_{1/3}Nb_{2/3})_{0.5}$ $(Zr_{0.47}Ti_{0.53})_{0.5})O_3$ ceramics, J. Am. Ceram. Soc. 84 (3) (2001) 636–638.
[5] H. Yudong, Z. Mankang, G. Feng, et al., Effect of MnO_2 addition on the structure and electrical properties of $Pb(Zn_{1/3}Nb_{2/3})_{0.20}$ $(Zr_{0.5}Ti_{0.5)0.80}O_3$ ceramics, J. Am. Ceram. Soc. 87 (5) (2004) 847–850.
[6] T.K. Vasileva, M.M. Nadoliisky, S.D. Toshev, Study of PZT ceramics doped with Cr_2O_3, Phys. Status Solidi 86 (1984) 109–111.
[7] K. Toshio, S. Toshimasa, T. Takaaki, et al., Effects of manganese addition on piezoelectric properties of $Pb(Zr_{0.5}Ti_{0.5})O_3$, Jpn. J. Appl. Phys. 31 (9B) (1992) 3058–3060.
[8] M. Furuya, T. Mori, A. Ochi, et al., Dielectric properties and crystal structure in ternary system $Pb(Mg_{1/2}W_{1/2})O_3$–$Pb(Ni_{1/3}Nb_{2/3})$ O_3–$PbTiO_3$ ceramics, Jpn. J. Appl. Phys. 31 (9B) (1992) 3139–3143.
[9] B.H. Lee, N.K. Kim, J.J. Kim, et al., Perovskite formation sequence by B-site precursor method and dielectric properties of PFW–PFN ceramics, Ferroeletrics 211 (1998) 233–247.
[10] M. Orita, H. Satoh, K. Aizawa, et al., Preparation of ferroelectric relaxor $Pb(Zn_{1/3}Nb_{2/3})O_3$–$Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ by two-step calcinations method, Jpn. J. Appl. Phys. 31 (9B) (1992) 3261–3264.
[11] Y. Yamashita, Y. Hosono, K. Harada, et al., Effect of molecular mass of B-site ions on electromechanical coupling factors of lead-based perovskite piezoelectric materials, Jpn. J. Appl. Phys. 39 (9B) (2000) 5593–5596.
[12] B. Jaffe, W.R. Cook, H. Jaffe, Piezoelectric Ceramics, Academic Press Inc., New York, 1971.