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Piezoelectric properties of $Pb(Ni_{1/3},Sb_{2/3})O_3$–$PbTiO_3$–$PbZrO_3$ ceramics modified with MnO_2 additive

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Abstract

Effects of MnO_2 additive on the ceramic and piezoelectric properties of 0.12PNS–0.48PT–0.40PZ (PNS–PT–PZ) ceramics were investigated. Addition of small amount of MnO_2 increased the sintered density and promoted the grain growth of PNS–PT–PZ. The grain size increased to the maximum at 0.15 wt.% MnO_2, further increasing MnO_2 to 0.2 wt.% decreased the grain size. Addition of 0.15 wt.% MnO_2 to PNS–PT–PZ produced a relatively higher density and maximum grain size which gave the best piezoelectric properties of kp ~ 68%, $\varepsilon_r \sim 3069$, Qm ~ 181 and $\tan\delta \sim 5.4 \times 10^{-3}$ for applications.

Keywords: Piezoelectric properties; PZT; MnO_2; Grain size

1. Introduction

Piezoelectric ceramics with high electromechanical coupling coefficient kp, k_{33}, etc., high dielectric constant ε_r, and high piezoelectric constants d_{33}, d_{31}, etc., are desirable for transducers in ultrasonic motor, actuator and acoustic applications. Previous papers concerning $Pb(Ni_{1/3},Nb_{2/3})O_3$–$PbTiO_3$–$PbZrO_3$ (hereafter abbreviated to PNN–PT–PZ) ceramics have been extensively studied, and reported that the composition with the highest performance ($\varepsilon_r \sim 5000$, kp ~ 70%) appeared at 0.5PNN–0.345PT–0.155PZ.[1,2] This composition need 50 mol% PNN which contains high price niobium oxide as a raw material, it seems too costly. Therefore, developing cheaper ceramics with similar performance will be desired. A previous report disclosed that $Pb(Ni_{1/3},Sb_{2/3})O_3$–$PbTiO_3$–$PbZrO_3$ (abbreviated as PNS–PT–PZ hereafter) compositions near the TiO_2:ZrO_2 = 0.48:0.40 form a morphotropic phase boundary and have high values of ε_r and kp.[3] But the piezoelectric properties of PNS–PT–PZ were not as high as PNN–PT–PZ. In order to improve the piezoelectric properties, MnO_2 was added in 0.12PNS–0.48PT–0.40PZ.

2. Experimental

Ceramic disk samples of 0.12PNS–0.48PT–0.40PZ + α wt.% MnO_2 were prepared by the solid-state reaction of powder materials, where $\alpha = 0.05$, 0.1, 0.15 and 0.2 wt.%. Starting materials were Pb_3O_4, TiO_2, ZrO_2, NiO, Sb_2O_3 and MnO_2. High pure (>99.5%) raw materials of a given composition were weighed based on 350 g/batch, wet-milled in a 1500 ml ball mill with 10 mm yttria stabilized zirconia balls for 20 h mixing, then dried and crushed. The crushed powders were calcined at 880 °C for 2 h in a covered alumina crucible. The calcined powders were ground and pressed into disks. Stacked disks were sintered at 1150 °C for 2 h in a covered alumina crucible. The silver painted disks were poled at 130 °C for 20 min by applying a field strength of 3 kV/mm. The piezoelectric properties of poled disks were measured using an impedance analyzer (HP-4194A). The kp and ε_r were measured by a method conform to that of the Institute of Radio Engineers Standard.[4]

The sintered density of each disk was obtained by Archimedes method from the sample weights in air W_d, in water W_w, and with absorbed water in air W_s. The volume fraction of open porosity (abbreviated as Vop) was computed from $(W_s - W_d)/(W_s - W_w)$. The grain size was measured by the line intercept method counting a minimum of 100 grains/specimen.

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Table 1
Effects of MnO_2 additive on the ceramic properties of 0.12PNS–0.48PT–0.40PZ + α wt.% MnO_2 ceramics

α	Sintered density (g/cm^3)	Percent theoretical density (%)[a]	Vop (%)	Grain size (μm)
0	7.78	94.3	1.64	2.5
0.05	7.91	95.9	1.01	2.8
0.10	7.95	96.4	0.64	4.6
0.15	8.00	97.0	0.40	7.8
0.20	8.05	97.6	0.53	3.7

[a] The true density was taken as 8.25 g/cm^3.

3. Results and discussion

3.1. Sintered density and microstructure

Table 1 shows the effects of different amount of MnO_2 on the sintered densities and grain sizes of the basic composition 0.12PNS–0.48PT–0.40PZ. Small amount of MnO_2 increased the sintered density obviously. The microstructures of the basic composition and MnO_2 added compositions were shown in Fig. 1. The microstructure of basic composition was shown in Fig. 1(a), the grain size was about 2.5 μm and grain growth was inhibited. Some open pores appear in the microstructure as shown in Fig. 1(a). The Vop of the basic composition was about 1.64%. Addition of MnO_2 to the basic composition promoted densification and grain growth those were proportional to the amount of MnO_2 additive up to 0.15 wt.%, and then decrease grain growth when further added MnO_2 to 0.2 wt.%. The maximum grain size about 7.8 μm were obtained for 0.15 wt.% MnO_2 added composition, while the grain size of 0.2 wt.% MnO_2 added composition was only 3.7 μm.

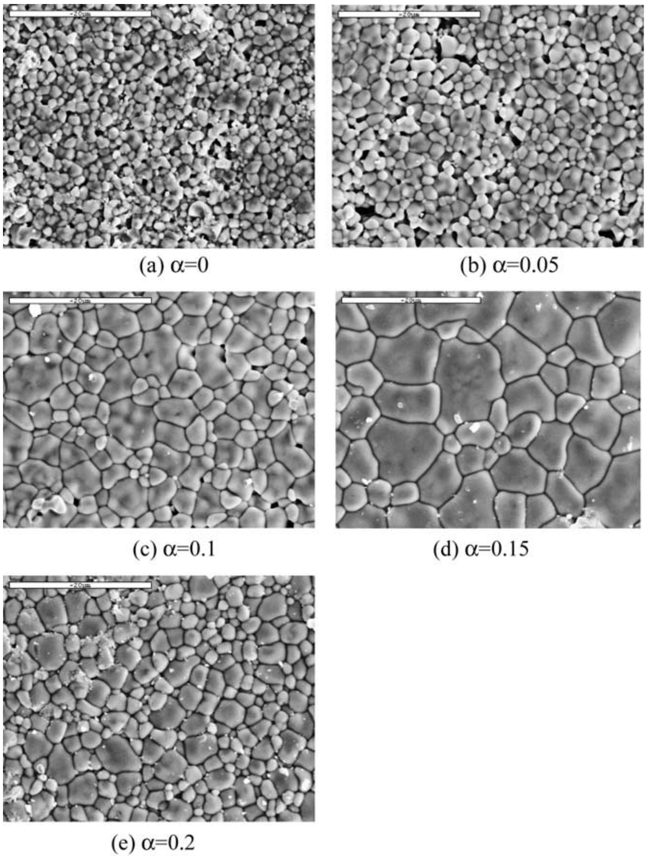

Fig. 1. SEM micrographs of 0.12PNS–0.48PT–0.40PZ ceramics modified with α wt.% MnO_2 (bar = 20 μm).

It has been reported that Mn oxide could have duality behavior as an acceptor and a donor in PT and PZT.[5,6] The effects of MnO_2 on the densification and grain growth of PNS–PZ–PT were interpreted by the formation of oxygen vacancies by replacing Mn^{+3} into the B-site of perovskite (ABO_3) lattice in this study. It was due to the existence of oxygen vacancies in MnO_2 doped PNS–PZ–PT, the pores in the ceramics were easily diffused through the movement of oxygen vacancies and eliminated at the grain boundaries. Therefore, the densities of the MnO_2 added PNS–PZ–PT ceramics were increased with the amount of MnO_2.

The grain growth of ceramic was retarded by both of the pores and the impurities. It was due to the movement of grain boundary was dragged by these defects. When MnO_2 increased, the pore of ceramics decreased, the boundary drag effect was limited, therefore the grain size increased gradually up to the maximum at 0.15 wt.% MnO_2. However, when MnO_2 further increased to 0.2 wt.%, not only the amount of Mn impurity increased, oxygen vacancies were also increased. Grain boundary was dragged by the local lattice distortion due to the large size of oxygen vacancy,[7] therefore the grain size of 0.2 wt.% MnO_2 doped ceramic was reduced. The increase of oxygen vacancy could be conjectured indirectly by the dramatic increase of Qm in 0.2 wt.% MnO_2 doped ceramics.

3.2. Piezoelectric properties

The kp and ε_r of 0.12PNS–0.48PT–0.40PZ + α wt.% MnO_2 are shown in Fig. 2. The kp and ε_r increased with increasing amount of MnO_2, the maximum value of kp and ε_r occurred at 0.15 wt.% of MnO_2, for example, the kp increased form 46% to 68%, and ε_r increased from 1938 to 3069, respectively. The decrease in kp and ε_r was occurred when MnO_2 further added to 0.2 wt.%. The effects of MnO_2 on the mechanical quality factor Qm, and dissipation factor tan δ of 0.12PNS–0.48PT–0.40PZ were shown in Fig. 3. The Qm was increased gradually by addition of MnO_2 up to 0.15 wt.%, and then increased dramatically up to 0.2 wt.%, for example, Qm increased from 98 to 181, and then was jumped to 423. The tan δ decreased proportionally to the

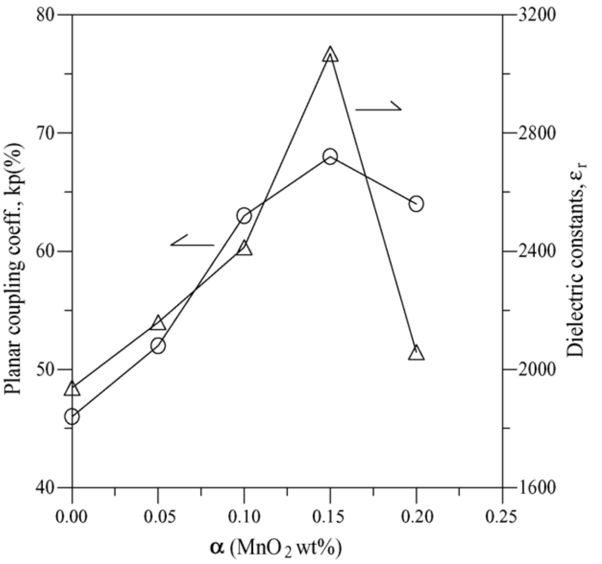

Fig. 2. Planar coupling coefficient kp and relative dielectric constants ε_r of 0.12PNS–0.48PT–0.40PZ ceramic modified with α wt.% MnO$_2$.

amounts of MnO$_2$ additive, and obtained the lowest value at 0.2 wt.% MnO$_2$ doped ceramics.

The electromechanical coupling coefficient and dielectric constants are positively correlated to the saturation polarization in PZT. The magnitude of the maximum polarization is proportional to the extent of electric domain boundary motion. Larger grain has a larger domain size and less domain boundary, therefore the maximum polarization is larger.[8] Therefore, kp and ε_r reached the maximum values at the 0.15 wt.% MnO$_2$ doped composition, which has the biggest grain size and a higher density. The motion of domain boundary is also sensitive to the oxygen vacancies those will pin the walls of domains. Although the 0.2 wt.% MnO$_2$ doped composition have the highest density, but more domain boundaries in smaller grains and high concentration of oxygen vacancies retarded the motion of domain boundary, the kp and ε_r were thus decreased.

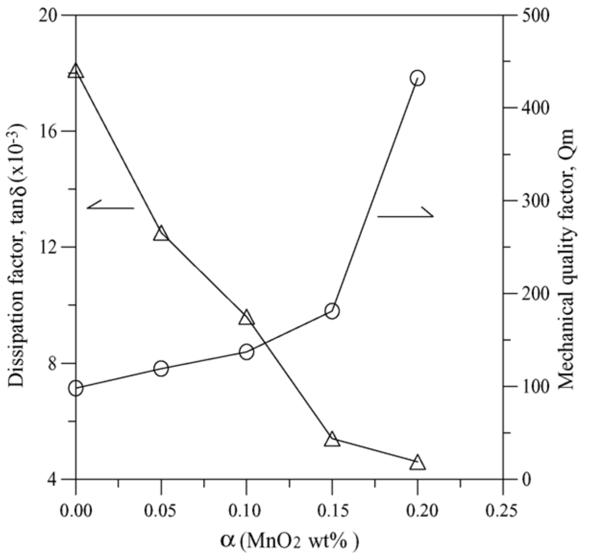

Fig. 3. Mechanical quality factor Qm and dissipation factor tan δ of 0.12PNS–0.48PT–0.40PZ ceramic modified with α wt.% MnO$_2$.

The Qm increased gradually as MnO$_2$ has increased, but dramatically increased by adding MnO$_2$ from 0.15 to 0.2 wt.%. Acceptor effect become strong when larger numbers of oxygen vacancies were formed in 0.2 wt.% MnO$_2$ added composition. In this case, bigger oxygen vacancies more effectively pin the walls of ferroelectric domains by local strain of lattice. This is consistent to the interpretation of the Mn^{3+} effects on the densification and grain growth of MnO$_2$ doped 0.12PNS–0.48PT–0.40PZ ceramics.

4. Conclusions

Additions of small amount of MnO$_2$ to the PNS–PT–PZ ceramics increased the sintered density and grain size. Small amounts of MnO$_2$ additives also improved the kp, ε_r, Qm and reduced the tan δ. The maximum grain size about 7.8 μm and 97% theoretical density were obtained for 0.15 wt.% MnO$_2$ doped 0.12PNS–0.48PT–0.40PZ, the kp increased from 46% to 68%, ε_r increased from 1038 to 3069 as compared to those of the basic composition. The experimental results may be explained by the presence of oxygen vacancies. These defects appear in the perovskite lattice to charge compensate the lower valence B-site dopant Mn^{3+}.

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