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 $k_p \sim 68\%$, $\varepsilon_r \sim 3069$, $Q_m \sim 181$ and $\tan \delta \sim 5.4 \times 10^{-3}$ for applications.

Keywords: Piezoelectric properties, MnO$_2$, PZT

1 Introduction

Piezoelectric ceramics with high electromechanical coupling coefficient $k_p$, $k_{33}$, etc., high dielectric constant $\varepsilon_r$, 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 ($\varepsilon_r \sim 5,000$, $k_p \sim 70\%$) appeared at 0.5PNN-0.345PT-0.155PZ.$^{1,2}$ This composition need 50 mole% 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 $\varepsilon_r$ and $k_p$.$^3$ 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 + $\alpha$ 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$_3$O$_4$, TiO$_2$, ZrO$_2$, NiO, Sb$_2$O$_3$ and MnO$_2$. High pure (>99.5%) raw materials of a given composition were weighed based on 350 g per batch, wet-milled in a 1500 ml ball mill with 10 mm Yttria stabilized zirconia balls for 20 hours mixing, then dried and crushed. The crushed powders were calcined at 880 for 2 hours 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 εr were measured by a method conform to that of the Institute of Radio Engineers Standard.4

The sintered density of disks were obtained by Archimedes method from the sample weights in air Wd, in water Ww, and with absorbed water in air Ws. The volume fraction of open porosity (abbreviated as Vop) was computed from (Ws - Wd)/(Ws - Ww). The grain size was measured by the line intercept method counting a minimum of 100 grains per specimen.

3 Results and Discussion

3.1 Sintered density and microstructure
Table 1 shows the effects of different amount of MnO2 on the sintered densities and grain sizes of the base composition 0.12PNS-0.48PT-0.40PZ. Small amount of MnO2 increased the sintered density obviously. The microstructures of the basic composition and MnO2 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 MnO2 to the basic composition promoted densification and grain growth those were proportional to the amount of MnO2 additive up to 0.15 wt%, and then decrease grain growth when further added MnO2 to 0.2 wt%. The maximum grain size about 7.8 µm were obtained for 0.15wt% MnO2 added composition, while the grain size of 0.2 wt% MnO2 added composition was only 3.7 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 MnO2 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 pervoskite(ABO3) lattice in this study. It was due to the existence of oxygen vacancies in MnO2 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 MnO2 added PNS-PZ-PT ceramics were increased with the amount of MnO2.

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 MnO2 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% MnO2. However when MnO2 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% MnO2 doped ceramic was reduced. The increase of oxygen vacancy could be conjectured indirectly by the dramatic increase of Qm in 0.2 wt% MnO2 doped ceramics.

3.2 Piezoelectric properties
The kp and εr of 0.12PNS-0.48PT-0.40PZ + α wt% MnO2 are shown in Fig. 2. The kp
and $\varepsilon_r$ increased with increasing amount of MnO$_2$, the maximum value of $k_p$ and $\varepsilon_r$ occurred at 0.15 wt% of MnO$_2$, for example, the $k_p$ increased from 46% to 68%, and $\varepsilon_r$ increased from 1938 to 3069, respectively. The decrease in $k_p$ and $\varepsilon_r$ 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$\delta$ 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$\delta$ decreased proportionally to the 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. Therefore, $k_p$ and $\varepsilon_r$ reached the maximum values at the 0.15wt% 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 0.2wt% 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 $k_p$ and $\varepsilon_r$ were thus decreased.

The Qm increased gradually as MnO$_2$ has increased, but dramatically increased by adding MnO$_2$ from 0.15wt% to 0.2 wt%. Acceptor effect become strong when larger numbers of oxygen vacancies were formed in 0.2wt% 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 $k_p$, $\varepsilon_r$, Qm and reduced the tan$\delta$. The maximum grain size about 7.8 $\mu$m and 97% theoretical density were obtained for 0.15 wt% MnO$_2$ doped 0.12PNS-0.48PT-0.40PZ, the $k_p$ increased from 46% to 68%, $\varepsilon_r$ increased from 1038 to 3069 as compared to those of the basic composition. Mn$^{+3}$ substituted into the B site of perovskite structure induced the formations of oxygen vacancies were employed to interpret these results.

References

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Table 1. Effects of MnO$_2$ additive on the ceramic properties of 0.12PNS–0.48PT–0.40PZ + $\alpha$ wt% MnO$_2$ ceramics.

<table>
<thead>
<tr>
<th>$\alpha$ (MnO$_2$ wt%)</th>
<th>Percent Density (g/cm$^3$)</th>
<th>Theoretical Density (%)</th>
<th>Size (%Ø)</th>
<th>Grain size ($\mu$m)</th>
</tr>
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<td>0</td>
<td>7.78</td>
<td>94.3</td>
<td>1.64</td>
<td>2.5</td>
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<tr>
<td>0.05</td>
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<td>95.9</td>
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<tr>
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<td>96.4</td>
<td>0.64</td>
<td>4.6</td>
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<tr>
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<td>8.00</td>
<td>97.0</td>
<td>0.40</td>
<td>7.8</td>
</tr>
<tr>
<td>0.20</td>
<td>8.05</td>
<td>97.6</td>
<td>0.53</td>
<td>3.7</td>
</tr>
</tbody>
</table>

*Note: The true density was taken as 8.25 g/cm$^3$.*

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Fig. 1. SEM micrographs of 0.12PNS-0.48PT-0.40PZ ceramics modified with $\alpha$ wt% MnO$_2$. (Bar = 20 $\mu$m)

Fig. 2. Planar coupling coefficient $k_p$ and relative dielectric constants $\varepsilon_r$ of 0.12PNS-0.48PT-0.40PZ ceramic modified with $\alpha$ wt% MnO$_2$.
Fig. 3. Mechanical quality factor Qm and dissipation factor tanδ of 0.12PNS-0.48PT-0.40PZ ceramic modified with α wt% MnO₂.