Relaxor ferroelectric properties of PZT-PZN-PMnN Ceramics

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$x\text{Pb}(\text{Zr}_{0.47}\text{Ti}_{0.53})\text{O}_3-(0.925-x)\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.075\text{Pb}(\text{Mn}_{1/3}\text{Nb}_{2/3})\text{O}_3+0.7\%\text{wt Li}_2\text{CO}_3$ (PZT-PZN-PMnN) ceramics with $x=0.65-0.9$ have been prepared by two-stage calcination method. The effect of the PZT content on the relaxor behavior and ferroelectric properties of ceramics has been investigated. The degree of diffuseness ($\gamma$) from 1.72 to 1.85 indicates that all of compositions show a diffused phase transition with the strong frequency dispersion, which is characteristic of relaxor ferroelectric materials. The sharpness of the permittivity peak shows that the compositions are gradually approached normal ferroelectric behavior when the mol fraction of PZT increases. At $x = 0.80$, dielectric and ferroelectric properties of ceramics are optimal with the mass density ($\rho$) of 7.81 g/cm$^3$, the dielectric constant ($\varepsilon_r$) of 1230, the dielectric loss (tan$\delta$) of 0.005 and the remanent polarization (Pr) of 27 $\mu$C/cm$^2$.

**Keyword:** PZT-PZN-PMnN ceramics, Ferroelectric, Dielectric loss, Dielectric constant, Degree of diffuseness, Mass density

Relaxor ferroelectric materials have high dielectric constant, broad ferroelectric-paraelectric transition (the diffuse phase transition) and strong frequency dependence of dielectric properties$^{1,2}$. So far, researchers have been interested in the Pb-based relaxors Pb(B$^{1+}$,B$^{2+}$)$_2$O$_3$ because these are promising materials for multilayer capacitors, transducer and actuators$^{2,3}$. Although Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$ (PZN) is one of the most important relaxor ferroelectric materials, pure PZN in the perovskite structure is very difficult to prepare by conventional method due to the formation of pyrochlore phases and the reduction of desirable properties$^4$. The addition of other perovskite materials such as PbTiO$_3$, BaTiO$_3$ and PbZr$_{0.47}$Ti$_{0.53}$O$_3$ (PZT) is necessary to stabilize the perovskite structure for PZN ceramics$^{1,3,4}$. When PZT is added to PZN to form a PZN-based solid solution, the structure and electrical properties of the ceramics become strongly dependent on the PZT content$^{1,2}$. The B-site ions in the PZT perovskite structure (Zr$^{4+}$, Ti$^{4+}$) might have been partially substituted by the B-site ions of the relaxor-type PZN structure (Zn$^{2+}$, Nb$^{5+}$), which allowed the PZT-PZN solid-solution system to retain the perovskite structure and the high sinterability of lead-based relaxor ceramics$^{1,3,4}$. Based on the preparation of pyrochlore-free Pb(Ni$_{1/3}$Nb$_{2/3}$)O$_3$ (PNN), Vittayakorn and Cann$^5$ studied the effects of PZT contents on dielectric and ferroelectric properties of 0.5PNN-(0.5-x)PZN-xPZT ceramics. The results showed that the dielectric constant ($\varepsilon_r$), the remanent polarization ($P_r$) and Curie temperature ($T_c$) increase with the increase in PZT content. With the complementary features of PZT, PZN and PMnN, the PZT-PZN-PMnN solid solutions are expected to combine the prominent properties of normal ferroelectric PZT and relaxor ferroelectric PZN and PMnN, which could exhibit better piezoelectric and dielectric properties simultaneously.

In this study, in order to improve electrical properties we have prepared $x\text{Pb}(\text{Zr}_{0.47}\text{Ti}_{0.53})\text{O}_3-(0.925-x)\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.075\text{Pb}(\text{Mn}_{1/3}\text{Nb}_{2/3})\text{O}_3+0.7\%\text{wt Li}_2\text{CO}_3$ ceramics with the content of PZT from 0.65 to 0.90.

**Experimental Procedure**

The general formula of the materials was $x\text{Pb}(\text{Zr}_{0.47}\text{Ti}_{0.53})\text{O}_3-(0.925-x)\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.075\text{Pb}(\text{Mn}_{1/3}\text{Nb}_{2/3})\text{O}_3+0.7\%\text{wt Li}_2\text{CO}_3$ (PZT-PZN-PMnN), where $x$ is 0.65, 0.70, 0.75, 0.80, 0.85, 0.90 and are denoted by M65, M70, M75, M80, M85, M90, respectively. Reagent grade oxide powders (purity $\geq 99\%$) of PbO, ZnO, MnO$_2$, Nb$_2$O$_5$, ZrO$_2$, TiO$_2$ and Li$_2$CO$_3$ were used as starting materials.

Firstly, the powders of (Zn,Mn)Nb$_3$(Zr,Ti)O$_8$ were prepared with reactions of ZnO, MnO$_2$, Nb$_2$O$_5$, ZrO$_2$ and TiO$_2$ at 1000°C for 2 h. Secondly, (Zn,Mn)Nb$_3$(Zr,Ti)O$_8$ and PbO were weighed and milled (the PM 400/2 milling machine) for 8 h using zirconia balls and ethanol as the medium. Then, the
powders were calcined at 850°C for 2 h, that produces the PZT-PZN-PMnN compound. Thirdly, Li$_2$CO$_3$ was mixed into the calcined PZT-PZN-PMnN powder, as a liquid-phase sintering aid$^6,7$, and powders milled for 16 h. The ground materials were pressed into circular pellets with 12 mm of diameter and 1.5 mm of thickness under 100 MPa. These pellets were coated with PbZrO$_3$ powder then were sintered in a sealed alumina crucible at 950°C for 2 h.

The crystal structure of the sintered samples were examined by X-ray diffraction (XRD, D8 ADVANCE). The densities of samples were measured by Archimedes method. The synthesized pellets were poled in a silicone oil bath at 120°C by applying the DC electric field of 30 kV cm$^{-1}$ for 20 min then cooling down to room temperature (RT). They were aged for 24 h prior to testing.

The piezoelectric properties were determined by the resonance and antiresonance frequencies using an impedance analyzer (Agilent 4196B and RLC HIOKI 3532). Temperature dependence of dielectric constant were determined using RLC HIOKI 3532 with automatic programming; temperature of the samples were measured using Digital Multimeter 7562. The ferroelectric property was measured by Sawyer-Tower method. X-ray energy dispersive spectra (EDS) were measured using a Hitachi S-3400N scanning electron microscope with an EDS system Thermo Noran.

**Results and Discussion**

**Phase analysis and the lattice constant**

Figure 1 shows XRD patterns of the PZT-PZN-PMnN ceramics at various contents of PZT. As observed, all ceramics have pure perovskite phase with dominantly tetragonal structure. The lattice parameters ($a$, $c$) of the samples have been evaluated from the (002) and (200) peaks of diffraction patterns which are shown in Fig. 2. When PZT content increases, the tetragonality $c/a$ ratio increases. According to the PbZrO$_3$–PbTiO$_3$ phase diagram, Pb(Zr$_{0.47}$Ti$_{0.53}$)O$_3$ is of the tetragonal phase (space group P4mm) near the morphotropic phase boundary region at RT$^6$. Meanwhile, Pb(Mn$_{1/3}$Nb$_{2/3}$)O$_3$ is cubic structure and the PZN composition was determined to be the rhombohedral (space group R3m)$^{1,2}$. Therefore, with increasing molar fraction of PZT, the crystal symmetry of the PZT-PZN-PMnN should change due to the tetragonal distortions of PZT$^{1,5}$.

In order to determine what chemical composition of the PZT-PZN-PMnN ceramic change during sintering, the EDS analysis is performed and shown in Fig. 3. The presence of lithium (Li) is not plotted here because its atomic number is low and the mass percentage is too small$^8$. Table 1 also showed the comparison in mass of Pb, Zr, Ti, Nb, Zn and Mn.

![Fig. 1 – XRD patterns of PZT-PZN-PMnN ceramics at various content of PZT](image1)

![Fig. 2 – The tetragonality $c/a$ ratios of ceramics as a function of PZT content](image2)

![Fig. 3 – EDS spectrum of 0.8PZT-0.125PZN-0.075PMnN ceramics](image3)
elements between before and after sintering of the PZT-PZN-PMnN ceramics. It is quite clear that the chemical composition of the synthesized ceramic obtained by EDS analysis can roughly accord with the general formula of the material without Pb. The reason could be explained by the evaporation of PbO during sintering. Therefore, it is necessary to add excess 5 wt% PbO to compensate for lead loss during sintering. Based on the EDS analysis, it can be confirmed that the qualitative and quantitative chemical composition of the PZT-PZN-PMnN ceramic are quite good.

Microstructure and density

Figure 4 shows microstructures of the PZT-PZN-PMnN ceramics at various contents of PZT. The average grain size of these samples is increased with the increase of PZT content as given in Table 2. On the other hand, the average grain size is reduced when \( x \) increases above 0.8 mol.

Figure 5 shows the density of the PZT-PZN-PMnN ceramics as a function of the PZT content. With the increase of PZT content up to 0.8 mol, the mass density of PZT-PZN-PMnN ceramics increases. It achieves a maximum value (\( \rho = 7.81 \text{ g/cm}^3 \)) at PZT content of 0.8 mol, and then decreases. This is explained by the change in content of PZT: If less than 0.8 mol PZT was added to the ceramic system, a large number of pores were present, indicating insufficient densification of the sample as shown in Fig. 4.

The grain size and the density of ceramic have a strong effect on dielectric, piezoelectric and ferroelectric properties of ceramic materials. The relationships between the grain size and the density of ceramic and electrical properties are discussed.

Dielectric properties

The PZT content dependence of the dielectric constant (\( \varepsilon_r \)), dielectric loss (\( \tan \delta \)) and mass density (\( \rho \)) of the PZT-PZN-PMnN ceramics at 1 kHz and RT is illustrated in Fig. 5. It can be seen that dielectric properties are strongly influenced by the composition of the ceramics. When the content of PZT increases from 0.65 to 0.8 mol, values of \( \varepsilon_r \) increase and reach to the maximum of 1230 at 0.8 mol of PZT. Then, these rapidly decrease with increasing \( x \), while \( \tan \delta \)
decreases with increasing PZT content. The minimum tanδ of 0.005 is obtained at $x = 0.8$ and then increased. It could be explained with the combination of large and homogeneous grain size, and the highest densification for the composition of 0.8PZT-0.125PZN-0.075PMnN ceramic.

In order to characterize the dielectric loss of all samples, the measurement of dependent dielectric constant on temperature is carried out at 1 kHz in Fig. 6. With increasing PZT content, the dielectric constant peak increases and becomes sharpened. Hence, the material properties changes from relaxor ferroelectricity to normal ferroelectricity. The permittivity maximum temperature ($T_m$) of the ceramics are shown in Fig. 7. It shows that the $T_m$ increases with increasing PZT content and in the range of 206-275°C. There is a difference between the phase transformation temperatures of PZN ($T_m \sim 140°C$) and PZT ($T_C \sim 390°C$), so it is significant to study the dependence of phase transition temperature of the PZT-PZN-PMnN ceramics on PZT content.

When temperature is higher than $T_m$, the function $\varepsilon(T)$ is out of order the Curie-Weiss law in the normal ferroelectric materials. In fact, $\varepsilon$ versus $T$ in the following expression:

$$\frac{1}{\varepsilon} - \frac{1}{\varepsilon_{max}} = \frac{(T - T_m)^\gamma}{C} \quad \ldots \quad (1)$$

where, $\varepsilon_{max}$ is the maximum value of dielectric constant at $T_m$, $\gamma$ is the degree of diffuseness, and $C$ is the Curie-like constant. $\gamma$ is ranging from 1 (normal ferroelectric) to 2 (ideal relaxor ferroelectric). The plot of $\ln(1/\varepsilon - 1/\varepsilon_{max})$ versus $\ln(T - T_m)$ of $x$PZT-(0.925-x)PZN-0.075PMnN ceramics at 1 kHz is shown in Fig. 8. The slopes of the fitting curves are used to determine the $\gamma$ value. At 1kHz, $\gamma$ changes from 1.70 to 1.88. Thus, it is indicated that the transitions are of diffuse type and the ceramics are highly disordered. The broadness in the expression curve of $\varepsilon$ versus temperature is one of the most important characteristics of the disordered perovskite structure with diffuse phase transition.

Figure 8 also shows that the increase of PZT content causes the decrease in the diffusiveness exponent ($\gamma$), inducing more ferroelectric clusters. This is more confirmed by the enlarged (002) and (200) peaks in XRD patterns in Fig. 1.

Figure 9 shows the temperature dependence of the dielectric constant $\varepsilon$ and dielectric loss tanδ of
the ceramics measured at frequency of 1, 10, 100 and 1000 kHz, respectively. It shows that the shape of the $\varepsilon$ peaks is broad. When the frequency is increased, the maximum of $\varepsilon_{\text{max}}$ is decreased and shifted to higher temperature while dielectric loss is increased near the Curie point, which is the typical character of a relaxor material\textsuperscript{11-14}.

To analyze the frequency dependence of $T_m$, it is necessary to use Vogel-Fulcher law\textsuperscript{14,15}:

$$F = f_o \exp\left(-\frac{T_o}{(T-T_f)}\right) \quad \ldots (2)$$

$$\ln(f) = f_o - T_o(T_m - T_f) \quad \ldots (3)$$

where, $T_f$ is the freezing temperature of polar region in the materials regarded as the temperature at which the dynamic reorientation of dipolar cluster polarization can be no longer thermally activated. The fitting curves are shown in Fig. 10 and the fitting parameters $T_o$ and $T_f$ are listed in Table 3. An excellent fit of Vogel–Fulcher law with the experimental data constitutes strong evidence for a static freezing temperature of thermally activated polarization fluctuations in PZT-PZN-PMnN.
Ferroelectric properties

Figure 11 shows \(P-E\) hysteresis loops of the PZT-PZN-PMnN ceramics measured at room temperature. The dependence of \(P_r\) and \(E_c\) on PZT content, is plotted in Fig. 12. When PZT content increases from 0.65 to 0.90, the remanent polarization increases and reaches the highest value of 27 \(\mu\)C/cm\(^2\) with M80 sample. Then, the value decreases gradually. This result is in good agreement with the studied dielectric properties of the ceramics. The coercive field decreases with the increase of PZT content and reaches smallest \(E_c\) of 9.0 kV/cm at \(x = 0.8\), and then increases.

<table>
<thead>
<tr>
<th>Sample</th>
<th>M65</th>
<th>M70</th>
<th>M75</th>
<th>M80</th>
<th>M85</th>
<th>M90</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T_0) (°C)</td>
<td>398</td>
<td>254</td>
<td>302</td>
<td>331</td>
<td>217</td>
<td>253</td>
</tr>
<tr>
<td>(T_f) (°C)</td>
<td>179</td>
<td>198</td>
<td>208</td>
<td>218</td>
<td>237</td>
<td>255</td>
</tr>
</tbody>
</table>

Table 3 – The value of fitting parameters to Vogel-Fulcher relationship

Taking into account the above results, the PZT-PZN-PMnN ceramics with various PZT content have been investigated and the composition with \(x = 0.8\) is selected since it has the best dielectric and ferroelectric properties.

Conclusions

We have prepared well crystallized \(x\)Pb\((Zr_{0.47}Ti_{0.53})_O_3-(0.925-x)\)Pb\((Zn_{1/3}Nb_{2/3})_O_3-0.075\)Pb\((Mn_{1/3}Nb_{2/3})_O_3+0.7\%\)wt Li\(_2\)CO\(_3\) (PZT-PZN-PMnN) ceramics with \(x = 0.65-0.90\) by two-stage calcination method at sintering temperature of 950°C for 2 h. All ceramics seem to be pure perovskite phase mainly tetragonal structure. With \(x = 0.8\), the characteristic parameters such as density, dielectric constant, and remanent polarization are optimal, which are \(\rho = 7.81\) g/cm\(^3\), \(\varepsilon_r = 1226\) and \(P_r = 27\) \(\mu\)C/cm\(^2\), respectively. The experimental \(T_m\) data points are in good agreement with the Vogel–Fulcher relation constitutes strong evidence for a static freezing temperature of thermally activated polarization fluctuations in PZT-PZN-PMnN.

Acknowledgments

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References