Effect of Sintering and Poling Conditions on the Properties of \([\text{Pb, Sr}][(\text{Zr, Ti})(\text{Zn, Nb})(\text{Mg, Nb})]_3\) Piezoelectric Ceramics System

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The \((\text{Pb, Sr})(\text{Zr, Ti})(\text{Zn, Nb})(\text{Mg, Nb})]_3\) piezoelectric ceramic system with compositions close to the morphotropic phase boundary (MPB) was studied. The dielectric and piezoelectric properties of the system \(\text{Pb}_{0.96}\text{Sr}_{0.04}[(\text{Zr}_{1-y}\text{Ti}_y)_{0.74}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.06}](\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.20}]_3\) were investigated, where the compositions of \(0.44 \leq y \leq 0.60\) were selected. From the results of XRD and piezoelectric measurement, it was supposed that the composition with \(y = 0.50 - 0.51\) corresponded to MPB between tetragonal and pseudocubic phase. By the way of the variation of the fabrication process, the influence of sintering and poling processes on the properties of the ceramic were studied, and we expected to find the optimal conditions of these processes. Some developed phenomena or models were introduced. After the optimal choice of the process conditions, the planar coupling factor close to 0.73 and the dielectric constant close to 3000 can be approached simultaneously in this multicomponent system.

Key words: Piezoelectric ceramics, phase boundary, domain wall

I. INTRODUCTION

After Jaffe\(^1\) discovered the very strong piezoelectric activity of poled \(\text{Pb(Zr, Ti)}_3\) (PZT) ceramics at compositions near the morphotropic phase boundary (MPB), many papers have reported on the piezoelectric properties of PZT solid solution.

In order to reach requirements in practical applications, a number of minor additives had been added to the PZT ceramics.\(^2\)-\(^6\) But when those two or more minor additives were added simultaneously, much improved piezoelectric properties were not obtained. Therefore, ternary or quaternary solid solution ceramics in place of the binary ceramics consisting of a complex perovskite compound were synthesized.\(^7\)-\(^12\)

In this paper, the properties of the \([\text{Pb, Sr}][\text{Zr, Ti)})(\text{Zn, Nb})(\text{Mg, Nb})]_3\) system with compositions close to the MPB are studied. The composition \(\text{Pb}_{0.96}\text{Sr}_{0.04}[(\text{Zr}_{1-y}\text{Ti}_y)_{0.74}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.20}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.66}]_3\) with \(0.44 \leq y \leq 0.60\) is used as the main composition in this study.

Many papers\(^13\)-\(^17\) showed that for achieving completely single phase and densification, every condition in the fabrication process (especially the sintering process) should be carefully selected. If the sintering temperature was too low, the reaction of the solid solution was incompletely and the formation of the parasitic phase was increased. On the other hand, too high a sintering temperature and too long a sintering time would produce a second phase owing to the vaporization of \(\text{PbO}\).\(^18\)-\(^19\) In a system containing the \(\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_3\) composition, the second phase was considered a pyrochlore phase (\(\text{PbNb}_2\text{O}_6\)), and this pyrochlore phase degraded the dielectric and piezoelectric properties of the ceramic body.\(^20\)

It was well known that ferroelectric ceramic materials had not net polarization due to the random orientation of the axes of their constituent crystals. Such ceramics could be made piezoelectrically active by the application of an external dc electric field, this process was referred to as poling. The properties of the piezoelectric ceramic were controlled by the poling process.

Besides the properties of the piezoelectric ceramic system, the influence of sintering conditions and poling processes on the properties of the system were also discussed in this paper.

II. EXPERIMENTAL PROCEDURE

In this study, the samples are prepared from high purity (\(\geq 99\%\) \(\text{PbO}, \text{TiO}_2, \text{ZrO}_2, \text{Nb}_2\text{O}_5, \text{SrCO}_3\) and \(\text{MgO}\). The basic composition is chosen to be \(\text{Pb}_{0.96}\text{Sr}_{0.04}[(\text{Zr}_{1-y}\text{Ti}_y)_{0.74}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.20}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.66}]_3\) with \(0.44 \leq y \leq 0.60\) in this study, and excess 0.5 wt.
\% PbO is added to the solid solution to enhance the formation of the liquid phase. Corresponding molar fractions of the starting materials are weighed and mixed with D.I. water in an alumina ball mill for 2 hr. After drying, the mixture is calcined at 850°C for 2 hr in a covered high alumina crucible. The calcined powder is ground and pressed into a disc about 15 mm in diameter and 1–2 mm in thickness.

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For the purpose of studying the influence of sintering conditions, the samples are heated by a fixed heating rate at 4°C/min, the sintering temperature is from 1220 to 1270°C, and the sintering time is from 2 to 7 hr. In sintering, the samples are surrounded by a packing powder, the packing powder used in this study is PbZrO$_3$ + 3 wt.% PbO.

After sintering, the samples are then lapped to a thickness of 1 mm. After lapping, silver electrodes are fired onto the faces of samples at 750°C for the measurement of its properties.

In order to determine crystal structure, crystal system and lattice parameters, the sintered ceramic samples are polished, and measurements are carried out at room temperature by the x-ray diffraction (XRD) method using CuK$\alpha$ radiation. By using the scanning electron microscope (SEM), the free surface of the sintered ceramic body is observed. The mean grain size is calculated by the line intercept method.

Before measuring the properties, the samples are poled in silicon oil. For the purpose of studying the influence of the poling process, the poling field (0.5-4 kV/mm), and poling temperature (20-140°C) are taken as variants for the poling study, progressively, and the poling time is for 30 min.

24 hr after poling, the dielectric and piezoelectric properties are measured with HP4192A L.F. Impedance Analyzer in reference of the IRE Standard. Polarization against the electric field is measured using a Sawyer-Tower circuit.

III. RESULTS AND DISCUSSION

III.1 Properties of the System

For studying the properties of the system, the samples are sintered at 1250°C for 3 hr, and poled by 3 kV/mm at 100°C for 30 min.

Figure 1 shows the XRD patterns of Pb$_{0.96}$Sr$_{0.04}$[(Zr$_{1-y}$Ti$_y$)$_{0.74}$ (Mg$_{1/3}$Nb$_{2/3}$)$_{0.20}$ (Zn$_{1/3}$Nb$_{2/3}$)$_{0.06}$]O$_3$ system with different $y$ values at room temperature. The perovskite phase appears to have the pseudocubic symmetry for $y \leq 0.50$, and the tetragonal symmetry for $y \geq 0.51$. It means that there is a phase boundary between pseudocubic and tetragonal phase at compositions nearly equal to $y = 0.50 - 0.51$ in this system.

The coercive field and remanent polarization of the system are shown in Table I. From the results of Table I, it finds the coercive field $E_c$ increased with an increase in PbTiO$_3$, and the remanent polarization $P_r$ also increases until it reaches a peak value at the phase boundary, then decreases for higher Ti concentration.

Table I. The coercive field and remanent polarization of Pb$_{0.96}$Sr$_{0.04}$[(Zr$_{1-y}$Ti$_y$)$_{0.74}$ (Mg$_{1/3}$Nb$_{2/3}$)$_{0.20}$ (Zn$_{1/3}$Nb$_{2/3}$)$_{0.06}$]O$_3$ system at room temperature.

<table>
<thead>
<tr>
<th>$y$</th>
<th>$E_c$ (kV/mm)</th>
<th>$P_r$ (µC/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>44</td>
<td>0.68</td>
<td>13</td>
</tr>
<tr>
<td>47</td>
<td>0.65</td>
<td>21</td>
</tr>
<tr>
<td>50</td>
<td>0.75</td>
<td>25</td>
</tr>
<tr>
<td>51</td>
<td>0.75</td>
<td>24</td>
</tr>
<tr>
<td>52</td>
<td>0.80</td>
<td>21</td>
</tr>
<tr>
<td>54</td>
<td>1.00</td>
<td>20</td>
</tr>
<tr>
<td>57</td>
<td>1.25</td>
<td>19</td>
</tr>
</tbody>
</table>

In piezoelectric ceramics, the properties depend on the composition and crystal structure; the dielectric constant may be increased or decreased through the poling treatment. Figure 3 shows the dielectric constant $K$ (before poling) and $K_{33}$ (after poling) of the system. After poling the dielectric constant increases for the tetragonal compositions but decreases for the pseudocubic compositions. Moreover, variations of the dielectric constant through poling also rely on the domain alignment. The increase of the dielectric constant when poling the tetragonal compositions is previously explained as being due to the elimination of the effect of compression of the 180-degree domains. This occurs due to the virtually complete 180-degree domain orientation along the poling direction, and dominates the decrease in dielectric constant from the 90-degree domain reorientation. For the pseudocubic compositions, the dielectric constant decreases when poling the samples. This net decrease may be caused by the 90-degree domain reorientation dominating the effect of the removal of compression.

As far as the dielectric constant of the poled ceramic is concerned, the maximum point of the dielectric constant in the multicomponent system is displaced into the tetragonal phase and does not coincide with the maximum point of the electromechanical coupling factor. Before poling, the dielectric constant of the piezoelectric ceramic can be written as:

$$K = K_i + K_{or}$$

where $K_i$ is caused by induced polarization and $K_{or}$ is caused by orientational polarization.