Microstructure and Dielectric Properties of PZN-PT-BT Relaxor Ferroelectric Ceramics

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ABSTRACT

Paraelectric Ba(Zn\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3} (BZN) is realized as an implicit component in Pb(Zn\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3}-PbTiO\textsubscript{3}-BaTiO\textsubscript{3} (PZN-PT-BT), which decreases phase transition temperature and weakens dielectric properties. The dielectric behaviors under high electrical field have been investigated. In the broad temperature range of the diffuse phase transition, PZN-PT-BT ceramics show highly induced polarization. An unusual linear relation of the polarization with electrical field has been observed near the central portion of the hysteresis loops of some samples, which are both temperature and composition dependent. The observed ferroelectric properties may be understood using a model of PZN-based matrix containing ferroelectric PT and paraelectric BZN nano-phase regions.

INTRODUCTION

Perovskite structure is one of the most common crystal structures in advanced functional ceramics. Compositions of mixed perovskite materials are normally in the form of solid solution. But limited by the processing of conventional solid-state reaction, local chemical compositions on the nano scale of some solid solution ceramics can be inhomogeneous [1-5]. Up to date, it is unclear how wide the distribution of the inhomogeneous compositions in nano-regions could spread, and on an even more fundamental aspect, whether these compositionally inhomogeneous nano-regions do or do not exist in solid solution ceramics. Diffuse phase transition of ferroelectric solid solutions stems basically from nano-compositional inhomogeneity. The temperature \( T_n \) of maximum dielectric constant of some ferroelectrics with diffuse phase transition shifts towards high temperature as measuring frequency increases. These materials are specially named as “relaxor ferroelectrics”. Pb(Zn\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3} belongs to such a group of materials.

Perovskite ceramics of Pb(Zn\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3}-PbTiO\textsubscript{3}-BaTiO\textsubscript{3} (PZN-PT-BT) are complicated solid solution system. In order to understand the abnormal decrease of the average phase transition temperature with increase of BT content in PZN-PT-BT ceramics, expression of Pb(Zn\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3}-PbTiO\textsubscript{3}-BaTiO\textsubscript{3}-Ba(Zn\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3} (PZN-PT-BT-BZN) has been used to replace the normal formula, PZN-PT-BT [6-9]. Ba(Zn\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3} (BZN) is a linear dielectric with dielectric constant around 30, while the dielectric constant of PZN single crystal is higher than 10,000 [10].

It is well known that an effective way to decrease Curie temperature \( T_C \) of a ferroelectric is to add some non-polar materials or ferroelectrics with lower \( T_C \) to it. The resultant ceramics have been assumed to be in the solid-solution form. No theoretical description has been given on the mechanism for the \( T_C \) decrease. However, thermodynamic analysis, done on a model of a
ferroelectric single crystal with embedded dispersed para-electric micro regions, indicates that the \( T_c \) of the ferroelectric system will decrease with increase of the size and concentration of the para-electric micro regions [6].

In this paper, we focused on analyzing the dielectric properties between unannealed and annealed samples in PZN-PT-BT ceramics to infer the influence of para-electric BZN nano-regions.

**Variation of \( T_m \)**

Ceramics of 0.75PZN-0.15PT-0.10BT and 0.70PZN-0.15PT-0.15BT are of tetragonal perovskite structure at room temperature according to the X-ray diffraction results. Figure 1 and 2 show the dependence of dielectric constant and dissipation factor with temperature at different frequencies for the unannealed and annealed samples, respectively. Comparison data of the dielectric properties for both ceramics are listed in Table 1.

<table>
<thead>
<tr>
<th>PZN/PT/BT</th>
<th>( T_{m} ) (°C) at 100 KHz</th>
<th>( \Delta T_{m}^* ) (°C)</th>
<th>( \Delta T_{m}^{**} ) (°C)</th>
<th>( K_m ) at 100 KHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>75/15/10</td>
<td>Unannealed: 133</td>
<td>34</td>
<td>6</td>
<td>6800</td>
</tr>
<tr>
<td></td>
<td>Annealed: 167</td>
<td>0.2</td>
<td>7500</td>
<td></td>
</tr>
<tr>
<td>70/15/15</td>
<td>Unannealed: 109</td>
<td>51</td>
<td>6</td>
<td>7300</td>
</tr>
<tr>
<td></td>
<td>Annealed: 160</td>
<td>0.3</td>
<td>6800</td>
<td></td>
</tr>
</tbody>
</table>

\( \Delta T_{m}^* \) = \( T_{m, \text{1kHz}} \) (Unannealed) - \( T_{m, \text{1kHz}} \) (Annealed);

\( \Delta T_{m}^{**} \) = \( T_{m, 100 \text{kHz}} \) - \( T_{m, 100 \text{Hz}} \).

These two compositions show typical relaxor ferroelectric properties before annealing. But after annealing, the \( T_m \)'s of the two compositions do not vary with measuring frequency, and are all higher than unannealed ones. The frequency dispersion of the dielectric constants substantially weakens as well. Both the dielectric constants and dissipation factors in the temperature range below \( T_m \) decrease.

After annealing at sufficiently high temperatures, the chemical compositions of nano-regions would presumably distribute more homogeneously. If inhomogeneous nano-regions of PZN-PT-BT ceramics are only composed of solid solution phases with different proportional components, the \( T_m \) and the dielectric relaxation should not be affected as appreciably by annealing.
Figure 1. Plots of (A) dielectric constant and (B) dissipation factor with temperature and frequency for 0.75PZN-0.15PT-0.10BT ceramics. (Open circle: unannealed; black spot: annealed.)

Figure 2. Plots of (A) dielectric constant and (B) dissipation factor with temperature and frequency for 0.75PZN-0.15PT-0.15BT ceramics. (Open circle: unannealed; black spot: annealed at 880°C for 16 hours.)

Another possibility of chemical compositional inhomogeneity in solid solution ceramics is that there exist nano-phase regions of significantly different amounts of solutes dispersed in the matrix of a solid solution. For ceramics of 0.75PZN-0.15PT-0.10BT and 0.70PZN-0.15PT-0.15BT, the possible solutes are PT, BT and BZN. BZN is a linear dielectrics. The existence of BZN non-polar
nano-phase would lower the $T_m$ of PZN-PT-BT ceramics. Long time annealing could promote ions in different concentration areas to diffuse more uniformly, so that the solute nano-phase regions could shrink gradually, or even disappear entirely. If there are BZN-rich nano-phase regions in PZN-PT-BT ceramics, then annealing could dilute the nano-phase regions, and the $T_m$ could increase. Table 2 gives the corresponding components of PZN-PT-BT-BZN system for 0.75PZN-0.15PT-0.10BT and 0.70PZN-0.15PT-0.15BT. The latter has more content of BZN than the former. Before annealing, the $T_m$ of 0.70PZN-0.15PT-0.15BT is 24°C lower than that of 0.75PZN-0.15PT-0.10BT. After annealing, this difference becomes 7°C only. This hypothesized model is consistent with the experimental results.

Table 2. Corresponding components of PZN-PT-BT-BZN system for 0.75PZN-0.15PT-0.10BT and 0.70PZN-0.15PT-0.15BT

<table>
<thead>
<tr>
<th>PZN-PT-BT</th>
<th>PZN-PT-BT-BZN</th>
</tr>
</thead>
<tbody>
<tr>
<td>PZN PT BT</td>
<td>PZN PT BT BZN</td>
</tr>
<tr>
<td>0.75 0.15 0.10</td>
<td>0.675 0.225 0.025 0.075</td>
</tr>
<tr>
<td>0.70 0.15 0.15</td>
<td>0.595 0.225 0.045 0.105</td>
</tr>
</tbody>
</table>

Variation of Relaxation Behaviors
Dielectric properties of many solid solution ferroelectric ceramics containing PT and with tetragonal perovskite structure do not show relaxation behaviors [11-14]. The ceramic structures of 0.75PZN-0.15PT-0.10BT and 0.70PZN-0.15PT-0.15BT are tetragonal perovskite phase. Before annealing, both ceramics belong to relaxor ferroelectrics. After annealing, e.g. at 880°C for 16 hours, however, their dielectric relaxation almost vanishes (see Figure 1 and 2). This behavior can also be explained using the model of BZN non-polar nano-phase.

Unusual Linear Region of P-E Hysteresis Loop
Further evidence of the existence of the paraelectric BZN phase may be inferred from the unusual behavior of P-E loops as shown in Figure 3. It was found that an elongated P-E loop exists with linear slope near the center, which is composition and temperature dependent. Calculated dielectric constants, taken from the slope of the P-E curve, show a constant plateau – a behavior like a paraelectric system.

A SUGGESTED MODEL
A model is hypothesized to explain the observed dielectric behaviors. The microstructure of a grain in the ceramics of 0.75PZN-0.15PT-0.10BT or 0.70PZN-0.15PT-0.15BT at room temperature is schematically drawn in Figure 4. The shaded areas indicate BZN non-polar nano-regions. Electric fields of spontaneous polarizations of ferroelectric domains cause movable space charges to concentrate around the non-polar areas. Therefore, the non-polar nano-regions are equivalent to big dipoles, contributing to the dielectric and ferroelectric properties. The presence of these paraelectric nano-regions could also account for the dielectric plateau seen in Figure 3.
Figure 3. Polarization versus electrical field and the corresponding dielectric constants for a 75PZN-10PT-15BT ceramics.

The macro ferroelectric domains transform into para-electric phase as the temperature increases beyond the Curie point. The induced dipoles on the non-polar nano-regions would disperse away when the polar domains around them disappear. The dielectric frequency dispersion and relaxation of PZN-PT-BT ceramics may be related to the induced dipoles. Long time annealing would make BZN non-polar nano-regions becoming smaller, and even vanish, so that the dominant tetragonal PZN-PT-BT ceramic matrix phase exhibits weak dielectric relaxation, similar to other tetragonal solid solutions of PT-type. Furthermore, the induced dipoles still contribute to the dissipation factor of the samples. After annealing, when the induced dipoles decrease largely, the dissipation factor lessens.

X-ray diffraction patterns failed to show any impurity phase because the nano nature of in homogeneities. This is not surprising because power x-ray diffraction using conventional x-ray sources do not have sufficient sensitivity. We have taken some preliminary data using transmission electron microscopy (TEM). Figure 5 shows a TEM bright field image of one PZN-5PT-10BT sample. It is clear that the system is far from homogeneous. Many nano-regions of different contrasts are seen. Due to the small size of these inhomogeneous regions, composition analysis using fluorescent x-rays of a Philips CM-10 microscope turned out to be inconclusive. Much higher resolution TEM must be utilized in order to obtain accuracy information on composition fluctuation on the nano scale.

CONCLUSIONS

Comparing the variations of the dielectric properties with respect to composition, temperature and annealing, it is reasonable to believe that there are BZN-rich non-polar nano-phase regions in PZN-PT-BT ceramics. In a sense, PZN-PT-BT ceramics are self-assembling nano-composites exhibiting unusual properties.
ACKNOWLEDGMENTS

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REFERENCES