Relaxor ferroelectric properties of 85PZN–15BT transparent ceramic at low temperatures

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Dielectric, hysteresis (P – E) loops and TSDC properties of transparent 85PZN–15BT ceramic over -150 – 150°C were investigated. The sample was found to exhibit a strong relaxor behavior and a relatively small remanent polarization. TSDC studies showed that there existed an electric field-dependent peak in the p versus T . Such interesting features were attributed to the electric field-induced transition and coexistence of polar nanoregion, long-range ordered polar region and nonpolarizable BZN-rich region.

Keywords: PZN; BT; relaxor; electric field-induced transition; TSDC.

1. Introduction

Lead-based relaxor ferroelectric materials, known for their strong frequency dispersion of dielectric response,^{1–3} high dielectric constant,¹ large electrostrictive coefficient^{4,5} and good transmittance,⁶ have been intensively studied over the past decades. It is commonly recognized that relaxors are highly inhomogeneous materials, which consist of randomly oriented polar nanoregions (PNRs) and chemically ordering regions (CORs).⁷ Moreover, the CORs block the PNRs growth to micrometer. An external electric field could overcome the energy barrier and transform the material into a long-range ordered polar state.

$\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PZN) is a typical relaxor ferroelectrics. It undergoes a diffused phase transition above 140°C . The perovskite structure PZN is thermal unstable and will turn to pyrochlore phase in the preparing process due to its inherently low tolerance factor and small absolute value of the bond valence sum of oxygen.⁸ To stabilize the perovskite structure, addition of a little amount of BaTiO_3 (BT) is purposed as an effective way.⁹ Structurally, the nonpolarizable BZN-rich region was found to exist in BT stabilized PZN by TEM analysis.¹⁰ However, the dynamical responses of PNR with strong electric field and temperature in such relaxor ferroelectrics are still less studied.

Here, we investigated the evolution of dielectric, hysteresis (P – E) loops and domain with strong electric field and temperature of 85PZN–15BT transparent ceramic.

2. Experiments

Transparent 85PZN–15BT ceramic was fabricated by using a two-stage sintering method. The detailed preparation procedure

can be found in our previous report.¹¹ The sintered sample was polished to 0.2 mm and deposited with gold as electrodes for different property measurements. Dielectric properties were measured by using a Novocontrol Broadband Dielectric Spectrometer with a 500 V DC high voltage booster. Thermally simulated depolarization current (TSDC) properties were measured by using a Keithley 6517 Electrometer. Ferroelectric hysteresis (P – E) loops and curves of current versus electric field were characterized by using a TF2000 using the Sawyer-Tower circuit at 10 Hz. Temperature with a precision of 0.01 K was controlled by using a Novocontrol Quatro Cryosystem.

3. Results and Discussion

3.1. Dielectric properties under DC bias

Figure 1 shows dielectric property as a function of temperature for the 85PZN–15BT ceramic under various conditions (ZFH: zero-field-heating, FC: field-heating under DC bias after ZFH). The broad maximum and frequency dispersion of dielectric permittivity indicates its relaxor-like behavior. With increasing DC bias, a drop of dielectric permittivity within a wide temperature range and a shift of T_m can be observed. Such features reveal an electric-field-induced transition from relaxor state to a long-range ordered ferroelectric phase or a mixed state phase as reported in many previous works. Threshold field E_{th} has also been observed by measuring dielectric permittivity (at 1 kHz) of the sample that has been prepoled under DC field within 1 min at room temperature, as shown in the insert of Fig. 2. Anomalous drop in dielectric permittivity near 5 kV/cm was observed, indicating the presence of E_{th} for the 85PZN–15BT ceramic.

Fig. 1. Dielectric property as a function of temperature and DC bias for the transparent 85PZN-15BT ceramic.

There is no obvious shrink of dielectric permittivity, even under high electric field of 20 kV/cm. Such strong relaxor feature indicates that certain amount of PNRs still exist at measured lowest temperature. Generally, PNRs are not stable and easily grow under electric field at low temperatures; as a consequence, the permittivity is expected to shrink at low temperatures under electric field, which is commonly less than 10 kV/cm. For example, dielectric permittivity of 4% La-doped 75PMN-25PT shrinks below electric field of 4 kV/cm.¹² One main mechanism suggests to enhance local random fields derived from the existence of nonpolarizable BZN-rich region.

Fig. 2. Dielectric permittivity at 1 kHz as a function of applied DC field at room temperature.

3.2. Ferroelectric properties

Figure 3 shows hysteresis (P - E) loops at various temperatures, ranging from -150°C to 140°C . Clearly, the evolution of P - E loops gives a direct evidence that there are paraelectric-relaxor and relaxor-normal transition. Below the freezing temperature of -75°C calculated using Vogel-Fulcher model, or in the temperature from relaxor to normal ferroelectric phase

Fig. 3. Evolution of ferroelectric properties of the sample at 10 Hz with temperature.

transition in our previous report,¹¹ one can see that the 85PZN–15BT ceramic has square hysteresis loop which is a characteristic of typical normal ferroelectrics, indicating the existence of long-range ordered polarization derived from electric field and temperature. The saturated and remanent polarizations of the 85PZN–15BT are very small with comparison to that of typical ferroelectrics. Such phenomenon can be explained by the coexistence of polar nanoregion, long-range ordered polar region and nonpolarizable BZN-rich region. This is also supported by dielectric analysis.

3.3. TSDC properties

To better investigate dynamical evolution of PNRs under electric fields and thermal stability of long-range ordered polar state, TSDC was measured, as shown in Fig. 4. The samples were heated to 100°C, polarized at various DC electric fields, and rapidly cooled to –150°C while keeping DC fields. The samples were stayed at –150°C for 5 min after removing the DC fields, then were heated to 70°C at 3°C/min while measuring the current. Similar to what have been reported by Cross *et al.*,¹³ the sample has very small magnitude of maximum current $I_{\max}$, relatively not too high remanent polarization and a broad peak. It is well known that the peak in the current versus T represents the transition from long-range ordered domain to microdomain state. Obviously, such well-defined broad peak can be observed for all electric fields. However, while increasing electric field, the current peak increases and shifts to lower temperature until reaching saturation state at 15 kV/cm. The peak temperature shift indicates that there is no structure phase transition in the temperature range of –150 ~ –50°C, and high current at high electric fields reveals that higher electric field could induce larger macrodomain state, but larger macrodomains are more unstable because the peaks of $I_{\max}$ shift to lower temperature.

Fig. 4. TSDC properties of 85PZN–15BT as a function of temperature cooled under various electric fields. Insert is calculated polarization versus temperature.

The calculated remanent polarization is shown in the insert of Fig. 2. Small remanent polarization was obtained, which coincides with what observed from ferroelectric measurement.

3.4. Discussion

Dielectric, hysteresis (P – E) loops and TSDC properties suggested that 85PZN–15BT ceramic has an electric field-induced transition from relaxor state to a long-range ordered ferroelectric phase or a mixed state phase. The polar nanoregions appeared at high temperatures beyond the temperature of maximum dielectric constant versus temperature, T_m , and then formed nuclei for the field-induced long-range order at low temperatures. In such transition, the competition, as well as coexistence between short-range and long-range polar order, were dominated by local random fields. For BT stabilized PZN, it was suggested that there existed nonpolarizable BZN-rich regions. Such regions resulted in high local random fields which enhanced the relaxor characteristics or, in other words, increased the energy barrier that would inhibit the field-induced phase transition. Thus, there appeared strong relaxor behavior, quite broad TSDC peak and relatively small remanent polarization in 85PZN–15BT transparent ceramic. At measured lowest temperatures in the present work, it could be expected that there was a coexistence of polar nanoregion, long-range ordered polar region and nonpolarizable BZN-rich region.

4. Conclusion

In summary, we studied dielectric, ferroelectric and pyroelectric properties of transparent 85PZN–15BT ceramic. A clear feature of polar nanoregions and electric field-induced long-range order was drawn. Nonpolarizable BZN-rich region was suggested to exist and enhance local random fields. The existence of nonpolarizable region resulted in strong relaxor behavior, quite broad pyroelectric peak and relatively small remanent polarization.

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