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Poling induced dielectric anomalies in a PZT ceramic

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Abstract

Dielectric properties of $Pb_{0.99375}(Zr_{0.52}Ti_{0.48})_{0.9875}Nb_{0.0125}O_3$ (PZTN) ceramics were measured during heating and cooling processes before and after poling. A dielectric anomaly from 220 K to 290 K was only observed in poled PZTN samples. The frequency dependence of the ε'' peaks was fitted using the Vogel–Fulcher law, which indicated that this dielectric anomaly could be associated with the poling induced monoclinic distortion. Meanwhile, the existence of the low-temperature transformation involving rotations of the octahedra was confirmed by the broadening peaks in ε''–T curves and the variation of slopes in ε'–T curves in both unpoled and poled samples.

Keywords: Poling process; Dielectric dispersion; Monoclinic distortion; Nb-doped PZT

1. Introduction

Great attention has been paid to ferroelectric ceramics $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) with perovskite structure, due to their extremely high electromechanical coupling coefficients [1,2] near the morphotropic phase boundary (MPB). Although its phase diagram has been well accepted during the past few decades [3], there is a resurgence of interest for PZT-based ceramics with the MPB compositions, since an unexpected ferroelectric monoclinic phase has been discovered within the MPB by Noheda and his coworkers [4]. The investigations on the new phase have been carried out with different measurements [5–8]. The temperature dependent dielectric responses, which is the basic parameter characterizing the ferroelectric ceramics, were also measured to provide more information [5,9–12]. However, the controversy over the origin of the dielectric anomaly observed at about 260 K has not stopped. Ragini et al. and Cordero et al. attributed the dielectric anomaly to the existence of the monoclinic phase [5,13]. Meanwhile, Zhang et al. and Garcia et al. associated this dielectric anomaly with the domain wall pinning effect related to the oxygen vacancies [11,14,15]. Yet, Sheen and Kim ascribed this dielectric behavior to the phase coexistence in the MPB region [12].

As is experimentally known, poling is a crucial process in PZT preparation. During the poling process, the original isotropic symmetry, which can be associated with the random orientation of the spontaneous polarization between different domains, is broken and an induced polar axis along the direction of the applied electric field appears [16]. Hence, there is an intimate relationship between poling, domain walls, and phase structures. On one side, poling can align the dipole defects and space charges under the external electric field, which restructures the lattice into perfection [17], decreasing the frequency dependence of the dielectric responses. Yet, on the other side, poling can induce the lattice distortion in the ceramics [18], which would lead to the instability of the phase structures, increasing the frequency dependence of the dielectric responses. That means there are competing contributions to the dielectric responses resulting from the poling process.

In this paper, the temperature dependent dielectric properties were measured on Nb-doped PZT ceramics before and after poling. Both real (ε') and imaginary (ε'') parts of the dielectric constants showed anomalies of frequency dispersions only in the poled samples. This specific dielectric behavior provided new information on the nature of the phases within the MPB.

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2. Experimental details

$Pb_{0.99375}(Zr_{0.52}Ti_{0.48})_{0.9875}Nb_{0.0125}O_3$ ceramics were prepared by the traditional solid-state reaction method. Appropriate PbO, ZrO_2, TiO_2, and Nb_2O_5 according to the formula stoichiometry were mixed by ball milling for 6 h. The dried mixtures were calcined at 850 °C for 2 h. Then the synthesized powders were remilled for 24 h, dried, and sieved. The powders were finally pressed into disks with 0.5 mm thickness and 5 mm diameter. Then, in order to minimize the lead loss, the disks were sintered under a PbO-rich atmosphere at 1250 °C for 2 h. The density of the samples was about 95% of the theoretical value. The electrodes were made of fired-on silver paste.

The crystal structures of the samples were checked by powder X-ray diffraction (D/max2550V, Rigaku, Tokyo, Japan) using CuKα radiation from 20° to 80°. The XRD diffraction patterns confirmed the tetragonal phase of all samples. The low-temperature electrical properties were characterized in a vacuum chamber (Janis ST-500) with two feeler pins. The relative dielectric constant (ε_r) and dissipation factor ($\tan\delta$) of the samples were measured before and after poling by an HP4294A LCR meter (Hewlett-Packard, Palo Alto, CA). The poling condition is under a dc electric field of 4 kV/mm for 20 min at 140 °C in a silicon oil bath.

3. Results and discussion

3.1. Dielectric properties of unpoled samples

Fig. 1 shows the temperature dependent variation of ε' and ε'' through cooling and heating processes (1 K/min) from 100 K to 290 K of unpoled samples for a frequency range from 100 Hz to 100 kHz. Both were calculated from Eqs. (1) and (2), respectively:

$$\varepsilon' = \varepsilon r, \tag{1}$$

$$\varepsilon'' = \varepsilon_r \tan\delta, \tag{2}$$

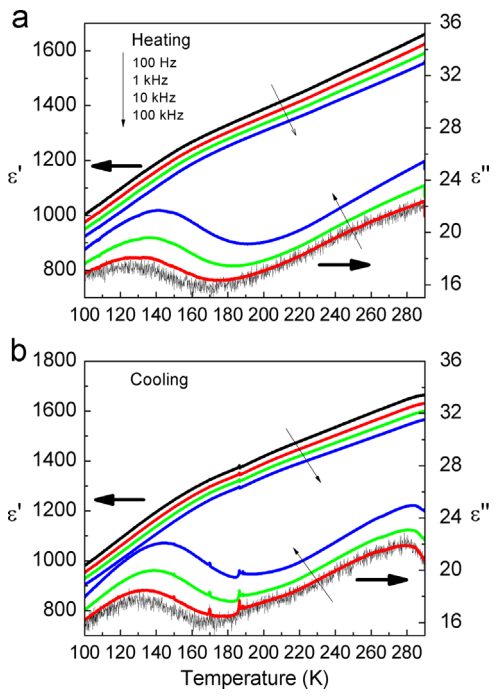

Fig. 1. The dielectric properties of unpoled samples during (a) heating and (b) cooling processes.

The ε' is observed to decrease with the increasing frequency, while the ε'' increases with it. The ε'–T plot displays a nearly monotonous increase with a little change of its slope at about 150 K for all frequencies in the studied temperature range. Simultaneously, the ε''–T plot shows a complex variation. The ε'' increases initially with increasing temperature, reaches the maximum at about 140 K, decreases rapidly until 190 K, then again slightly increases up to 290 K. The broad peak observed at about 140 K in the ε''–T curve agrees well with the investigation of Cordero et al. in their dielectric susceptibility spectroscopy measurements [13]. They attributed this broadening peak to the phase transition involving rotations of the octahedra. And the slope change temperature in the ε'–T curve is a little higher than the broadening peak temperature in our study. However, there is a little difference between the curves observed in the cooling and heating processes. The ε''–T curve shows a decreasing tendency at about 280 K in the cooling process, while there is no tendency of decreasing in the heating process. And the peaks in ε'' at about 280 K show no frequency dispersion. It might demonstrate that there is a thermal hysteresis process at about 280 K.

3.2. Dielectric properties of poled samples

For poled samples, the dielectric properties were measured as a function of temperature from 100 Hz to 100 kHz. The results obtained from 100 K to 290 K in the heating process are shown in Fig. 2(a). Compared with the ε''–T curves above 1 kHz, the ε''–T curve at 100 Hz is really unstable, especially below 200 K. Therefore, we cut off the ε''–T curve for 100 Hz below 220 K. In ε''-T curves, the broadening peak indicating a lower-temperature transformation at about 140 K still appears. The significant difference between the unpoled and poled samples should be the frequency dispersion in both ε'-T and ε''–T curves obtained from 220 K to room temperature. Especially in ε''–T plot, the peak temperature increases with increasing frequency. This frequency dependence of peaks in ε'' has been reported in previous MPB studies of PZT films by Sheen and Kim [12], whereas no similar dielectric anomalies near the MPB have been observed in PZT ceramics to the best of our knowledge. Cordero et al. have reported the frequency dispersion behavior in their dielectric susceptibility spectroscopy at 1 kHz and 100 kHz [13], but no more information was provided. As was proposed for PZT ceramics with MPB compositions, this dielectric anomaly observed between 230 K and 290 K might be associated with a tetragonal–monoclinic phase transition [5,12]. Fig. 2(b) shows the dielectric properties obtained in the cooling process. The frequency dependent dielectric anomaly was still observed in the cooling process, but it shifts to a lower temperature. The existence of the

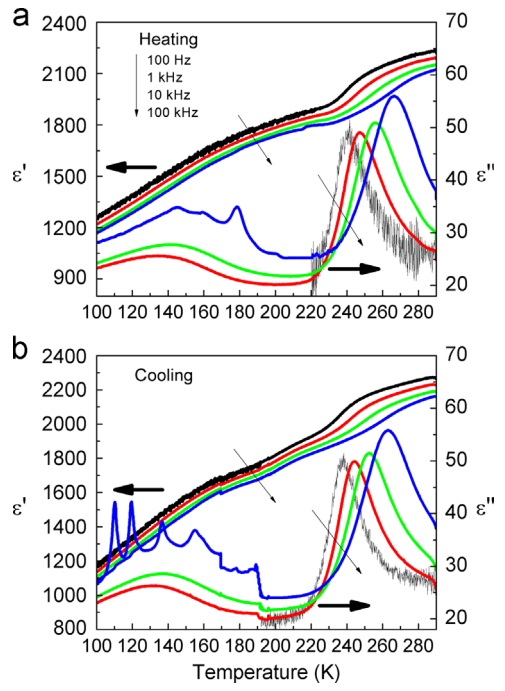

Fig. 2. The dielectric properties of poled samples during (a) heating and (b) cooling processes.

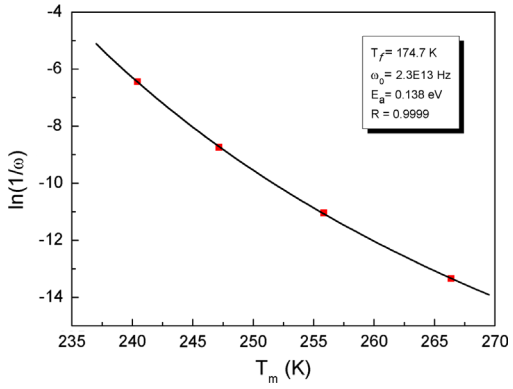

Fig. 3. Vogel–Fulcher plots of $\ln(1/\omega)$ versus T_m for PZTN.

temperature hysteresis in the heating and cooling ε''–T plots indicates that the transformation is of first order in the samples.

3.3. Vogel–Fulcher relationship

The frequency dispersion in ε'' can be described by the Vogel–Fulcher law [12,19]:

$$\omega = \omega_0 \exp[-E_a/k(T_m - T_f)], \quad (3)$$

where $\omega=2\pi f$ is the measuring frequency, ω_0 is the attempt frequency, which has a meaning of the inverse minimum relaxation time, k is the Boltmann constant, E_a is the activation energy, T_m is the peak temperature in ε''–T curves, and T_f is the freezing temperature. Fig. 3 shows the Vogel–Fulcher plots of $\ln(1/\omega)$ versus T_m in the heating process. It can be seen that the dielectric dispersion data are sufficiently fitted with reasonable standard deviations of fitting parameters. The frequency ω_0 is 2.3×10^{13} Hz, which is in the frequency range of lattice vibration for ionic solids on the order of 10^{11}–10^{13} Hz. The activation energy and freezing temperature are found to be about 0.138 eV and 174.7 K, respectively, which are close to the E_a and T_f obtained in PZT films by Sheen and Kim [12]. The dielectric dispersion observed in poled samples but not in unpoled ones implies that the dispersion is directly induced by the poling process.

In the poling process, the applied electric field aligns the dipole defects induced by oxygen vacancy in the perovskite cells [20], reducing their contribution to the dielectric constant and weakening the dielectric dispersion induced by them. Therefore, the dielectric dispersion observed in our case cannot be attributed to the thermally activated motion of mobile charged defects [11,14], since the dispersion behavior only appears in poled samples. And another fact, that the E_a calculated by the Vogel–Fulcher law is much smaller than the activation energy for the migration of the oxygen vacancy [19], also disproves the above mechanism. As was proposed in previous literatures, the poling effect of the applied electric field in PZT ceramics with MPB compositions is partially retained after the field is removed [18,21], and a definite elongation is induced along those directions associated with a monoclinic distortion [18]. In addition, Damjanovic et al. proposed that the relatively isotropic free-energy profile in tetragonal PZT, even in compositions close to the MPB, can be broken by external electric fields [22]. In our case, the unpoled ceramic is tetragonal phase, but the poling process induces an unstable monoclinic distortion [18,21,23]. This unstable phase structure results in the easiness of the polarization rotation [24], which is related to the flatness of the free energy [25]. And the change of the flatness free energy map versus temperature could induce the dielectric dispersion [25]. Hence, the dielectric dispersion observed in our case can be attributed to the monoclinic distortion induced by poling.

4. Conclusions

Dielectric measurements are conducted in $Pb_{0.99375}(Zr_{0.52}Ti_{0.48})_{0.9875}Nb_{0.0125}O_3$ ceramics in both heating and cooling processes before and after poling. The dielectric anomaly from 220 K to 290 K is significant in poled samples but not in unpoled ones. The frequency dispersion of the ε'' peaks follows the Vogel–Fulcher law. However, the frequency dispersion's only appearance in the poled ceramics and the small E_a calculated by the Vogel–Fulcher law disprove the thermally activated motion of mobile charged defect mechanism. Therefore, this dielectric dispersion should be associated with the poling induced monoclinic distortion. The temperature hysteresis exists in ε''–T plots indicating a first order transformation. Meanwhile, the broadening peaks in ε''–T curves and the change of slopes in ε'–T curves, which indicate the low-temperature transformation involving rotations of the octahedra, are observed both in poled and unpoled samples.

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