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Dielectric study of phase transitions in $Pb(Zn_{1/3}Nb_{2/3})O_3$–$PbTiO_3$

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Phase transitions in $Pb(Zn_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ were investigated by means of the dielectric constant measurement under the zero-field heating after field cooling. A sharp phase transition between ferroelectric phases in $Pb(Zn_{1/3}Nb_{2/3})O_3$ was confirmed to appear at 114°C, and to connect to the morphotropic phase boundary in the $Pb(Zn_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ solid solution system. It is therefore concluded that the phase transition between ferroelectric phases of $Pb(Zn_{1/3}Nb_{2/3})O_3$ is the one between the tetragonal and rhombohedral phases.

Key-words : $Pb(Zn_{1/3}Nb_{2/3})O_3$, Dielectric constant, Ferroelectricity, Morphotropic phase boundary, Relaxor

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1. Introduction

Solid solutions of perovskite-type ferroelectrics $Pb(Zn_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ (PZN–xPT) characterized by the morphotropic phase boundary (MPB) at $x = 9\%$ have been of fundamental and practical interest for many years, because of their giant dielectric and piezoelectric responses.[1)] The mechanism of giant responses in PZN–xPT was proposed to be due to the transversal instability near the MPB, where the dielectric response perpendicular to the spontaneous polarization becomes extremely large.[2),3)] The dielectric anisotropy near the MPB of PZN–xPT was confirmed by the authors to show transversal instability.[4)] It is known that physical properties in the vicinity of the MPB of PZN–xPT are sensitive to external fields such as stresses and electric fields, reflecting the giant dielectric and piezoelectric responses.[5)–9)]

On the other hand, PZN shows the diffuse phase transition with a broad peak of the dielectric constant as a function of temperature, because of heterogeneity in this material such as polar nanoregions (PNRs).[10)] It is conceivable that in relaxors the random fields due to either frustration-induced or compositionally induced disorder form PNRs in the paraelectric matrix below the Burns temperature, and impede the growth of the long range order of the polarization in the temperature range, where the dielectric constant shows as a maximum.[10),11)] For physical properties of the relaxor, Cross proposed the superparaelectric model assuming the thermal fluctuation of the spontaneous polarization in the PNR,[12)] while Westphal et al. proposed the domain state model, in which the static PNR is considered to be induced by the random field.[13)] These models seem to contradict each other. On the other hand, Iwata et al. reported that the sign of the third order nonlinear dielectric susceptibility, which is positive, does not favor a superparaelectric model in the relaxor PMN.[14)] Bobnar et al. and Glazounov and Tagantsev claimed that the experimental results of the third order nonlinear dielectric susceptibility support the spherical random bond-random field (SRBRF) model,[15)–17)] which is based on the superparaelectric model. Thus, it seems that the mechanism of the appearance of relaxors is still controversial.

Recently, a sharp phase transition at 114°C below the paraelectric-ferroelectric phase transition point in PZN has been found under the conditions of the zero-field heating (ZFH) after field cooling (FC),[18)–20)] implying that decrease of heterogeneity owing to the applied electric field on the FC may make the phase transition sharp, which is usually smeared by the complex domain structures such as PNRs. The critical slowing down and temperature dependences of the second- and third-order nonlinear dielectric constants near this transition point were reported.[21)] However, no detail of this phase transition observed under ZFH after FC has been clarified. Under this circumstance, we report the investigation of phase transitions under ZFH after FC in $Pb(Zn_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ by means of the dielectric constant measurement, and discuss these phase transitions.

2. Experimental

Single crystals of PZN–xPT were grown by the flux method from the PbO–ZnO–Nb_2O_5–TiO_2 system. The mixture in a platinum crucible was heated to 1150°C and held at this soak temperature for 10 h, and then the melt was cooled to 850°C at the rate of –5°C/h. The single crystals obtained were yellowish in color and were typically 3 mm in size. All of the synthesized crystals were confirmed by the X-ray powder diffraction studies as being the single perovskite phase.

For the measurement of the dielectric constant, (111) crystal plates in a cubic coordinate with Au electrodes deposited on their faces were prepared; the samples have an area of about 4 mm^2 and a thickness of about 200 μm. For the measurement on ZFH after FC, the biasing field was applied on cooling at a rate of 1 K/min, before the dielectric constant measurement with no dc biasing field on heating. The measurements of dielectric dispersions with no dc biasing field were carried out using an LCR hitester (Hioki 3532–50). Complex dielectric constants were obtained at 51 frequencies in the range from 40 Hz to 5 MHz.

3. Results

Temperature dependence of the dielectric constant measured on ZFH without poling in PZN is shown in **Fig. 1**(a). The typical behavior of the diffuse phase transition like in a relaxor is found, where the temperature showing the maximum value of the

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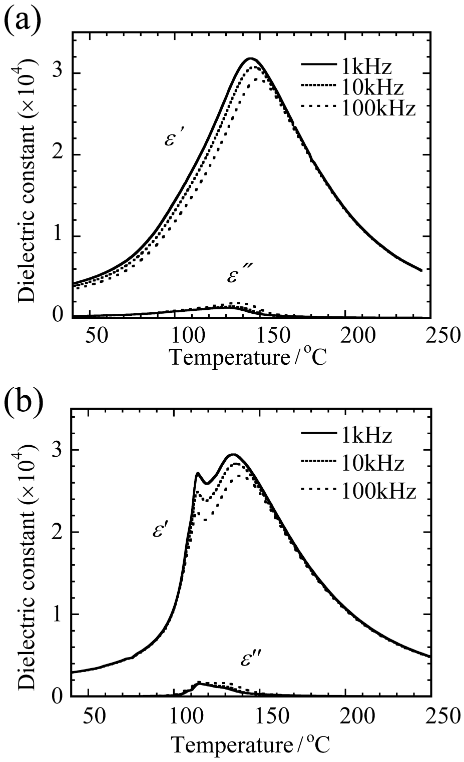

Fig. 1. Temperature dependences of dielectric constants along (111) direction in PZN measured on ZFH without poling (a) and ZFH after FC (b). The biasing field on FC process is 5.8 kV/cm with temperature changed at a rate of 1 K/min.

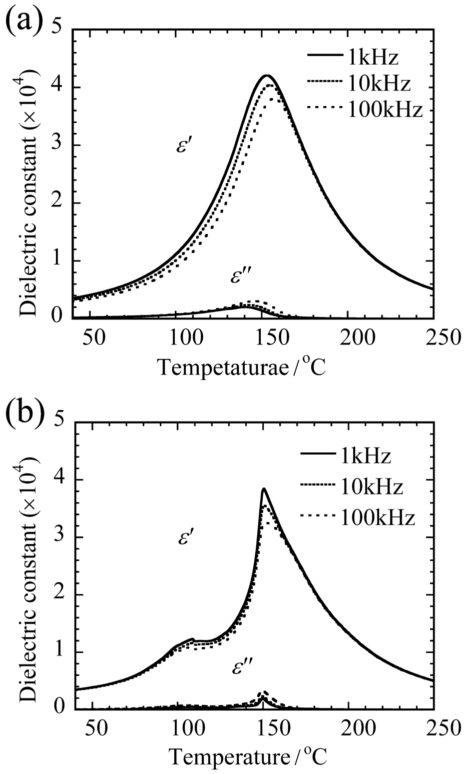

Fig. 2. Temperature dependences of dielectric constants along (111) direction in PZN–5%PT measured on ZFH without poling (a) and ZFH after FC (b). The biasing field on FC process is 10 kV/cm with temperature changed at a rate of 1 K/min.

dielectric constant at 1 kHz is about 144°C. No anomaly corresponding to a phase transition is found below 144°C in non-poled PZN. Figure 1(b) shows the temperature dependence of the dielectric constant on ZFH after FC in PZN, where the biasing field on the FC process is 5.8 kV/cm with temperature changed at a rate of 1 K/min. In addition to the broad peak at 144°C in Fig. 1(a), a sharp peak showing a phase transition at 114°C is newly found in PZN under ZFH after FC. This peak temperature shows no frequency dependence unlike the relaxor.

In order to clarify this new phase transition found in PZN at 114°C, we investigated the dielectric constants on ZFH after FC in PZN–*x*PT mixed crystals, where the biasing field on the FC is about 5–10 kV/cm higher than the coercive filed in the *P*–*E* hysteresis loop. **Figures 2**(a) and 2(b) show temperature dependences of the dielectric constants in PZN–5%PT measured on ZFH without poling and ZFH after FC, respectively. The biasing field on the FC is 10 kV/cm, with temperature changed at a rate of 1 K/min. It is seen that a diffuse phase transition like in relaxors appears in Fig. 2(a), where the temperature showing the maximum value of the dielectric constant at 1 kHz is about 153°C. From Fig. 2(b), we find two dielectric anomalies at 150 and 108°C. The higher and lower ones are considered to correspond to the original diffuse transition, and to the sharp phase transition found in PZN, respectively.

Figure 3(a) and 3(b) show temperature dependences of the dielectric constants in PZN–8%PT measured on ZFH without poling and ZFH after FC, respectively. The biasing field on the FC is 10 kV/cm with temperature changed at a rate of 1 K/min. It is found that two anomalies showing the diffuse phase transitions appear in Fig. 3(a), where one is a peak showing the maximum value of the dielectric constant at about 160°C, and the

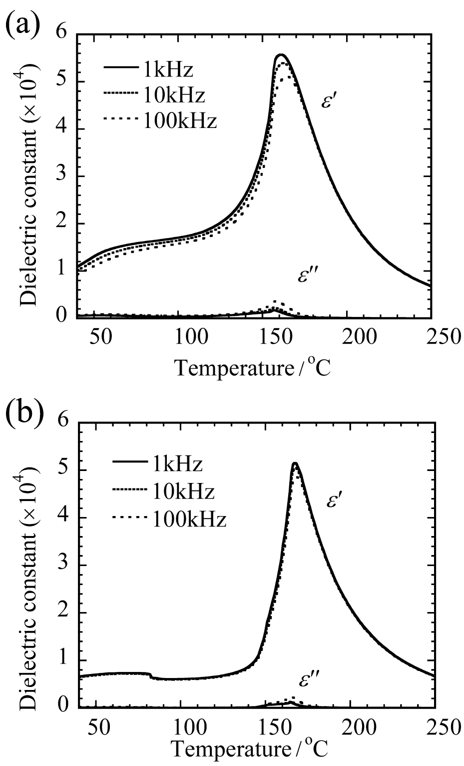

Fig. 3. Temperature dependences of dielectric constants along (111) direction in PZN–8%PT measured on ZFH without poling (a) and ZFH after FC (b). The biasing field on FC process is 10 kV/cm with temperature changed at a rate of 1 K/min.

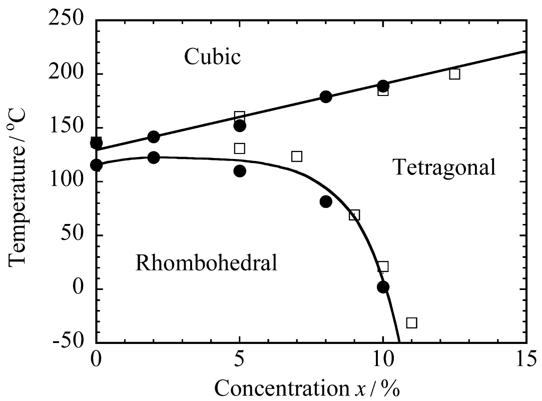

Fig. 4. Phase diagram of PZN–*x*PT mixed crystal system. Open squares indicate the phase boundary reported by Kuwata et al.,[1)] and solid circles indicate the present experimental result.

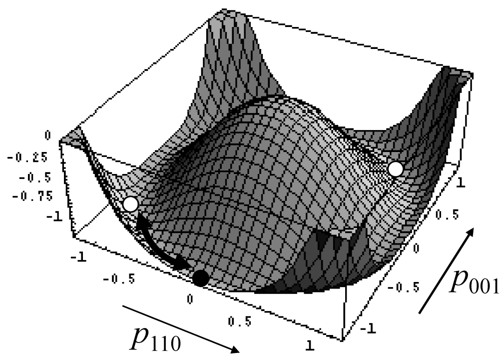

Fig. 5. Thermodynamic potential f near the MPB in the tetragonal phase, where the abscissa axes are parallel to the (001) and (110) directions. The solid and open circles indicate the stable points of the tetragonal phase and metastable points of the rhombohedral phase, respectively.

other is a shoulder near 57°C. In PZN–8%PT, it is known that there exists the phase transition between tetragonal and rhombohedral phases, which is the MPB on the concentration-temperature (x–T) phase diagram. In Fig. 3(b), it is seen that the phase transition at the MPB becomes sharp at 82°C, which is higher than that of as-grown samples.

Figure 4 shows the phase diagram in PZN–*x*PT system, where the open squares indicate the phase boundary reported by Kuwata et al.,[1)] and solid circles indicate our experimental result. We found that the phase transition found in PZN under ZFH after FC connects to the MPB.

4. Discussion

In this study, we have investigated the phase transition between ferroelectric phases under the condition of ZFH after FC in PZN–*x*PT mixed crystals. It has been confirmed that the phase transition in the ferroelectric phase under the condition of ZFH after FC appears at 114°C in PZN. We have shown that the MPB between the tetragonal and rhombohedral phases bends and extends to the phase transition between ferroelectric phases found in PZN, indicating that the phase transition newly found in PZN is the transition between the tetragonal and rhombohedral phases at the MPB.

In the phase diagram of PZN–*x*PT previously reported by Kuwata et al., the phase boundary between rhombohedral and tetragonal phases in the low x region below 5% was not determined because of the diffuseness of the phase transition. Note that, in general, the boundary separates phases of different symmetry, and cannot simply terminate at a point on the phase diagram. It is guessed that the diffuseness of the phase transition due to an inhomogeneous structure from the complex domain structure such as PNRs obscures the phase boundary between the tetragonal and rhombohedral phases in the low concentration range ($x < 5\%$) of PZN–*x*PT. The phase transition between ferroelectric phases found in PZN may appear when the complex domain structures such as PNRs vanish owning to the electric field during the FC process. We conjecture from our experimental result that the tetragonal and rhombohedral phases coexist around the ferroelectric phase transition in non-poled PZN.

Next, to discuss the origin of the large dielectric response near the MPB, let us write the Landau-Devonshire-type energy function in terms of polarization components as[2),3)]

$$f = \frac{\alpha}{2}\left(p_1^2 + p_2^2 + p_3^2\right) + \frac{\beta_1}{4}\left(p_1^4 + p_2^4 + p_3^4\right) + \frac{\beta_2}{2}\left(p_1^2p_2^2 + p_2^2p_3^2 + p_3^2p_1^2\right) + \frac{\gamma_1}{6}\left(p_1^6 + p_2^6 + p_3^6\right) + \frac{\gamma_2}{2}\left[p_1^4\left(p_2^2 + p_3^2\right) + p_2^4\left(p_3^2 + p_1^2\right) + p_3^4\left(p_1^2 + p_2^2\right)\right] + \frac{\gamma_3}{2}p_1^2p_2^2p_3^2 \ , \tag{1}$$

where α is temperature-dependent as shown by $\alpha = a\ (T - T_0)$, and a, β_1, β_2, γ_1, γ_2, and γ_3 are all constants. Within the model in which terms only up to the fourth order are taken into account, the MPB appears when the above β_1 and β_2 are equal, because then the free-energy function becomes isotropic in the space spanned by p_1, p_2 and p_3, i.e., the free energy becomes a function of only $p_1^2 + p_2^2 + p_3^2$.[2)] This isotropy induces an instability in the direction perpendicular to spontaneous polarization, which is called the transversal instability.[2)] Ishibashi and Iwata pointed out that this transversal instability is an essential origin of a large dielectric response.[2),3)] Note that a polarization-rotation path induced by the transversal instability exists near the MPB, and the polarization rotation can result in a marked piezoelectric response. We point out that the phase boundary between tetragonal and rhombohedral phases shown in Fig. 4 can be explained using the free energy function in Eq. (1), even if the phase boundary is not perpendicular to the concentration axis. The transversal instability would be induced near the transition point between tetragonal and rhombohedral phases even in the pure PZN. **Figure 5** shows a thermodynamic potential f near the MPB in the tetragonal phase, where the abscissa axes are parallel to the (001) and (110) directions. The solid circles indicate the stable points of the tetragonal phase, and the open circles indicate the metastable points corresponding to the rhombohedral phase. It is seen that the potential barrier between the tetragonal and rhombohedral phases is extremely small and there is a pass with the low energy value between the tetragonal and the rhombohedral phases.[2),3)] Consequently, it is guessed that the tetragonal and rhombohedral phases easily coexist in PZN around the ferroelectric phase transition, since the polarization direction can be easily changed due to the transversal instability.

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