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Temperature–field phase diagrams in $Pb(Zn_{1/3}Nb_{2/3})O_3$–4.5%$PbTiO_3$ II

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Abstract

Temperature and field dependences of the dielectric constants under the DC biasing fields along the [011]- and [111]-directions in the cubic coordinate in $Pb(Zn_{1/3}Nb_{2/3})O_3$–4.5%$PbTiO_3$ were investigated. The temperature–field phase diagrams were constructed in the field range below 10 kV/cm. It was confirmed that in $Pb(Zn_{1/3}Nb_{2/3})O_3$–4.5%$PbTiO_3$ the intermediate tetragonal phase as a ground state of the system exists even without the DC field, and the tetragonal phase disappears in the external field above 4 and 3 kV/cm along the [011]- and [111]-directions, respectively. The field-induced orthorhombic-phase in the field along the [011]-direction was also found.

Keywords: PZN; Relaxor; Ferroelectric; Morphotropic phase boundary

1. Introduction

It is well known that giant dielectric and piezoelectric responses appear in the vicinity of the morphotropic phase boundary (MPB) of solid solution systems such as $Pb(Zn_{1/3}Nb_{2/3})O_3$–$x PbTiO_3$ (PZN–xPT), where MPB in PZN–xPT is located at $x=9\%$ at room temperature [1–3]. Ishibashi and Iwata claimed that such giant responses essentially come from the transversal instability near MPB based on the Landau-type free energy, where the transversal instability is induced by decreasing the anisotropy of the free energy function in the order-parameter space [4]. It was also reported on the basis of first-principles calculations that a similar mechanism works for such a giant response in $BaTiO_3$ [5]. The dielectric anisotropy near MPB in PZN–xPT was experimentally confirmed to show the transversal instability [6]. Physical properties in the MPB region of PZN–xPT seem to be sensitive to external fields, reflecting the giant dielectric and piezoelectric responses owing to the transversal instability [7–10]. On the other hand, it was discovered by Kutnjak et al. that a critical end point (CEP) appears in the three-dimensional concentration–temperature–field phase diagram in $Pb(Mg_{1/3}Nb_{2/3})O_3$–$x PbTiO_3$ (PMN–xPT); they proposed that the giant electromechanical response in PMN–xPT is the manifestation of CEP in addition to MPB [11,12]. It was also experimentally confirmed that CEP exists on the temperature–field phase diagrams in PZN–xPT and PMN–xPT [13–17]. A detailed and semi-quantitative analysis of such phase diagrams were presented on the basis of the Landau free energy [18]. These results imply that the essential part of giant dielectric and piezoelectric responses in relaxor ferroelectrics can be explained within the Landau theory.

It was found that a new sharp phase transition at 114 °C below the paraelectric–ferroelectric phase transition point in PZN appears only on zero-field heating (ZFH) after field cooling (FC) process [19–22], implying that decrease of heterogeneity owing to the external field on FC may make the phase transition sharp, which is usually smeared by the complex domain structures such as polar nano-regions (PNRs). We reported a new phase diagram in poled samples of PZN–xPT (see Fig. 1), and found that the new sharp transition in the poled PZN and the transition at MPB are the same kind, showing that this new transition is the one between the tetragonal and rhombohedral phases [23,24]. Recently, Chang et al. reported the result of the X-ray diffraction study that the tetragonal and rhombohedral phases coexist [25,26]. It seems, however, that the existence of the intermediate tetragonal phase in the low concentration range ($x<5\%$) of PZN–xPT is still controversial.

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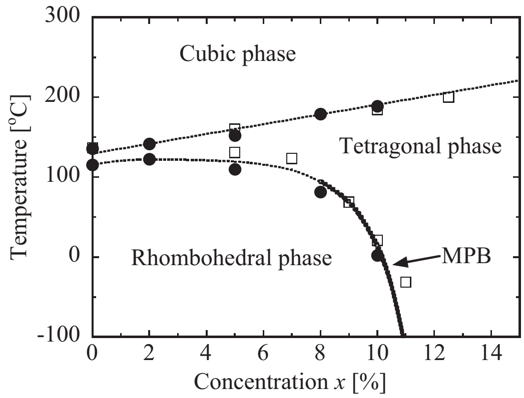

Fig. 1. Phase diagram of the poled sample in PZN–xPT. Open squares and solid circles indicate the phase boundary reported by Kuwata et al. [1] and Iwata et al. [23,24], respectively. The thick curve indicates MPB.

Under these circumstances, in our previous paper, the temperature–field phase diagram under the electric fields along the [001]-direction in the cubic coordinate was clarified, and the existence of the stable tetragonal phase as an average structure in PZN–4.5%PT was experimentally confirmed [27]. In the present paper, we report our experimental results of the DC field dependences of the dielectric constants and the temperature–field phase diagrams with the electric field applied along the [011]- and [111]-directions in the cubic coordinate.

2. Experimental

PZN–4.5%PT single crystal plates were acquired from Microfine Technologies in Singapore. The size of the platelike sample is $3 \times 3 \times 0.2\ mm^3$ perpendicular to the [011]-, and [111]-directions in the cubic coordinate. For the measurement of the dielectric constant, the sample plates with Au electrodes deposited on their faces were prepared. Measurements of the dielectric constant with and without the DC biasing field were carried out using an impedance/gain phase analyzer (NF ZGA5900), where an AC electric field to measure the dielectric constant is about 25 V/cm. The maximum value of the DC biasing voltage to the sample during measurement is 800 V. Complex dielectric constants were obtained at 41 frequencies in the range from 100 Hz to 1 MHz.

3. Results

In order to construct the temperature–field phase diagrams with the electric field applied along the [011]- and [111]-directions in PZN–4.5%PT, we measured the dielectric constant by the two methods; one is the temperature dependence of the dielectric constant under a certain biasing field, and the other is the field dependence of that under a constant temperature.

3.1. Dielectric constant along [011]-direction

Fig. 2 shows a typical result of temperature dependence of the dielectric constants on cooling under the DC biasing field of 2.0 kV/cm along the [011]-direction in the cubic coordinate in PZN–4.5%PT. It is seen that three dielectric anomalies appear at 152.6, 118.1, and 77.3 °C with no significant dispersion. These phases are assigned to be the cubic, tetragonal, orthorhombic, and rhombohedral phases from the high temperature side. The electric field dependence of the dielectric constant at 128.8 °C is presented in Fig. 3 as a typical result. A sharp peak is found at 2.83 kV/cm, implying the field induced tetragonal–orthorhombic phase transition.

On the basis of our experimental results, the temperature–field phase diagram with the electric field applied along the [011]-direction in PZN–4.5%PT was obtained as shown in Fig. 4, where open and solid circles indicate the transition points on heating and cooling measurements, and upward and downward triangles show measurements of those on the field increasing and decreasing, respectively. The solid upward triangles present the dielectric anomaly points due to the polarization reversal on the field increasing measurement.

3.2. Dielectric constant along [111]-direction

Fig. 5 shows temperature dependences of the dielectric constants on cooling under the DC biasing field of 0.8 kV/cm

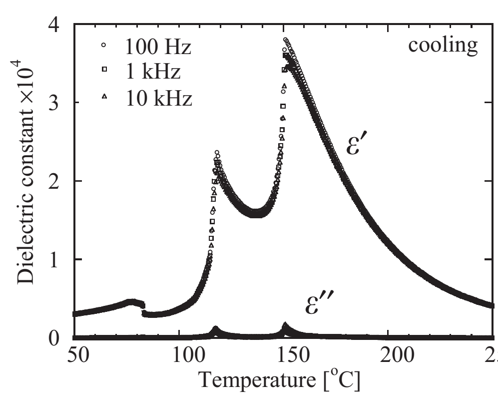

Fig. 2. Temperature dependence of the dielectric constant under the DC biasing field of 2.0 kV/cm along the [011]-direction in PZN-4.5%PT.

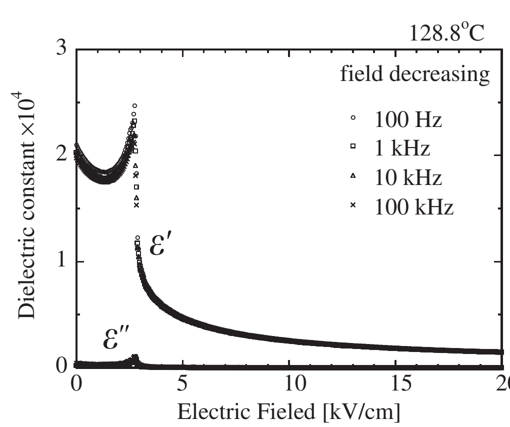

Fig. 3. Electric field dependence of the dielectric constant along the [011]-direction at 128.8 °C in PZN–4.5%PT.

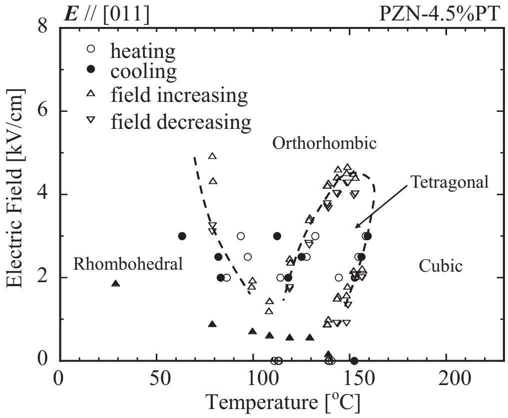

Fig. 4. Temperature–field phase diagram with the electric field applied along the [011]-direction in PZN–4.5%PT. The broken curves are the eye-guide for the concerned phase boundaries.

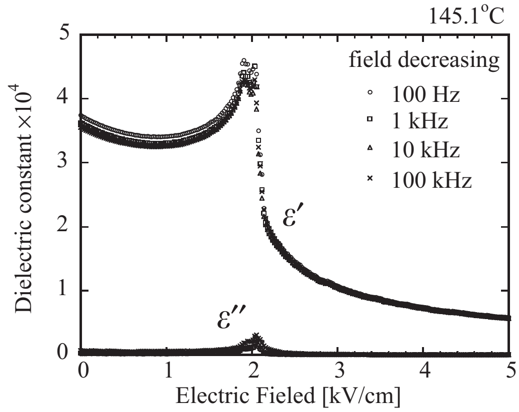

Fig. 6. Electric field dependence of the dielectric constant along the [111]-direction at 145.1 °C in PZN–4.5%PT.

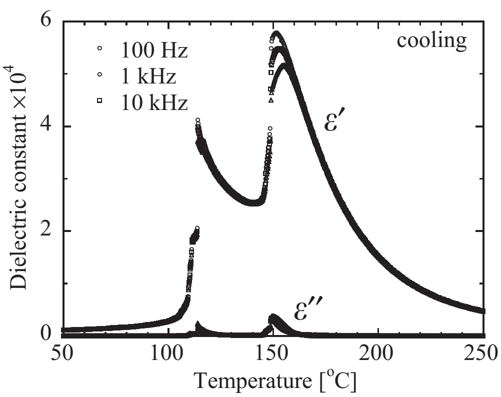

Fig. 5. Temperature dependence of the dielectric constant under the DC biasing field of 0.8 kV/cm along the [111]-direction in PZN–4.5%PT.

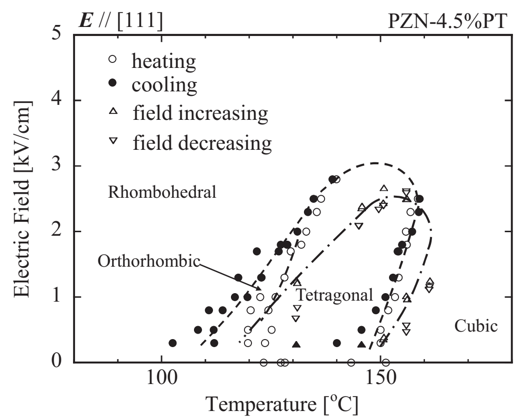

Fig. 7. Temperature–field phase diagram with the electric field applied along the [011]-direction in PZN-4.5%PT. The broken and dashed-dotted curves are the eye-guide for the phase boundaries obtained from the temperature dependence and field dependence measurements, respectively.

along the [111]-direction in the cubic coordinate in PZN–4.5%PT as an example. It is seen that three anomalies appear at 148.9, 113.9, and 110.8 °C. Except for the region near the diffuse phase transion around 148.9 °C, no significant dispersion appears. These phases are assigned to be the cubic, tetragonal, orthorhombic, and rhombohedral phases from the high temperature side. The electric field dependence of the dielectric constant at 145.1 °C is presented in Fig. 6. A sharp peak is found at 2.08 kV/cm, implying the field induced tetragonal–rhombohedral phase transition.

Fig. 7 shows the field–temperature phase diagram with the electric field applied along the [011]-direction in PZN–4.5%PT obtained from our experimental results, where open and solid circles indicate the transition points on heating and cooling measurements, and upward and downward triangles show those on the field increasing and decreasing measurements, respectively. The solid upward triangles show the dielectric anomaly points due to the polarization reversal on the field increasing measurements. The broken curves and dashed-dotted curve are the eye-guide for the phase boundary obtained from the temperature dependence and field dependence measurements, respectively. It is seen that the phase boundary slightly moves depending on the measurement method due to the hysteresis effect.

4. Discussion

In a series of our studies [23,24], we reported that the new sharp transition found in the poled PZN and the phase transition at MPB are the same kind, indicating that this new transition is the one between the tetragonal and rhombohedral phases (see Fig. 1). We also proposed that the intermediate tetragonal phase as a ground state exists even in the low concentration region below 5% in the poled PZN–xPT. In our previous paper [27], we confirmed that the stable tetragonal phase in PZN–4.5%PT exits as a macroscopic average structure based on the dielectric constant measurement in the DC biasing field along the [001]-direction in the cubic coordinate. On the other hand, it is known that only one broad peak in the dielectric constant without DC field is observed in PZN–4.5%PT, showing the diffuse phase transition, where the existence of the intermediate tetragonal phase cannot be recognized. It is guessed that heterogeneity characteristic to relaxors due to PNRs makes the stable tetragonal phase invisible.

In the present paper, we clarified the temperature–field phase diagrams with the electric field applied along the [011]- and [111]-directions in the cubic coordinate. We found that the critical end point (CEP) does not appear when the electric fields are along the [011]- and [111]-directions in PZN–4.5%PT, unlike the case along the [001]-direction [27]. Here, CEP found in the (001)-plate of PZN–4.5%PT was discussed in detail in Ref. [27].From our experimental results, we conclude that all of the phase transition found in the temperature–field phase diagram shown in Figs. 4 and 7 are the first order transition.

We also clarified that the intermediate tetragonal phase disappears in the external field above 4 and 3 kV/cm along the [011]- and [111]-directions, respectively (see Figs. 4 and 7). In our experiment, it was found that the dielectric anomaly showing the transition near the top of the tetragonal region on the phase diagram is detectable only by using the measurement method of the filed dependence under a constant temperature, although we cannot detect it with the method of temperature dependence under a certain field. It should be noticed that the dielectric anomaly cannot be detected by using the method of temperature dependence when the slope of the phase boundary curve line becomes small on the temperature–field phase diagram. We claim that the filed dependence measurement under a constant temperature is important when the phase diagram is investigated.

On the other hand, it was reported that the orthorhombic phase exists in the poled sample of PZN–PT [2,3]. However, the stable region of the orthorhombic phase on the temperature–field phase diagram has not been clarified yet as far as the authors know. In this study, we clearly showed that the stable region of the orthorhombic phase on the temperature–field phase diagram under the electric field along the [011]-direction. In the low field region below 1 kV/cm, however, we cannot determine the stable region of the orthorhombic phase because of the diffuseness of the dielectric anomaly due to the heterogeneity such as polar nanoregion.

The study of relaxors such as PZN–xPT and PMN–xPT seems to be still inconclusive in spite of a long history of the study more than 40 years and many articles. Davis compared this situation to a parable of the four blind men and the elephant in his review paper of the relaxor [28]. The reason of the chaotic situation in the relaxor study may be considered to come from heterogeneity having a hierarchical structure over a wide spatial range. If so, the detailed investigation of the local crystal structure by means of a synchrotron X-ray diffraction or other atomic level study with a high-performance equipment may not be the best method for complex materials such as the relaxors. In order to establish the framework of the physical property in these materials, the study of the macroscopic average structure may be important.

Under this situation, in this study, we investigated the dielectric constant under DC field in PZN–4.5%PT, and found that the diffuseness of the phase transition considerably decreases when the DC biasing field is applied. This implies that decrease of heterogeneity owing to the applied electric field on FC may make the phase transition sharp, which is usually smeared by the complex domain structures such as PNRs. When the DC biasing field is applied, the physical properties in relaxor ferroelectrics seem to become more similar with those of normal ferroelectrics.

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