Field induced effect near MPB in $Pb(Zn_{1/3}Nb_{2/3})O_3$-9%$PbTiO_3$

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Abstract. Temperature dependences of the dielectric constants under the DC biasing fields along the [001]- and [111]-directions in the cubic coordinate were measured in $Pb(Zn_{1/3}Nb_{2/3})O_3$-9%$PbTiO_3$. The temperature-field phase diagrams were clarified in the field range below 3.5 kV/cm. The existence of the critical end point at 185^{o}C and 1.7 kV/cm was confirmed. The aspect of the temperature-field phase diagram depending on the direction of the field was discussed.

1. Introduction

Relaxor ferroelectrics typified by $Pb(Zn_{1/3}Nb_{2/3})O_3$-$x$$PbTiO_3$ (PZN-xPT) and $Pb(Mg_{1/3}Nb_{2/3})O_3$-$x$$PbTiO_3$ (PMN-xPT) have attracted considerable attention in view of their unique physical properties due to the polar nanoregion (PNR) [1]. On the other hand, PZN-xPT and PMN-xPT are also known as technologically important materials because they show giant dielectric and piezoelectric responses near the morphotropic phase boundary (MPB) at x = 8% and 30%, respectively [1,2]. It was claimed that the origin of such giant responses is essentially the transversal instability near MPB on the basis of the Landau-type free energy, where the dielectric constant perpendicular to the spontaneous polarization becomes extremely large because anisotropy of the free energy in the parameter space becomes small [3-5]. A similar mechanism for the giant response was also reported in $BaTiO_3$ based on the first principle studies [6].

It was experimentally discovered by Kutnjak *et al*. that the critical end point (CEP) appears on the concentration-temperature-field phase diagram in PMN-xPT, and they claimed that the giant electromechanical response in PMN-xPT is the manifestation of CEP in addition to MPB [7]. The CEP in PMN-xPT was investigated in detail by many authors [8-12], while CEP in PZN-8%PT was also experimentally confirmed on the temperature-field phase diagram [13-16]. Iwata *et al*. presented detailed and semi-quantitative analysis of such phase diagrams based on the Landau-type free energy [17,18]. The static modulation structure of the phase front at the first order transition point near CEP was discussed based on the Landau-type free energy [19].

However, the temperature-field phase diagram on the CEP in PZN-9%PT has not yet been reported, as far as the authors know. Under this circumstance , experimental results of temperature dependences of the dielectric constants under the DC biasing fields along the [001]- and [111]-directions in the cubic coordinate will be shown to clarify the phase diagram in PZN-9%PT. The aspect of the temperature-field phase diagram depending on the direction of the field was discussed.

2. Experimental

Single crystals of PZN-9%PT used for our experiments were acquired from Microfine Technologies in Singapore, where the size of the platelike samples is 3×3×0.2 mm^3 perpendicular to the [001] and [111] directions in the cubic coordinate. For the measurement of the dielectric constant, crystal 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 LCR hi-tester (Hioki 3532-50), where the temperature changes at a rate of 2 K/min. An AC electric field to measure the dielectric constant is about 25 V/cm.

3. Results and Discussion

Figures 1(a) to 1(d) show temperature dependences of the dielectric constants measured on cooling at 1 kHz in the (001)-plate of the PZN-9%PT. The DC biasing fields, *E*, in Figs. 1(a) to 1(d) are 0, 1.0, 1.7, and 2.5 kV/cm, respectively. It is found that two anomalies showing the phase transitions appear in Fig. 1(a). These are attributed to the cubic-tetragonal and tetragonal-rhombohedral phase transitions, respectively. It is seen that the anomaly showing the tetragonal-rhombohedral phase transition shifts to lower temperature side below room temperature due to the field. The broad peak showing the cubic-tetragonal transition at $E = 0$ changes to the sharp phase transition with approaching about $E = 1.7$ kV/cm, and above this field, a broad peak appears again. This indicates that CEP exists in the vicinity of 1.7 kV/cm.

Figures 2(a) to 2(d) show temperature dependences of the dielectric constants measured on cooling at 1 kHz in the (111)-plate of the PZN-9%PT. The DC biasing fields, *E*, in Figs. 2(a) to 2(d) are 0, 0.5, 2.0, and 3.5 kV/cm, respectively. It is found that two anomalies showing the cubic-tetragonal and tetragonal-rhombohedral phase transitions appear in Figs. 2(c) and 2(d). The tetragonal-rhombohedral phase transition exists below room temperature in Figs. 2(a) and 2(b). Both anomalies showing phase transitions are seen to shift to higher temperature side due to the field.

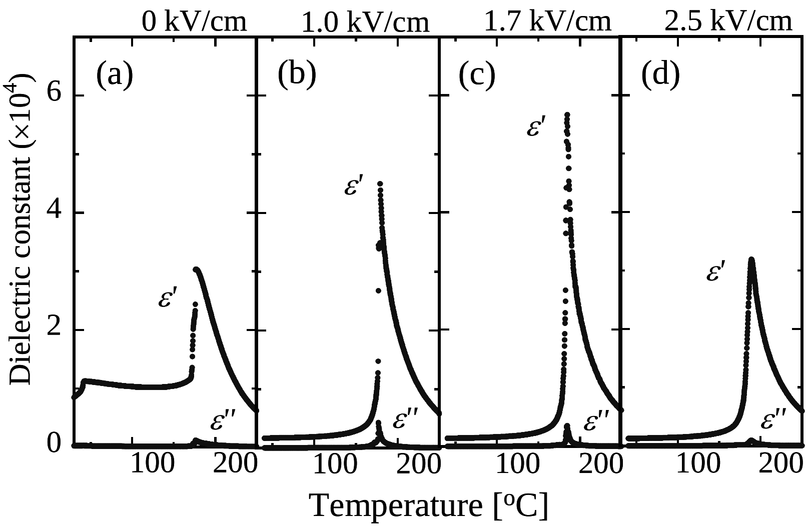

Figure 1. Temperature dependences of the dielectric constants measured on cooling at 1 kHz under the DC biasing field along the [001]-direction in the cubic coordinate. The DC biasing fields, *E*, are (a) 0, (b) 1.0, (c) 1.7, and (d) 2.5 kV/cm. The electric field 1.7 kV/cm corresponds to CEP.

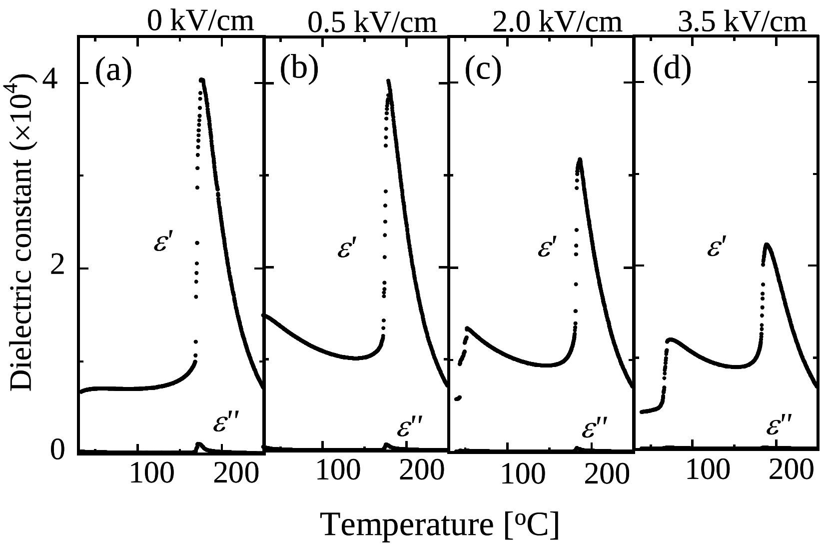

Figure 2. Temperature dependences of the dielectric constants measured on cooling at 1 kHz under the DC biasing field along the [111] direction in the cubic coordinate. The DC biasing fields, E, are (a) 0, (b) 0.5, (c) 2.0, and (d) 3.5 kV/cm.

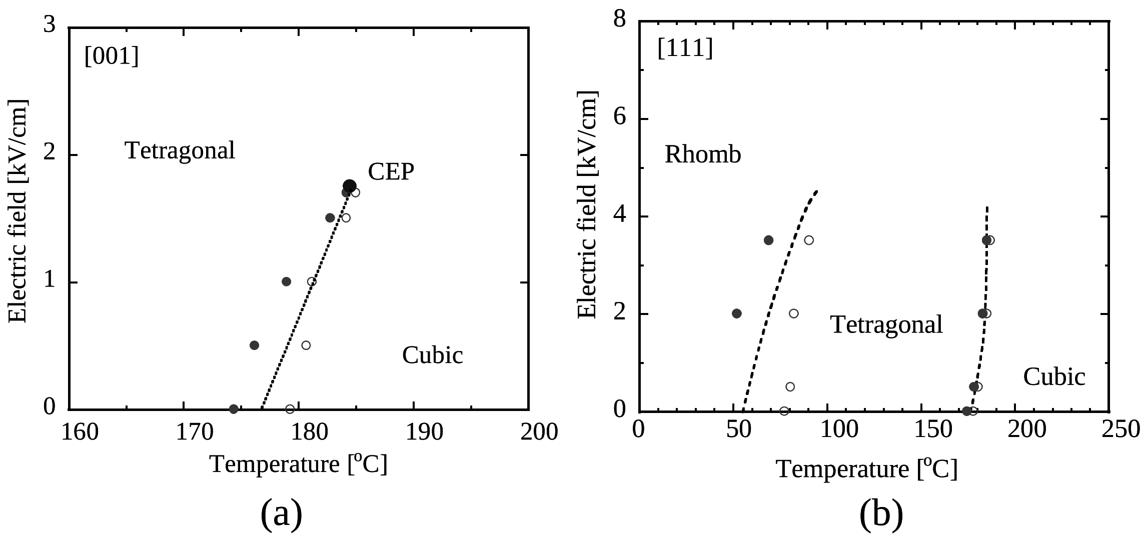

Figure 3. Temperature-field phase diagrams in PZN-9%PT. The electric field is along (a) the [001]- and (b) [111]-directions in the cubic coordinate.

Figures 3(a) and 3(b) show the temperature-field phase diagrams under the electric fields along the [001]-and [111]-directions in PZN-9%PT, respectively. Here, solid and open circles indicate the transition temperatures obtained from the dielectric constants measured on cooling and heating processes, respectively. It is seen in Fig. 3(a) that due to the electric field along the [001]-direction, the region of the tetragonal phase increases with increasing the field, and CEP is found at about 185°C and 1.7 kV/cm. It should be noticed that the critical field 1.7 kV/cm is very small compared with that in ordinary perovskite ferroelectrics such as $BaTiO_3$. The slope of the phase boundary between cubic and tetragonal phases was estimated to be about dE/dT = 0.23 $kVcm^{-1}K^{-1}$ under the field along the [001] direction. Note that the critical field E_{CEP} in PZN-9%PT is slightly higher than that in PZN-8%PT [12-14].

In Fig. 3(b), it is seen that owing to the electric field along the [111]-direction, the region of the stable rhombohedral phase increases with increasing the field, while the region of the tetragonal phase decreases. The slope of the boundary between cubic and tetragonal phases was estimated to be about dE/dT = 0.14 $kVcm^{-1}K^{-1}$ in the [111]-direction. Note that this value is about $1/\sqrt{3}$ times of that in the [001]-direction.

In our experiment, no evidence of the second-order phase transition or CEP for both transitions was observed below 3.5 kV/cm along the [111]-direction. In PMN with the rhombohedral symmetry, Zhao *et al*. [10] reported that CEP observed by Kutnjak *et al*. [7,8] in the electric field along the [111]-direction is not observed in the [011]- and [001]-directions up to the field of 7.5 kV/cm. From the viewpoint of symmetry, we point out that CEP is not necessary to exist in the above cases, i.e., the tetragonal crystal in the field along the [111]-direction and the rhombohedral crystal in the field along the [001]- or [011]-direction [17].

In this study, we investigated temperature dependences of dielectric constants under DC biasing fields in PZN-9%PT. The temperature-field phase diagrams were clarified in the field range below 3.5 kV/cm. In order to clarify the relationship between CEP and giant response, experimental results of the concentration dependence of critical field and critical temperature are required, and the investigation along this line is now in progress.

Acknowledgments

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