The Critical End Point in $Pb(Zn_{1/3}Nb_{2/3})O_3$-8%$PbTiO_3$

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Temperature dependence of the dielectric constant under the DC biasing field was measured in $Pb(Zn_{1/3}Nb_{2/3})O_3$-8%$PbTiO_3$. The temperature-field phase diagram was clarified in the field range below 2.5 kV. The existence of the critical end point at 172 ± 3^{o}C and 1.75 ± 0.25 kV/cm was confirmed.

KEYWORDS： PZN, relaxor, ferroelectric, morphotropic phase boundary, phase diagram, critical end point

1. Introduction

It is known that $Pb(Zn_{1/3}Nb_{2/3})O_3$-$x$$PbTiO_3$ (PZN-xPT) shows the morphotropic phase boundary (MPB) at x = 9% and giant dielectric and piezoelectric responses appear in the vicinity of MPB [1]. It was claimed that the origin of such giant responses essentially is 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 anisotopy of the free energy in the parameter space becomes small [2,3]. A similar mechanism for the giant response was also reported in $BaTiO_3$ based on the first principles studies [4]. In order to clarify the transversal instability experimentally, we investigated the dielectric anisotropy near MPB in PZN-xPT, and confirmed that the dielectric constant perpendicular to the spontaneous polarization significantly increases with approaching MPB [5]. It was reported that physical properties near MPB in PZN-xPT are sensitive to external fields such as stresses and electric fields, reflecting that the giant dielectric and piezoelectric responses are due to the transversal instability [6,7].

Recently, it was found that a new sharp phase transition at 114^{o}C below the paraelectric-ferroelectric phase transition point in PZN appears only on zero-field heating (ZFH) after field cooling (FC) process [8.9]. This may imply that the nature of the phase transition smeared by complex domain structures such as PNRs can be clarified by decreasing heterogeneity owing to the electric field on the FC process. We reported a new phase diagram in poled samples of PZN-xPT, 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 corresponds to that between the tetragonal and rhombohedral phases [10-13].

On the other hand, Kutnjak *et al*. experimentally discovered the critical end point (CEP) on the concentration-temperature-field phase diagram in $Pb(Mg_{1/3}Nb_{2/3})O_3$-$x$$PbTiO_3$ (PMN-xPT), and pointed out that the giant electromechanical response in PMN-PT is the manifestation of CEP [14]. To clarify the detail of CEP in PMN-xPT, many experimental investigations were carried out [15-19]. These phase transitions were discussed on the basis of the Landau-type free energy, and it was shown that the fourth order anisotropy of the polarization in the free energy plays an important role in the determination of the aspect in this phase diagram [20,21]. With respect to PZN-*x*PT, some results were reported mainly using the electrostrictive loop measurments [22-26]. There is, however, no report on the CEP in PZN-PT, as far as the authors know. Under this circumstance, temperature dependence of the dielectric constant under the DC biasing field was measured in PZN-8%PT to clarify the phase diagram and to confirm the existence of CEP.

2. Experimental

Single crystals of PZN-8%PT used for our experiments were acquired from Microfine Technologies in Singapore, where the size of the platelike sample is 3×3×0.4 mm^3 perpendicular to the [001] direction in the cubic coordinate. For the measurement of the dielectric constant, the (001)-crystal plates in the cubic coordinate 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.

3. Results and Discussion

Figures 1(a) to 1(d) show temperature dependences of the dielectric constants in the (001)-plate of the PZN-8%PT, where christcrosses and open circles indicate the dielectric constants measured on cooling and heating processes after field cooling, respectively. The biasing DC fields, E, in Figs. (a) to (d) are 0, 1.0, 1.5, 2.5 kV/cm, respectively. It is found that two anomalies showing the phase transitions appear in each figure. These are attributed to the cubic-tetragonal and tetragonal-rhombohedtral phase transitions, respectively. It is seen that the broad peak showing the cubic-tetragonal transition at E = 0 changes to the sharp phase transition with approaching about E = 1.5 kV/cm, and above 1.5 kV/cm, a broad peak appears again. This indicates that CEP exists in the vicinity of 1.5 kV/cm.

Figure 2 shows temperature-field phase diagram under the electric field along the [001] direction in PZN-8%PT. It is seen that due to the electric field along the [001] direction, the region of the tetragonal phase increases with increasing the field, and CEP in the phase diagram is found, at about 172 ± 3^{o}C and 1.75 ± 0.25 kV/cm. It should be noticed that the critical field 1.75 kV/cm is very small compared with that in ordinary perovskite ferroelectrics such as $BaTiO_3$. The slopes of the phase boundaries between cubic and tetragonal phases and between tetragonal and rhombohedral phases were estimated to be about dE/dT = 0.2 and -0.06 kV/cmK, respectively.

In this study, we have investigated temperature dependence of the dielectric constant under the DC biasing field in PZN-8%PT. The temperature-field phase diagram was clarified in the field range below 2.5 kV. 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 of it is in progress.

Acknowledgement

This work was supported in part by Grants-in-Aid for Scientific Research (B) (No. 22340081) from the Japan Society for the Promotion of Science for MI.

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Figure captions

Fig. 1 Temperature dependence o open circles indicate dielectric constants measured on cooling process and heating process after field cooling, respectively.
The biasing DC fields, *E*, are (a) 0, (b) 1.0, (c) 1.5, and (d) 2.5 kV/cm.

Fig. 2 Temperature-field phase diagram in PZN-8%PT. The electric field is along the [001] direction.

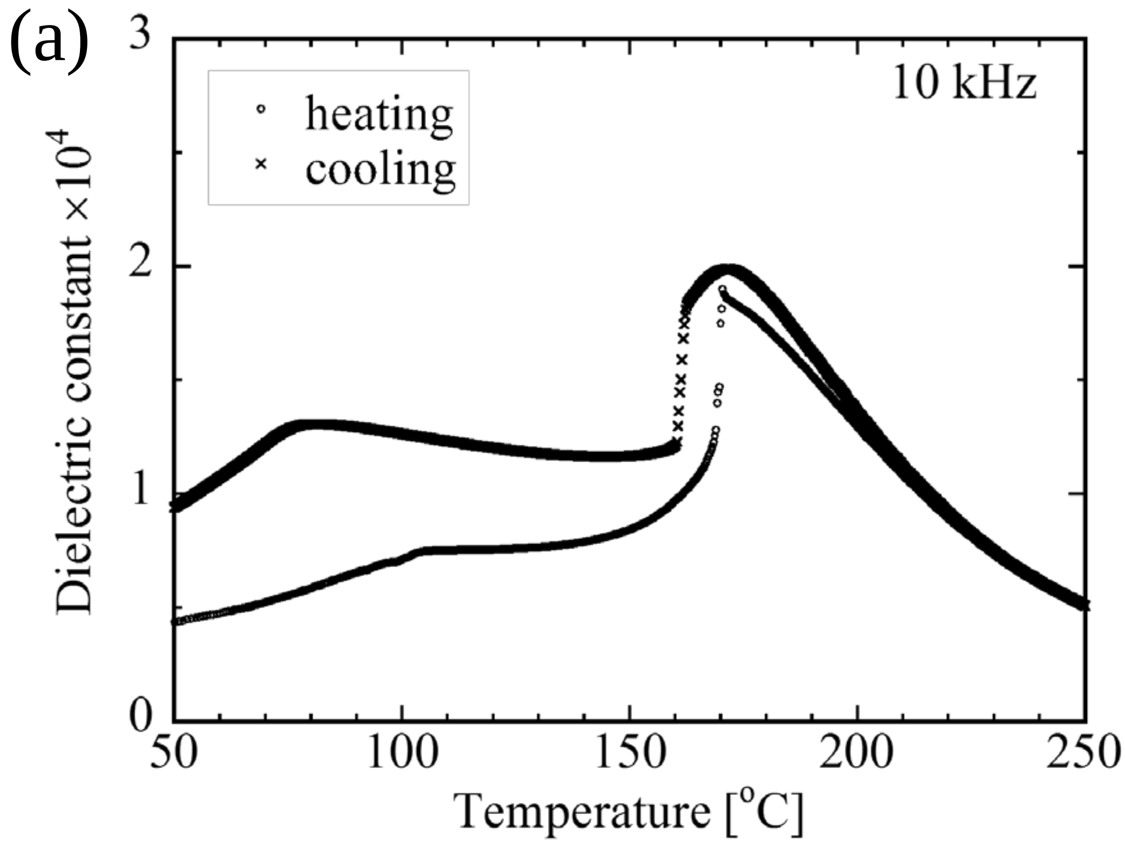
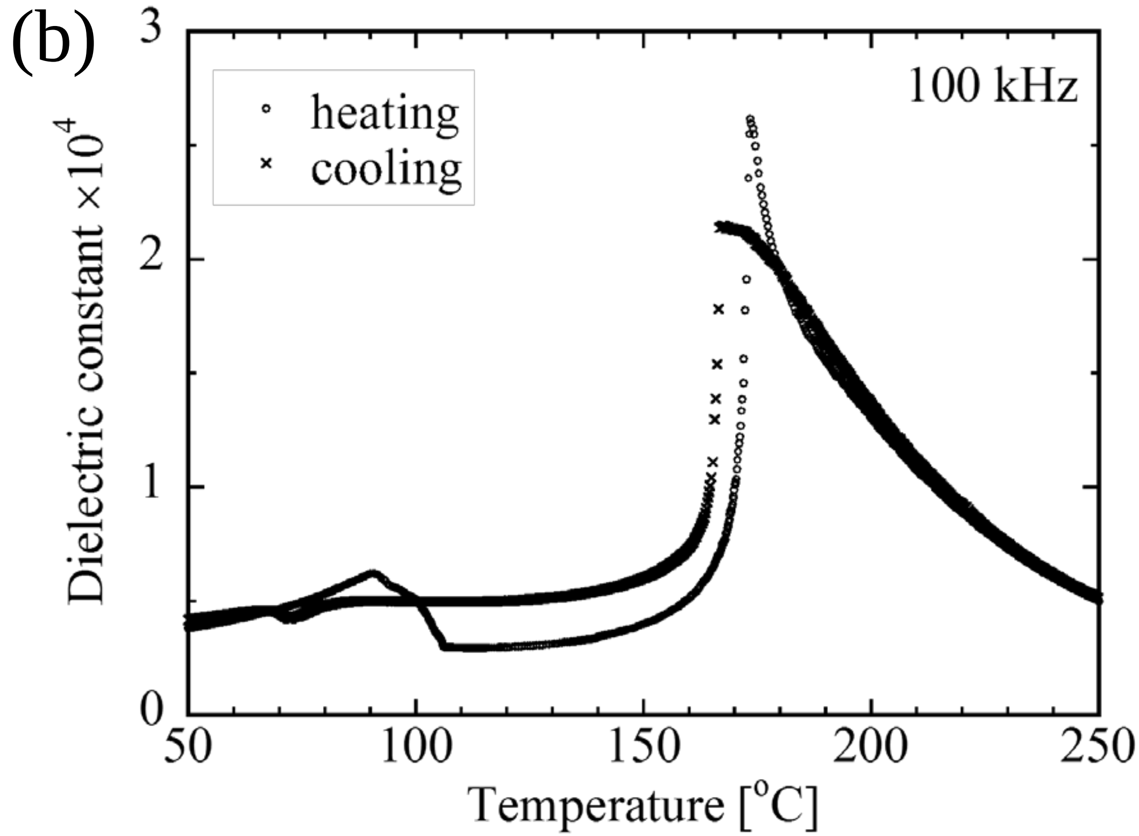


Fig. 1(a) M. Iwata et al.



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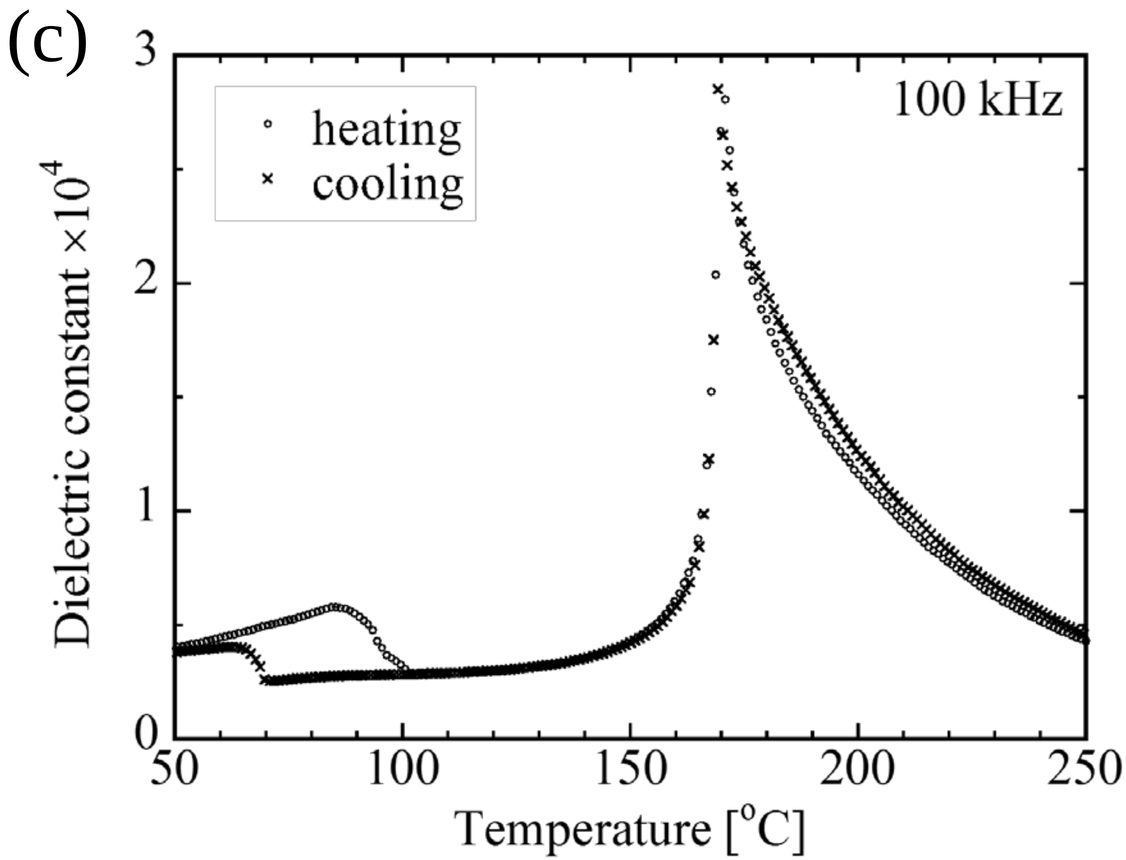
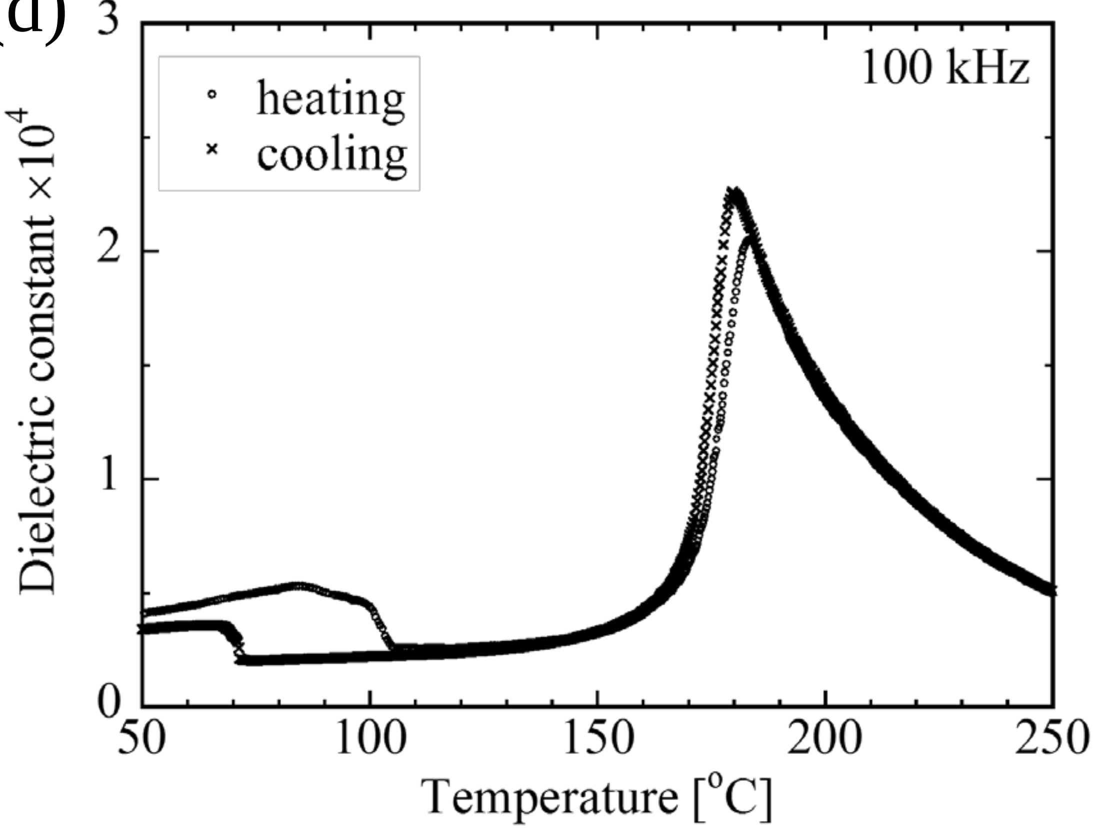


Fig. 1(c) M. Iwata et al.

(d)



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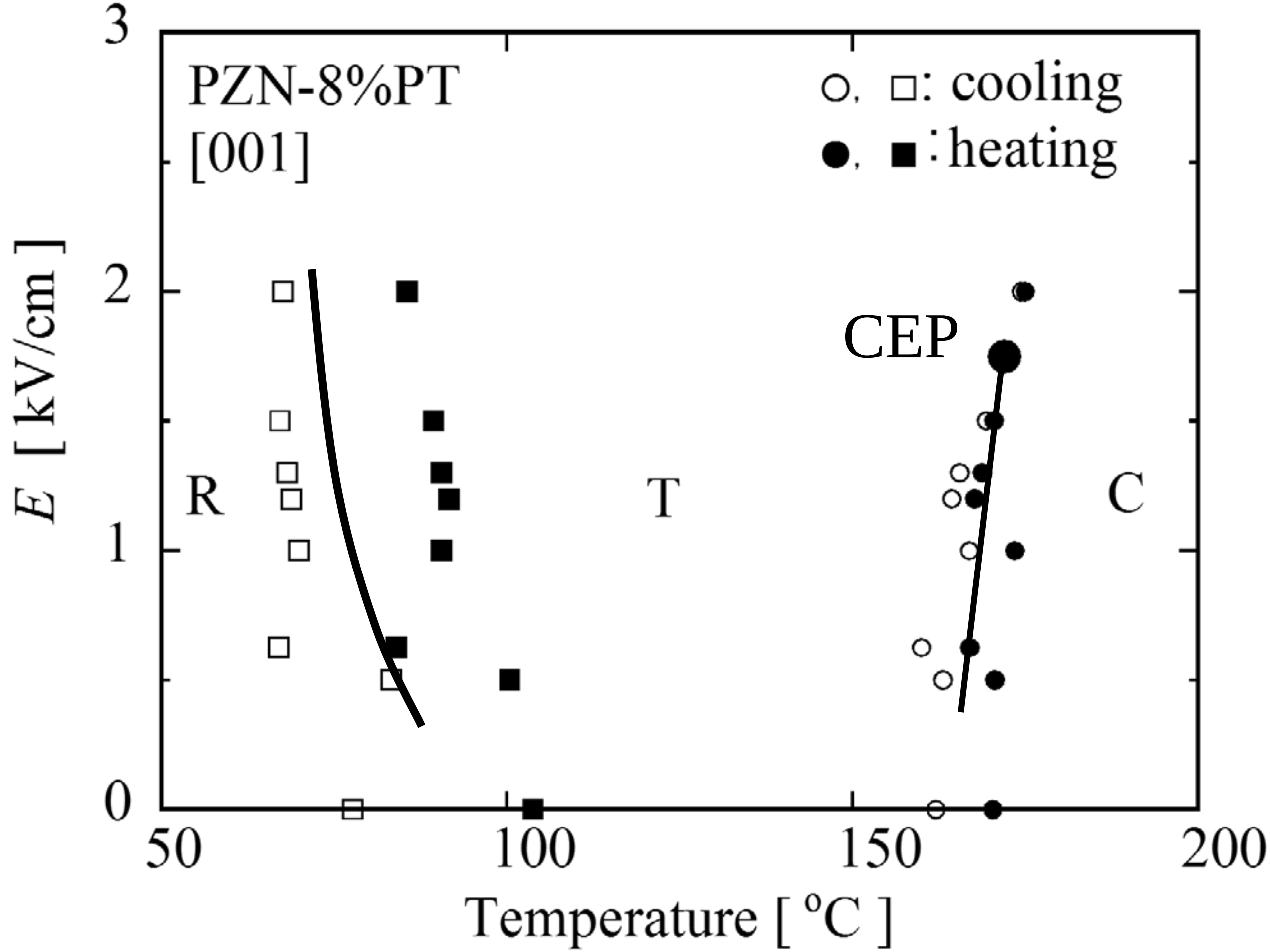

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