Field Induced Phase Transition in $Pb(Zn_{1/3}Nb_{2/3})O_3$-8%$PbTiO_3$

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Field induced phase transition in $Pb(Zn_{1/3}Nb_{2/3})O_3$-8%$PbTiO_3$ (PZN-8%PT) was investigated by measuring temperature dependence of the dielectric constant under the DC biasing field. It was clarified that the critical end point exists at 172 ± 3^{o}C and 1.75 ± 0.25 kV/cm in the temperature-field phase diagram. The entropy change at the transition point was discussed based on the Clausius-Clapeyron relation. The phase transition in PZN-8%PT was found to be very close to the second-order.

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

1. Introduction

Mixed crystals of Pb based relaxor and ferroelectric $PbTiO_3$ are known to show giant dielectric and piezoelectric responses near the morphotropic phase boundary (MPB). Among them, $Pb(Zn_{1/3}Nb_{2/3})O_3$-$x$$PbTiO_3$ (PZN-xPT) shows MPB at x = 8-9% at room temperature [1]. It was claimed that such giant responses essentially come from 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 such giant response in $BaTiO_3$ was reported based on the first principles studies [4]. On the experimental side, it was confirmed that the dielectric constant perpendicular to the spontaneous polarization in PZN-xPT significantly increases with approaching MPB [5]. Furthermore, 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]. On the other hand, a new sharp phase transition at 114^{o}C below the paraelectric-ferroelectric phase transition point in PZN was found to appear only on zero-field heating (ZFH) after field cooling (FC) process [8,9]. It is guessed 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].

Kutnjak *et al*. experimentally discovered the critical end point (CEP) on the three dimentional concentration-temperature-field phase diagram in $Pb(Mg_{1/3}Nb_{2/3})O_3$-$x$$PbTiO_3$ (PMN-xPT), and claimed that the giant electromechanical response in PMN-xPT is the manifestation of CEP in addition to MPB [14]. 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 [15,16].

Many experimental results with respect to CEP in PMN-*x*PT were reported to clarify its detail [17-21]. 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 the entropy change at the transition point was discussed based on the Clausius-Clapeyron relation.

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 $3\times3\times0.4$ 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.

The D-E hysteresis loop was measured using a Sawer-Tower circuit at 100 Hz in order to determine remanent polarization.

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 open and solid 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.

Figure 3 shows P-E hysteresis loop along the [001] direction in PZN-8%PT, where the frequency of the field and temperature are 100 Hz and 33^{o}C, respectively. Figure 4 shows temperature dependence of the remanent polarization along the [001] direction in the cubic coordinate in PZN-8%PT. In the P-E hysteresis loop observation, the sample same as that used in the dielectric constant measurement was used. Although the jump of the remanent polarization at transition temperature is not sharp, the polarization change Δp at the transition point can be roughly estimate to be about 3.7 $\mu C/cm^2$ from the fact that the transition temperature under no biasing field is at 170^{o}C on heating in Fig. 1(a).

Next, let us evaluate the entropy change ΔS at the transition point using the Clausius-Clapeyron (CC) relation [27], where CC relation is written by

$$\frac{\mathrm{d}E}{\mathrm{d}T} = -\frac{\Delta S}{\Delta p}. \qquad (1)$$

Using the values of dE/dT and Δp obtained in our experiment, ΔS is estimated to be about 0.03 J/Kmol, where the lattice constant c = 0.405 nm in PZN-8%PT was used. Note that this value ΔS is one order of magnitude smaller than that in $BaTiO_3$ (ΔS = 0.5 J/Kmol) [27]. It seems that the phase transition in PZN-8%PT is very close to the second-order.

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.

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Figure captions

Fig. 1 Temperature dependence of the dielectric constant in the (001)-plate of PZN-8%PT, where christcrosses and 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. 4 P-E hysteresis loop along the [001] direction in PZN-8%PT, where the frequency of the field and temperature are 100 Hz and 33^{o}C, respectively.

Fig. 4 Temperature dependence of the remanent polarization along the [001] direction in the cubic coordinate in PZN-8%PT.

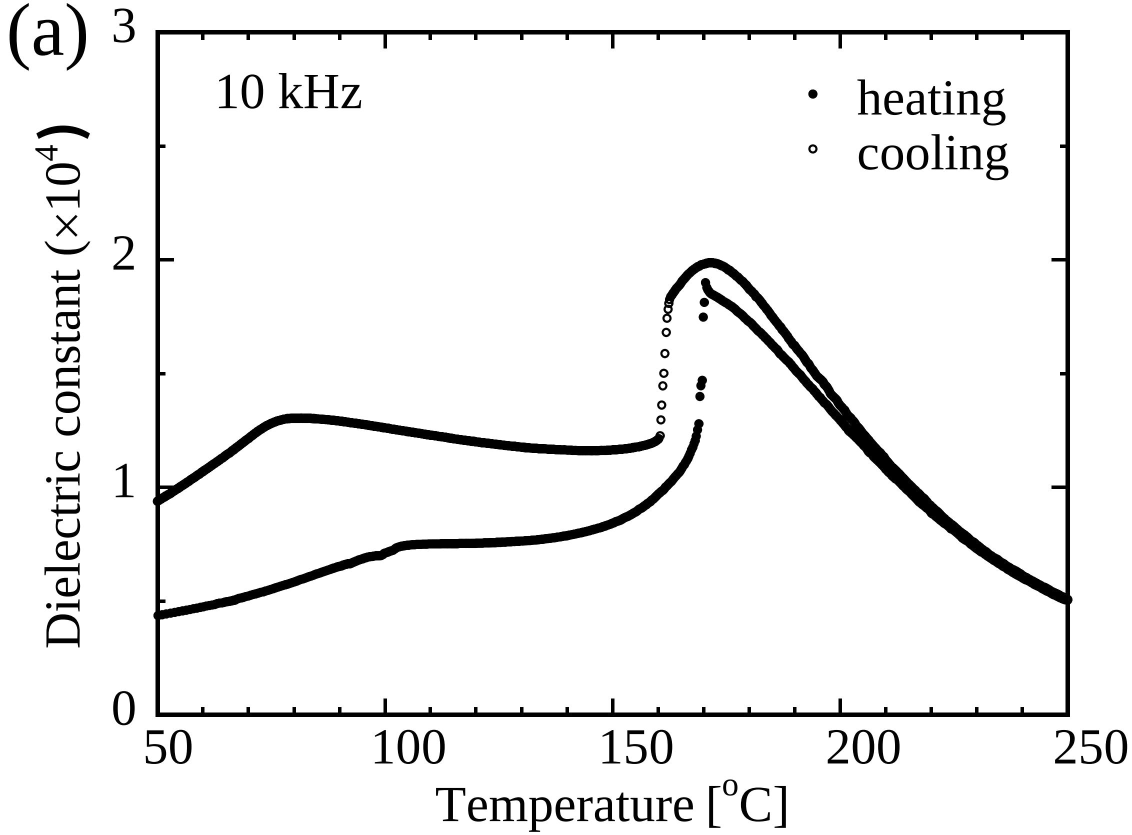


Fig. 1(a) M. Iwata et al.

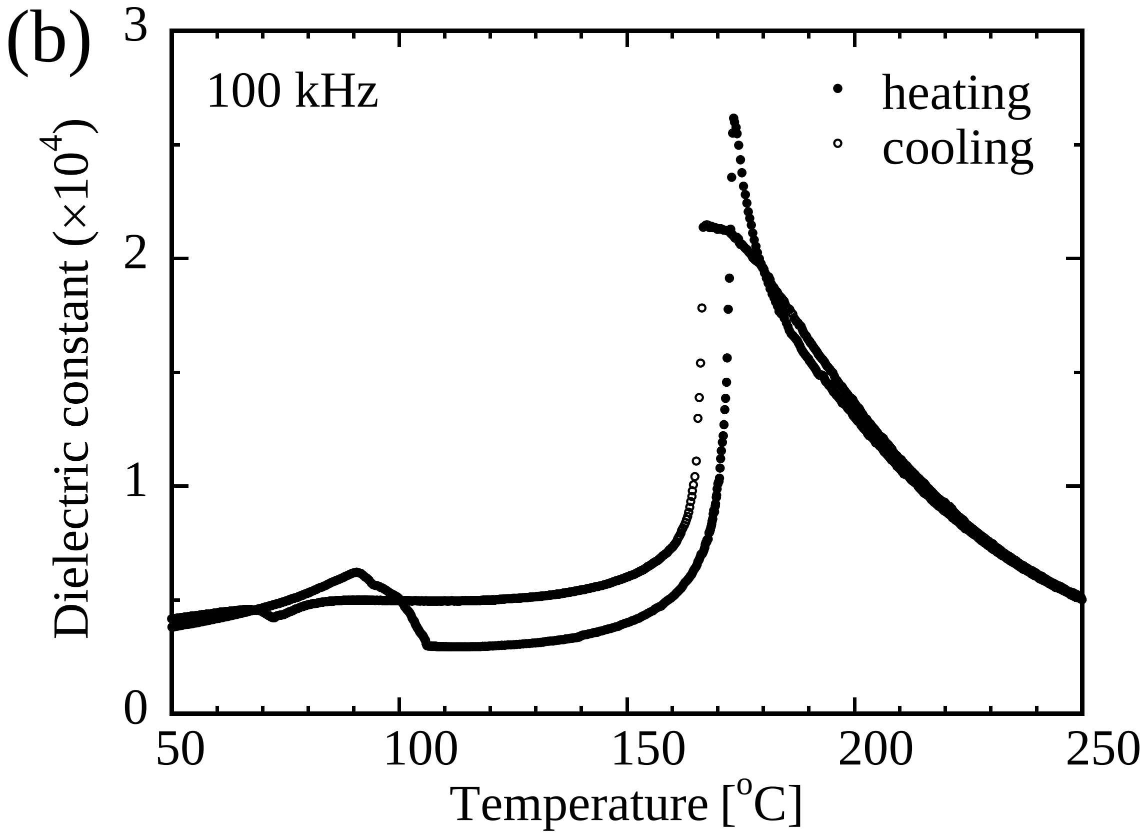
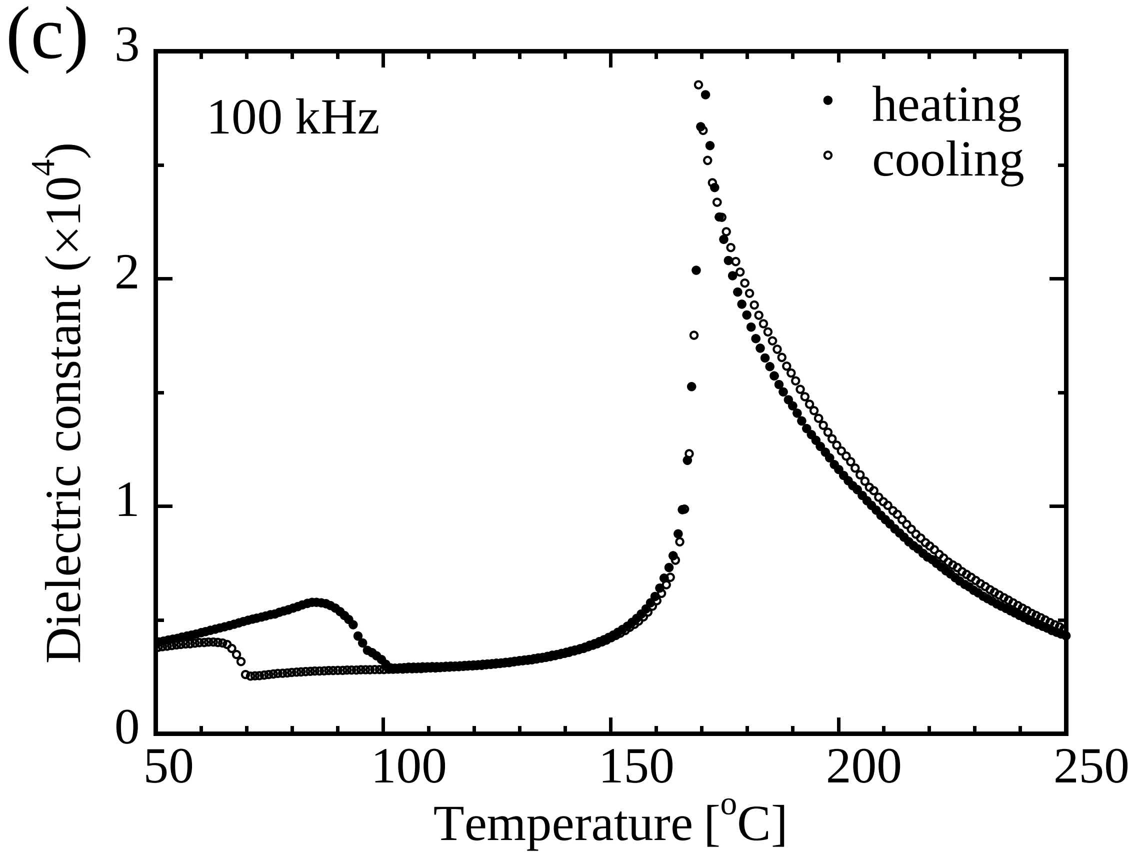


Fig. 1(b)   M. Iwata et al.



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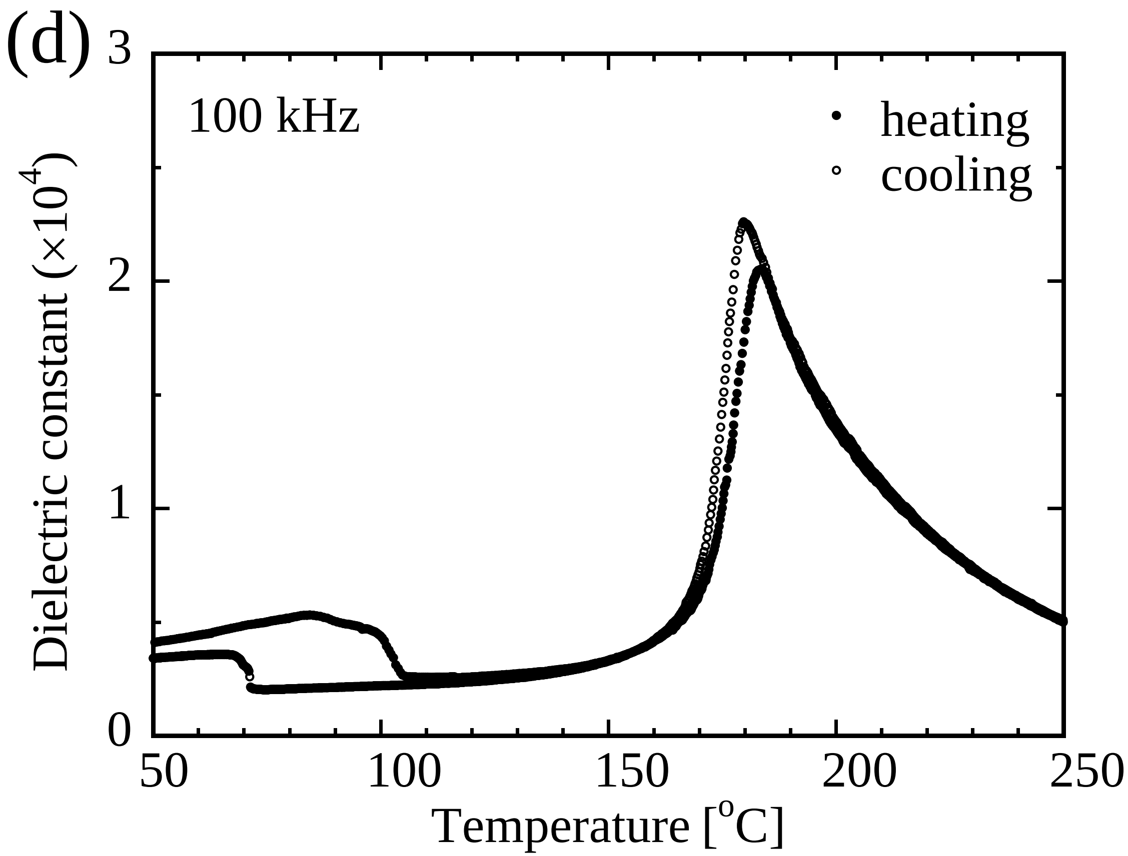

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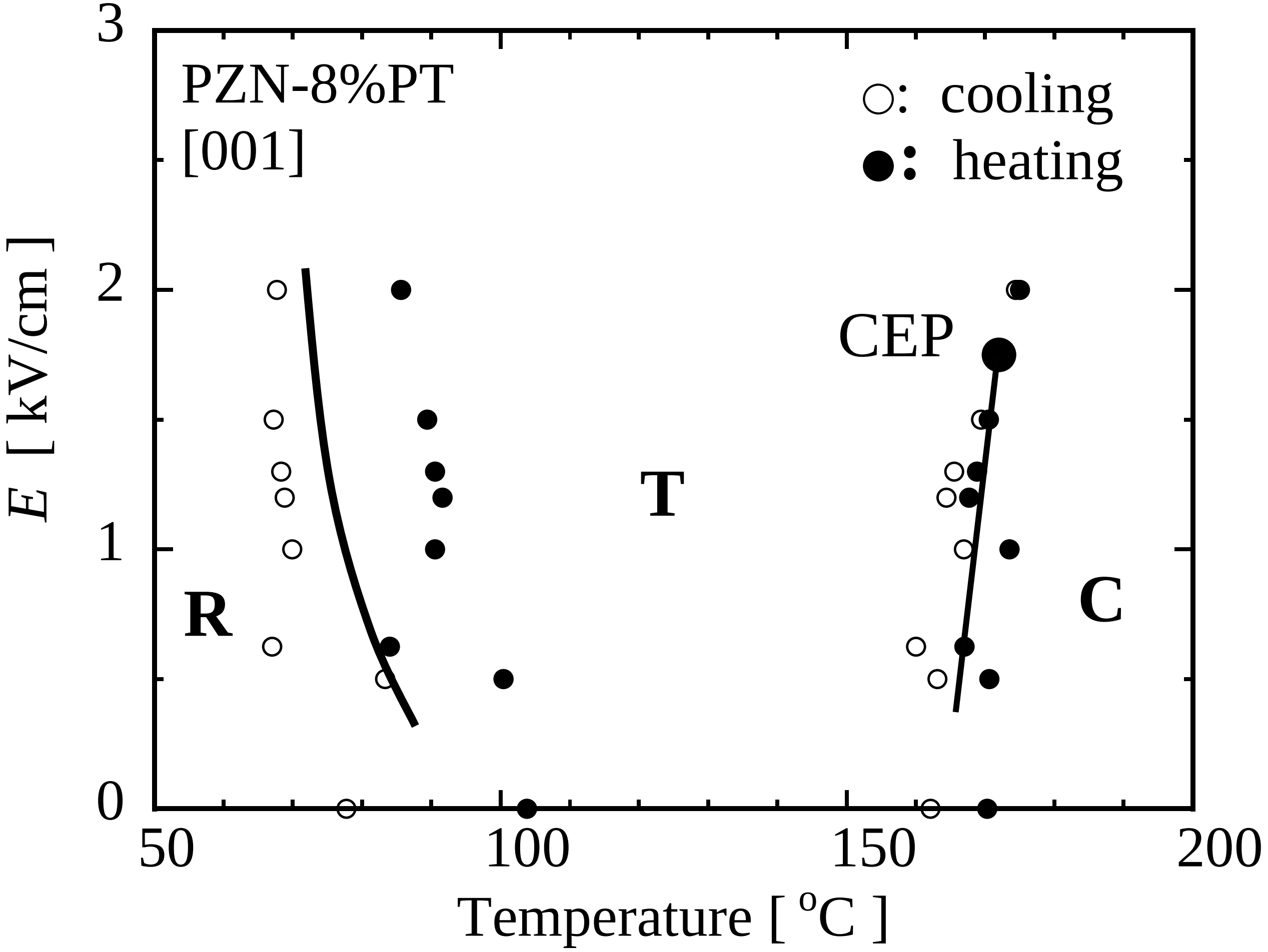

Fig. 2 M. Iwata et al.

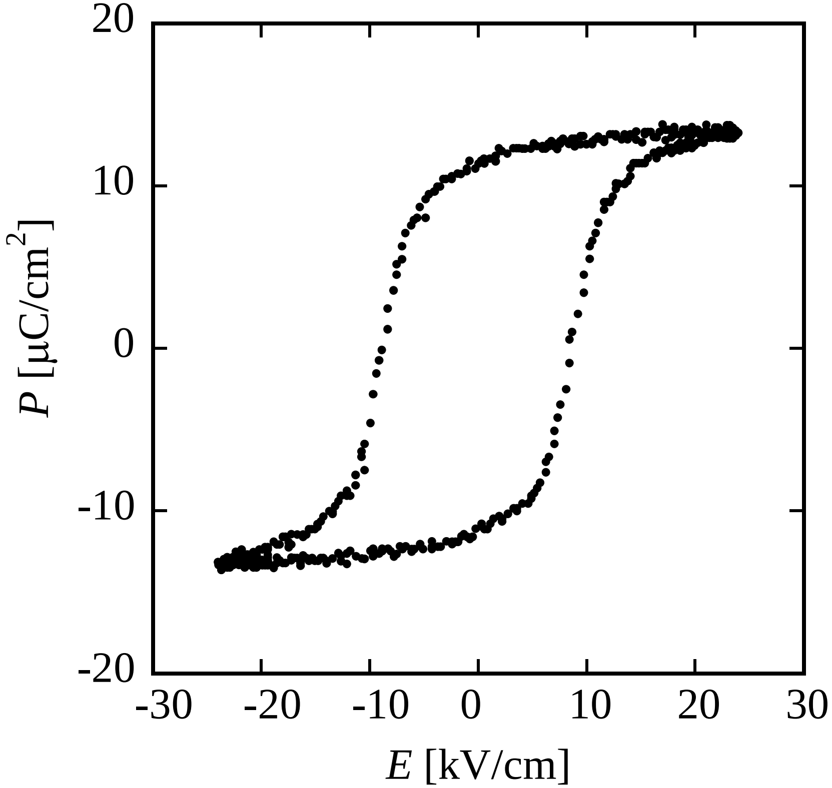

Fig. 3 M. Iwata et al.

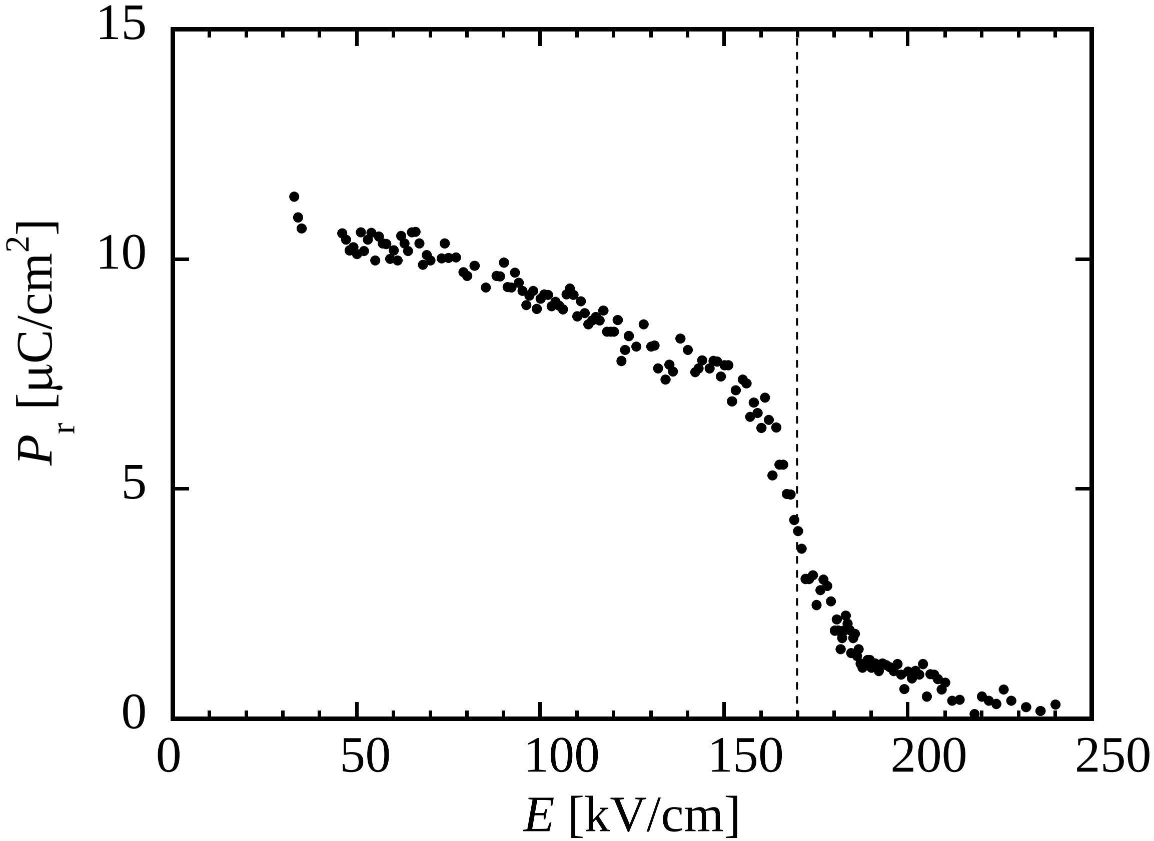

Fig. 4 M. Iwata et al.