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Dipolar Behavior in PZN Relaxor Single Crystals under Bias Field

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Pure $Pb(Zn_{1/3}Nb_{2/3})O_3$ (=PZN) single crystal is the typical relaxor ferroelectrics with an optical isotropic property. However, PZN crystals with defects showed a defect-induced domain configuration with very small birefringence. This birefringence decreased drastically around 120°C and this decrease suggested the change of the polar state in polar micro regions (PMR) at 120°C under a weak stress-field. Moreover, polarization and strain behaviors showed normal ferroelectric hysteresis below 120°C and double hysteresis loop above 120°C. This difference suggested that there was a transition around 120°C between relaxor states under no electric(E)-field and ferroelectric domains under a high E-field. The temperature dependence of dielectric constant in as-grown PZN crystal showed a strong frequency dependence. On the other hand, the dielectric property in the PZN crystal poled at 20°C showed no frequency dependence below 110°C while the strong frequency dependence reappeared above 110°C. The above results revealed that under bias fields such as stress and E-fields, all anomalous changes were observed around 110~120°C, while under no bias field, there was no change around 120°C. We concluded that the significant change around 110~120°C observed under bias fields was a kind of transition between flipping and frozen polar directions in PMR.

Key word: PZN single crystal, defect-induced domain, polar micro regions, relaxer behavior, bias field

1. INTRODUCTION

PZN single crystal is the typical relaxor ferroelectrics with a maximum dielectric constant around 140°C, and has an optical isotropic property[1-5]. Many researchers have considered that PMR is the origin of the relaxor behavior with an optical isotropic state[5-9]. Therefore, PMR is the most important factor in the relaxor behavior. At present, there are some models about PMR state, *i.e.*, (i) superparaelectric model[6], (ii) dipolar and spin glass model[7], (iii) dipolar dielectric with random field model[8] and (iv) breathing model[9]. First three models are on the basis of flipping polar vector in PMR, whereas the last model is on the basis of fixed polar vector. Therefore, it is important to understand PMR, but the polar state in PMR has been still unclear. Previously, it was considered that chemically ordered domains (COD) observed by TEM might be PMR, but Akbas and Devis[10-11] revealed that COD did not relate with the relaxor behavior.

Nomura *et al.* reported that a DC-bias exposure on an optical isotropic PZN crystals induced a ferroelectric state with normal ferroelectric domains[5]. However, in PZN single crystal with the inhomogeneous defect structure, a domain-like configuration with very low birefringence was observed clearly under crossed-nicols, as shown in Fig. 1[12]. This domain-like pattern was investigated crystallographically, and it was clarified that this pattern was due to the polar vector ordered by a weak stress-field originated from the physical defects[12]. We called this pattern a "defect-induced domain configuration". The study on the defect-induced domain possibly gives important information on relaxor mechanism in PZN crystals because the defect-induced domain involves the direct information on PMR.

Our final objective is to elucidate the relaxor behavior in PZN crystals and its origin. In this study, we investigated the defect-induced domain, dielectric properties, polarization and strain as a function of temperature and bias field.

2. EXPERIMENTAL

PZN single crystals were grown by a conventional flux method using a PbO flux. Further details on the crystal growth were reported elsewhere[13]. These crystals were oriented along [111] direction using a back reflection Laue method. For *in-situ* domain observation from -100°C to 200°C, thin crystals with thickness of around 50 μm and two mirror-polished (111) surfaces were prepared. Domain configuration was observed under crossed-nicols at transmittance configuration using a polarizing microscope (Carl Zeiss, D-7082). Prior to the domain observation, all crystals were annealed at 250°C for 15hr in air in order to remove ferroelastic domains. On the other hand, samples with a size around 2x2x0.2 mm³ were prepared for the measurements of dielectric constant and polarization.

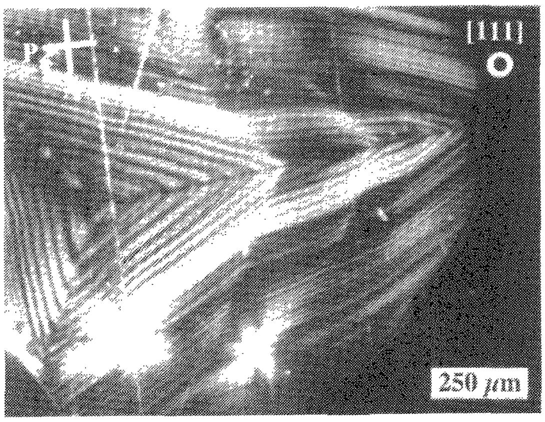

Fig. 1 Domain configuration of PZN single crystal oriented along [111].

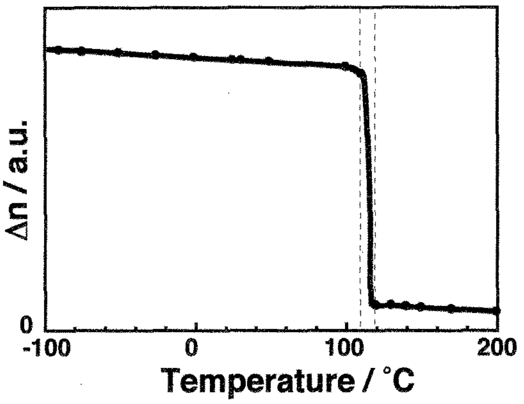

Fig. 2 Temperature dependence of birefringence Δn in the defect-induced domain.

Dielectric properties were measured using a multifrequency LCR meter (HP4274A and HP4275A) while polarization and strain were measured at 0.2Hz using a modified Sawyer-Tower circuit and a linear variable differential transducer (LVDT).

3. RESULTS AND DISCUSSION

3.1 Temperature dependence of the defect-induced domain configuration:

In-situ domain observation was done at temperatures from -100°C to 200°C. Between -100°C and 110°C, the domain configuration did not changed while its birefringence slightly increased with decreasing temperature. This slight increase of the birefringence suggests an increase of spontaneous polarization. On the other hand, a drastic decrease of the birefringence was observed between 110°C and 120°C, as shown in Fig. 2, although the domain configuration was still observed even at 200°C[12]. Pure PZN crystal has a strong frequency dependence of dielectric property. Yokomizo and Nomura[3] reported that the temperature at maximum dielectric constant (T_{max}) extrapolated to the zero frequency was estimated to be about 120°C. This temperature was corresponded to the change of birefringence in this study. Previously, we reported that the origin of the defect-induced domain was assigned to the ordered PMR, in which the polar directions in PMR were ordered by the weak stress-field, in the disordering PMR matrix with the randomly oriented polar vectors[12]. Therefore, this significant birefringence change around 120°C means the change of polar states in the ordered PMR. Crystallographically, the birefringence is proportional to the magnitude of crystal anisotropy. Thus, as the origin of the change of birefringence, the following factors would be considered, *i.e.*, (1) the change of spontaneous polarization, (2) the volume change of the ordered PMR, and (3) the change of flipping behavior in the ordered PMR.

3.2 Temperature dependence of polarization and strain: To investigate the origin of the above drastic change of the birefringence around 120°C, both polarization and strain were measured, as shown in Figs. 3 and 4. Fig. 3(a) shows a normal ferroelectric hysteresis loop at 25°C. This is because although PZN crystal was a relaxor before E-field exposure, the poled PZN crystal changed to a normal ferroelectrics with ferroelectric domains[12]. In Figs. 3(a)-(c), with increasing temperature from 25°C to 110°C, the spontaneous polarization decreased slightly while the coercive field decreased significantly. Around 120°C, polarization curve became to a double hysteresis loop (Fig. 3(d)). The appearance of double hysteresis means that ferroelectric domains induced by E-field did not exist stably at 120°C, and disappeared easily by the removal of E-field, *i.e.*, polar directions ordered along applied E-field changed to polar directions randomly oriented between eight equivalent <111> directions without E-field. On the contrary, below 120°C, the ferroelectric domains induced by E-field existed stably despite the removal of E-field. We consider that this difference is originated from the difference of the thermal fluctuation between below and above 120°C. In other words, below 120°C, the polar directions ordered by E-field were frozen

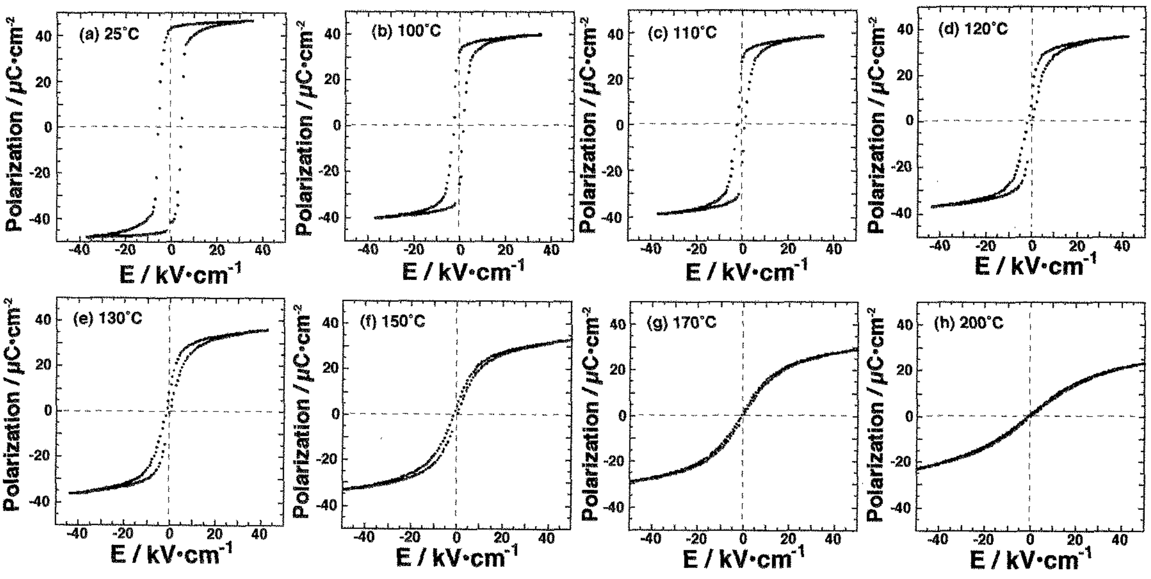

Fig. 3 Temperature dependence of polarization in PZN single crystal measured at 0.2Hz using a triangle wave function.

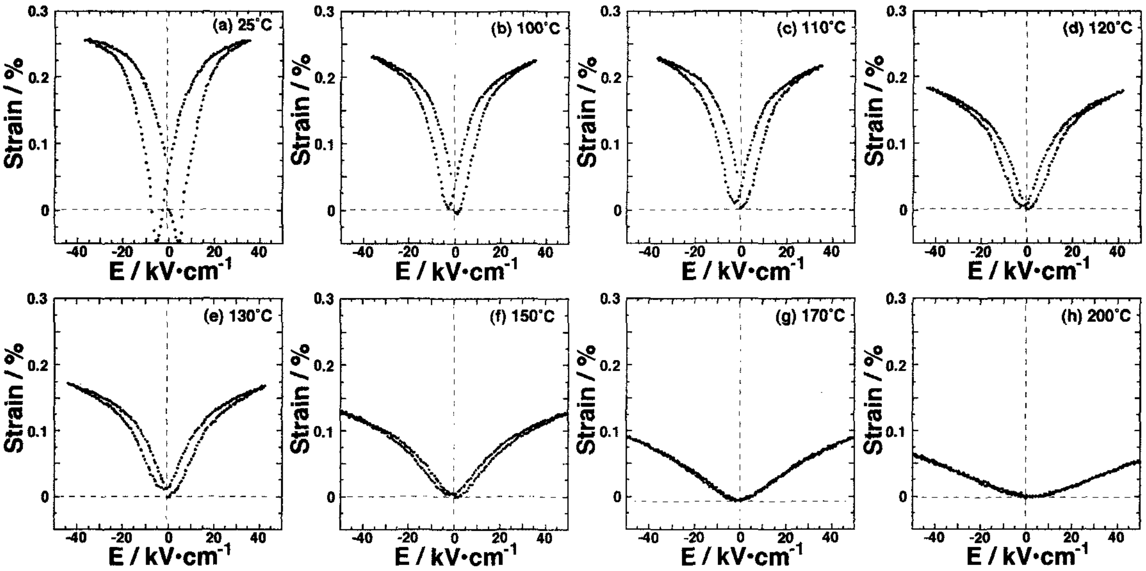

Fig. 4 Temperature dependence of strain in PZN single crystal measured at 0.2Hz using a triangle wave function.

without bias, whereas above 120°C, the polar vector ordered by E-field flipped between eight equivalent polar directions by the thermal fluctuation without E-field. This result supported the "superparaelectric model" proposed by Cross[6]. Above 170°C, hysteresis behavior disappeared completely (Fig. 3(g)), and with increasing temperature from 170°C to 200°C, "*S*" curves approached to linear. The polar state of PMR above 170°C was almost similar to that observed in pure Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ (PMN) around room temperature[6]. These results were corresponded to *in-situ* domain observation of PZN crystals under AC-bias field reported by Mulvihill[14].

The strain behavior as a function of E-field shows almost the same behavior as that of the polarization. The strain behavior at 25°C (Fig. 4(a)) looks like normal ferroelectric one characterized by the domain reorientation. Below 110°C, hysteresis due to domain reorientation was also observed in Figs. 4(a)-(c). However, above 120°C (Figs. 4(d)-(h)), all strain curves indicated zero strain at the zero E-field. However, from 120°C to 150°C, the hysteresis behavior was observed clearly under high E-field. This observation suggests that above zero E-field, the ferroelectric domain structure was induced, and also supports the prediction from Fig. 3 that around 120°C, the ferroelectric domains were induced by electric-field. Above 170°C, no hysteresis was observed (Figs. 4(g)-(h)) and this is almost similar to the electrostrictive strain behavior[6]. This also means that there was no domain reorientation above 170°C.

The polarization and strain behaviors revealed that around 120°C, the polar vector in PMR is flipping between eight equivalent <111> directions without E-field, whereas under E-field, its polar direction is oriented along the applied E-field directions. Moreover, it should be noted that although the spontaneous polarization decreased with increasing temperature, there was no drastic decrease around 120°C in their spontaneous polarization. This means that the origin of the change of birefringence around 120°C was not assigned to the change of spontaneous polarization. The observation of the E-field induced transition between relaxor and ferroelectrics around 120°C suggests that the change of the birefringence around 120°C is originated from the change of flipping behavior of polar vector in the PMR.

3.3 Temperature dependence of dielectric properties:

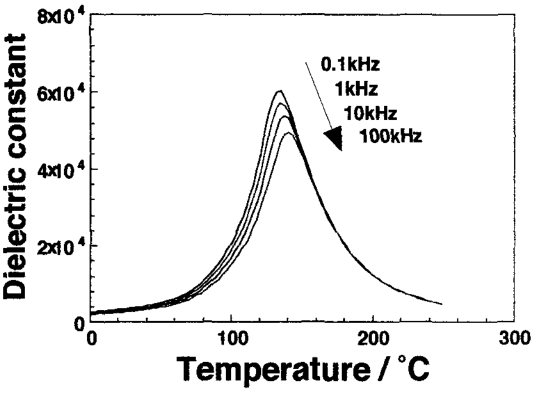

Fig. 5 Temperature dependence of dielectric constant in as-grown PZN single crystal.

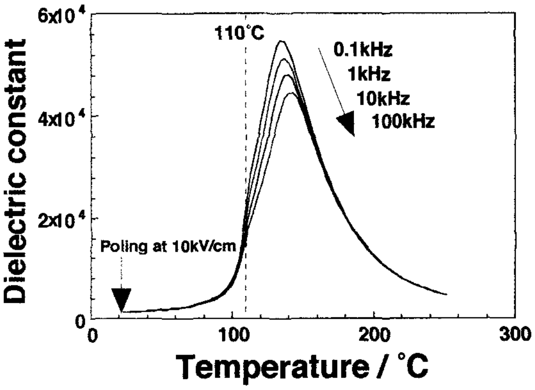

Fig. 6 Temperature dependence of dielectric constant in PZN single crystal poled at 20°C.

Fig. 5 shows temperature dependence of dielectric constant for the as-grown PZN single crystal along [111]. Dielectric constant and T_{max} measured at 100Hz was around 60000 and 134°C, respectively, and T_{max} shifted to higher temperatures with increasing frequency, whereas dielectric constant also decreased at the same way as that of T_{max}[13]. Moreover, it should be noted that the PZN crystal with the defect-induced domain exhibited almost the same dielectric properties with those in Yokomizo's isotropic PZN[3-4]. The optical isotropic PZN crystals showed no anomalous change around 120°C in dielectric properties. The difference between two PZN crystals is the existence of stress-field.

The observation of the defect-induced domain using a polarized microscope directly indicated the existence of PMR with the polar vector frozen by a weak stress-field. The temperature dependence of the birefringence showed that the polar state in PMR changed remarkably around 120°C, whereas the defect-induced domain was still remained at 200°C. On the contrary, the polarization and strain behaviors in the PZN crystal with the defect-induced domain exhibited that above 120°C, most of PMR had the flipping polar vector under no E-field, and a contribution of PMR with the frozen polar vector was not observed (Figs. 3 and 4). These results suggested that a volume fraction of PMR with the fixed polar direction was a little. Thus, the similar dielectric properties in between two kinds of PZN crystals were explained by the above reason.

Fig. 6 shows temperature dependence of dielectric constant measured using the PZN crystal poled at 20°C. Although PZN crystal was relaxor before E-field exposure, PZN crystal after E-field exposure was normal ferroelectrics with domain structure[12]. In Fig. 6, below 110°C, no frequency dependence in dielectric constants was observed, whereas above 110°C, the normal frequency dependence was observed. This indicates that around 110°C, the ferroelectric state changed to the relaxor state, and also supports that around 110~120°C, the fixed polar vector changed to the flipping polar vector.

3.4 Dipolar behavior in PZN crystals under bias field:

The temperature dependences of properties measured under stress-field (Fig. 2) and E-field (Figs. 3, 4 and 6) revealed an anomalous change around 110~120°C. Especially, under a weak stress-field, the anomalous change was the transition between the fixed polar vector and the flipping one in PMR around 120°C while under strong E-field, the anomalous changes was the transition between ferroelectric one and relaxor state around 110~120°C. On the other hand, in the optical isotropic PZN crystal without any bias field[3] and the PZN crystal with a weak stress-field (Fig. 5), there was no anomalous change around 120°C for their dielectric properties. These results suggested that a dipolar behavior under bias field is completely different from that under no bias field. In Fig. 6, below 110°C, there was no frequency dependence of dielectric constants, whereas in Fig. 5, below 110°C, the strong frequency dependence was observed. This difference may be caused by a difference of dipolar behavior, *i.e.*, the fixed polar direction under bias field and the flipping polar direction under no bias field. This means that the origin of relaxor behavior is the flipping polar direction in PMR. Ohwa *et al.*[15] measured the temperature dependence of Raman scattering using PZN crystals, and reported that Raman spectra did not change significantly from 25°C to 200°C. Wada *et al.* measured E-field dependence of Raman scattering in PZN crystals, and also reported that Raman spectra did not change in the both relaxor and ferroelectric states[16]. These results indicated that in the phonon frequency region of GHz~THz order, there is no difference between relaxor and ferroelectric states. This suggests that the flipping frequency of polar vector is much slower than phonon frequency. To clear flipping frequency for relaxor behavior, more study is required.

4. CONCLUSION

Using the PZN crystal with the defect-induced domain, its temperature dependence was investigated. As a result, its birefringence decreased significantly around 120°C and this decrease suggested the change of the polar state under a weak stress-field, *i.e.*, a transition between the fixed and flipping polar directions in PMR. Their polarization and strain behaviors also showed the transition between ferroelectric state and relaxor one around 120°C under a high E-field. In the PZN crystal poled at 20°C, its dielectric properties showed no frequency dependence of dielectric constants below 110°C and the strong frequency dependence reappeared above 110°C. These results showed that under some bias fields, the polar state in PMR changed around 120°C. We concluded that the change around 110~120°C was the transition between flipping and frozen polar directions in PMR.

5. ACKNOWLEDGEMENTS

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