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Defect-induced Domain Configuration in Relaxor PZN Single Crystal and Its Origin

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$Pb(Zn_{1/3}Nb_{2/3})O_3$ single crystal is typical relaxor ferroelectrics and has optical isotropic property . However, our PZN single crystal showed real domain configuration with very small birefringence at room temperature. This domain configuration can not satisfy crystallographic configuration, and its temperature dependence indicated that the domain configuration existed even at 200°C. Moreover, the complete same domain patterns can be always regenerated despite repeated heat annealing at 250°C. The characterization of the PZN crystal revealed that there were growth twinning structures, lattice defect, and inhomogeneity of chemical composition. Therefore, it suggests that very weak local stress field caused by these defect structure can make polar micro region ordering and thus can make the defect-induced domain configuration.
Key word: PZN single crystal, defect-induced domain configuration, polar micro region, relaxor, defect structure

1. INTRODUCTION

It was well known that $Pb(Zn_{1/3}Nb_{2/3})O_3$ (=PZN) single crystal is typical relaxor ferroelectrics and has an optical isotropic property[1-5]. To date, many researchers have considered that a polar micro region (=PMR) must be the origin in the relaxation behavior, and PMR could also cause an optical isotropic state[5-9]. Therefore, PMR is the most important factor in the relaxation behavior. At present, there are some models about state of PMR, 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 were on the basis of flipping polar vector in PMR while the last model was on the basis of fixed polar vector. Therefore, it was very important to observe PMR directly and reveal the state of PMR. Before, it has considered that chemically ordered domain (COD) observed by TEM might be PMR, but Akbas and Devis revealed that COD did not relate with relaxation behavior, i.e., PMR[10-11]. Therefore, to date, no one has observed PMR directly.

Nomura et al. reported that before DC-bias exposure, pure PZN crystal showed an optical isotropic property although after DC-bias exposure, the relaxor state changed to the ferroelectric state with a normal ferroelectric domain[5]. However, in PZN single crystal which we grew by a flux method, a domain configuration with very low birefringence was observed clearly under crossed-nicols, as shown in Fig. 1. This domain configuration has some strange features, i.e., (1) very unclear domain wall, (2) partially curved domain wall, (3) very low birefringence, (4) unexpected angle between neighbored domain, and (5) graduation of birefringence in one domain. Moreover, it should be noted that our PZN crystal with the strange domain configuration exhibited the almost same dielectric properties as those in Yokomizo's isotropic PZN[3-4]. These results mean that the relaxation behavior in the optical isotropic PZN crystal is almost same as that in PZN crystal with the strange domain configuration, i.e., there is no difference between states of PMR in two PZN crystals. Therefore, it is so important to discuss about the domain configuration on the basis of crystallography, and reveal its origin.

Our objective is to clear the strange domain configuration crystallographically, and discuss about its origin. In this study, we analyze the domain configuration crystallographically, and also do in-situ domain observation as a function of temperature.

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[12]. Flux grown crystals were characterized using XRD and ICP.

These crystals were oriented along [111] direction using a back reflection Laue camera. After the orientation, the crystals were cut and polished. For in-situ domain observation from -100°C to 200°C and crystallographic interpretation, very 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

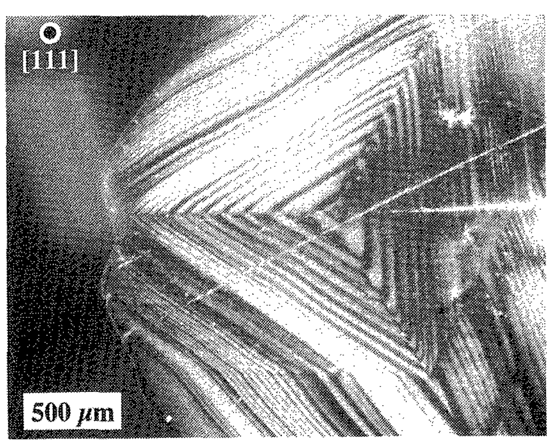

Fig. 1 Domain configuration of PZN single crystal oriented along [111].

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.

3. RESULTS AND DISCUSSION

3.1 Characterization of PZN crystal: Powder XRD measurement of as-grown PZN crystal indicated that an average symmetry can be assigned to rhombohedral R3m, and *a*-axis and α is 0.4056nm and 89°55', respectively[12]. These lattice parameters were almost consistent with those in Yokomizo's crystal[4]. On the other hand, ICP measurement of the as-grown PZN crystal revealed that each wt% of lead (Pb), zinc (Zn), niobium (Nb), and oxygen (O) was 59.9, 5.7, 20.7 and 13.7, respectively, while in an ideal PZN crystal, each wt% of Pb, Zn, Nb, and O is 61.1, 6.4, 18.3 and 14.2, respectively[12]. This indicated that a chemical composition in the as-grown crystal is slight Nb-rich, while Yokomizo et al. grew PZN crystal with almost its stoichiometric composition[4]. Therefore, as considered electroneutrality condition, there must be lattice defects such as $Nb_{Zn}^{\bullet\bullet\bullet}$, $V_O^{\bullet\bullet}$, V_{Pb}'', V_{Zn}'' and V_{Nb}''''' in our PZN crystal.

Fig. 2 shows temperature dependence of dielectric constant in the as-grown PZN single crystal oriented along [111]. T_{max} and dielectric constant measured at 100Hz was 134°C and around 60000, respectively, and T_{max} at various frequencies shifted to higher temperature with increasing frequency while and dielectric constant also decreased at the same time[12]. Moreover, the dielectric properties in our crystal were the almost same as those in Yokomizo's crystal[3-4].

The above characterization suggested that about the average crystal structure and dielectric property, there is no difference between our and Yokomizo's crystals while about chemical composition, there is a significant difference between both crystals. Thus, it can be possible that this difference in defect structure can cause the domain configuration (Fig. 1) in our crystal while the optical isotropy in Yokomizo's crystal.

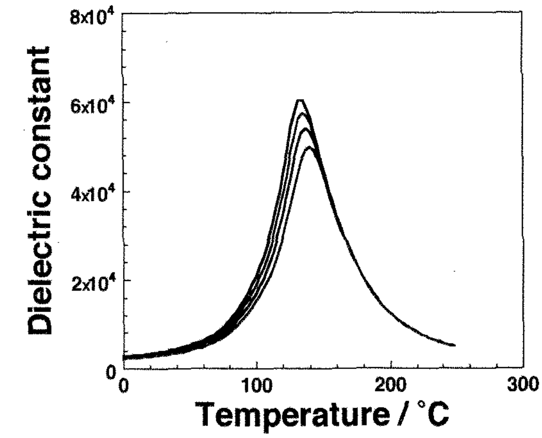

Fig. 2 Temperature dependence of dielectric constant in PZN single crystal oriented along [111].

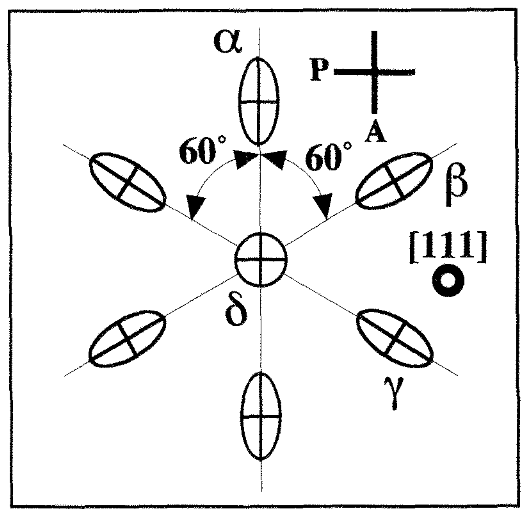

Fig. 3 Projection of indicatrix for 8 domains on (111) plane in R3m crystal.

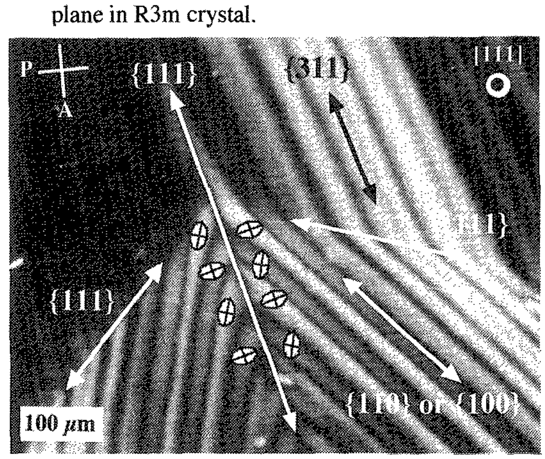

Fig. 4 Crystallographic assignment on a part of the domain configuration shown in Fig. 1.

3.2 Crystallographic domain assignment: A crystallographic assignment of the domain configuration (Fig. 1) was done using a polarized microscope. R3m crystal can have 8 equivalent domains with polar directions of <111>. Fig. 3 shows a projection of indicatrix for 8 domains on (111) plane. Under fixed crossed-nicols, α, β and γ-domains with 6 polar directions of $[\bar{1}11]$, $[1\bar{1}\bar{1}]$, $[\bar{1}1\bar{1}]$, $[1\bar{1}1]$, $[\bar{1}\bar{1}1]$ and $[11\bar{1}]$ have an extinction position by 90°, and the angle between the extinction position of these domains must be 30° or 60°, while δ-domains with 2 polar directions of [111] and $[\bar{1}\bar{1}\bar{1}]$ have always an optical isotropic state. Therefore, by rotating crystal under fixed crossed-nicols, we can obtain the crystallographic information about domain configuration[13-14]. Fig. 4 shows the crystallographic assignment performed on a part of the domain configuration in Fig. 1. The relationship between neighbored domains satisfied a crystallographic configuration in R3m ferroelectric crystal. Moreover, it was confirmed that there are growth twinning structures of {111}, 71° domain walls of {100} or 109° domain walls of {110}. However, there is still remained a significant question about crystallographic assignment, i.e., it is impossible to explain the high Miller indices of planes such as {311} as non-180° domain wall in R3m crystal crystallographically. Moreover, as above mentioned, there are other questions in Fig. 1 such as (1) very unclear domain wall, (2) partially curved domain wall, (3) very low birefringence and (4) graduation from dark to bright even in one domain. Especially, it is impossible to consider one region with the graduation of birefringence as one ferroelectric domain. Therefore, the above crystallographic assignment revealed that these domains can not be regarded as a normal ferroelectric domain.

3.3 Temperature dependence of domain configuration: The in-situ domain observation was done from -100°C to 200°C. From 25°C to -100°C, there is no change of domain configuration while its birefringence increased slightly with decreasing temperature. This slight increase of the birefringence suggests an increase of spontaneous polarization. On the other hand, from 25°C to 200°C, a drastic decrease of the birefringence was observed around 115°C while there is no change of the domain configuration as shown in Fig. 5. Pure PZN has a phase transition around 140°C. Therefore, if the domain configuration is induced on a ferroelectric phase transition from R3m to Pm3m, we can expect a disappearance of the domain configuration around 140°C. However, the domain configuration was observed even at 200°C, which means that the domain configuration is not normal ferroelectric domain.

3.4 Domain configuration before and after poling: Figs. 6-(a) and (b) show the domain configuration before and after poling. By the poling at 42kV/cm, a normal ferroelectric domain configuration expected in R3m crystal was observed as shown in Fig. 6-(b). This detail was described elsewhere[15-16]. The ferroelectric domain configuration induced by poling was quite different from the domain configuration in Fig. 6-(a), and thus poling can break the strange domain configuration. However, when poled PZN crystal was annealed at 250°C for 15h, it was confirmed that the original domain configuration was regenerated completely as shown in Figs. 6-(a) and (c). Moreover, annealing at 500°C resulted in the complete regeneration of the original domain configuration. These facts suggested that the domain configuration in Fig. 6-(a) has some memory effect on its configuration. As one of factors affecting in the memory effect on the domain configuration, the defect structure is well known[17]. In this study, characterization of PZN crystal revealed that there were the defect structure such as the lattice defects, inhomogeneity of chemical compositions and growth twinning structures. Therefore, we must consider the defect structure as an origin of the strange domain.

3.5 Defect-induced domain configuration: In general, an inhomogeneously distributed defect structure can be the origin of very weak local stress field. On the other hand, relaxor material must have PMR intrinsically as the origin of relaxation behavior, and PMR is considered as the nm-sized region with flipping or fixed polar vector. Moreover, Cross proposed that PMR in relaxor can be present above T_{max}[6]. Therefore, we propose the following model about the strange domain

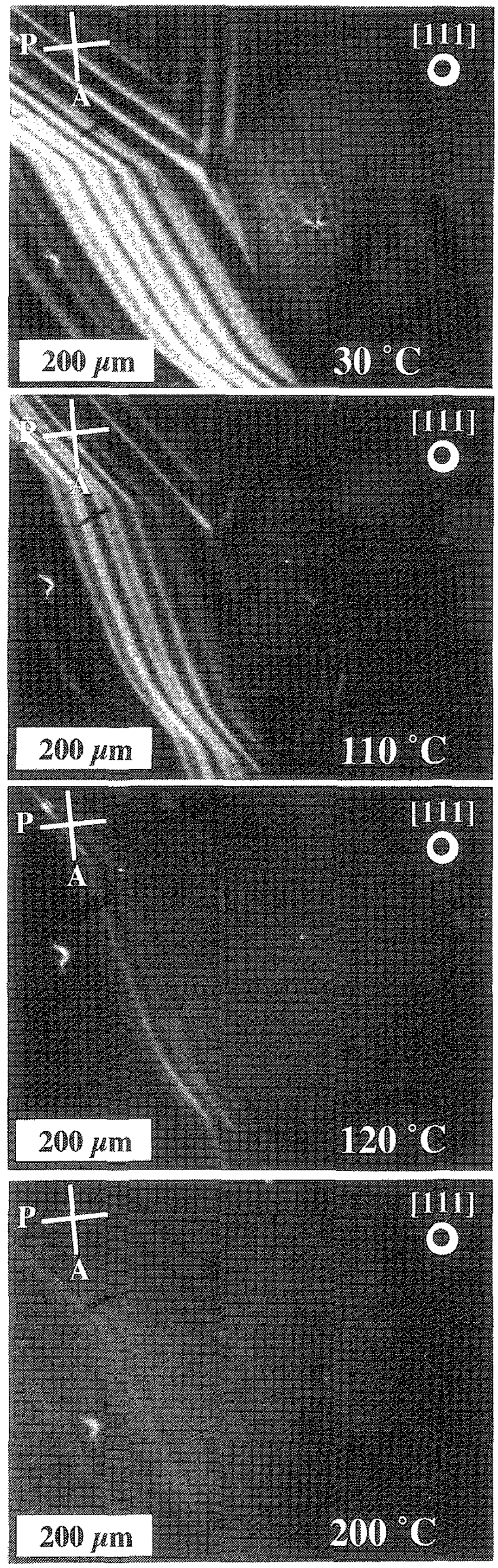

Fig. 5 Temperature dependence of the domain configuration from 30°C to 200°C

configuration, i.e., the weak local stress field occurred by the inhomogeneously distributed defect structures made polar direction of a part of PMR ordering, and thus its ordering region was observed as a domain under crossed-nicols. This model can also explain all of questions about the strange domain configuration. Now, we believe that the strange domain configuration in this study should be a defect-induced domain configuration, and the defect-induced domain configuration can be observed only in relaxor materials. This is because for an formation of the defect-induced domain configuration, the both PMR and inhomogeneously distributed defect structures must be required. Moreover, it should be noted that PMR may be first observed indirectly in this study. Therefore, it is possible that the important information about PMR can be obtained through the study about the defect-induced domain configuration, and now we are doing so.

4. CONCLUSION

Our flux-grown PZN crystal exhibited the strange domain configuration with very small birefringence. The crystallographic assignment revealed that this domain configuration can not be a normal ferroelectric domain. The temperature dependence of this domain configuration indicated that the domain configuration existed even at 200°C. Moreover, the same domain patterns can be always regenerated despite of repeated heat annealing at 250°C. Our PZN crystal also included growth twinning structures, lattice defects, and an inhomogeneity of chemical composition. Therefore, it suggests that very small local stress field caused by these defect structures can make PMR ordering, and thus can make the defect-induced domain configuration. Therefore, it is possible to obtain the information about relaxation mechanism of PZN from the study about the defect-induced domain configuration. Thus, a significant decrease of the birefringence around 115°C suggested that the state of the polar vector changed remarkably.

5. ACKNOWLEDGEMENTS

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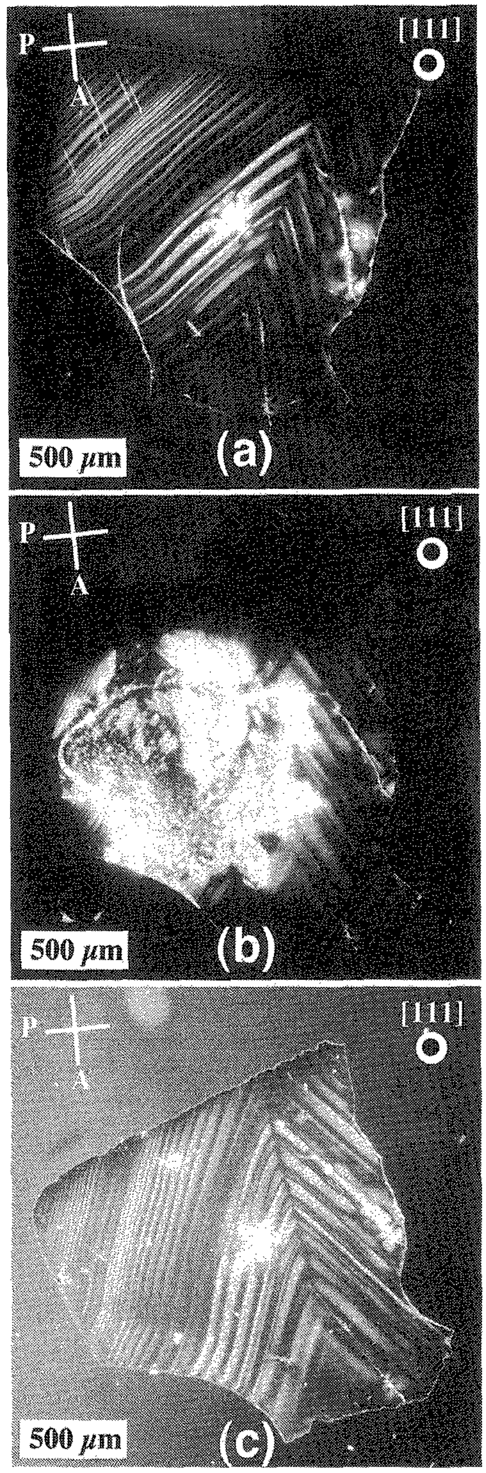

Fig. 6 Domain configuration at 25°C before poling (a), after poling at 42kV/cm (b) and after heat annealing at 250°C for 15h (c).

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