Transactions of the Materials Research Society of Japan 25 [1] 19-24 (2000)

Change of Macroscopic and Microscopic Symmetries in Relaxor PZN Single Crystal under DC-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. Using the PZN crystal, two kinds of symmetries were investigated by using a polarized microscope and a Raman scattering spectroscopy under DC-bias field to obtain some important informations about polar micro regions (PMR). In the relaxor state, its macroscopic symmetry on the basis of domain observation was assigned to the highest symmetry *i.e.*, *m3m*. However, DC-bias exposure to the PZN crystal with the relaxor state induced the ferroelectric domains, and finally all regions in the crystal became to ferroelectrics. This domain configuration was analyzed crystallographically, and its macroscopic symmetry was assigned to acentrosymmetric *3m*. On the other hand, no change between Raman scattering spectra in relaxor and ferroelectric states was observed. This means that their microscopic symmetries of acentrosymmetric *3m* and phonon damping states did not changed in the both states. These results revealed that for the relaxor state, the existence of the disorder system in the structure is very important.

Key word: PZN single crystal, Raman scattering, domain configuration, polar micro regions, DC-bias

1. INTRODUCTION

It was well known that 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 was 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 were on the basis of flipping polar vector in PMR while the last model was on the basis of fixed polar vector. Therefore, it is important to understand PMR. However, the polar state in PMR has been still unclear, and moreover, a time scale and a spatial magnitude in PMR were also unknown. Previously, it has been 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.

Time scale t / Spatial magnitude d	Dynamic t < 1 ns	Intermediate 1 ns < t < 10 μs	Quasi-static 10 μs < t
Microscopic d < 1~2 nm	Raman Scattering Spectroscopy		Transmittance Electron Microscopy
Mesoscopic 2 nm < d < 0.5 μm	Brillouin Scattering Spectroscopy		X-ray Diffraction Spectroscopy
Macroscopic 0.5 μm < d		Microwave Dielectric Spectroscopy	Polarized Microscopy

Table I Relationship between measurement method and spatial magnitude and time scale of measured physical phenomenon[12].

Nomura *et al.*[5] reported that a DC-bias exposure on an optical isotropic PZN crystals induced a ferroelectric state with normal ferroelectric domains. This means that using DC-bias field, two states, *i.e.*, the relaxor and ferroelectric states, were controlled in PZN crystals. Therefore, if under the both states, some symmetries with various time scales and spatial magnitudes (Table I) are measured[12], it can be expected to obtain some important informations about the polar state in PMR. In this study, we focused two kinds of symmetries. One is a dynamic and local symmetry on the basis of the lattice vibration (phonon) which was measured by a Raman scattering spectroscopy. We call this symmetry a microscopic symmetry with a dynamic time scale (t < 1nsec) and a microscopic spatial magnitude (d < 1~2nm). The other is a statistic and macro symmetry on the basis of the domain configuration which was observed by a polarized microscope. We call this symmetry a macroscopic symmetry with a quasi-static time scale (t > 10μsec) and a macroscopic spatial magnitude (d > 0.5μm).

Our final objective is to elucidate the relaxor

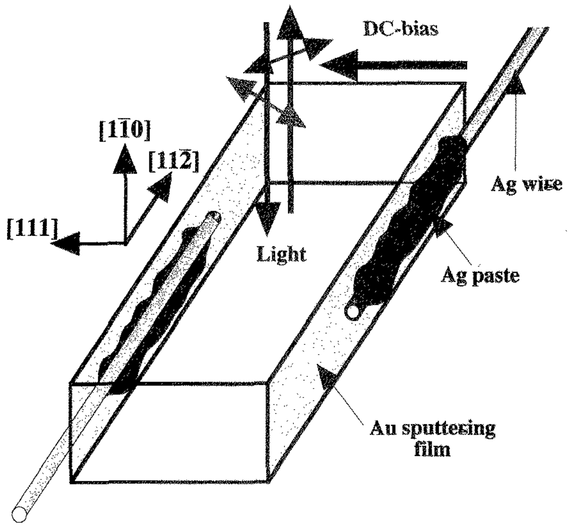

Fig. 1 A schematic diagram for *in-situ* Raman scattering measurement.

behavior in PZN crystals and its origin. In this study, we investigated about a change of the macroscopic and microscopic symmetries under DC-bias field, and discussed about PMR.

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 and Raman scattering measurement under DC-bias field, samples were prepared by polishing to an optimum size of approximately 0.2x0.5x4mm^3. Their top and bottom surfaces (0.5x4mm^2) were mirror-polished, normal to an incident light. Gold electrodes were sputtered on both sides (0.2x4mm^2), and the width between electrodes was around 0.5mm along [111] direction, as shown in Fig. 1. The details were described elsewhere[14,15]. Domain configuration was always observed under crossed-nicols using a polarized microscope (Carl Zeiss, D-7082). DC-bias exposure was done along [111] direction, being normal to the incident polarized light, using a Trek 610D high-voltage DC amplifier. Raman scattering spectra under DC-bias were measured in the backward scattering geometry using a Raman scattering spectrometer with a triple monochromator (Jobin-Yvon, T64000). DC-bias exposure was done in the same way as that in domain observation. The top surface (0.5x4mm^2) was excited by unpolarized and polarized Ar ion laser with a wavelength of 514.5nm and power below 20W/cm^2. The details are described elsewhere[16].

3. RESULTS AND DISCUSSION

3.1 in-situ domain observation under DC-bias field:
In-situ domain observation was done at 25°C. Figs. 2(a)-(l) show domain configurations under various DC-bias fields from 0 to 39kV/cm. Fig. 2(a) indicates a micrograph before a DC-bias exposure. When this crystal was rotated under fixed crossed-nicols, all regions in PZN crystal were always dark, except for some surface scratch. This means that the PZN crystal before the DC-bias exposure was the relaxor state with the optical isotropic property. Therefore, its indicatrix was a perfect sphere[17], and thus its macroscopic symmetry was assigned to the highest symmetry of *m3m*.

With increasing DC-bias field, ferroelectric domains appeared near the electrodes and grew. From 15 to 21kV/cm, the coexistence of relaxor regions and ferroelectric domains was observed in Figs. 2(b)-(d). Above 27kV/cm, all regions completely became to ferroelectric regions. The domain configuration was analyzed crystallographically, and these domain walls were assigned to 109° domain walls of {100} planes[18].

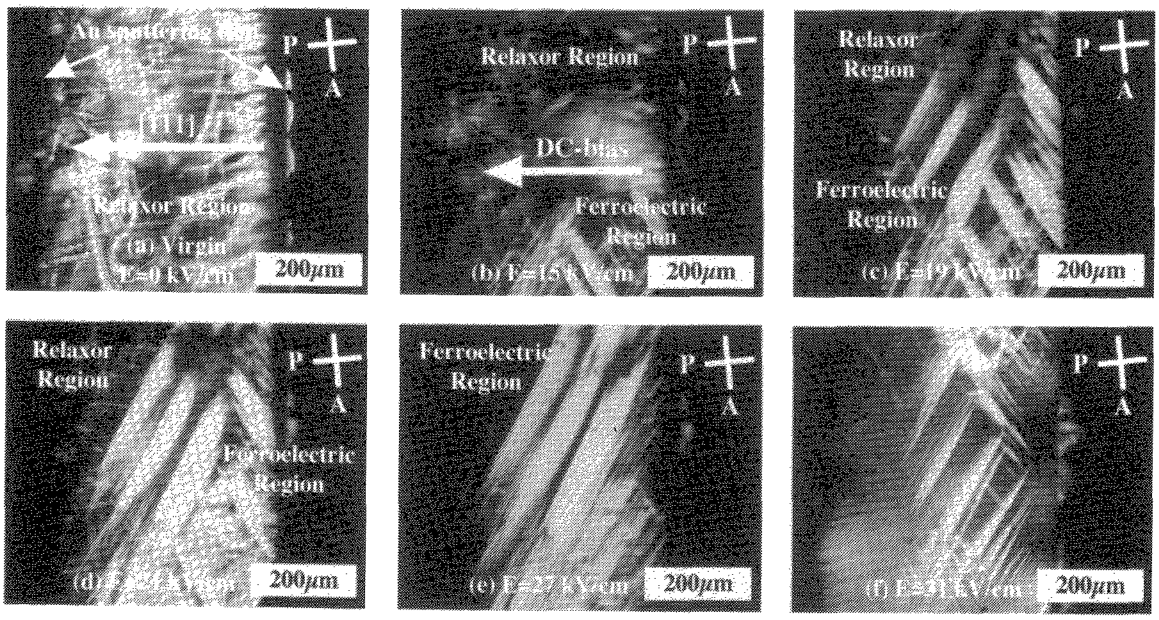

Fig. 2 Domain configuration under various DC-bias fields from 0 to 39kV/cm at 25°C.

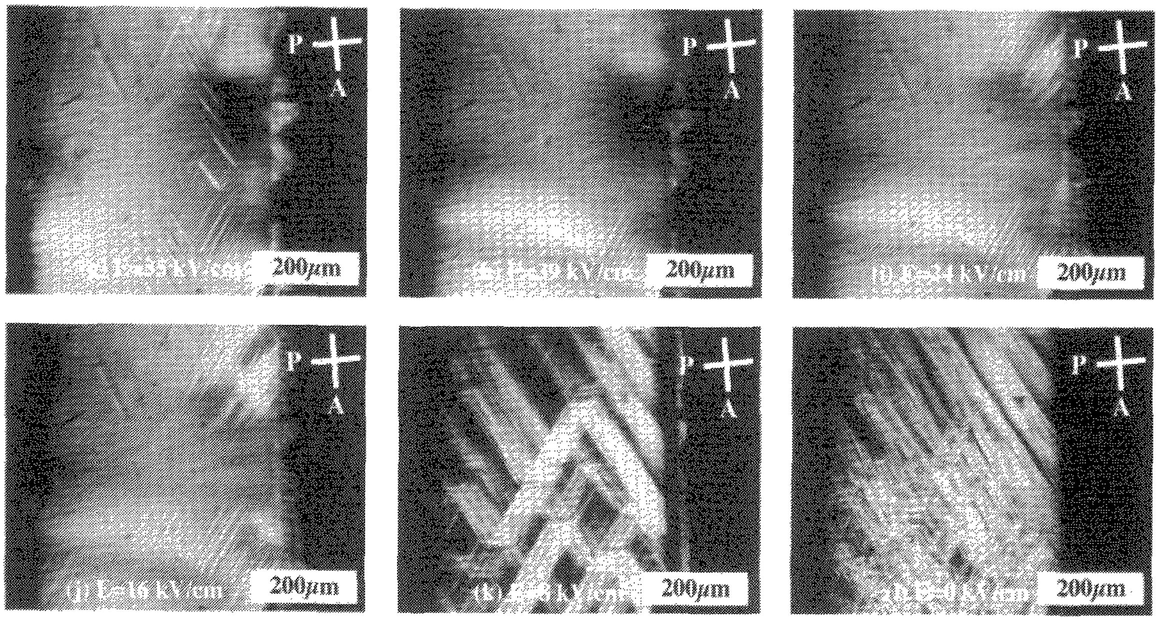

Fig. 2 Domain configuration under various DC-bias fields from 0 to 39kV/cm at 25°C. (*cont.*)

This domain configuration revealed that its macroscopic symmetry was assigned to rhombohedral symmetry *3m*. Moreover, the DC-bias exposure above 30kV/cm reduced domain wall density (Figs. 2(f)-(g)), and around 39kV/cm, most of PZN crystal became to a single domain state (Fig. 2(h)).

On the other hand, with decreasing DC-bias field, new domains appeared near the electrodes (Fig. 2(i)), and grew, as shown in Figs. 2(j)-(k). Finally a multidomain state was observed without DC-bias field (Fig. 2(l)). It should be noted that under no DC-bias field, its macroscopic symmetry after DC-bias exposure was assigned to *3m* acentric symmetry. The above result showed that the macroscopic symmetry in PZN crystal was changed from *m3m* to *3m* by the DC-bias exposure. Thus, we consider this phenomenon as a kind of phase transition induced by an electric-field. The ferroelectric state in Fig. 2(l) was completely disappeared by annealing at 250°C for 16h, and returned to the relaxor state as shown in Fig. 2(a).

3.2 in-situ Raman scattering measurement under DC-bias field:

In-situ Raman scattering measurement was done at 25°C using polarized and unpolarized lights. Through this manuscript, the scattering configuration is denoted by $A(BC)\bar{A}$, which means that the incident light polarized along "B" direction propagates along "A" direction, and the scattered light polarized along "C" direction propagates along opposite "A" direction ($\bar{A}$). In domain observation, we used "*cubic-axis*" notation system such as [111], but in Raman scattering measurement, we changed the notation system from "*cubic-axis*" notation system to "*principle-axis*" notation system. In *3m* rhombohedral crystal, $[1\bar{1}0]$, $[11\bar{2}]$ and [111] in "*cubic-axis*" notation system (Fig. 1) correspond to X, Y and Z in "*principle-axis*" notation system, respectively. In this study, Raman scattering measurement was done in three kinds of backward scattering geometries, *i.e.*, $X(NN)\bar{X}$, $X(ZZ)\bar{X}$ and $X(ZY)\bar{X}$ (N: unpolarized light).

Fig. 3 shows Raman scattering spectra measured in $X(NN)\bar{X}$ geometry under upward DC-bias field from 0 to 28.4kV/cm while Fig. 4 shows those measured under downward DC-bias field from 28.4 to 0.04kV/cm. In Raman spectra using unpolarized lights, all Raman-active phonon modes could be observed. PZN crystal before DC-bias exposure exhibits 12 peaks, as shown in the bottom of Fig. 3. XRD measurement using crashed PZN crystals was assigned to rhombohedral *3m* symmetry[13]. If a microscopic symmetry on the basis of phonon is *3m* symmetry, there are 14 Raman-active modes, *i.e.*, $3A_1(TO)+3A_1(LO)+4E(TO)+4E(LO)$. Thus, we regarded the microscopic symmetry of PZN crystal before DC-bias exposure as *3m* symmetry.

With increasing DC-bias field to 28.4kV/cm, the peak positions and their FWHM did not change while only intensity of some peaks changed irregularly, especially peaks around 600.9 and 784.6cm^{-1}. Now, we can not assign these Raman peaks to the corresponding phonon modes. Peak position means vibration energy and peak FWHM means damping of phonon. Thus, no change of peak position means that the microscopic symmetries before and after DC-bias exposure were the same, and no change of peak FWHM also indicates that the phonon damping states did not change by the DC-field exposure.

With decreasing DC-bias field from 28.4 to 0.04kV/cm, peak positions and their FWHM also did not change whereas only intensity of some peaks changed irregularly (Fig. 4). Therefore, the above result revealed that the microscopic symmetry of *3m* and phonon state, except for the intensity, did not change between the relaxor and the ferroelectric states.

Fig. 5 shows Raman scattering spectra measured in $X(ZZ)\bar{X}$ geometry under upward DC-bias field from 0 to 28.4kV/cm while Fig. 6 shows those measured under downward DC-bias field from 28.4 to 0.04kV/cm. If *3m* crystals is a single domain state, Raman scattering

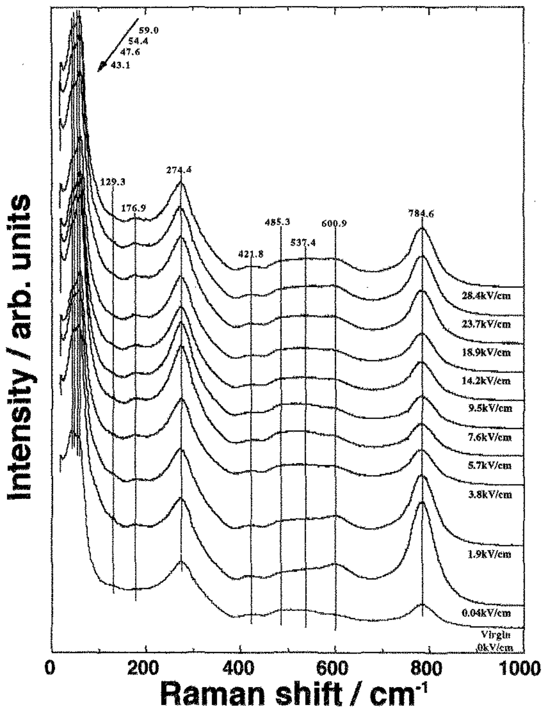

Fig. 3 Raman scattering spectra measured in X(NN)$\bar{X}$ geometry under upward DC-bias fields.

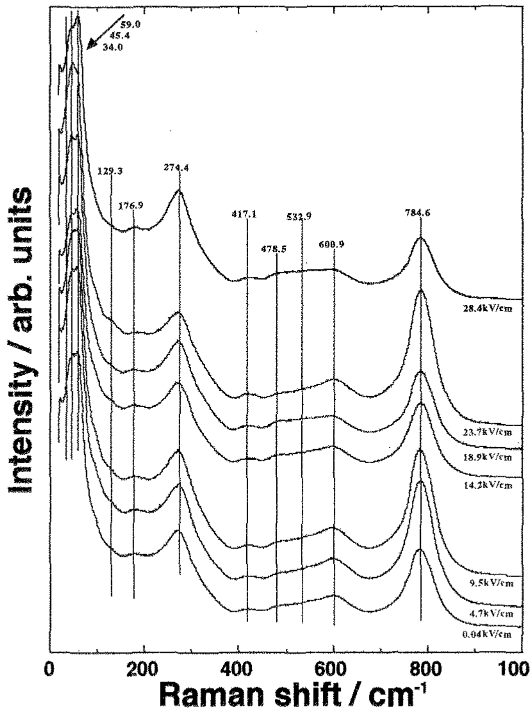

Fig. 4 Raman scattering spectra measured in X(NN)$\bar{X}$ geometry under downward DC-bias fields.

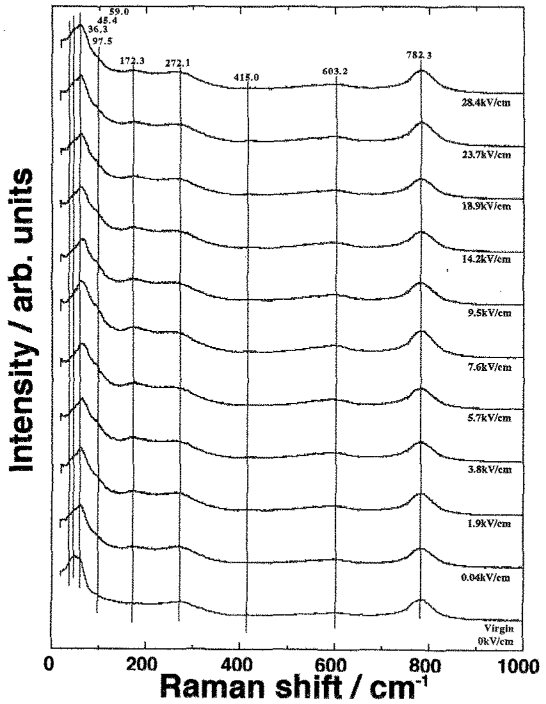

Fig. 5 Raman scattering spectra measured in X(ZZ)$\bar{X}$ geometry under upward DC-bias fields.

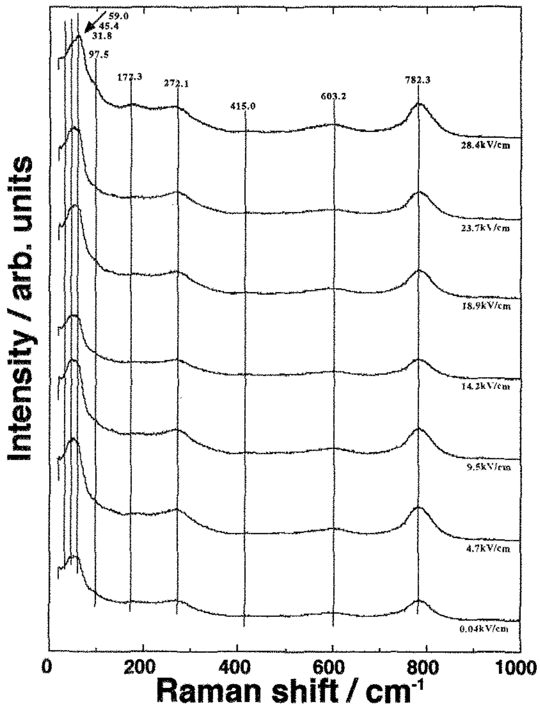

Fig. 6 Raman scattering spectra measured in X(ZZ)$\bar{X}$ geometry under downward DC-bias fields.

spectra measured in the X(ZZ)$\bar{X}$ geometry exhibit only mixed modes of A_1(TO) and A_1(LO). With increasing DC-bias field from 0 to 28.4kV/cm, no change in peak positions, their FWHM and intensity was observed (Fig. 5). Similarly, With decreasing DC-bias field from 28.4 to 0kV/cm, no change in peak positions, their FWHM and intensity was also observed (Fig. 6). A_1 modes are phonon modes vibrating along Z axis. This means that the phonon state along Z axis was not affected by DC-bias exposure. Therefore, about A_1 modes, there was no difference between the relaxor and ferroelectric states.

Fig. 7 shows Raman scattering spectra measured in X(ZY)$\bar{X}$ geometry under upward DC-bias field from 0 to 28.4kV/cm while Fig. 8 shows those measured under downward DC-bias field from 28.4 to 0.04kV/cm. If *3m* crystals is a single domain state, Raman scattering

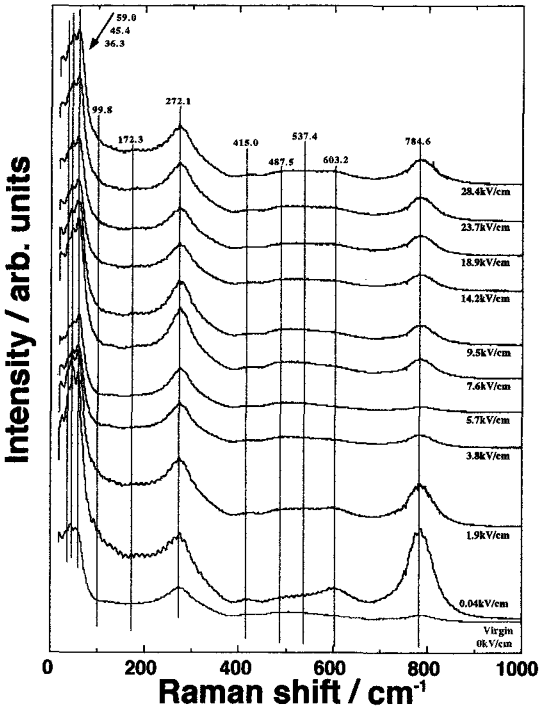

Fig. 7 Raman scattering spectra measured in $X(ZY)\bar{X}$ geometry under upward DC-bias fields.

spectra measured in the $X(ZY)\bar{X}$ geometry exhibit only mixed modes of E(TO) and E(LO). With increasing DC-bias field from 0 to 28.4kV/cm, the peak positions and their FWHM did not changed while only their intensity, especially the intensity of some peaks with higher frequencies, changed irregularly (Fig. 7). Moreover, with decreasing DC-bias field from 28.4 to 0kV/cm, the similar tendencies were observed (Fig. 8). E modes are phonon modes vibrating along X or Y axis. This result suggests that the irregular change of some peak intensity in Fig. 3 was originated from the change of peak intensity in E modes. However, all peak frequencies and their FWHM did not changed, which indicates that the microscopic symmetry and phonon damping were not affected by DC-bias exposure. At present, we can not explain the change of intensity in E modes. Perhaps, a contribution of the 109° domain wall motion to the phonon intensity by DC-bias exposure may be more significant along X or Y direction than along Z direction.

Time scale t / Spatial magnitude d	Dynamic t < 1 ns	Intermediate 1 ns < t < 10 μs	Quasi-static 10 μs < t
Microscopic d < 1~2 nm	*3m*		Transmittance Electron Microscopy
Mesoscopic 2 nm < d < 0.5 μm	Brillouin Scattering Spectroscopy		X-ray Diffraction Spectroscopy
Macroscopic 0.5 μm < d		Microwave Dielectric Spectroscopy	*m3m*

Table II Various symmetries in PZN crystals with the relaxor state before the DC-bias exposure.

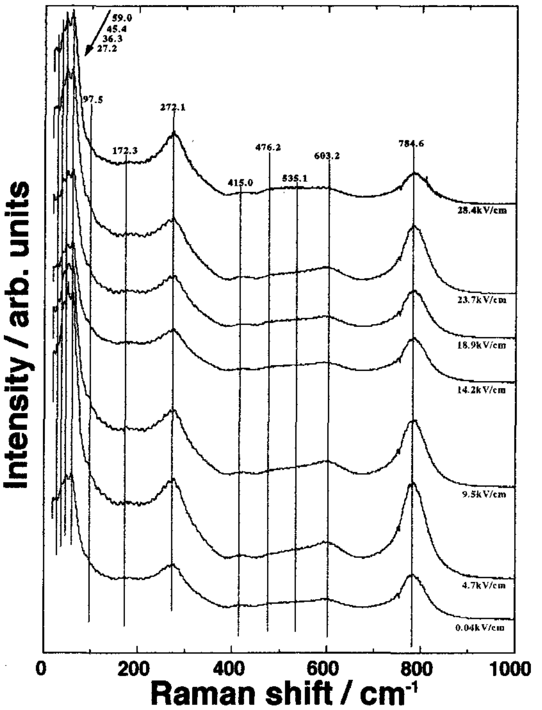

Fig. 8 Raman scattering spectra measured in $X(ZY)\bar{X}$ geometry under downward DC-bias fields.

Raman scattering measurement of PZN crystals using DC-bias field revealed that its microscopic symmetry of *3m* and phonon damping did not change between the relaxor and ferroelectric states.

3.3 Change of macroscopic and microscopic symmetries by DC-bias field:

Table II shows the macroscopic and microscopic symmetries in virgin PZN crystal before DC-bias exposure. In the relaxor state with the optical isotropic property, its macroscopic symmetry was assigned to centrosymmetrical *m3m* while its microscopic symmetry was assigned to acentrosymmetrical *3m*, *i.e.*, a symmetry with a spontaneous polarization, as shown in Table II. This difference between two symmetries suggests that PZN crystal with the relaxor state had a disorder system in the structure.

On the other hand, in the PZN crystal with the ferroelectric domains, the both macroscopic and microscopic symmetries were assigned to acentrosymmetrical *3m*, *i.e.*, a symmetry with a spontaneous polarization, as shown in Table III. Thus, no difference between two symmetries indicates that in the ferroelectric state after the DC-bias exposure, there was no disorder system. Thus, this study revealed that for the relaxor state, the existence of the disorder system in the structure is an important factor. This supports the validity of some models using "flipping polar vector"[6-8] as the origin of relaxor behavior. It should be also noted that in the both states, *i.e.*, relaxor and ferroelectrics in PZN, their microscopic symmetries were assigned to same *3m*, and there was no difference between phonon

Time scale t / Spatial magnitude d	**Dynamic** t < 1 ns	**Intermediate** 1 ns < t < 10 μs	**Quasi-static** 10 μs < t
Microscopic d < 1~2 nm	***3m***		**Transmittance Electron Microscopy**
Mesoscopic 2 nm < d < 0.5 μm	**Brillouin Scattering Spectroscopy**		**X-ray Diffraction Spectroscopy**
Macroscopic 0.5 μm < d		**Microwave Dielectric Spectroscopy**	***3m***

Table III Various symmetries in PZN crystals with the ferroelectric state after the DC-bias exposure.

damping states. In $BaTiO_3$ single-domain crystal, it was known that just above Tc of 133°C, phonon damping increased remarkably, which suggested a coupling between phonon frequency and flipping frequency of polar vector[12]. On the other hand, in PZN crystal, phonon damping was almost same between relaxor and ferroelectric states. This means that the origin of relaxor behavior is "flipping polar vector" in PMR.

Therefore, to clarify relaxor behavior, it is important to investigate other symmetries with intermediate time scale and/or mesoscopic spatial magnitude under DC-bias field. Our next strategy is to study a symmetry with dynamic time scale ($t <$ 1nsec) and mesoscopic spatial magnitude (2nm $< d <$ 0.5μm). This symmetry can be measured by a Brillouin scattering spectroscopy under DC-bias field. We expect that in this symmetry, some difference will be obtained between the relaxor and ferroelectric states.

4. CONCLUSION

Using pure PZN single crystal, two kinds of symmetries were measured by a polarized microscope and a Raman scattering spectroscopy under DC-bias field. In the relaxor state, its macroscopic symmetry on the basis of domain observation was assigned to the highest symmetry *m3m*. However, DC-bias exposure to PZN crystal with the relaxor state induced the ferroelectric domains. This domain configuration was analyzed crystallographically, and its macroscopic symmetry was assigned to acentrosymmetric *3m*. On the other hand, Raman scattering spectra exhibited no change under between relaxor and ferroelectric states. Thus, their microscopic symmetries of acentrosymmetric *3m* did not changed in the both states. These results revealed that for the relaxor state, the existence of the disorder system in the structure is important. Moreover, this study also suggested that it is important to investigate a mesoscopic symmetry in order to obtain valuable informations about PMR.

5. ACKNOWLEDGEMENTS

The authors thank Mrs. Lei and Mr. Liu for great help with PZN crystal growth, and also thank Dr. Newnham, Dr. Fousek, Dr. Cao and Dr. Randall of MRL, PennState university for helpful discussion about domain configuration.

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