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HETERO STRUCTURE AND ELECTRO-OPTIC EFFECT IN RELAXOR $Pb(Mg_{1/3}Nb_{2/3})O_3$

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Temperature and frequency dependences of the electro-optic response were measured in the relaxor ferroelectrics $Pb(Mg_{1/3}Nb_{2/3})O_3$(PMN). Heterogeneity and anisotropy in the dielectric and electro-optic properties of the relaxor PMN were discussed.

Key words: electro-optic effect, relaxor, PMN, phase transition, ferroelectrics.

1. INTRODUCTION

It is well known that relaxor ferroelectric materials with the perovskite structure are of very much importance in applications because of a large dielectric constant and high electro-mechanical coupling constant.[1] It has been pointed out that dielectric properties of the relaxor originate from the existence of the polar micro regions (PMR).[2,3] In order to obtain the information from the PMR, measurements of the nonlinear dielectric constant[4-8] and electro-optic coefficient which are the responses induced by the higher order of the applied electric field are important, since the averaged value of the polarization from the PMR in the whole crystal is zero and there is no long range order in relaxor materials.

In the present study, temperature and frequency dependences of the electro-optic response were investigated in the relaxor $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) single crystal. The PMN is a typical perovskite-type relaxor ferroelectrics, where the averaged structure is considered to be pseudo-cubic below and above the diffuse phase transition temperature.[9]

2. ELECTRO-OPTIC EFFECT

Let us consider the transmitted light intensity in the polarizing microscope. The change of the transmitted light intensity, ΔI, due to the application of an electric field to a crystal sample between the crossed polarizers is expressed as[10,11]

$$\begin{aligned}\Delta I/I_0 = {} & 2\sin 4\alpha_0 \sin^2(\beta n_{a0})\Delta\alpha \\ & + \beta\sin^2 2\alpha_0 \sin(2\beta n_{a0})\Delta n_a \\ & + 4\cos 4\alpha_0 \sin^2(\beta n_{a0})\Delta\alpha^2 \\ & + \beta^2 \sin^2 2\alpha_0 \cos(2\beta n_{a0})\Delta n_a{}^2 \qquad (1) \\ & + 2\beta\sin 4\alpha_0 \sin(2\beta n_{a0})\Delta\alpha\Delta n_a + \cdots,\end{aligned}$$

where $\beta = \pi d/\lambda$, I_0 is the incident light intensity, d the sample thickness, λ the wave length of the incident light, α_0 and n_{a0} are the angle of the optical axis with respect to one of the polarizer directions and the anisotropy of the refractive index in the absence of the filed, respectively, and $\Delta\alpha$ and Δn_a are electrically induced parts. In experiment, a sinusoidal electric field, E, at the frequency, f, is applied to the sample, i.e.

$$E = E_0\cos 2\pi f. \qquad (2)$$

When a sample has no inversion symmetry, first and second terms in eq. (1) show the first order response for the electric field due to the Pockels effect, i.e., $\Delta\alpha \propto E$, $\Delta n_a \propto E$, where the transmitted light intensity, ΔI, at the frequency, f, ($1f$ response) is observed. If a sample has inversion symmetry without anisotropy of the refractive index ($n_{a0} = 0$), then the lowest order of the electro-optic response is of the 4th power of the electric field because of $\Delta I \propto \Delta n_a{}^2 \propto E^4$ (the Kerr effect). Then, in this case, the response at the frequency of $4f$ ($4f$ response) is observed as the lowest frequency response. On the other hand, if a sample has inversion symmetry with anisotropy of the refractive index ($n_{a0} \neq 0$), then the lowest order of the electro-optic response is of the 2nd power of the electric field, and the signal at the frequncy of $2f$ ($2f$ response) is observed as the lowest frequency response.

3. EXPERIMENTAL

3.1 Crystal growth

Single crystals of PMN were grown by the flux method from the PbO-MgO-Nb_2O_5 system. The mixture in a platinum crucible was heated up to 1150°C and held at this soak temperature for 5 hours, then the melt was cooled to 950°C at a rate of 3°C/h and down to 800°C at a rate of 5°C/h. PMN crystals obtained are yellowish in color and 5 mm in the typical size. Synthesized crystals were confirmed by the X-ray powder diffraction as a single perovskite phase.

3.2 Electro-optic measurement

For the electro-optic measurement, PMN (001)-plate with an area of about 25 mm^2 and thickness of about 0.3 mm were cut out and polished with a polishing sheet (0.3 μm size). The sample plate with electrodes was mounted in a hot stage, then set on the polarizing microscope

(Olympus, BH-2), where the gap between two electrodes is about 1 mm. White light from an electric bulb and an Ar-ion laser at 488nm were used as an incident light. A external electric field along the [100] direction of the PMN was applied, where the direction of the electric field, [100], is perpendicular to the incident light, [001]. The crystal sample was placed between the crossed polarizers and the polarizer direction was set at $\theta = 45°$, where θ is the angle between one of the polarizers and electric field. In the electro-optic measurement, the transmitted optical response was detected by a photodiode (Hamamatsu Photonics, C6386) attached to the microscope, then the amplitudes and phases of the 1st-, 2nd- and 4th-order responses were measured by a vector signal analyzer (HP, 89410). For the n-th order response (nf response), we use complex intensity, $I = I' - iI''$, defined as $I = ae^{i\phi}$, where a and ϕ are the amplitude and the phase in each response, respectively.

In general, the intensity of the nf response is proportional to the n-th power of the electric field applied to the sample, if the field is weak enough. In our measurement, it is confirmed that the complex intensity is proportional to the n-th power of the electric field. Figure 1 shows the field dependence of the $2f$ response. It is seen that the complex intensities of the $2f$ response are proportional to the square of the electric field, E^2.

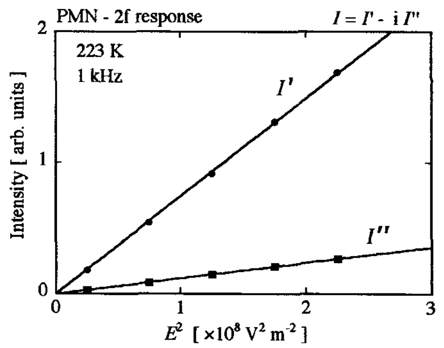

Fig. 1 Typical dependence of the $2f$ complex intensity, I' and I'' on E^2 at 223K. White light was used as an incident light.

4. RESULTS AND DISCUSSIONS

Figures 2 and 3 show temperature dependence of the dielectric constant and $2f$ response of the electro-optic effect, where white light is used as an incident light in the electro-optic measurement. It is seen in Fig. 3 that $2f$ response as a function of temperature shows a broad peak, and with increasing frequency, the temperature, T_m, showing the maximum intensity increases, while the magnitude of the peak decreases.

In the present study, no $1f$ response of the electro-optic effect was detected within acceptable range of experimental error. Namely, no Pockels effect in PMN appears. This indicates that there is no long range order of the polarization. On the other hand, the intensities of the $2f$ and $4f$ responses are comparable near the field range of about 100 V/cm, and the intensities of the $2f$ and $4f$ responses are confirmed to be in proportion to E^2 and E^4, respectively. Then, it is guessed that the lowest order of the electro-optic effect in PMN is of the 2nd order. This indicates that the averaged symmetry in the PMN over the macroscopic scale is lower than the cubic $m\bar{3}m$, which is due to the anisotropy of the refractive index without long range order of the polarization.

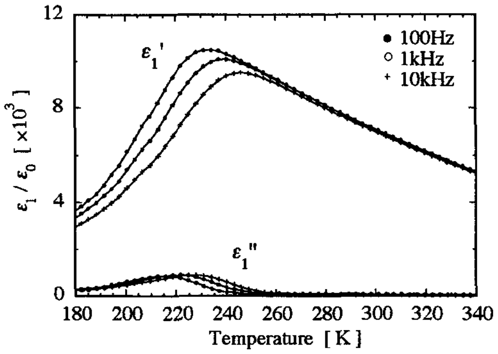

Fig. 2 Temperature dependence of the dielectric constant in PMN

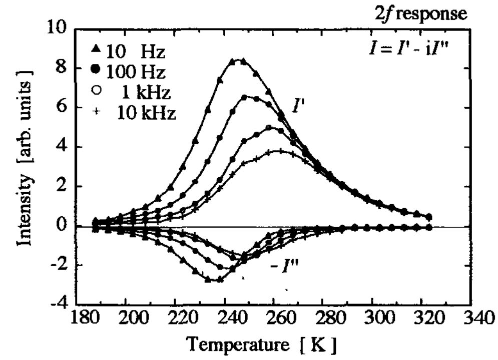

Fig. 3 Temperature dependence of the $2f$ complex intensity, I' and I'', in PMN. White light was used as an incident light.

In order to clarify the anisotropy of the PMN, angle, θ, dependence of the $2f$ response was investigated by using a laser light, where θ is the angle between one of the polarizers and electric field. Figure 4 shows the angle dependence of the square of the $2f$ intensity at some positions, where the diameter of the focus point of the laser light is about 50 μm. The solid lines show results of the fitting by

$$|\Delta I|^2 = \left|A\sin^2 2\alpha_0 + B\sin 4\alpha_0\right|^2, \qquad (3)$$

and

$$\alpha_0 = \theta - \phi, \qquad (4)$$

where A and B are the complex constants and ϕ is the angle between the principle axis of the indicatrix and electric field applied. The result of the fitting in Fig.4

seems to be good. It is seen in Fig. 4 that square of the $2f$ intensity, $|\Delta I|^2$, and the angle, θ_m, showing the maximum intensity strongly depend on the sample position. This implies that the heterogeneous strain field without long range order of the polarization exists in the relaxor PMN.

Next, let us consider the relation between the electro-optic response and dielectric constant. If a sample is homogeneous and there is no anisotropy of the dielectric constant, ε, in the frequency range of kHz order, then the $2f$ response should be in proportion to the square of the dielectric constant, i.e., $\Delta I_{2f} \propto \varepsilon^2$. Figure 5 shows the comparison between the real part of the $2f$ response and square of the real part of the dielectric constant at 1kHz.

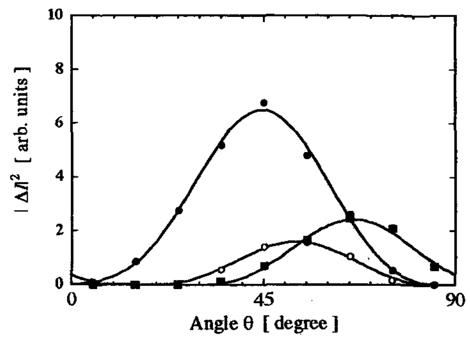

Fig. 4 Angle θ dependence of the $2f$ intensity. An Ar-ion laser at 488 nm was used as an incident light.

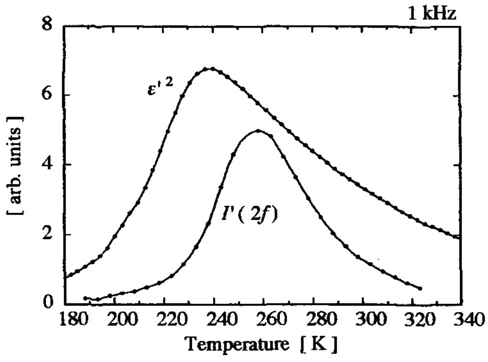

Fig. 5 Comparison between the real part of the $2f$ response and square of the dielectric constant.

It is found that temperature dependence of the $2f$ response, ΔI_{2f} in the relaxor PMN does not obey the relation $\Delta I_{2f} \propto \varepsilon^2$. This admits of two possibilities. One is the existence of the anisotropy of the dielectric constant in the frequency range of kHz order, and the other is due to heterogeneity of the strain field.

It was reported on the basis of the Landau theory that there is an anisotropy of the dielectric constant in the perovskite-type ferroelectric solid solutions located near the morphotropic phase boundary (MPB), and the dielectric constant perpendicular to the spontaneous polarization, P_s, is much larger than that parallel to the P_s, and pointed out that the instability perpendicular to the P_s, called transverse instability, is important in the dielectric property of the solid solution near the MPB.[12-14] On the other hand, the PMN is known to be located near the MPB form the experimental result of the solid solution system between PMN and $PbTiO_3$.[15] In the present study, we conjectured the possibility that the PMR in PMN shows the dielectric anisotropy in kHz region. However, we were not able to determine the dielectric anisotropy of the PMR in PMN qualitatively. In order to clarify the dielectric property in relaxor, the determination of the dielectric anisotropy of the PMR is required.

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