Mechanism of Diffuse Phase Transition in Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3}

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Electrostriction and dielectric dispersion of lead magnesium niobate (PMN) was measured as a function of temperature. And crystal structure of PMN was refined by Rietveld analysis method. The results of structure refinement indicated that the volume of polar microregions (PMR) increased with decreasing temperature. The dielectric property of PMN was well explained by 'universal' law of dielectric dispersion. The decrease in dielectric permittivity, observed on the low temperature side of the peak temperature (T\textsubscript{m}) in dielectric permittivity vs. temperature curve, was explained by a simple dielectric relaxation theory, but on the contrary the increase in dielectric permittivity on the high temperature side of T\textsubscript{m} was explained by the volume increase of PMR. It was concluded that the diffuse phase transition was a overlapping phenomenon of volume increase of PMR, freezing process of fluctuating dipoles and dielectric dispersion around measuring frequency.

1. INTRODUCTION

Ferroelectrics with diffuse phase transition or relaxor ferroelectrics (RF) are extensively studied due to their technological importance and scientific interest. The model of diffuse phase transition has been proposed by many research groups[1-7]. Most of models proposed the formation of randomly oriented polar micro regions (PMR) in paraelectric crystals[1]. The model proposed by Smolensky[2] related the formation of PMR with composition fluctuations. Burns et al.[3,4] found a glassy polar phase existed in RF by means of optical index refraction measurements and Raman spectroscopy. Cross et al.[5,6] suggest that PMR are thermally fluctuating at high temperatures, and that the fluctuations have a freezing temperature in analogy with spin glasses. However, the analyses of electric properties and crystal structure of RF from the view point of the formation of PMR, thermal fluctuation and freezing of PMR have been limited so far.

In the present study, electrostriction and dielectric dispersion of lead magnesium niobate (PbMg\textsubscript{1/3}Nb\textsubscript{2/3}O\textsubscript{3}, PMN) are measured as a function of temperature. And, the crystal structure of PMN is refined by Rietveld method. The behavior of dielectric dispersion is analyzed by using 'universal' dielectric response theory[8] in order to clarify the thermal fluctuation and freezing behavior of PMR. Finally, we propose a model of diffuse phase transition to explain various experimental results.

2. EXPERIMENTAL

Powder of PMN was prepared by the columbite precursor method[9] in order to produce phase-pure compositions. It was sintered at 1200°C for 4 hours. The density of the ceramics obtained was above 95% of the theoretical value. The electrically induced strain was measured by means of a laser interferometer (Suntechno OM-15D) from -80°C to 60°C. The crystal structure of PMN was refined by Rietveld analysis method (program RIETAN[10]) from -60°C to 200°C. The dielectric dispersion of the specimen was measured using impedance analyzers (hp4192A, hp4191A) from 1KHz to 1GHz.

We used the following 'universal' theory to analyze dielectric dispersion data. Polarization P can be expressed by an integral expression

\[ P(t) = \int_{-\infty}^{t} E(u) \psi(t - u) du \]  

(1)

where E is an electric field and \( \psi \) is a response function. The dielectric susceptibility \( \chi \) can be calculated from the Fourier transform of eq.(1).

\[ \chi(\omega) = \chi(0) \int_{-\infty}^{+\infty} \psi(t) \exp(i\omega t) dt \]  

(2)

In the 'universal' theory proposed by Ngai[8], the response function is expressed by

\[ \psi(t) = \beta \left[ \exp \left( \frac{t}{\tau} \right) \right] t dt \]  

(3)

where \( \beta \) is a constant which represents degree of correlation between fluctuating dipoles in this case.
3. RESULTS AND DISCUSSION

3.1 Crystal Structure Refinement

The crystal system of PMN was cubic and no additional diffraction lines nor distortion of lattice was observed in the temperature range examined. The thermal vibration parameters of cations are shown in Fig.1 as a function of temperature. It was found that the vibration parameters was too large in comparison with other oxides and that the parameters increased with decreasing temperature. These distinct features could be interpreted by assuming that cations displace from special positions. Similar result was reported by Bonnue et al. [11] as a structure of PMR. The apparent increase in vibration parameters, which was resulted from the increase in the occupancy of displaced cations, indicated that the volume of PMR increased with decreasing temperature [5].

3.2 Dielectric and Electrostrictive Properties

The temperature dependence of dielectric permittivity measured at different frequencies was consistent with well-known behavior of RF (Fig.2). A large dielectric dispersion was observed on the low temperature side of the maximum temperature (T_m) of dielectric permittivity. Figure 3 shows electrostriction curves of PMN measured at different temperatures. PMN showed a ferroelectric property as the temperature decreased, though the cubic crystal system was maintained. This may be related with the increase in the volume of PMR. An electrostrictive coefficient Q_{33} was about 1.6x10^{-2} m^4/C^2 which was independent of temperature as reported by Kuwata et al. [12].

3.3 Dielectric Dispersion

Figure 4 shows frequency dependence of dielectric permittivity. The solid lines in the figures were those calculated using eq.(2) and eq.(3). The experimental results were well explained by the 'universal' law, which meant that the dielectric dispersion of PMN was not special. The similar agreement was obtained in the case of tantalum-bearing strontium barium niobate with tungsten bronze structure[13].

Figure 5 is a change of β as a function of temperature. The low β values (0.15-0.3) indicated a strong correlation of fluctuating dipoles existed in the...
The temperature dependence of $\beta$ implied that the correlation increased with decreasing temperature.

In Ngai's theory[8], the temperature dependence of dielectric relaxation frequency $\omega_p$ is represented by

$$\omega_p = \omega_0 \exp\left(-\frac{E_A^*}{kT}\right)$$  \hfill (4)

where $E_A^*$ is an apparent activation energy of $E_A^* = E_A/\beta$, $\omega_0$ is an attempt frequency, and $k$ is the Boltzmann's constant. Figure 6 shows a relation between the relaxation frequency $\omega_p$ and $1/\beta T$. It was found that the temperature dependence of relaxation frequency obeyed eq.(4) with an activation energy $E_A = 0.048$eV. This result evidenced the thermally fluctuating dipoles in PMN and their freezing behavior. However, we could not find the Vogel-Fulcher relationship[6,14] which evidenced the existence of the freezing temperature. The wave number corresponding to the frequency $\omega_0$ was about $50$cm$^{-1}$ which was consistent with the wave number of soft mode phonons. It seems to be reasonable that the attempt frequency of the fluctuation was the frequency of soft mode phonons.

From the analysis of dielectric dispersion, it is concluded that the dielectric dispersion of RF is determined by the thermally fluctuating dipoles in PMR and their freezing process. A large dielectric relaxation is observed when the measuring frequency is close to the fluctuation frequency.

### 3.4 Mechanism of Diffuse Phase Transition

Dielectric dispersion was distinguishably observed on the low temperature side of $T_m$ (Fig.2). It implies that the mechanism of the change in dielectric permittivity is different between low and high temperature sides of $T_m$.

The decrease in dielectric permittivity on the low temperature side is simply explained by dielectric relaxation: if the relaxation frequency becomes lower than the measuring frequency as the temperature decreases, the real part of dielectric permittivity decreases. On the other hand, the increase in dielectric permittivity on the high temperature side can be explained as follows. The electrically induced polarization should increase with increasing volume of PMR because dipoles are fluctuating in PMR.

Therefore, the real part of dielectric permittivity which is mainly determined by electrically induced polarization increases with decreasing temperature.
The dielectric properties of RF can be explained by an overlap of three phenomena; 1) the volume increase of PMR which are formed at temperatures much higher than $T_m$, 2) freezing of the fluctuating dipoles in PMR and 3) dielectric relaxation in measuring frequency range. This conclusion implies that phase transformation do not take place around $T_m$ which is consistent with experimental results that changes in electrostrictive coefficient, optical index of refraction[3,4] and crystal system was not observed around $T_m$. This model is basically similar to the superparaelectric model proposed by Cross[5] and can explain a lot of experimental results reported for RF.

REFERENCES
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