Effect of quenching temperature on the dielectric properties of lead metaniobate

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The effect of quenching temperature on the dielectric properties of $PbNb_2O_6$ was studied. The dielectric properties were dependent on the quenching temperature. The Curie temperature increased and the maximum dielectric constant decreased as the quenching temperature increased. The sample quenched from 1300°C exhibited a relaxor behavior, such as broad-diffuse phase transition and frequency dispersion of the Curie temperature, whereas the sample quenched from 700°C did not exhibit such a relaxor behavior. The changes in the dielectric properties with the quenching temperature were explained by the distribution of Pb^{2+} ions and vacancies in the A sites of the tungsten bronze structure.

1. INTRODUCTION

Lead metaniobate $(PbNb_2O_6)$ is a ferroelectric and piezoelectric material with the tungsten bronze structure; the paraelectric and the ferroelectric phases are tetragonal and orthorhombic, respectively, and the Curie temperature is about 560°C [1]. $PbNb_2O_6$ has attracted considerable attention because of the large anisotropy in electromechanical coupling factors between thickness and planar modes as well as small mechanical quality factor Qm [2].

The projection of the tungsten bronze structure along [001] axis is shown in Fig. 1. It consists of corner-linked NbO_6 octahedra, and other cations occupy A1, A2 and C sites. The tetragonal unit cell contains two A1 sites, four A2 sites, four C sites, two B1 sites, eight B2 sites and thirty oxygen ions in this structure. In $PbNb_2O_6$, Pb^{2+} ions occupy only 5 sites among six of the A sites. One of the A sites and all C sites are vacant [3].

The variations of the Curie temperature and the dielectric constant in the tungsten bronze structure ceramics are attributed to the differences in cation and vacancy occupancy among the A sites [4-5]. The dielectric properties of $PbNb_2O_6$ are expected to depend on the thermal history which affects the vacancy distribution in the A site.
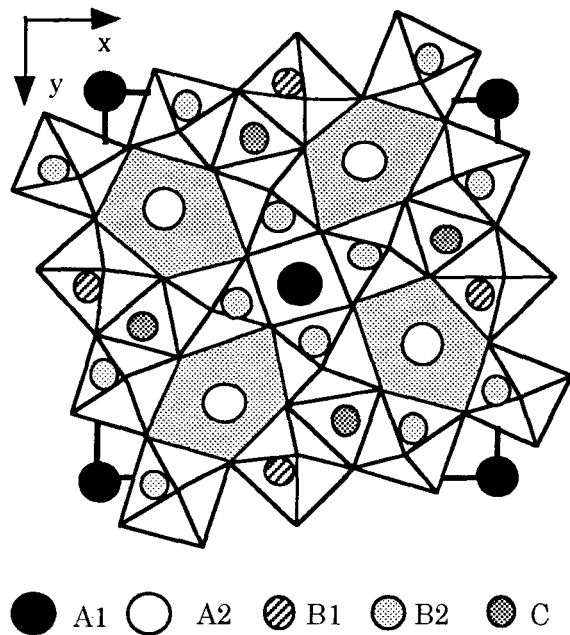
The purpose of this work was to study the

● A1 ○ A2 ⊘ B1 ◎ B2 ⊛ C

Fig. 1 Projection of tetragonal $PbNb_2O_6$.

effect of vacancy distribution on the dielectric properties of $PbNb_2O_6$ by controlling the quenching temperature.

2. EXPERIMENTAL PROCEDURE

Reagent grade PbO and Nb_2O_5 powders were mixed in a ball-mill for 24h. The calcined powder was obtained by heating the mixture at 1300°C for 1 h and by grinding with a planetary ball-mill for 3h. Green compacts were made by uniaxial pressing in a cylindrical die under a pressure of 98 MPa. The compacts were isothermally sintered at 1300°C for 1h and then quenched in air.

To prepare samples quenched at 700° or 1000°C, the samples were sintered at 1300°C for 1h, cooled at a rate of 10°C /min down to 700° and 1000°C, soaked at these temperatures for 1h, and then quenched in air.

The density of the obtained samples was 92.3 % of theoretical density $(6.64gcm^{-3})$, irrespective of the quenching temperature. The microstructure was observed by a scanning electronic microscope. Gold electrodes were coated on both surfaces of the samples. The dielectric constant up to 600°C was measured at 0.1, 1 and 10kHz, at a heating rate of 5°C /min by a computerized automatic measuring system using a LCR meter.

3. RESULTS AND DISCUSSION

3.1 Effect of quenching temperature on the dielectric behavior

Figure 2 shows the temperature dependence of dielectric constant for the samples quenched from various temperatures. The Curie temperature, defined as the temperature at which the dielectric constant is maximum, decreased with decreasing quenching temperature; by 2° and 12°C decreased for the samples quenched from 1000° and 700°C, respectively, as compared
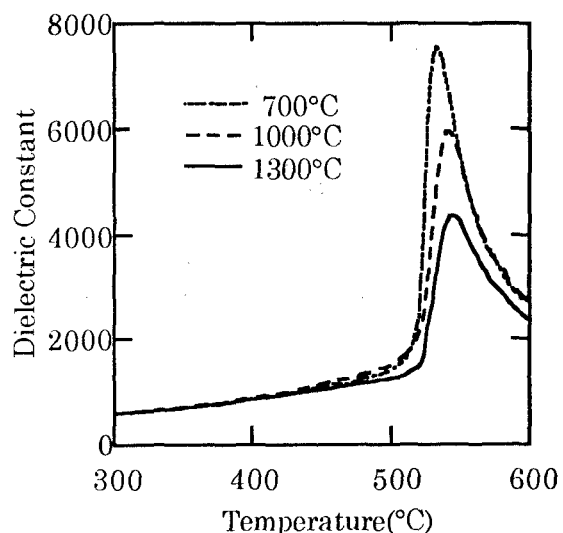

Fig. 2 Dielectric Constant for the samples quenched from various temperatures (10kHz).

with that of the sample quenched from 1300°C.

The Curie temperature and dielectric constant depend on the microstructure; the Curie temperature is high for samples containing a large amount of pores and cracks, and an increase in grain size of samples with same density decreases the Curie temperature [6].

Figure 3 shows the microstructures of samples quenched from various temperatures. Little difference in microstructure was observed irrespective of the quenching temperature. Thus, the variation of the Curie temperature shown in Fig. 2, cannot be explained by the difference in the microstructure. The Curie temperature is also influenced by the distribution of cations in the A sites of the tungsten bronze structure.

$PbNb_2O_6$ has a disordered structure, since the five cations and one vacancy are distributed in two A1 and four A2 sites. Three types of vacancy occupancy in the A sites are possible. One is that vacancies occupy only A1 sites. The other is that vacancies
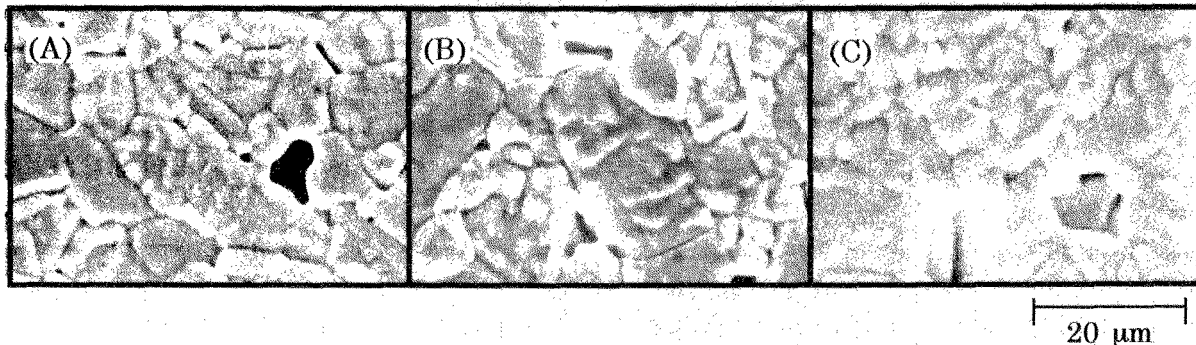
Fig. 3 SEM micrographs of the samples quenched from (A); 1300°, (B); 1000°, and (C); 700°C.

occupy only A2 sites. The last is mixed state that vacancies are randomly distributed in both A1 and A2 sites. Because the size of the A2 site is larger than that of A1 site, the structure with vacancies occupying the A1 sites is energetically stable at low temperature. Vacancies tend to occupy the A2 sites as the temperature increases, due to thermal agitation. Thus, the second type of vacancy occupation is improbable. The vacancy ordering is defined based on the vacancy distribution. The degree of vacancy ordering is high when most of vacancies occupy the A1 sites. As the temperature increases, the degree of vacancy ordering decreases and the population of Pb^{2+} ions in the A1 sites increases.

The increase in the Curie temperature at higher quenching temperature is explained by the population of Pb^{2+} ions in the A1 sites. The bonding energy between Pb^{2+} ion and surrounding oxygens is larger for Pb^{2+} in the A1 site than Pb^{2+} in the A2 site, because of the shorter distance between Pb^{2+} and oxygen ions. Thus, the free energy of the ferroelectric state decreased as the population of Pb^{2+} in the A1 site increased, so that the Curie temperature shifted to high temperature.

The maximum dielectric constant and the sharpness of the phase transition peak increased as the quenching temperature

decreased, as seen in Fig. 2. When quenched from high temperatures, an increased population of Pb^{2+} cations in the smaller A1 sites may cause nonuniformly built-up strain to deform the oxygen octahedra and to reduce the polarizability along the c axis. Therefore, a decrease in A site vacancy ordering is also responsible for broadening of the phase transition peak.

3.2 Effect of vacancy ordering on the dielectric dispersion behavior

Figure 4 shows the frequency dependence of dielectric constant of samples quenched from different temperatures. The sample quenched from 1300°C(Fig. 4A) exhibited distinct relaxor characteristics such as broad-diffuse phase transition and frequency dispersion of the Curie temperature compared with the sample quenched from 700°C(Fig. 4B). This is attributed to the fact that quenching from higher temperature endowed the sample with the low degree of vacancy ordering in A sites as discussed in 3.1.

The dispersion of the Curie temperature in response to frequency almost vanished and the sharpness of the phase transition peak was significantly increased by lowering the quenching temperature. This indicates that the disorder in the polarization is reduced by an increase in the vacancy ordering, which is in
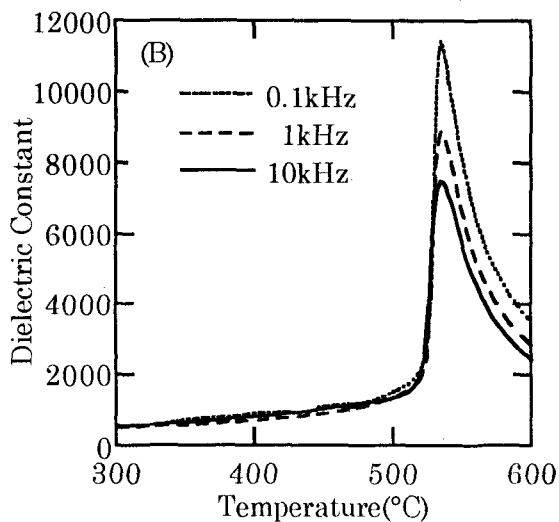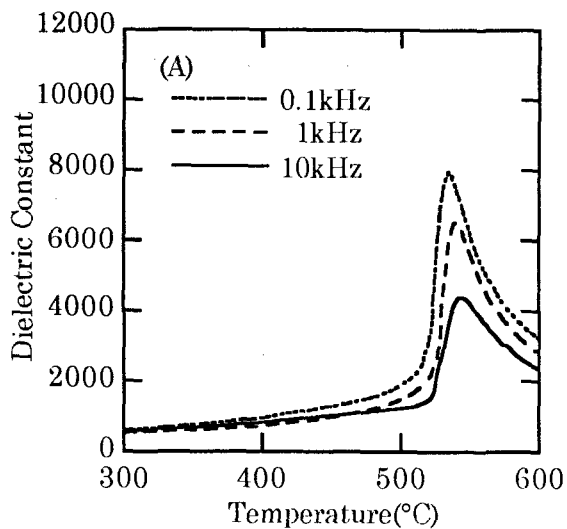
Fig. 4 Frequency dispersion of dielectric constant for the samples quenched from (A) ; 1300 and (B) ; 700°C.

good agreement with the local polarization model [7-8].

4. CONCLUSION

Quenching from high temperatures was found to decrease the degree of vacancy ordering in the A site. The sharpness of the phase transition peak and the maximum dielectric constant decreased as the vacancy ordering decreased. Since highly disordered state decreased the free energy of the ferroelectric state due to stronger ionic bonding energy, the disordered state resulted in the shift of the Curie temperature toward higher temperature than the ordered state. Structure disorder in A sites led to the diffuse phase transition, which can be explained by the disorder in the polarization.

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