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Growth and physical properties of $Sr_xBa_{1-x}Nb_2O_6$ (x = 0.60, 0.75) single crystals

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Abstract $Sr_{0.6}Ba_{0.4}Nb_2O_6$ (60SBN) and $Sr_{0.75}Ba_{0.35}Nb_2O_6$ (75SBN) single crystals were grown by Czochralski method. Growing direction was <001>, and as-grown crystals has well-developed (001) plane. Temperature- and frequency dependence of dielectric constant represent relaxor ferroelectrics. 60SBN has wider optical transmittance than 75SBN.

Key words Crystal morphology, Czochralski method, $Sr_xBa_{1-x}Nb_2O_6$(SBN), Relaxor ferroelectric materials

1. Introduction

The tungsten-bronze type relaxor ferroelectric material strontium barium niobate $Sr_xBa_{1-x}Nb_2O_6$ (SBN) is a interesting material due to the variety of its potential applications, particularly in the areas of pyro-electricity, piezoelectricity, electro-optics, photo-refractive optics and non-linear optics [1-4]. However it has been difficult to obtain high-quality SBN single crystals. Since the thermal conductivity of SBN is very small, approximately 1/60 of that of sapphire. In the conventional Czochralski growth of SBN crystals, a strong temperature gradient needs to be applied in order to maintain a plannar growth interface, which is necessary for the growth of large single crystals. To obtain SBN crystals of high compositional homogeneity, Stepanov technique or double crucible Stepanov technique [5-7] and vertical Bridgman technique [8].

The nature of the relaxor phase transition can only be found out having detailed knowledge of the influence of internal charge carriers and electric fields in the paraelectric and ferroelectric regime [9, 10]. This influence is of paramount importance for the “random field Ising model”, which has been put forward to explain the relaxor behavior of SBN [11]. Relaxor ferroelectrics are characterized by a significant frequency dependence of their peak permittivity, persistence of the local polarization far above the phase transition temperature T_C, and absence of macroscopic spontaneous polarization and structural symmetry breaking after zero-field cooling.

Optical properties are dependent of the Sr/Ba ratio in the solid solution and of the temperature. In particular, the refractive index of the extraordinary wave n_e is extremely sensitive both to compositional and to temperature change [12].

The purpose of this study is investigation of growing condition and morphology of $Sr_{0.60}Ba_{0.40}Nb_2O_6$ (60SBN), $Sr_{0.75}Ba_{0.25}Nb_2O_6$ (75SBN) single crystals. We discussed on the Sr/Ba ratio influence on temperature- and frequency-dependence of the dielectric properties in 60SBN and 75SBN single crystals. We also showed optical properties of 60SBN and 75SBN.

2. Experimental Procedure

$SrCO_3$ (99.99 %, Alfa Aesar), $BaCO_3$ (99.999 %, CERAC), and Nb_2O_5 (99.999 %, H.C. Starck) were used as starting material. $Sr_xBa_{1-x}Nb_2O_6$ was wet-ball mixed. Mixing was preformed with ethyl alcohol for 24 hr, using Teflon balls. The mixed slurry were dried, pressed, and calcined at 1150°C for 5 hr. The phases in the calcined powder was identified by XRD (Rigaku Geigerflex X-ray diffractometer) using a CuKα radiation at 30 kV and 20 mA, and was identified by comparing spectra with standard data in JCPDS (39-0265) file index. Single phase calcined powder was re-pressed in a mold of 10 mm in-diameter under a uniaxial pressure, and the pressed discs were sintered at 1300°C for 4 hr.

Single crystals of 60SBN and 75SBN were grown from the Czochralski method. A Pt crucible with 40 mm in diameter, 40 mm in height and 1 mm in thickness

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was positioned under the suitable thermal conditions for crystal growth. Pt wires were used as seed. In order to grow good-quality crystals, growth conditions such as pulling rate and seed rotation rate were adjusted in range of 2~4 mm/hr and 8~15 rpm, respectively.

For dielectric properties and electrical conductivity measurements, polished specimens were electrode with silver paste (Dae-Joo, DS-0081IE) and were heat-treated at 400°C for 1 hr. The frequency and temperature dependence of dielectric and electrical properties were estimated from room temperature to 150°C, using a Hioki 3532 LCR HiTester at 50 Hz~5 MHz. Heating and cooling rate of specimens were 0.2°C/min.

For its optical transmittance measurement, specimens were polished using a UV/Vis spectrometer (OPTIZEN 2120UV).

3. Results and Discussion

Fig. 1 shows as-grown 60SBN, 75SBN single crystals and its facets. As-grown crystals had a yellowish color. In Table 1, detailed condition of crystal growth was described.

In general, tetragonal tungsten bronze crystal, for example, $Sr_xBa_{1-x}Nb_2O_6$ (SBN), $Sr_2KNb_5O_{15}$ (SKN), $Ba_6Ti_2Nb_8O_{30}$ (BTN) etc, have a distinct cylindrical growth habit with 24 well-defined facets, each facet corresponding to a definite crystallographic orientation [13]. Growing direction of 60SBN and 75SBN crystals was <001>, and as-grown crystals had well-developed (110) plane.

The conoscope image/XRD pattern for growing direction and etch pit of as-grown crystals are shown in Fig. 2 and Fig. 3, respectively. Etching condition was HF : HNO_3 = 1 : 3 during 1 hr at 80°C. Etch pit of non-uniform represents the internal stress of crystals for previous annealing process.

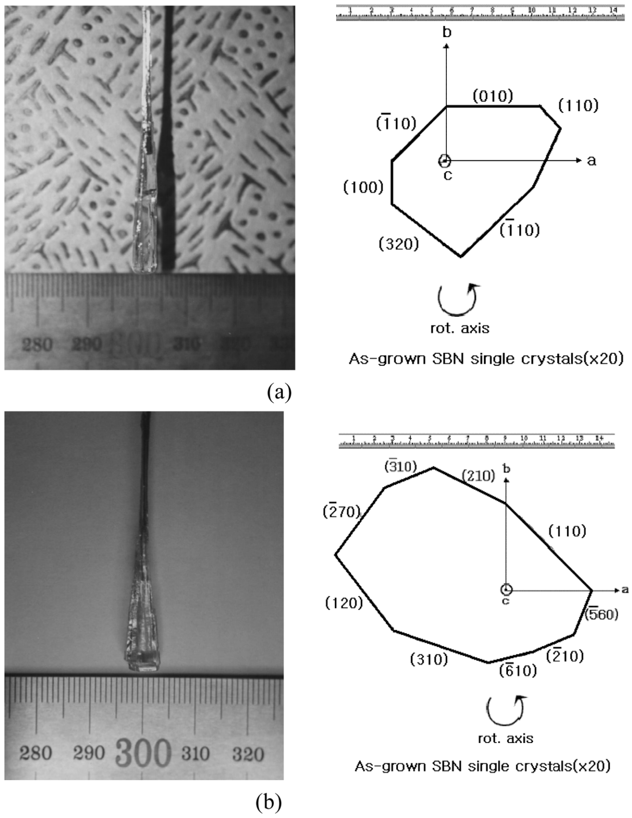


Fig. 1. As-grown 60SBN (a) and 75SBN (b) single crystals and its facets.

Table 1
Growth condition of 60SBN and 75SBN

	Pulling rate (mm/hr)	Rotation rate (rpm)	Atmosphere
60SBN	2	8	O_2 gas
75SBN	4	15	O_2 gas

Fig. 4(a), (b) illustrate the temperature and frequency dependence of the dielectric constants of 60SBN and

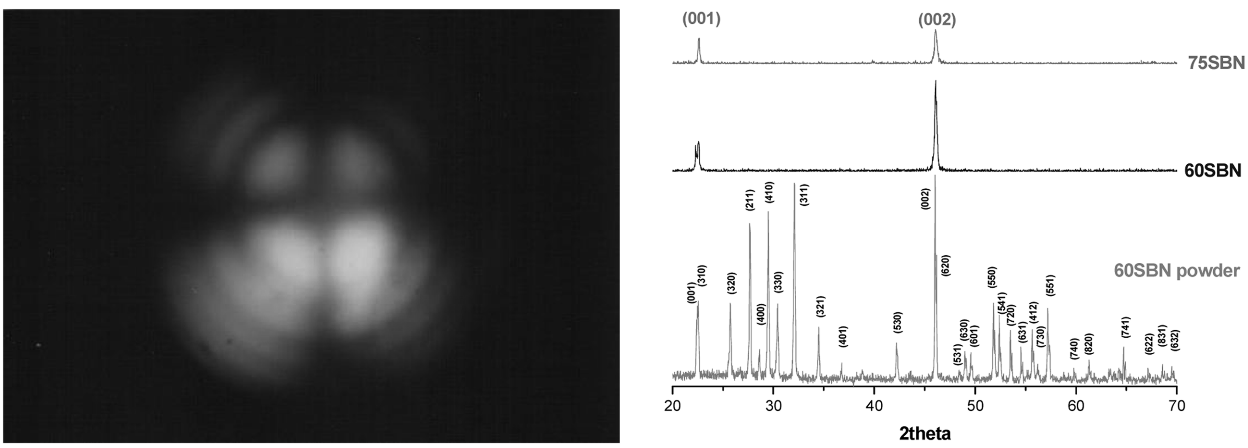


Fig. 2. Conoscope image and XRD patterns of as-grown crystals (c-axis//pulling direction).

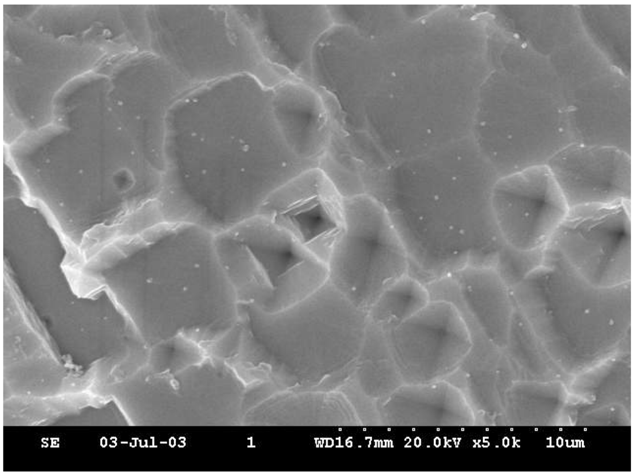


Fig. 3. Etch pit of 60SBN single crystals.

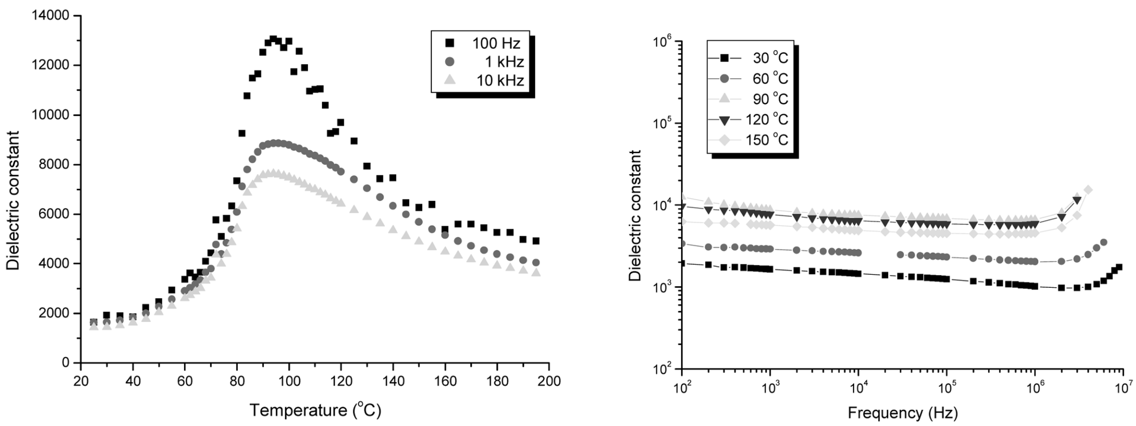
75SBN single crystals. Situation of the phase transition in SBN ceramics was explained by relaxor-type, that is to say “smeared” or “diffused”. To describe this situation of the conventional transition behavior, a “random-field Ising model” as a consequence of structural and compositional inhomogeneity was introduced. When the temperature is lowered below the transition, domains become more and more cooperative, until a ferroelectric state is reached [14]. The dielectric maxima peaks shift to higher temperature with increasing frequency that is similar to what is observed in typical diffusive phase transition (DPT) ferroelectrics.

Both specimens had almost same frequency dependence of the dielectric constants, but at high frequency above 100 kHz dielectric constants increase significantly [15, 16]. These results represent implying a promising candidate for electro-optics device applications.

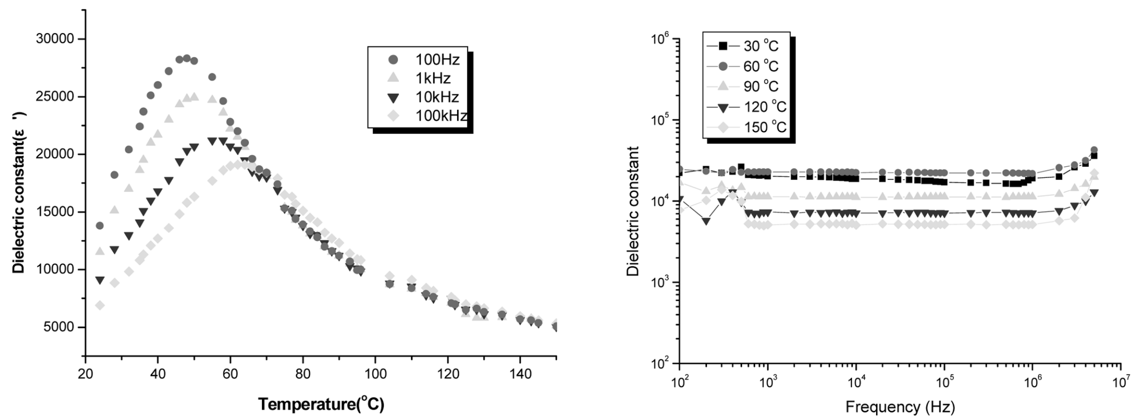
Fig. 5 shows the absorption coefficient of as-grown 60SBN and 75SBN single crystals. Optical transmittance of 60SBN has a wide range than 75SBN single crystals. These optical properties are being studied.

4. Conclusions

60SBN and 75SBN single crystals grown by Czo-



(a)



(b)

Fig. 4. Temperature- and frequency-dependence of dielectric constant for 60SBN (a) and 75SBN (b) single crystals.

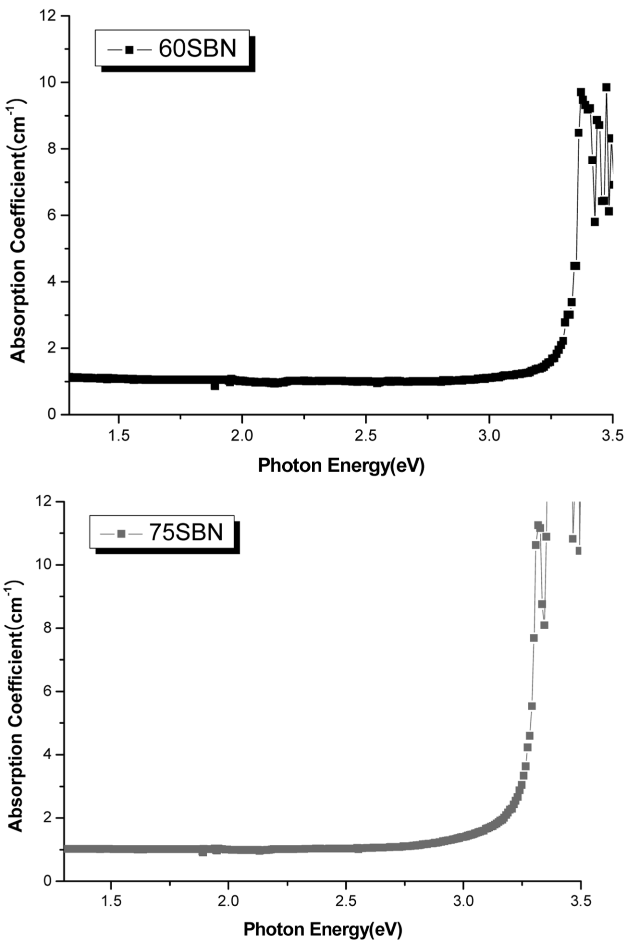


Fig. 5. Absorption coefficient of 60SBN and 75SBN single crystals.

chralski method using Pt wire seed. Growing direction was <001>, and as-grown crystals had well-developed (110) plane. Situations of the phase transition in SBN crystals were explained by relaxor-type and dielectric properties of temperature dependence indicated a strongly diffused phase transition (DPT). From these results, we suggested implying a promising candidate for electro-optics device applications.

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