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Structural, dielectric and optical properties of barium strontium sodium niobate $(Sr_{0.7}Ba_{0.3})_2NaNb_5O_{15}$ single crystals

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Abstract

Barium strontium sodium niobate $(Sr_{0.7}Ba_{0.3})_2NaNb_5O_{15}$ (SBNN70) crystals were grown by the Czochralski method. X-ray energy dispersive spectrometry showed that SBNN70 crystals have a stoichiometric composition nearly identical to the starting materials. X-ray diffraction of crushed powder indicated that the SBNN70 crystals are orthorhombic with $a = 1.2748$ nm, $b = 1.1402$ nm and $c = 0.3898$ nm. The measured temperature dependence of dielectric constants showed strongly anisotropic relaxor behaviour. The Curie temperature of the SBNN70 crystals is 186.7°C, which is 116°C higher than that of the $(Sr_xBa_{1-x})_5Nb_{10}O_{30}$ (SBN) crystal. The transmissivity and refractive index of [001] oriented SBNN70 single crystals were measured, and a deep energy level of 3.54 eV was found. The SBNN70 crystal has better than 70% optical transmittance for wavelengths above 500 nm. The refractive index of SBNN70 is 2.004 at 632.8 nm, which is lower than 2.3117 for SBN crystals.

1. Introduction

The strontium barium sodium niobate system $(Sr_xBa_{1-x})_2NaNb_5O_{15}$ (SBNN), with a tungsten bronze structure, is a lead-free ferroelectric system [1]. Many properties of SBNN ceramics, such as crystallographic, optical, electro-optical and electrical properties, have been studied for applications in electro-optics and second-harmonic generation [2–4]. SBNN has a structure similar to $(Sr_xBa_{1-x})_5Nb_{10}O_{30}$ (SBN), but its Curie temperature can be much higher than that of SBN [4, 5]. SBN single crystals have been studied extensively for acoustic, pyroelectric, electro-optic and nonlinear optical applications because SBN has a large electro-optical coefficient and is also strongly nonlinear, which is useful for second harmonic generation [3–7]. However, SBN crystals have a low Curie temperature, making them easily depolarized near room temperature. If the Curie temperature can be increased, the material would be more useful for practical devices.

In SBNN, Na ions are introduced into the empty lattice sites of SBN. Similar to the function of K and Na ions in $(K_{0.5}Na_{0.5})_{0.2}(Sr_{0.75}Ba_{0.25})_{0.9}Nb_2O_6$ (KNSBN) crystal [8], the Na in the SBNN system increases the Curie temperature. Although the properties of SBNN ceramics have been evaluated, there are no reports on the properties of SBNN single crystals.

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Recently, we have fabricated some SBNN70 single crystals ($x = 0.7$) in an attempt to find a new a kind of lead-free ferroelectric materials with a high Curie temperature and better functional properties. In this paper, we will report the structural, dielectric and optical properties of SBNN70 crystals measured experimentally.

2. Experimental details

The SBNN70 single crystals were grown at 1500˚C by the Czochralski technique using high purity $SrCO_3$, $BaCO_3$, Nb_2O_5 and Na_2CO_3. The crystal growth procedures have been reported in detail in [5]. The crystals obtained have excellent optical quality. From experimental results obtained with an eagle x-ray spectrometer, SBNN70 crystals have congruent composition. Platelet samples of single crystal SBNN70 with thickness 1–2 mm were cut along the crystallographic plates [100], [010] and [001] of the orthorhombic phase and then polished to optical quality. Gold film was deposited onto the large surfaces of each sample as electrodes. Polycrystalline fine powder samples for differential scanning calorimeter (DSC) and x-ray diffraction (XRD) were prepared by grinding the as-grown single crystals.

The crystal structure and lattice parameters of SBNN70 were measured using a SIEMENS D5000 powder x-ray diffractometer using Cu_Kα1 radiation. DSC was utilized to study the nature of the phase transition using a Perkin Elmer DSC-2910 DSC, and the polycrystalline powder samples were sealed in aluminium pans and then heated up to 300˚C at a rate of 10˚C min^{-1}. The dielectric constants were studied as a function of temperature using an Agilent 4294A LCR meter at frequencies of 10^3 Hz, 10^4 Hz, 10^5 Hz and 10^6 Hz, respectively. Samples were placed in a delta chamber, where the temperature was controlled within ± 0.1˚C, and data were collected in the temperature range 20–300˚C. The dielectric constant ε was calculated from the parallel-plate approximation. The optical transmittance of these samples was measured using a Lambda2s UV/VIS spectrophotometer, and the wavelength dispersion curve of the refractive index of [001] oriented SBNN single crystals was studied by a phase modulator type spectroscopic ellipsometer UVISEL.

3. Results and discussions

Figure 1 shows the powder XRD pattern with assigned (hkl) values of the SBNN70 single crystal, which indicates that the crystal has orthorhombic symmetry at room temperature. Some reports showed that there is a tetragonal–orthorhombic morphotropic phase boundary (MPB) at $x = 0.5$–0.6 for SBNN ceramics [5, 9]. For SBNN ceramics with $x > 0.6$, their structures show orthorhombic symmetry. In our experiment, the SBNN70 single crystal has an orthorhombic structure with lattice parameters of $a = 1.2748$ nm, $b = 1.1402$ nm and $c = 0.3898$ nm. X-ray spectrometric analysis shows that the composition of SBNN70 has the mole ratio Sr : Ba = 0.73 : 0.27. The Ba^{2+} content is slightly lower than the Sr^{2+} content compared with the starting materials because the segregation coefficient of Sr^{2+} is larger than that of Ba^{2+} [5].

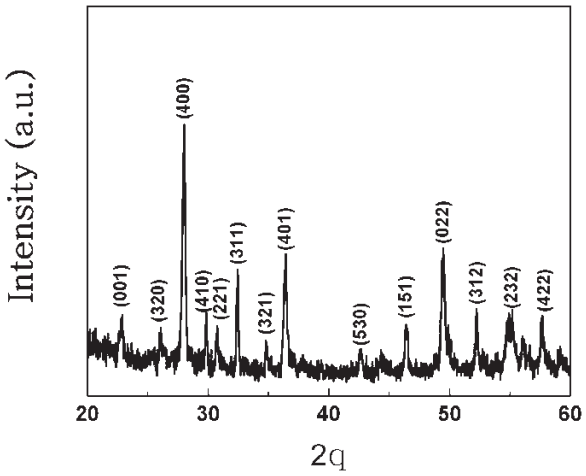

Figure 1. XRD patterns of SBNN70 single crystals grown by the Czochralski technique (crushed powder).

The dielectric dispersions of SBNN70 in the same temperature range along [100], [010] and [001] have been studied, and the data are shown in figures 2(a)–(c), respectively. A strong orientational dependence can be seen clearly. The peak temperature of the dielectric constant, T_c, for [100] and [010] oriented samples is 189.2˚C and 184.5˚C, respectively. No peak temperature shifting was found in these two samples of different orientations when the frequency was changed, but the amplitude of the peak decreases with frequency in both cases. On the other hand, for the [001] oriented sample, the peak temperature, T_{max}, increases from 185.7˚C to 188.5˚C as the frequency is increased from 1 kHz to 1 MHz. The maximum dielectric constant at T_{max} along [001] is about 70 times that along [100] and [010]. As shown in figure 2(c), as the frequency increases, the dielectric constant decreases and peak broadening occurs, accompanied with shifting of T_{max} to higher temperature. These results indicate that the SBNN70 crystal belongs to relaxor ferroelectrics, and the relaxor behaviour is strongly anisotropic.

At the ferroelectric phase transition, the dielectric constant of SBNN70 along the polar C-axis shows a very large peak. From figure 2, we can see that T_c of SBNN70 is between 184.5˚C and 189.2˚C. From the DSC data, the T_c value was indicated to be 186.7˚C. This Curie temperature is 117˚C higher than that of SBN single crystals, so that the material properties become much more stable at room temperature. The [001] oriented SBNN70 also shows a higher dielectric constant ($\sim 5 \times 10^4$) at T_{max} than that of the SBN crystal (3.3×10^4) at its peak temperature [10]. The frequency dispersion near the transition temperature reflects the dynamical nature of polar clusters, correlated by random fields above T_{max} and the slow domain wall dynamics below T_{max} [11]. The critical temperatures obtained from both the dielectric constant and DSC measurements show that SBNN70 single crystals exhibit higher T_c values than SBN crystals ($T_c \sim 70$˚C) at the same frequency. The T_c of SBNN is even higher than the T_c of the KNSBN crystal ($\sim$150˚C) [8]. From a crystallographic point of view, the SBNN70 crystal has an intermediate structure between SBN and $(Ba_2Na)Nb_5O_{15}$ (BNN). In BNN, both tetragonal and pentagonal interstices are completely occupied by Na and Ba ions, whereas the SBN is a rather disordered

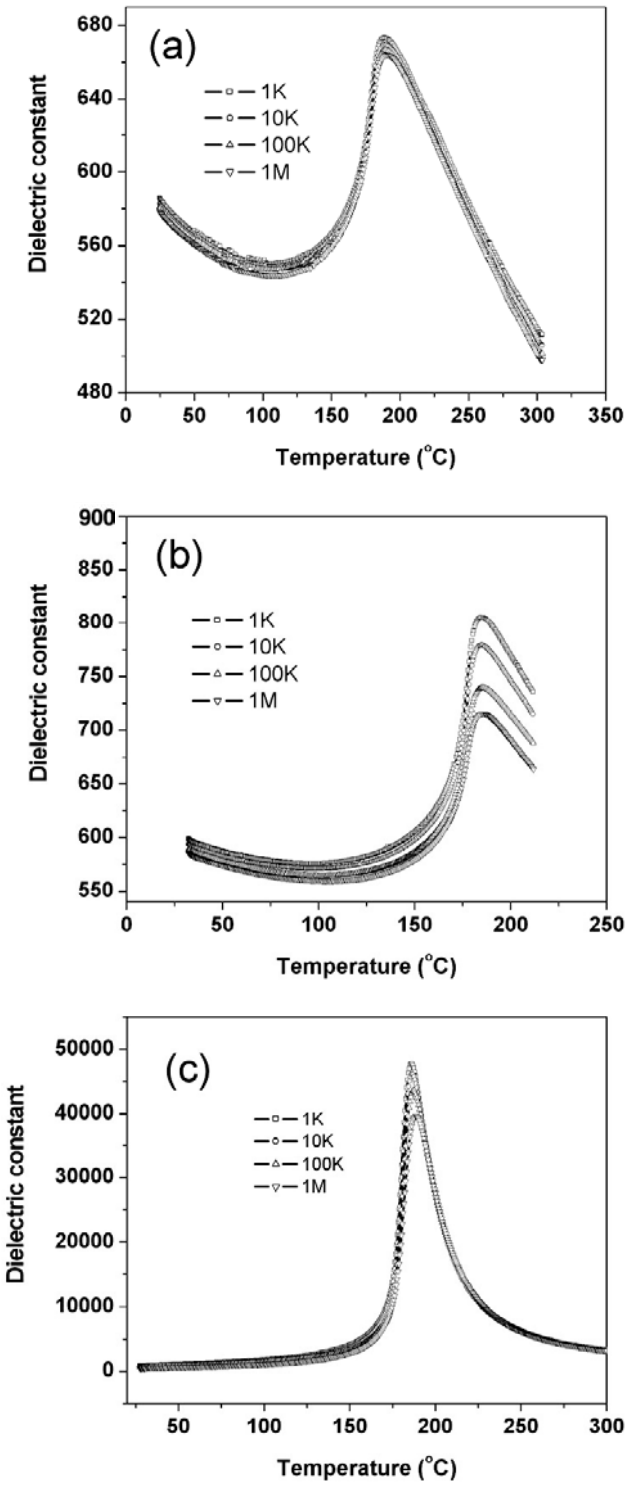

Figure 2. Dependence of the dielectric constant on temperature at different frequencies: 10^3, 10^4, 10^5, 10^6 Hz. (*a*) [100] orientation, (*b*) [010] orientation and (*c*) [001] orientation of SBNN70 single crystals.

system, in which Sr and Ba ions are distributed randomly and $\frac{1}{6}$ of the interstices remain vacant. So the BNN crystal shows a high Curie temperature of about 580°C [12] but the Curie temperature of SBN depends on the Sr–Ba composition. With the same Sr–Ba composition, addition of Na to the SBN increases its Curie temperature.

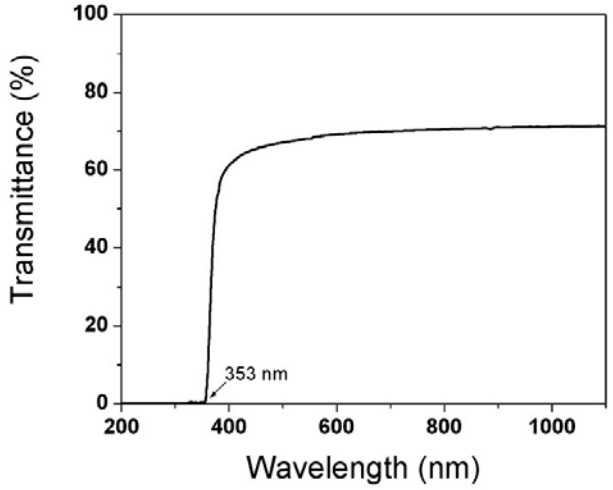

Figure 3. The wavelength dependence of the transmittance of [001] oriented SBNN70 single crystal.

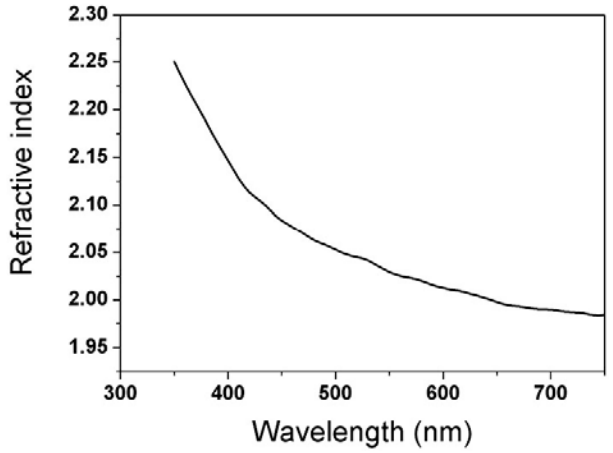

Figure 4. Dispersion of the refractive index of SBNN70 single crystal obtained by ellipsometry.

Figure 3 shows the transmission spectra of SBNN70 crystals. The transmittance decreases to zero at a wavelength of approximately 353 nm. For practical purposes, the optical transmittance of the SBNN70 crystal is high enough (∼70% transmittance at wavelengths above 500 nm) to make it a good candidate for many electro-optical applications. Based on the ligand field theory for transition metals, the curve implies the eigentransition of the d-electrons of Nb with an electron configuration (Kr) $4d^45s^1$ and shows a band gap of about 3.54 eV (353 nm) [13].

The linear refractive indices of the samples have been measured using ellipsometry. Figure 4 shows the wavelength dispersion curve of the refractive index of [001] oriented SBNN70 crystals. The linear index at 632.8 nm was determined to be 2.004. This value is smaller than that of bulk SBN (∼2.3117) [14].

4. Summary and conclusions

In summary, ferroelectric single crystal SBNN70 have been grown successfully by the Czochralski method. Powder XRD

data showed that the SBNN70 single crystal is orthorhombic with $a = 1.2748$ nm, $b = 1.1402$ nm and $c = 0.3898$ nm. X-ray spectrometric analysis shows that SBNN70 has a slightly lower Ba^{2+} content compared with the starting material because the segregation coefficient of Sr^{2+} is larger than that of Ba^{2+}. No relaxational behaviour was observed in [100] and [010] oriented samples, but the [001] oriented samples show an obvious relaxation behaviour and a very high dielectric constant value at T_{max}. These results clearly illustrate that the relaxor behaviour of SBNN70 is strongly anisotropic.

Adding Na ions makes the properties of SBNN70 changed greatly compared with SBN. The [001] oriented SBNN70 single crystal shows a very high dielectric constant peak of about 5×10^4 and a high Curie temperature of $T_c = 186.7^{\circ}$C. These values are much higher than those of SBN ($T_c \sim 70^{\circ}$C and peak value of 3.3×10^4). The crystals show excellent optical properties with optical transmittance greater than 70% at wavelengths above 500 nm. This value is high enough to make the SBNN70 crystal a good candidate for electro-optical applications. The linear index is 2.004 at 632.8 nm, which is smaller than that of bulk SBN (∼2.3117).

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