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Brillouin Scattering Study of Ferroelectric Instability of Calcium Strontium Barium Niobate Crystals

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1. Introduction

The ferroelectric materials with tetragonal tungsten bronze (TTB) structure are technologically important for the optical application such as electro-optic, nonlinear optic, and photorefractive devices. The direction of spontaneous polarization is only along the *c*-axis of TTB structure, and they are called uniaxial ferroelectrics. The structural formula of TTB ferroelectrics is expressed by $(A1)_2(A2)_4(C)_4$-$(B1)_2(B2)_8O_{30}$ with corner sharing distorted BO_6 octahedra as shown in **Fig. 1**. In ferroelectric $Ba_2NaNb_5O_{15}$, all A1 and A2 are occupied by Ba^{2+} and Na^{1+} ions. It belongs to the filled TTB ferroelectrics, which undergo a normal ferroeletric sharp phase transition [1].

However, in $Sr_xBa_{1-x}Nb_2O_6$ (SBN100*x*), the A1 sites are occupied only by Sr^{2+} ions and the A2 sites are occupied by both Ba^{2+} and Sr^{2+} ions. Since 1/6(A1+A2) sites are unoccupied, it belongs to unfilled TTB ferroelectrics. The empty sites at A1 and A2 sites are the main sources of quenched random fields by the charge disorder, which enhance the diffuseness of phase transition. The disadvantage of SBN in application are the relatively low Curie temperatures.

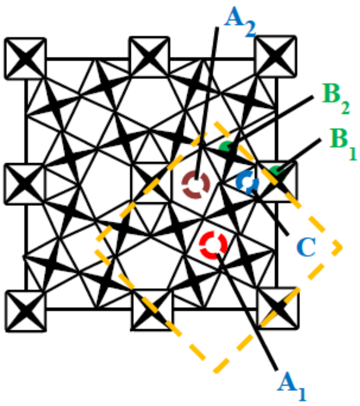

Fig. 1 Crystal structure of tetragonal tungsten bronze ferroelectrics along the *c*-axis perpendicular to the plane.

By the substitution of Sr by Ca, the Curie temperature of $Ca_xBa_{1-x}Nb_2O_6$ (CBN100*x*) increases more than 100 ºC [3]. The Curie temperatures of *x*CBN28-(1-*x*)SBN61 (CSBN100*x*) are shown in **Fig. 2**. As the CBN28 content increases, the Cuie temperature markedly increases by about 200 ºC. The CSBN25 was characterized by relaxor properties due to lower excess oxygen compared with CSBN50 and CSBN75 crystals. CSBN25 also has more nonuniform distribution of elements, which occupy the same position (A1) in TTB structure [4].

In 1922 L. Brillouin predicted inelastic light scattering by thermally excited sound waves. Since that time Brillouin scattering has been used as a non-contact and non-destructive method to measure sound velocity and attenuation [5]. In the present study, the elastic properties of CSBN100*x* crystals were investigated using Brillouin scattering spectroscopy.

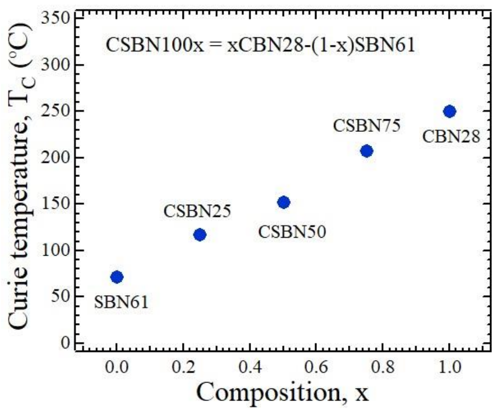

Fig. 2 Ferroelectric Curie temperatures of calcium strontium barium niobate crystals with TTB structure.

2. Experimental

CSBN100*x* single crystals were grown by the Czochralski method for the compositions, *x* = 0, 0.25, 0.5, 0.75, 1.0 (SBN61, CSBN25, CSBN50, CSBN75, CBN28). Single crystal plates were cut along [001] (*c*-plate) with optically polished 5 mm × 5 mm surfaces and 1 mm thickness. Brillouin scattering spectra were measured at the back scattering geometry using a high-contrast 3+3 passes tandem Fabry-Perot interferometer with a free spectral range of 75 GHz for longitudinal acoustic (LA) and transverse acoustic (TA) modes and 300 GHz for the

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central peak of polarization fluctuations along the ferroelectric c-axis. The exciting source was a diode-pumped solid state (DPSS) laser with a wavelength of 532 nm. The specimen temperature was controlled by a cooling/heating stage (Linkam THMS600) with a stability of ± 0.1 °C [6].

3. Results and discussion

The temperature dependence of frequency shift and width of the LA mode, which propagates along the ferroelectric *c*-axis, was measured as shown in **Fig. 3**. Upon cooling from the high temperature above Burns temperature, the LA frequency shows the remarkable softening toward the Curie temperature, T_C = 152 ºC. The LA mode width shows marked increase toward T_C. This elastic anomaly is related to the temperature evolution of polar nanoregions (PNRs) caused by the random fields. In a ferroelectric phase, the width does not decrease markedly by the scattering of LA modes at frozen PNRs.

The composition variation of LA frequency shift is shown as a function of temperature in **Fig. 4**. The elastic anomaly of CBN28 with very weak random fields is different from that of SBN61 with strong random fields. In SBN61, the temperature dependence of the LA mode frequency in the vicinity of T_C = 72 ºC, is diffusive and no remarkable change near T_C is observed. On the other hand, in CBN28, the elastic anomaly is more remarkable. These differences can be caused by the variation in the strength of the random fields which suppress the sharp changes in the vicinity of T_C.

The temperature dependences of relaxation time of polarization fluctuations determined by a central peak along the c-axis shows the critical slowing down toward $_T$C. However, as the Sr content increases, the slowing down is stretched by the strengthened random fields.

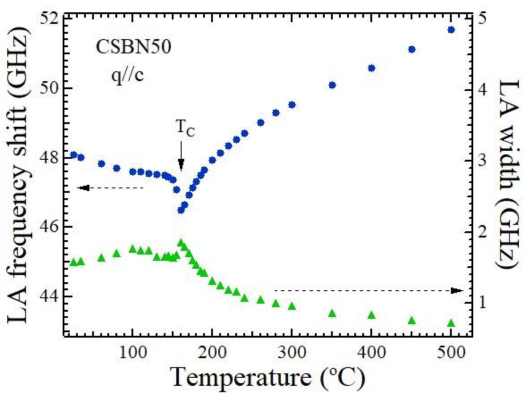

Fig. 3 Temperature dependence of LA frequency shift and width along the ferroelectric *c*-axis of a CSBN50 crystal.

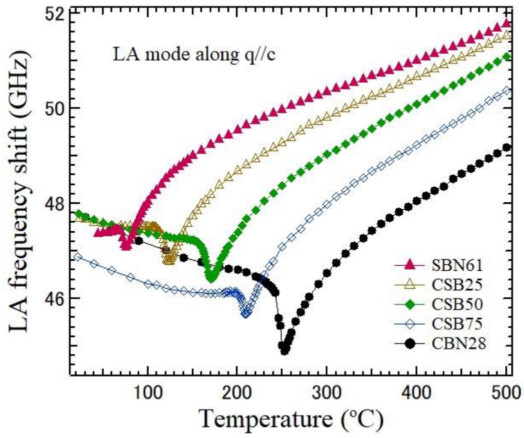

Fig. 4 Temperature dependence of LA frequency shift which propagates along the ferroelectric *c*-axis of CSBN crystals.

4. Conclusion

The elastic anomalies of uniaxial ferroelectric CSBN single crystals were studied by Brillouin scattering spectroscopy. A CBN28 crystal shows the sharp elastic anomaly toward T_C, however, those of CSBN75 and SBN61 crystals appear diffused due to stronger random fields. The elastic anomaly of CSBN crystals in the vicinity of T_C becomes sharp as the Ca content increases.

Acknowledgment

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