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Brillouin Scattering Spectroscopy of Uniaxial Relaxor Ferroelectric Calcium Barium Niobate

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1. Introduction

The uniaxial ferroelectric materials with tetragonal tungsten bronze (TTB) structure are technologically important for the optical applications such as electro-optic, nonlinear optic, and photorefractive devices. The direction of spontaneous polarization is only along the *c*-axis of TTB structure. At low temepratures, the polar instability pependicular to the *c*-axis appears, while the direction of a spontaneous polarization is invariant. 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**. The A1 and A2 sites are occupied by alkali or alkali earth ions. The B1 and B2 sites are occupied by Nb, Ta ions [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 [2]. The disadvantage of SBN in application is the relatively low Curie temperature.

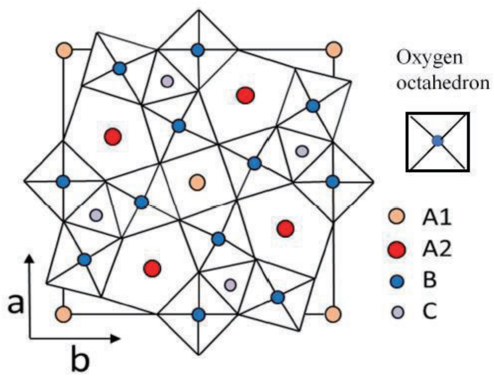

Fig. 1 Crystal structure of tetragonal tungsten bronze ferroelectrics on the (001) plane.

By the substitution of Sr by Ca in SBN, the Curie temperature of $Ca_xBa_{1-x}Nb_2O_6$ (CBN100*x*) increases more than 100 °C in comparison with that of SBN61 with T_C=72 °C [3,4]. The Ca content dependence of Curie temperatures of CBN100*x* are shown in **Fig. 2**. As the Ca content decreases from CBN32, the Cuie temperature markedly increases by about 100 °C. CBN26 undergoes a ferroelectric phase transition with weak relaxor nature, while CBN32 undergoes a typical relaxor ferroelectric phase transition.

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 temperature dependences of elastic properties of CBN100*x* crystals were investigated by using Brillouin scattering spectroscopy.

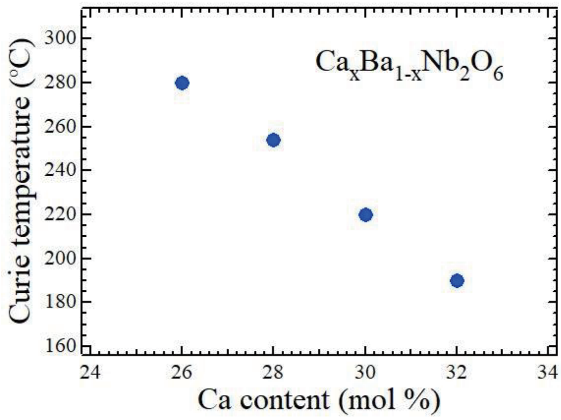

Fig. 2 Ferroelectric Curie temperatures of calcium barium niobate crystals.

2. Experimental

CBN100*x* single crystals were grown by the Czochralski method for the compositions, *x* = 0.26, 0.28, 0.30, 0.32 (CBN26, CBN28, CBN30, CBN32). 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 central

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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 [3].

3. Results and discussion

The temperature dependences of frequency shift and width of the LA mode, which propagates along the ferroelectric c-axis, was measured in CBN26 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 = 280 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 temperature dependence of LA frequency shift which propagates along the ferroelectric c-axis of a CBN32 crystal is shown in **Fig. 4**. The elastic anomaly of CBN32 with stronger random fields is different from that of CBN26 with weak random fields [6]. In CBN32, the temperature dependence of the LA mode frequency in the vicinity of T_C is diffusive and no remarkable change near T_C is observed. On the other hand, in CBN26, the elastic anomaly occurs in a narrow temperature range. This difference can be caused by the difference in the strength of the random fields which suppress the sharp elastic anomaly in CBN26 in the vicinity of T_C.

The temperature dependences of relaxation time of polarization fluctuations of a CBN26 crystal determined by a central peak along the c-axis shows the critical slowing down toward T_C. However, as the Ca content increases, the slowing down is stretched by the strengthened of random fields.

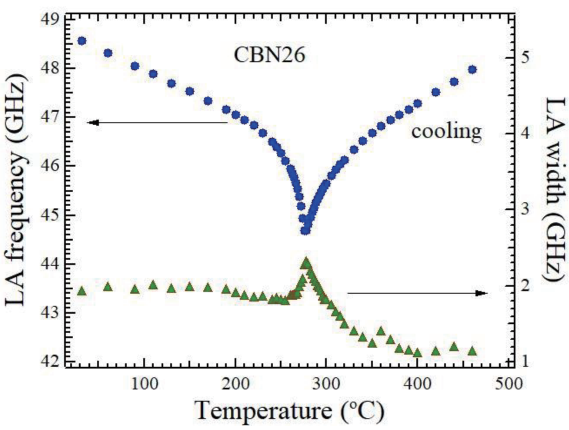

Fig. 3 Temperature dependence of LA frequency shift and width on cooling along the ferroelectric c-axis of a CBN26 crystal.

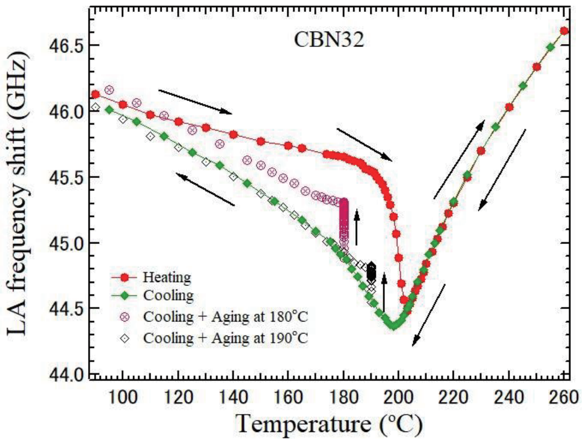

Fig. 4 Temperature dependence of LA frequency shift which propagates along the ferroelectric c-axis of a CBN32 crystal. Aging is observed at 180 and 190°C.

4. Conclusion

The elastic anomalies of uniaxial relaxor ferroelectric CBNx single crystals were studied by Brillouin scattering spectroscopy. A CBN26 crystal shows the sharp elastic anomaly toward T_C, however, those of CBN30 and CBN32 crystals exhibit diffused due to stronger random fields. The elastic anomaly of CBNx crystals in the vicinity of T_C becomes diffusive as the Ca content increases.

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