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Elastic anomaly and aging of new type of incommensurate phase transition in ferroelectric barium sodium niobate

強誘電体 $Ba_2NaNb_5O_{15}$ の新型不整合相転移の弾性異常

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1. Introduction

$Ba_2NaNb_5O_{15}$ (BNN) with a tungsten bronze crystal structure undergoes successive phase transitions at 833 K [1], and 573 K. At room temperature BNN is ferroelectric and ferroelastic with orthorhombic point group of *mm*2 [2]. At 573 K, it undergoes a ferroelastic to paraelastic phase transition in to the normal tetragonal phase with polar point group of 4*mm*. At 833 K it undergoes a phase transition from ferroelectric to a paraelectric tetragonal phase with nonpolar point group 4/mmm. The orthorhombic phase has the incommensurate (IC) modulation which couples a spontaneous strain e_6, and it was assigned the new type of IC instability [3]. The IC phase transforms to a normal phase at 573 K and the spontaneous strain disappears. The IC phase has a unique feature distinguishable from other kinds of normal phase transitions, of which modulation period is not a simple integral multiplication of its parent lattice [3].To provide better understanding of the elastic anomaly and aging in the new type of IC phase, detailed temperature and time dependences of Brillouin scattering spectra of BNN was studied.

2. Experimental

Single-crystal of $Ba_2NaNb_5O_{15}$ was grown using Czochralski method in NEC. The two surfaces of *a*-cut (100) plate with the size of 3.5×3.5×0.7 mm were polished to optical grade. The Brillouin scattering spectra were measured at the backward scattering geometry using a Sandercock-type 3 + 3 pass tandem Fabry-Perot interferometer and a conventional photon counting device. A green YAG laser with wavelength of 532 nm and 100 mW output was used as an exciting light source. A heating/cooloing stage (Linkam T1500) was utilized as a temperature controller in the temperature range from 303 K to 1073 K.

3. Results and Discussion

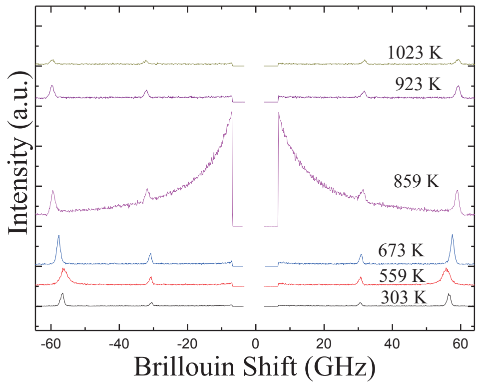

Fig 1. Temperature dependence of Brillouin scattering spectra of BNN at a(cc)$\bar{a}$.

The observed spectra at several selected temperatures are shown in **Fig 1**. As observed from Fig. 1, the LA peaks can be clearly observed around 57 GHz, and then it shifted to approximately 56 GHz at 559 K which is in the IC phase transition temperature range of BNN. TA peaks can be observed faintly at around 30 GHz at 303 K, and remained the same through 1023 K. In addition the strong central peak reflecting polarization fluctuation along the *c*-axis was observed in the vicinity of the Curie temperature, T_C=833 K. A CP appeared at the paraelectric phase transition temperature at 859 K and then gradually vanishes as temperature increases. Using the observed spectra, LA mode frequency and width were determined by the curve fitting. The obtained result is presented in **Fig. 2** displayed below.

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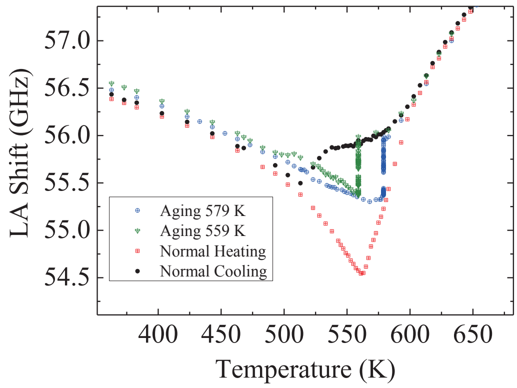

Fig 2. Temperature dependence of LA Frequency shift of BNN upon heating and cooling with aging.

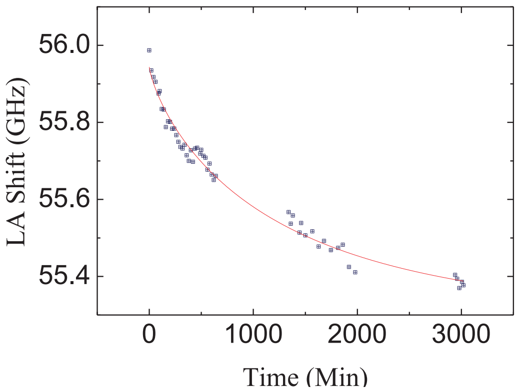

Fig 3. Aging of LA frequency shift at 559 K

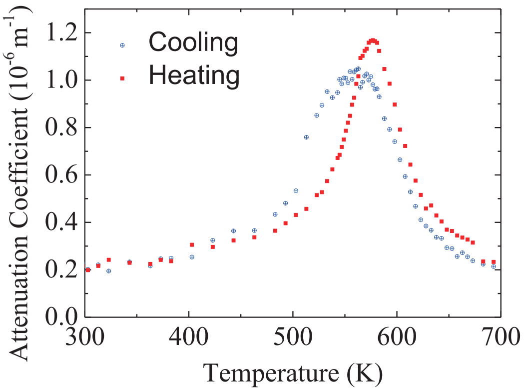

Fig 4. Temperature dependence of attenuation coefficient of LA mode.

From **Fig. 2**, it is clear that at the range of about 500 K to 600 K, thermal hysteresis occurred during cooling. Compared to normal ferroelastic phase transition, the appearance of this thermal hysteresis is improbable. At the IC phase transition, the crystal symmetry undergoes a change from the tetragonal to the orthorhombic. However, the order parameter of a ferroelastic phase transition is not a shear strain. For BNN, the lattice instability occurs at M-point ,[1/2, 1/2, 0] in the Brillouin zone, which is located far from the commensurate (C) lattice instability point of [1/4, 1/4, 1/2] in the Brillouin zone [3]. Upon heating, the IC modulation disappears conveniently at a IC to normal (N) transition temperature ≈ 573 K. In contrast, upon cooling it requires a considerable amount of time to form the IC modulation [4]. **Fig. 2** shows the aging compared with normal heating and cooling processes. On both 579 K and 559 K, before aging was started, sample was first heated up above T_C and then cooled down at the rate of 3 K/min. The change in the LA Shift related to time is plotted on **Fig. 3**. The observed curves were fitted using the Kohlrausch-Williams-Watts (KWW) function as shown below:

$$f_b(t) = A_0\, exp(-(t/\tau)^{\beta}),$$

where A_0 is a constant, τ is a relaxation time, and β acted as a stretched exponent with the value between 0 and 1. At 559 K, $A_0 = 55.30$, $\beta = 0.78$, and $\tau = 1290$ min were determined. As can be seen from **Fig. 4**, upon heating a broad peak of attenuation coefficient was observed at 579 K, while upon cooling at around 565 K. These temperatures are related to the thermal hysteresis of the N-IC phase transition temperature. This remarkable increase of attenuation coefficient of the LA mode is attributed to the appearance of the macroscopic shear strain [4].

4. Conclusion

Brillouin scattering were measured on a $Ba_2NaNb_5O_{15}$ (BNN) crystal. Heating and cooling processes were measured at a heating/cooling rate on average of 3 K/min. The remarkable thermal hysteresis of the LA frequency shift was observed on the N-IC phase transition. In addition, the aging was investigated at several temperatures. The KWW type relaxation was recorded for 559 K reflecting the metastable nature of the IC phase. The attenuation coefficient shows a broad peak near the N-IC phase transition temperature of 573 K.

References

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