Normal-incommensurate phase transition in (Sr$_{1-x}$Ba$_x$)$_2$Nb$_2$O$_7$ ferroelectric single crystals

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Abstract

Micro-Brillouin and Raman light scattering experiments were performed on (Sr$_{1-x}$Ba$_x$)$_2$Nb$_2$O$_7$ single crystals to investigate the effect of Ba addition on the normal-incommensurate phase transition. From the Brillouin frequency shift results, it was observed that the onset temperature of the normal-incommensurate phase decreased with increasing Ba concentration. This was associated to the suppression of the octahedra tilting due to substitution of larger ion on the A-site. The Raman intensity of the Q soft mode measured at room temperature also showed a similar behaviour with increasing $x$.

Keywords: Phase transition; Inelastic light scattering; Acoustic properties

1. Introduction

Sr$_2$Nb$_2$O$_7$ is a layered perovskite-type ferroelectric material with exclusively very high Curie temperature ($T_c = 1342 \pm 2 ^\circ$C). Its single crystals have been studied extensively due to their remarkable piezoelectric properties [1–3]. It has low dielectric constant, coercive field and high heat resistance is expected because of its high melting point ($\sim 1700 ^\circ$C). Owing to its interesting properties, attention has been focused for its applications in high density non-volatile ferroelectric random access memory (FERAM) cells [4]. Moreover, its bismuth and lead free nature makes it good candidate as a green material from environmental point of view.

It belongs to the family of compounds with the crystal chemical formula $A_nM_4O_{3n+2}$ with $n=4$. Sr$_2$Nb$_2$O$_7$ consists of NbO$_6$ octahedra framework that distorts and tilts with temperature changes, undergoing successive phase transitions. In the paraelectric phase (above $T_c$), $Cmcm$ space group has been proposed. In the ferroelectric phase, the space group changes to $Cmc2_1$ [2] and the spontaneous polarization appears along the orthorhombic c-axis. At room temperature, the spontaneous polarization $P_s = 9 \times 10^{-2}$ C.m$^{-2}$ is parallel to the c-axis and the coercive field is $E_c = 6 \times 10^3$ V.cm$^{-1}$. At $T_c = 215 ^\circ$C, it undergoes into a second order normal-incommensurate (IC) ferroelectric phase transition modulated with the wave vector $q = (1/2 - \delta)a^*$, $\delta$ being temperature-dependent. This transition was observed in the elastic compliance coefficients, electromechanical coupling, permittivity, and birefringence. The lattice instability studies revealed the soft optic modes responsible for the first and second phase transitions, and for the normal-IC phase transition [5]. As for Ba doped (Sr$_{1-x}$,Ba$_x$)$_2$Nb$_2$O$_7$ single crystals, it was shown that $T_c$ decreases from 1342 to $\sim 127 ^\circ$C for $x = 0.6$ [1] and the low temperature phase transition ($T \sim 177 ^\circ$C) with appearance of a new ferroic phase at $T \sim 127 ^\circ$C [6]. However; the effect of Ba doping on the normal-IC phase transition is unknown. In continuation of our previous work [7,8], here we report for the first time the effects of Ba doping on the normal-IC phase transition temperature $T_c$ by using micro-Brillouin and Raman light scattering techniques.

The present investigations were carried out for $x$ values up to 0.16 only, because it was more difficult to grow single crystals of reasonable size with increasing Ba concentration.
Moreover; the purpose of the present studies was to investigate the effect of Ba addition on the normal-incommensurate phase transition, and the acoustic anomaly could be observed only along $b$-axis [7]. Therefore; the experiments were carried out for the scattering wave-vector only along $b$-axis.

2. Experimental

(Sr$_{1-x}$Ba$_x$)Nb$_2$O$_7$ ferroelectric single crystals were grown by a floating zone technique [6]. Micro-Brillouin light scattering experiments were carried out by using a Sandercock tandem Fabry-Pérot interferometer in the 180° backscattering geometry with a free spectral range (FSR) of 75 GHz. A single frequency, Ar$^+$-ion laser at a wavelength of 514.5 nm and a power of about 100 mW was used to excite the crystals. The crystals were placed in a cryostat cell (THMS 600) and the temperature was varied from ~600 to −190 °C with an accuracy of ±1 °C and a stability of ±0.1 °C.

To study the doping effect of Ba on the behaviour of an optical soft mode related to the normal-IC phase transition, the Raman spectra were also measured at room temperature. The crystals were excited with a solid state laser with a wavelength of 532 nm and a power of ~50 mW. The scattered light was collected by a focal lens in the $b_{cc}b$ backward scattering geometry and analyzed by a triple grating spectrometer (Jobin Yvon, T64000) with a resolution of 2.5 cm$^{-1}$.

3. Results and discussion

The sample temperature was initially raised to ~600 °C and then micro-Brillouin spectra were measured by cooling the crystals subsequently down to ~−190 °C. Typical Brillouin spectra associated with the acoustic phonon modes in (Sr$_{1-x}$Ba$_x$)Nb$_2$O$_7$ crystals for $x=0.08$ at some selected temperatures are plotted Fig. 1. The incident and the scattered wave vectors were taken along $b$-axis for all the measurements reported here. It can be seen (Fig. 1) that the measured spectra is composed of only one longitudinal acoustic (LA) mode. No transverse acoustic phonon modes could be observed in these measurements in the temperature range of interest. The instrumental function was assumed as a Gaussian and the phonon peaks were fitted with a Lorentzian function to obtain frequency shift ($\nu_{LA}$) of the Brillouin component. The resulting temperature dependence of the LA phonon mode frequency shift for all the measured compositions are shown in Fig. 2. The sound velocity of the LA mode ($V_{LA}$) can be obtained from the observed $\nu_{LA}$, which is related to the corresponding elastic stiffness coefficients $c_{ij}$ through the following relations.

\[ q = \frac{4\pi}{\lambda} n \sin \left( \frac{\theta}{2} \right) \]  
(1)

\[ V_{LA} = \frac{2\pi\nu_{LA}}{q} \]  
(2)

\[ c_{ij} = \rho (V_{LA})^2 \]  
(3)

where $q$ is the scattering wave vector with scattering angle $\theta$, $\rho$ is the crystal density (5.17×10$^3$ kg m$^{-3}$), $n$ is

![Fig. 1. Typical micro-Brillouin spectra of (Sr$_{1-x}$Ba$_x$)Nb$_2$O$_7$ single crystals for $x=0.08$, measured at some selected temperatures.](image1)

![Fig. 2. Temperature dependence of the observed Brillouin frequency shift ($\nu_{LA}$) of the longitudinal acoustic modes of (Sr$_{1-x}$Ba$_x$)Nb$_2$O$_7$ single crystals. The arrow indicates $T_i$ value for the crystal with $x=0.00$.](image2)
the refractive index $(2.15 \pm 0.02)$ and $\lambda = 514.5 \text{ nm}$ is the wavelength of laser, respectively. Although $n$ and $\rho$ will depend on $x$ and temperature, but for the purpose of present investigations they were assumed to be constant.

The temperature dependence of $n_{LA}$ (Fig. 2) was enhanced and exhibited a second order displacive type phase transition at $T_i \approx 215 \text{ °C}$. The interesting phenomenon observed in present measurements was that with increasing Ba concentration, normal-IC phase transition temperature lowered much as can be seen in Fig. 3. Moreover, the ratio of the slope of $n_{LA}$ in the IC phase to that of the normal ferroelectric phase also decreased markedly with increasing $x$ (Fig. 3).

The Raman spectra measured at room temperature in the $b(\overline{c}c)\overline{b}$ scattering geometry for all the compositions are plotted in Fig. 4. We could observe two optical soft modes P and Q, responsible for the paraelectric–ferroelectric and normal-IC phase transitions, respectively. It can be seen that the P mode does not show any $x$ dependence but the Q mode’s intensity decreased markedly with increasing Ba concentration. This behaviour is consistent with Brillouin light scattering results (Fig. 2). It is known that $T_i$ decreases with increasing $x$ [1] and the dielectric anomaly at $T \approx -177 \text{ °C}$ disappears for $x = 0.32$ ceramic [6]. Due to high sensitivity of the light scattering experiments, the present investigations show a clear change in $T_i$ with increasing Ba concentration.

Regarding the IC phase, a decrease in $\delta$ and appearance of higher harmonics usually results in the deformation of the modulation wave to a domain-like picture in which IC regions are reduced to periodic domain walls between the quasi-commensurate domains [9]. For pure crystals ($x = 0.00$), volume fraction of the IC regions might be very small due to appearance of the domain pattern and the crystal may be considered almost as a commensurate one. In the scenario observed here, $T_i$ decreases and also the concentration of the IC phase lowers (as seen by slope variations in Fig. 2), what happens to the R soft mode [5] that exists only in the IC phase (responsible for the low temperature dielectric anomaly at $\sim -177 \text{ °C}$) is not so clear. It is anticipated that due to substitution of larger atom (Ba) on A-site the tilting of the oxygen octahedra is suppressed that affects $T_i$ markedly. To elucidate these findings further investigations are in progress.

4. Conclusions

The effect of Ba addition on the normal-incommensurate phase transition temperature in the $b$-plate $(\text{Sr}_{1-x}\text{Ba}_x)_2\text{Nb}_2\text{O}_7$ single crystals were investigated using the micro-Brillouin and the Raman light scattering techniques. Temperature dependence of the acoustic phonon frequency shift showed a decrease in $T_i$ with increasing Ba that was associated to the suppression of the octahedra tilting due to substitution of larger ion on the A-site. The Raman spectra measured in $b(\overline{c}c)\overline{b}$ geometry showed that the intensity of the Q soft mode was also decreased for higher Ba contents.

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