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Order–disorder behavior of ferroelectric phase transition of KTa$_{1-x}$Nb$_x$O$_3$ probed by Brillouin scattering

Ryu Ohta,a) Junta Zushi, Takuma Arizumi, and Seiji Kojima
Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan

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The precursor dynamics of a cubic–tetragonal ferroelectric phase transition of potassium tantalate niobate (KTa$_{1-x}$Nb$_x$O$_3$ with $x=0.32$) is studied by Brillouin scattering. The appearance of the central peak (CP) and marked softening of the elastic constant $c_{11}$ are clearly observed above the Curie temperature, $T_{C-T}$, owing to the interaction between the LA mode and local polarization fluctuations of polar nanoregions (PNRs). The relaxation time determined by the CP width clearly shows a critical slowing down above $T_{C-T}$, indicating an order–disorder feature of the ferroelectric phase transition. The size of a dynamic PNR is evaluated, and it increases toward $T_{C-T}$. © 2011 American Institute of Physics [doi:10.1063/1.3560345]

Ferroelectric potassium tantalate niobate (KTa$_{1-x}$Nb$_x$O$_3$, KTN) is one of the well known lead free relaxor ferroelectrics with the perovskite structure. The KTN is the technologically important material by the huge quadratic electro-optic coefficient and good photorefractive effect. Recently, in perovskite ferroelectrics, precursor effects, broken local symmetry, and coexistence of order–disorder and displacive dynamics attract much attention. In BaTiO$_3$, the critical slowing down was clearly observed in the vicinity of a cubic–tetragonal phase transition temperature by the study of the central peak (CP). The KNbO$_3$ ($x=1$) undergoes a successive phase transition from cubic to tetragonal, orthorhombic, and rhombohedral phases. The low-frequency Raman scattering study reported the coexistence of the displacive soft mode and the relaxation mode. The soft optic mode is responsible for the instability to a rhombohedral phase, and the relaxation mode may contribute for cubic–tetragonal and tetragonal–orthorhombic phase transitions. In the KTN solid solutions for $x>0.05$, it undergoes a successive phase transition of a cubic–tetragonal–orthorhombic–rhombohedral sequence as same as KNbO$_3$ ($x=1.0$), and three phase transition temperatures of $x=1$ linearly decreases with decreasing the Nb content $x$. The KTN loses its relaxor properties at $x \approx 0.5$. The crystal of $x=0.008–0.05$ undergoes a cubic–rhombohedral phase transition without tetragonal and rhombohedral phases. The pure KTaO$_3$ ($x=0$) does not undergo any ferroelectric phase transition because of quantum fluctuations.

The KTN ($x<0.5$) in a cubic phase shows the polar nanoregions (PNRs) in which the off–center placed Nb ions in B-site cause the local polarizations. The Nb ion displacement in the KTN was accurately determined by the x-ray absorption fine-structure measurement. The formation of the PNRs is essential to relaxor behaviors. Sokoloff et al. discussed the Nb off-center by the eight site model in which Nb ions move among equivalent eight (111) direction sites. The existence of PNRs in a cubic phase was studied by various measurement such as inelastic neutron scattering, Raman scattering, infrared absorption, refractive-index, and linear-birefringence. The polarization fluctuations of PNRs in a cubic phase is the key factor of understanding a cubic–tetragonal phase transition. Therefore, the study of the dynamical property of the KTN is very important to make clear the dynamics of PNRs and the nature of a ferroelectric phase transition.

Brillouin scattering spectroscopy can give the information on dynamics such as elastic anomaly and slowing down in a gigahertz range. A CP, frequency shift and width of acoustic modes reflect the dynamic nature of a structural phase transition. Recently, the precursor dynamics of ferroelectric perovskite crystals such as (1−$x$)Pb(Zn$_{1/3}$Nb$_{2/3}$)$_3$O$_7$–$x$PbTiO$_3$ (Ref. 19) and BaTiO$_3$ (Refs. 4 and 20) has been studied by Brillouin scattering to clarify the precursor dynamics of PNRs. In this study, we report the results of the cubic–tetragonal phase transition of the KTN crystals investigated by Brillouin scattering to give the insights into the elastic and relaxation behaviors of the KTN crystals. We observe the critical slowing down indicating the order–disorder behavior contributes to a cubic–tetragonal phase transition by analyzing CPs. Furthermore, the critical slowing down above $T_{C-T}$ is accompanied by acoustic anomaly as a result of the growth of the fluctuating PNRs.

Brillouin scattering excited by a green YAG laser with a wavelength of 532 nm and a power of 50 mW was measured by using a high contract 3+3 pass Sandercock tandem Fabry–Perot interferometer. The free spectral range (FSR) of the spectrometer is fixed to be 75 or 300 GHz. The KTN crystals ($x=0.32$, MTI Corporation) grown by the top seed flux method were cut into the size of 5×5×1 mm$^3$ along the $a$, $b$, and $c$ axes in a cubic coordinate system, respectively. The largest two (100) faces were polished to an optical grade. The sample was put into a cooling/heating stage (Linkam THMS600), and measured at the backward scattering geometry using a c-plane. The temperature stability of a sample was within ±0.1 K over all temperatures.

Figures 1(a) and 1(b) show Brillouin scattering spectra of a KTN crystal ($x=0.32$) in a narrow and a wide frequency range at several temperatures, respectively. The spectra of Fig. 1(a) with the FSR (FSR)=75 GHz shows the doublet of a longitudinal acoustic (LA) mode and that of a transverse acoustic (TA) mode. LA and TA modes are related to the elastic constant $c_{11}$ and $c_{44}$, respectively. However, in this...
letter, the TA mode is not discussed, because the elastic constant $c_{44}$ related to TA mode is nearly constant over a wide temperature range. In contrast, the temperature dependence of the elastic constant $c_{11}$ shows the significant softening in the vicinity of a cubic-tetragonal phase transition temperature, $T_{C-T}$, as shown in Fig. 2.

On cooling from 383 K to $T_B=323\,\text{K}=T_{C-T}+65\,\text{K}$, the elastic constant $c_{11}$ is nearly constant, while, below $T_B$, it starts to soften with further cooling toward the Curie temperature, $T_{C-T}=258\,\text{K}$. The temperature dependence of $c_{11}$ of the KTN is in agreement with the result by the ultrasonic study within experimental accuracy.\cite{22,23} As to the precursor phenomenon of a cubic–tetragonal transition, the softening of $c_{11}$ from $T_B$ to $T_{C-T}$ on further cooling is caused by the interaction with dynamic PNRs in a cubic phase.\cite{22,23}

In order to obtain accurate data of the CP, we measured in the wide frequency range $\pm 560\,\text{GHz}$ with a bigger FSR = 300 GHz as shown in Fig. 1(b). Figure 3(b) shows that below the intermediate temperature, $T^*=280\,\text{K} (< T_B)$, the CP intensity drastically increases on cooling toward $T_{C-T}$, indicating the growth of the volume fraction of PNRs.\cite{12} The softening of the elastic constant $c_{11}$ from $T_B$ to $T_{C-T}$ on cooling (Fig. 2) is caused by the growth of PNRs. The local polarization fluctuation of PNRs in a cubic phase induces local strain fluctuations by piezoelectricity of PNRs.\cite{22,23} And the KTN with the high Nb concentration, the PNRs oriented between [111] directions tends to fix their orientation along one of [100] directions.\cite{23} Therefore, the softening of $c_{11}$ which correspond to longitudinal distortion indicates the interaction between the LA mode and the local polarization fluctuations of PNRs.

The full width at half maximum of the CP (CP width), which is inversely proportional to a relaxation time, also changes with temperature. Figure 3(a) shows the temperature dependence of the inverse of the relaxation time estimated by the equation of $r=1/\pi \Delta \Gamma$, where $r$ is the relaxation time and $\Delta \Gamma$ is the CP width.\cite{19} The inverse of the relaxation time, $1/r$, clearly shows a liner behavior from 300 K on cooling toward $T_{C-T}$, which indicates that the cubic–tetragonal phase transition of the KTN shows the order-disorder behavior. Such a behavior predicts the critical slowing down of an order-disorder phase transition given by the following equation:

$$\frac{1}{r} = \frac{1}{\tau_0} + \frac{1}{\tau_1} \left( \frac{T_{C-T}}{T_{C-T}} - 1 \right). \quad (1)$$

Using Eq. (1) in a cubic phase (temperature range of $T_{C-T} \sim T_{C-T}+42\,\text{K}$) yield $1/\tau_0=3.62 \times 10^{11}\,\text{s}^{-1}$, and $1/\tau_1=8.49 \times 10^{12}\,\text{s}^{-1}$. The finite value of $\tau_0$ may be caused by the lattice defects.\cite{24}

The Raman scattering measurements of KTN in a cubic phase show the spectra of first-order scattering peaks due to polar modes.\cite{14,15} The intensity of the peaks increases in the
In conclusion, we studied the precursor dynamics of a cubic–tetragonal ferroelectric phase transition of the potas-
sium tantalate niobate (KTa$_{1-x}$Nb$_x$O$_3$ with $x=0.32$) single crystals by Brillouin scattering. Above $T_{C-T}$, the elastic constant $c_{11}$ shows significant softening on cooling toward $T_{C-T}$ owing to the coupling between flipping PNRs and the LA mode. The intense CP appears in the vicinity of $T_{C-T}$. It reflects the enhancement of local polarization fluctuations of PNRs. The relaxation time determined the CP width clearly shows a critical slowing down above $T_{C-T}$, indicating a feature of an order–disorder behavior of a ferroelectric phase transition. The size of a dynamic PNR is estimated as a function of temperature above $T_{C-T}$.

FIG. 4. (Color online) Temperature dependence of the size of a dynamic PNR.