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Order–disorder behavior of ferroelectric phase transition of $KTa_{1-x}Nb_xO_3$ probed by Brillouin scattering

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The precursor dynamics of a cubic–tetragonal ferroelectric phase transition of potassium tantalate niobate ($KTa_{1-x}Nb_xO_3$ with $x=0.32$) crystals 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 ($KTa_{1-x}Nb_xO_3$, 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.[1,2] Recently, in perovskite ferroelectrics, precursor effects, broken local symmetry, and coexistence of order–disorder and displacive dynamics attract much attention.[3] 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).[4] 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.[5] The soft optic mode is responsible only for the instability to a rhombohedral phase, and the relaxation mode may contribute for cubic–tetragonal and tetragonal–orthorhombic phase transitions.[5] 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.[6] The KTN loses its relaxor properties at $x\geqq 0.5$.[7] 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 fluctuation.[8]

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.[9,10] The Nb ion displacement in the KTN was accurately determined by the x-ray absorption fine-structure measurement.[9] The formation of the PNRs is essential to relaxor behaviors.[7,11] Sokoloff *et al.*[12] discussed the Nb off-center by the eight site model in which Nb ions move among equivalent eight $\langle 111\rangle$ direction sites. The existence of PNRs in a cubic phase was studied by various measurement such as inelastic neutron scattering,[13] Raman scattering,[14,15] infrared absorption,[16] refractive-index, and linear-birefringence.[17] 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.[18] 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 $(1-x)Pb(Zn_{1/3}Nb_{2/3})O_3-xPbTiO_3$ (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.[18] 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 $5\times 5\times 1$ 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.[21] However, in this

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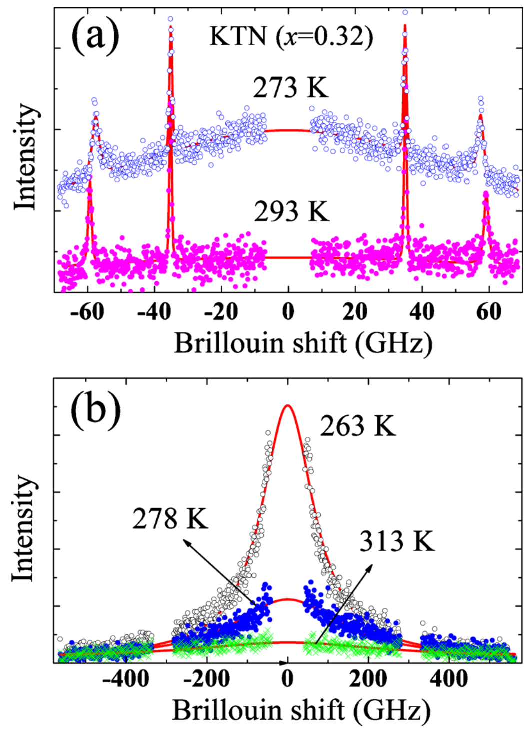

FIG. 1. (Color online) Brillouin spectra at selected temperatures of a KTN single crystal ($x=0.32$) in (a) narrow- and (b) a wide-frequency ranges. The solid lines indicate the fitted results.

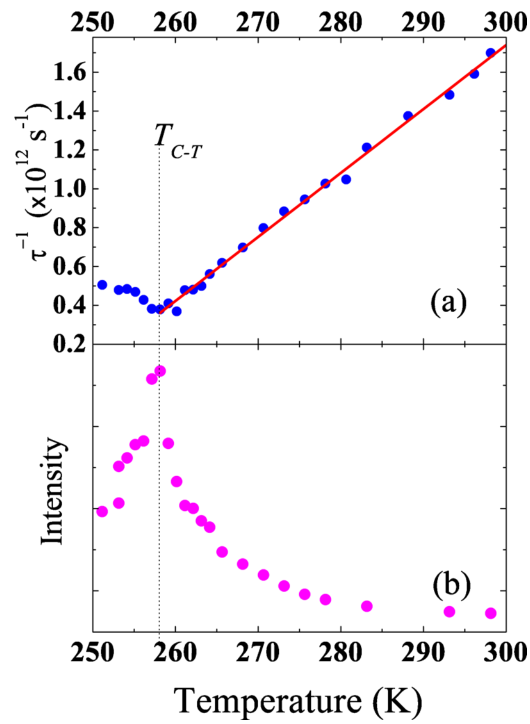

FIG. 3. (Color online) Temperature dependence of (a) the inverse of the relaxation time estimated from the CP width and (b) the CP intensity. The solid straight lines shown in (a) are fitted results by using Eq. (1).

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 $T_B=323$ K$=T_{C-T}+65$ K, the elastic constant c_{11} is nearly constant, while, below T_B, it starts to soften with further cooling toward the Curie temperature, $T_{C-T}=258$ K. The temperature dependence of c_{11} of the KTN is in agreement with the result by the ultrasonic study within experimental accuracy.[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.[22,23]

In order to obtain accurate data of the CP, we measured in the wide frequency range ± 560 GHz with a bigger FSR $=300$ GHz as shown in Fig. 1(b). Figure 3(b) shows that

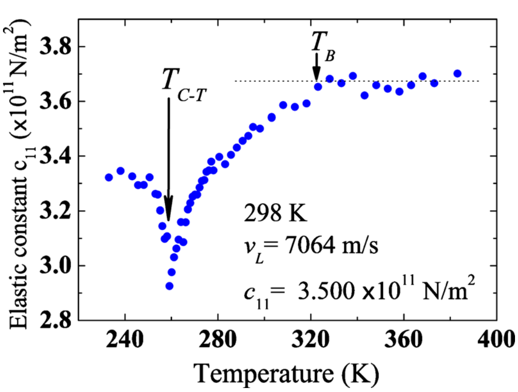

FIG. 2. (Color online) Temperature dependence of the elastic constant c_{11}. v_L denotes sound velocity of the LA mode.

below the intermediate temperature, $T^*=280$ K ($<T_B$), the CP intensity drastically increases on cooling toward T_{C-T}, indicating the growth of the volume fraction of PNRs.[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.[22,23] And the KTN with the high Nb concentration, the PNRs orientated between [111] directions tends to fix their orientation along one of [100] directions.[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 $\tau=1/\pi\Delta\Gamma$, where τ is the relaxation time and $\Delta\Gamma$ is the CP width.[19] The inverse of the relaxation time, $1/\tau$, 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:

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

Using Eq. (1) in a cubic phase (temperature range of $T_{C-T} \sim T_{C-T}+42$ K) yield $1/\tau_0=3.62\times 10^{11}$ s^{-1}, and $1/\tau_1=8.49 \times 10^{12}$ s^{-1}. The finite value of τ_0 may be caused by the lattice defects.[24]

The Raman scattering measurements of KTN in a cubic phase show the spectra of first-order scattering peaks due to polar modes.[14,15] The intensity of the peaks increases in the

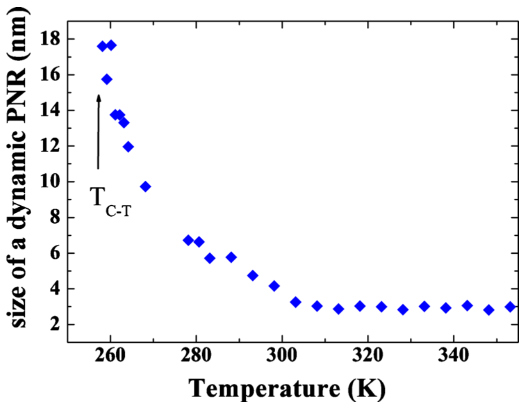

FIG. 4. (Color online) Temperature dependence of the size of a dynamic PNR.

vicinity of T_{C-T}. The Raman peaks in a cubic phase are generally Raman inactive. Therefore, it indicates that local distortions in a cubic phase are present and its magnitude increases toward T_{C-T}. The dielectric constant of the KTN obeys the Curie–Weiss law at a high temperature region, but deviates from it at $T_{C-T} \sim T_{C-T}+34$ K (the case of $x=0.3$) because of the rapid growth of PNRs.[11] Also, the studies of refractive index and birefringence suggest "cooperative dipole glass" model in which strain-induced collective ordered clusters appear at T_{C-T} by long range strain fields.[17] The drastic increase in relaxation times accompanied by extremely growing PNRs is related to the increase in the interaction among PNRs [Fig. 3(a)]. Furthermore, Fig. 3(a) clearly shows the critical slowing down of an order–disorder property of PNRs on cooling toward T_{C-T}, which indicates the growing process of static to dynamic change in PNRs.

We try to estimate the size of a dynamic PNR from the multiply the relaxation time by the sound velocity of the LA mode because the maximum of the characteristic length of flipping is given by the propagation length within a relaxation time.[25] Figure 4 shows the temperature dependence of the size of a dynamic PNR, and it increases toward T_{C-T} on cooling. The size is about 6 nm at T^*, which is in agreement with the size of dynamic polar clusters of 4–6 nm.[22] Therefore, a cubic–tetragonal phase transition of the KTN clearly indicates a critical slowing down of PNRs, which is in agreement with the increasing size of the PNRs. The growth of PNRs in a cubic phase also enhances the softening of c_{11} as shown in Fig. 2.

In conclusion, we studied the precursor dynamics of a cubic–tetragonal ferroelectric phase transition of the potassium tantalate niobate ($KTa_{1-x}Nb_xO_3$ 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}.

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