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Soft Mode Dynamics in ^{18}O-Exchanged $SrTiO_3$ as Inhomogeneous System

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Ferroelectric phase transition of quantum paraelectric $SrTiO_3$ is induced by an exchange of ^{16}O for its isotope ^{18}O in a low temperature region. The dynamics of ferroelectric soft mode in weakly ^{18}O-exchanged strontium titanate is studied by Raman scattering. A nominally Raman-inactive soft mode is observed in the paraelectric phase of $SrTi(^{18}O_{0.32}{}^{16}O_{0.68})_3$ due to the local symmetry-breaking. The observed soft mode spectrum shows the temperature dependence strongly affected by the inhomogeneity of the system. The soft mode nonuniformly freezes to induce the local ferroelectric order before the onset of ferroelectric phase. The dynamical inhomogeneity is concluded to play an essential role in the dielectric response of ^{18}O-exchanged strontium titanate.

Key words: quantum paraelectric, phase transition, strontium titanate, Raman scattering, inhomogeneity

1. INTRODUCTION

Strontium titanate, $SrTiO_3$ (STO16), shows quantum paraelectricity; quantum fluctuation suppresses the ferroelectric ordering of STO16 in a low temperature region [1-3]. It has continuously attracted huge attention since its discovery. The first observation of the quantum paraelectricity is an anomalous behavior of the dielectric constant in a low-temperature region near 0 K; the dielectric constant of STO16 becomes independent on temperature with huge value, $\varepsilon \sim 20{,}000$, after a divergent increase with decreasing temperature [1]. According to the result of several scattering experiments performed obviously, the soft mode softens with decreasing temperature but does not freeze until 0 K showing good correspondence to the Lyddane-Sachs-Teller (LST) relation [4-8]. It strongly suggests that the quantum fluctuation prevents the freezing of the soft mode to suppress the ferroelectric ordering of STO16.

Recently Itoh *et al.* successfully induced a ferroelectric phase of strontium titanate by an exchange of ^{16}O for its isotope ^{18}O [9-11]. The ferroelectricity of isotopically exchanged $SrTi(^{18}O_x{}^{16}O_{1-x})_3$ [hereafter $SrTi(^{18}O_x{}^{16}O_{1-x})_3$ is abbreviated as STO18-x] has been confirmed by the dielectric peak and the D-E hysteresis loop with the exchange rate x greater than x_c (= 0.33) [9-12]. This phenomenon is the first example of the direct controlling of quantum fluctuation in quantum paraelectrics because the oxygen isotope ^{18}O is chemically equivalent to ^{16}O. In order to reveal the phase transition mechanism, a series of light scattering experiment has been performed on the ferroelectric STO18-x ($x > 0.33$) [13-15]. Most recently, Takesada *et al.* observed the perfect softening of the soft mode at T_c in ferroelectric STO18-95 and concluded the ideal displacive-type phase transition of ferroelectric STO18-x [16].

In weakly exchanged STO18-x, on the other hand, the some unsolved problems are remaining. One of them is the anomalous temperature dependence of dielectric susceptibility. As reported in the previous study, the dielectric susceptibility of weakly exchanged STO18-x shows strongly rounded curve in the temperature dependence indicating large deviation from Curie-Weiss law. The dielectric behavior approaches to that follows Curie-Weiss law with increasing the exchange rate. It suggests the novel mechanism in the dielectric behavior of the weakly exchanged STO18-x.

In the present study, we focus on the soft mode dynamics in weakly exchanged quantum paraelectric STO18-32, whose exchange rate is critically close to x_c but less than it. Generally, the soft mode is Raman inactive due to the macroscopic centrosymmetry in the paraelectric phase of STO18-x. However, our previous studies reported the observation of the soft E_u mode due to the local symmetry-breaking in the low-temperature region of STO18-x ($x < 0.33$) [17,18]. By using the local symmetry-breaking induced Raman scattering, we can investigate the soft mode dynamics even in the paraelectric phase of STO18-x. The purpose of the present study is to elucidate the soft mode dynamics in weakly exchanged STO18-32 in association with the local symmetry-breaking developed in the low-temperature region.

2. EXPERIMENT

A single crystal of STO16 manufactured by Furuuchi Chemical Co. was cut with the $(110)_c$ wide surfaces. Dimensions of sample was designed with $7.0//[001]_c$ $*3.0//[-110]_c$ $*0.5//[110]_c$ mm^3 in order to obtain a tetragonal mono-domain with the c axis parallel to $[001]_c$ direction below the cubic-to-tetragonal phase transition temperature, where $[001]_c$ indicates the [001] axis in the cubic system. The wide surfaces were polished to optical quality. Oxygen-isotope exchange was performed by heating the plates at 1323 K in $^{18}O_2$ atmosphere. The final exchange rate $x = 0.32$ of $SrTi(^{18}O_x{}^{16}O_{1-x})_3$ was determined from the increment of the weight.

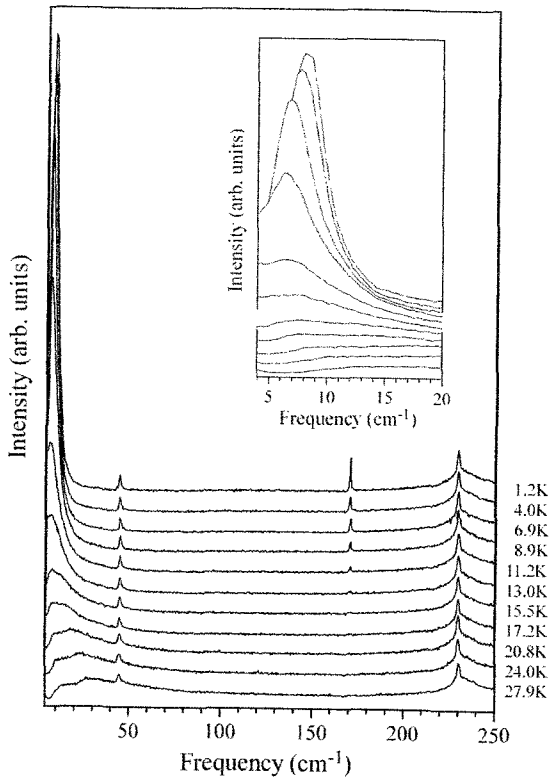

Fig. 1. Raman scattering spectra of STO18-32 observed in the $x(yy)$-x scattering geometry at several temperatures. The inset shows an expanded view of the soft E_u mode spectra.

The crystallographic axes used in the present study are denoted by a tetragonal set as follows: $x//[110]_c$, $y//[-110]_c$ and $z//[001]_c$. An Ar ion laser at a wavelength of 514.5 nm was used for the light source with an output power of 100 mW. The scattered light was collected in the back scattering geometries $x(yy)$-x and $x(yz)$-x and analyzed by a Jovin-Yvon T64000 triple monochromator with the subtractive dispersion mode. The spectral resolution of the present system attains 1.5 cm^{-1}.

A temperature of the sample was controlled by specially designed ^{3}He optical cryostat TS-HE3-C9 (Taiyo Toyo Sanso Co.) within ±0.05 K. This cryostat uses ^{3}He evaporation type cooling with the charcoal adsorbent and attained 520mK on the sample under a 100 mW laser irradiation input.

3. RESULTS AND DISCUSSION

Figure 1 shows the Raman spectra of weakly exchanged STO18-32 observed in the $x(yy)$-x scattering geometry at several temperatures. As obviously seen in the figure, a sharp and intense peak grows dramatically in a low frequency region with decreasing temperature. At 27.9K, a broad and weak spectrum, which is caused by phonon-branch scattering of the soft mode [19,20], and its higher harmonic component are seen in the frequency region below 100 cm^{-1}. The phonon-branch scattering spectrum shifts to the low frequency side and increases its intensity as lowering temperature. With further cooling, it develops to the sharp spectrum, and finally at 1.2 K, the spectral shape exhibits typical single-phonon scattering spectrum of underdamped

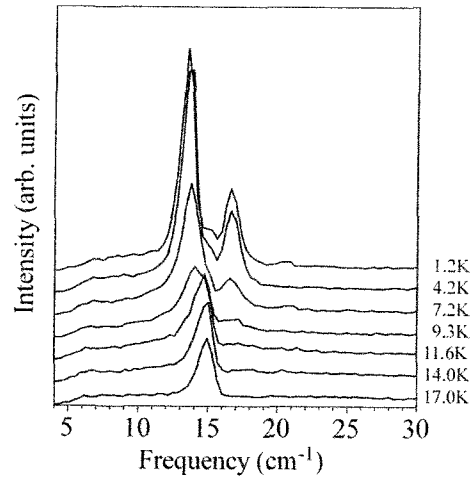

Fig. 2. Raman scattering spectra of STO18-32 observed in the $x(yz)$-x scattering geometry at several temperatures.

phonon. The sharp peak is assigned to a spectrum of ferroelectric soft E_u mode from its peak position and temperature dependence [17,18]. The observation of soft mode spectrum clearly indicates an occurrence of symmetry lowering in the low temperature region of STO18-32 because the soft E_u mode is Raman inactive in the centrosymmetric symmetry of paraelectric phase. The inset of Fig. 1 presents the expanded figure of the low frequency region from 4 cm^{-1} to 20 cm^{-1}. In the low temperature region below 10 K, the observed soft E_u mode spectrum shifts to a high frequency side with decreasing temperature. The hardening behavior of the soft mode is generally seen in a ferroelectric phase. Therefore, the observed behavior of the soft mode implies an occurrence of ferroelectric region in the low temperature region of STO18-32.

A small peak at 170cm^{-1} observed in the low temperature region confirms the occurrence of symmetry lowering. This peak is reported previously in the ferroelectric phase of strongly exchanged STO18-84 [15]. Therefore, the small peak is also observed in the local symmetry-breaking region. In the high temperature region, no peak is seen at around 170cm^{-1} indicating the macroscopic centrosymmetricity of STO18-32. On the other hand, the peaks at 45cm^{-1} and 230cm^{-1} do not show any noticeable changes on their peak positions and intensities.

Figure 2 presents the spectra observed in the $x(yz)$-x scattering geometry. As shown in the figure, the spectrum observed at 1.2 K clearly exhibits the established peaks at 14 cm^{-1} and 17 cm^{-1}. In comparison with previous study, these peaks locate at quite similar positions to $A_2(E_g)$ mode and $B_1(A_{2u})$ mode observed in the ferroelectric phase of STO18-84 [15]. This result confirms the occurrence of ferroelectric region in the low temperature region of STO18-32. On the other hand, only a peak for E_g mode is observed at 15 cm^{-1} in the high temperature region indicating the paraelectric symmetry of STO18-32. The E_g mode begins shifting to the low temperature region at around 13 K. It suggests the ferroelectric order appears at 13 K.

The temperature dependence of the soft E_u mode frequency is shown by solid squares in Fig. 3 (a). The

frequency shifts to the low frequency side with decreasing temperature indicating destabilization of the lattice vibration of soft E_u mode. Consequently, the soft mode begins to harden after the frequency minimum 7 cm^{-1} at 8 K, and finally it attains 8 cm^{-1} at 0 K. The hardening of the soft mode is considered to be caused by the occurrence of the ferroelectric order in the low temperature region of STO18-32. It should be noted that the linewidth of soft mode broadens at 13 K as shown in the Fig. 3 (b). The temperature of 13 K is a little above the temperature at which the frequency takes its minimum value. A mechanism for this anomaly will be discussed later.

Here, there is a problem what is a mechanism of the ferroelectric ordering in STO18-32. In the previous study, the critical value of ^{18}O-exchange rate x_c for the onset of ferroelectric phase in STO18-x is reported to be 0.33. However, the present result clearly indicates the occurrence of ferroelectric ordering in the low temperature region of STO18-32 in spite of its exchange rate is less than 0.33. Moreover, the observed soft E_u mode does not show any freezing in the entire temperature range observed here, though an occurrence of ferroelectric order in STO18-x must undergo the freezing of soft mode as obviously indicated by the light scattering study on STO18-95 [16]. The most plausible interpretation is an effect of inhomogeneity of the system. STO18-32 is fabricated by the partial exchanging of ^{16}O for ^{18}O, therefore the mass distribution of oxygen atoms is unavoidable. As a result, the system becomes intrinsically inhomogeneous. Since frequency of lattice vibration follows $\omega \sim m^{*-1/2}$ where m^* is the reduced mass, that of Slater type polar E_u mode, which includes oxygen atoms, is affected largely by the mass distribution of oxygen atoms. In the region where the concentration of ^{18}O atom is relatively large, the soft E_u mode frequency would become lower than that in the other region. Consequently, soft mode dynamics in STO18-32 is considered to become spatially inhomogeneous. Moreover, when the concentration of ^{18}O atom locally exceeds the critical value, sufficiently destabilized soft E_u mode would freeze at finite temperature. On the other hand, the soft E_u mode in the other region does not freeze until 0 K. Such a situation leads to the non-uniform freezing of the soft mode.

The present model is examined as follows. The freezing soft mode in the ^{18}O-concentrated region is assumed to follow the Curie-Weiss law as

$$\varpi_F^2 = A(T - T_C).$$

A broken line in Fig. 3 (a) is calculated with A = 13.5 for $T > T_c$ and A = 6.1 for $T < T_c$, where T_c is set to 13.0 K at which the E_g mode begins shifting. In the other region, on the other hand, the non-freezing soft E_u mode would follow the quantum Barrett's formula as

$$\omega_{NF}^2 = C\left\{\frac{T_1}{2}\coth\left(\frac{T_1}{2T}\right) - T_0\right\}$$

due to the relatively strong quantum fluctuation. A solid line in Fig. 3 (a) is calculated with C = 5.5, T_1 = 78.0 K and T_0 = 37.0 K which are consistent with the values reported previously. If the two regions are mixed in the scattering volume, the soft E_u mode spectrum observed as superposition of two kinds of spectra of the freezing

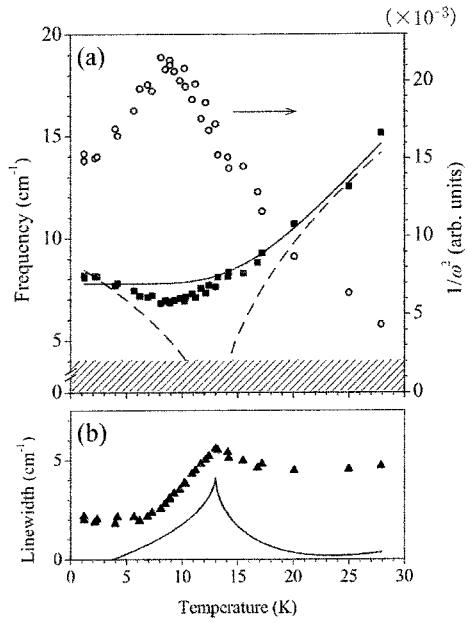

Fig. 3. (a) Temperature dependence of the soft E_u mode frequency (closed squares) and the reciprocal squared-frequency (open squares). Broken line and solid line denote the temperature dependence of the soft mode frequency calculated by Curie-Weiss law and Barrett's formula, respectively. Hatched region presents invisible region in the present experiment because of the slit. (b) Temperature dependence of the observed linewidth of the soft E_u mode (closed circles). Solid line indicates the calculated one [see text].

and non-freezing soft mode. The apparent line width of the soft E_u mode is considered to reflect the difference of the peak position of the two spectra. Therefore, we calculate the difference of the frequencies of the E_u modes, and result is presented by solid line in the inset of Fig. 3 (b). Surprisingly, such a simple assumption well explains qualitatively the temperature dependence of linewidth observed in the present study. This result strongly supports the present model. Thus, the observed non-freezing behavior of the soft E_u mode is concluded to be caused by the inhomogeneous distribution of soft mode due to the non-uniform mass distribution of the oxygen atoms. The ferroelectric ordering of STO18-32 is considered to be induced locally by freezing of the soft E_u mode.

Thus, the observed temperature dependence of the soft mode is explained as follows. In STO18-32, the partial exchange of ^{18}O makes a mass distribution of oxygen atoms to render the system intrinsically non-uniform. Since frequency of the soft E_u mode is depressed by the increase of reduced mass of the lattice vibration, the non-uniform mass distribution causes the inhomogeneous dynamics of the soft mode. In the temperature region around 13 K, the difference of the soft modes between the regions is enhanced especially. The soft mode freezes in one region, and does not freeze in the other region. The simultaneous observation of the soft modes in both regions makes the observed spectrum broaden, and the apparent peak exhibits finite frequency though the soft mode locally freezes. In the temperature

region below 13 K, the local ferroelectric region is induced by the freezing of the soft mode before the onset of the ferroelectric phase. The soft mode in the ferroelectric region begins hardening and increases its intensity with decreasing temperature. When the intensity of the freezing soft mode becomes dominating, the observed spectrum shows obvious hardening behavior.

Open circles in Fig. 3 (a) denote the values calculated by $1/\omega^2$, where ω is the observed soft mode frequency. They are corresponding qualitatively to the dielectric susceptibility according to the LST-relation. As shown in the figure, the calculated temperature dependence of the dielectric susceptibility shows the rounded peak at around 8 K. This behavior is in good agreement with the result of previous dielectric study in weakly exchanged STO18-*x*. The dielectric measurement observes macroscopic response of STO18-*x*. When the soft mode dynamics is spatially inhomogeneous, the simultaneous observation of dielectric response in the individual regions would make the temperature dependence of the dielectric susceptibility strongly deviated from Curie-Weiss law. Thus the rounded temperature dependent curve of the dielectric susceptibility in weakly exchanged STO18-*x* is considered to be caused by dynamical inhomogeneity of the system due to the spatially inhomogeneous soft mode dynamics.

4. CONCLUSION

In the present study, we observed the soft mode spectrum of STO18-32 as a function of temperature. The anomalous broadening of the soft mode spectrum at the low temperature indicates the spatial variation of the soft mode frequency in STO18-32 due to the non-uniform mass distribution of the oxygen atoms. The inhomogeneous dynamics of the soft mode is concluded to induce the local ferroelectric order before the onset of the ferroelectric phase in STO18-32. The rounded temperature dependence of the dielectric susceptibility in weakly exchanged STO18-*x* is suggested to be caused by the dynamical inhomogeneity of the system.

5. REFERENCES

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