Light scattering study of the ferroelectric phase transition in $SrTi^{18}O_3$

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Brillouin scattering measurements are reported for isotopically modified $SrTi^{18}O_3$, where a new ferroelectric phase transition at 23 K has been recently discovered. New acoustic anomalies have been revealed near the ferroelectric phase transition temperature T_C, including a remarkable softening of the c_{44} mode. Anomalies near the cubic-tetragonal phase transition in $SrTi^{18}O_3$ are also examined.

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In the last decade remarkable new directions emerged in the studies of $SrTiO_3$ and observed new phenomena continue to attract great attention to this extremely well known and most extensively studied perovskite.[1–6] Recent efforts have been focused on the quantum paraelectric regime of $SrTiO_3$, where large amplitudes of the zero-point motions of ions prevent transition to ferroelectric state.[7–11]

Recently, Itoh and co-workers have found that isotopically exchanged $SrTi^{18}O_3$ exhibits ferroelectric behavior.[12] They have reported that the temperature dependence of the dielectric constant shows a peak at around 23 K, very similar to the peak temperature in Ca-substituted $SrTiO_3$.[13] Furthermore, the presence of hysteresis in the D vs E measurements and the temperature dependence of Raman spectra provided strong evidence of ferroelectriciy in $SrTi^{18}O_3$.[12] This paper reports on ferroelectricity induced in $SrTiO_3$ without applying external fields[5,6] or introducing random field by A-cation substitution.[13] This important development in $SrTi^{18}O_3$ would justify a dedicated study.

We have carried out light scattering studies of the isotopically modified $SrTi^{18}O_3$ and observed remarkable anomalous features at low temperatures around ferroelectric phase transition point T_C. In this report, we describe interesting elastic anomalies near T_C in $SrTi^{18}O_3$ found by Brillouin scattering. A brief discussion of the anomalies observed near the cubic-tetragonal phase transition temperature T_o will also be given.

Brillouin scattering experiments were performed on a single crystal $SrTiO_3$ plate, $3\times5\times0.5$ mm^3 in size, with the edges parallel to the $[1\bar{1}0]$, [001], and [110] directions. The crystal was heated in $^{18}O_2$ gas of 99% purity. The isotope exchange rate was determined from the increase in weight. The final exchange ratio of the ^{18}O isotope was more than 90%. A detailed description of the sample preparation can be found in Ref. 12. The sample was mounted in a closed-cycle He-gas refrigerator. Brillouin scattering measurements were carried out in wide temperature range from 300 to 14 K. Ar^+ ion laser operated at $\lambda=514.5$ nm with a V-polarized longitudinal single mode was used as a light source. 90° scattering geometry with the phonon wave vector $Q//[001]$ was employed. The measurements were made using Sandercock-type six-pass tandem Fabry-Perot interferometer as a spectrometer.

Figure 1 shows Brillouin shifts of the c_{33} and c_{44} modes in $SrTiO_3$ as a function of temperature. Significant anomalies are observed around $T_o=108$ K and $T_C=23$ K, which correspond to the cubic (O_h) tetragonal (D_{4h}) and ferroelectric phase transitions, respectively. Before discussing the ferroelectric phase transition at T_C, let us briefly consider important features found in $SrTi^{18}O_3$ near T_o. The structural phase transition at T_o is triggered by the softening of the R_{25} mode at Brillouin-zone boundary.[14,6] In Fig. 1, the temperature dependence of the frequency shifts shows a downward stepwise change with decreasing temperature. This behavior is very similar to that observed in ''pure'' $SrTi^{16}O_3$;[15] the transition point T_o is found to be higher for $SrTi^{18}O_3$ ($T_o=108$ K) than for $SrTi^{16}O_3$ ($T_o=105$ K), but no other obvious differences are observed in our measurements. This stepwise behavior can be qualitatively understood from the third-order coupling between the square of the soft-mode amplitude and elastic strain, which is the lowest order coupling between the

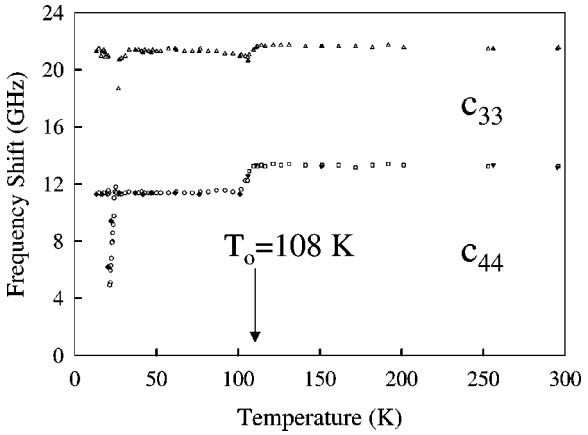

FIG. 1. Temperature dependence of Brillouin shifts of the c_{33} longitudinal and c_{44} transverse acoustic modes in $SrTi^{18}O_3$.

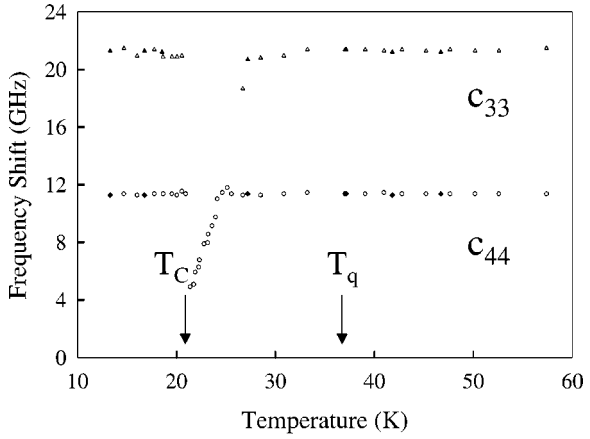

FIG. 2. Temperature dependence of Brillouin shifts of the c_{33} and c_{44} modes near the ferroelectric phase transition point T_C.

soft mode and elastic strain above T_o, also known as Landau-Khalatnikov mechanism.[16] The temperature T_o corresponds to the point where the downward stepwise change begins with decreasing temperature. This higher value of T_o for the isotopically exchanged $SrTi^{18}O_3$ is in good agreement with the results of heat-capacity measurements of Itoh *et.al.*, which showed T_o of 105 K for ''pure'' $SrTi^{16}O_3$, 106 K for 45% isotopically exchanged sample and 110 K for 93% exchanged sample.

In Fig. 1, strong elastic anomaly in $SrTi^{18}O_3$ at low temperatures (Fig. 1) is a remarkable feature that corresponds to the ferroelectric phase transition at T_C induced by the isotopic exchange. This anomaly is observed only in $SrTi^{18}O_3$, it has no counterpart in ''pure'' $SrTi^{16}O_3$. The temperature at which this anomaly was observed in our Brillouin scattering measurements agrees well with the results of the dielectric constants measurements of Itoh *et al.*, who reported that the temperature dependence of the real part of dielectric constant shows a peak around 23 K in the 93% exchanged sample. It is clear from Fig. 1 that the anomaly at T_C occurs in a narrower temperature range compared to the anomaly at T_o. This can be qualitatively understood in terms of the difference in the absolute values of phase-transition temperatures.

Figure 2 shows an expansion of the temperature dependence of frequency shifts in the low-temperature region of interest. The c_{44} transverse-acoustic mode shows clear softening near the phase-transition temperature T_c, however, no hardening process is observed below T_c. The acoustic-mode frequency changes rather abruptly, as seen in Fig. 2. The arrow near 37 K in Fig. 2 serves to indicate the temperature at which a small anomaly in heat capacity was reported for a sample with high isotopic exchange ratio. No anomalous behavior was observed around this temperature for c_{33} and c_{44} modes in our experiments.

Figure 3 shows the temperature dependence of Brillouin spectra above [Fig. 3(a)] and below [Fig. 3(b)] T_C. The spectra were taken in 90° scattering geometry with the acoustic phonon wave vector parallel to the [001] direction and the polarization of incident light parallel to the $[1\bar{1}0]$ direction. We used a plate sample in our measurements and the scattering angle inside the sample was smaller than 90°. One immediately notices in Fig. 3 that both frequency and intensity change largely around T_C. The linewidth increases remarkably between 26.2 and 24.0 K and the spectrum at 26.2 K shows a sharp doublet of the transverse acoustic mode [Fig. 3(a)]. As temperature is decreased toward T_C, the peak frequency becomes lower and the peak grows broader and stronger. In addition, the spectra above T_C show an intensity dip indicated by the arrows in Fig. 3(a). This dip is often observed in the spectra near structural phase transitions in crystals such as KDP, c-$BaTiO_3$, h-$BaTiO_3$, and others,[17–19] where a bilinear coupling exists between the order parameter and elastic strain. From the symmetry consid-

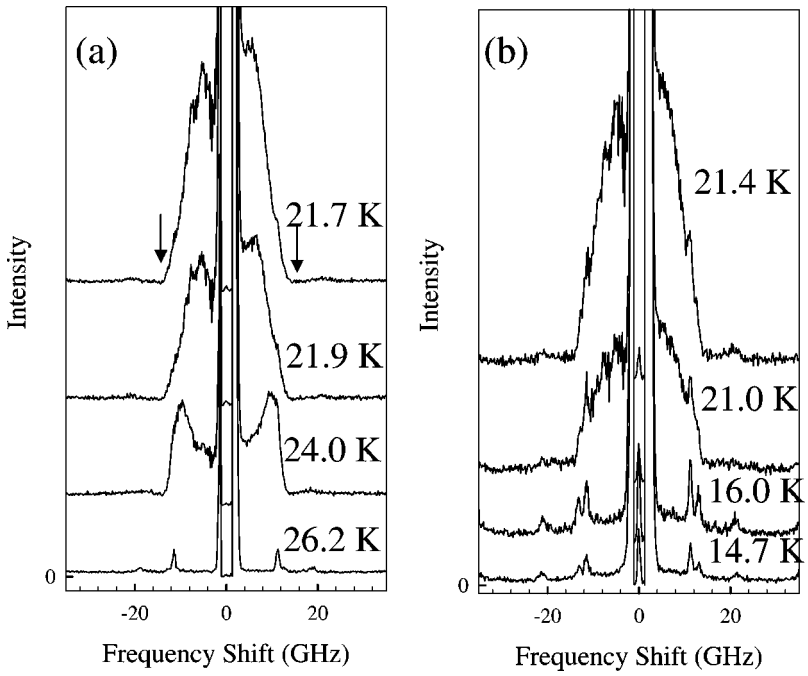

FIG. 3. Brillouin spectra of $SrTi^{18}O_3$ (a) above T_C and (b) below T_C.

erations, the bilinear coupling between the polarization and shear strain is not allowed in the tetragonal phase (D_{4h}) of $SrTiO_3$, which has inversion symmetry. It has been demonstrated, however, that the bilinear coupling between the strain and the gradient of polarization fluctuation in the tetragonal $SrTiO_3$ is allowed.[9] In ''pure'' $SrTiO_3$, the effects of such coupling have been observed in both neutron scattering and Brillouin scattering.[9,20,21] It has also been shown that although the strength of this coupling is proportional to the square q^2 of the wave vector q, the equation of motion can be expressed as a coupled harmonic oscillator.[21] In our case of $SrTi^{18}O_3$, this coupling could provide an explanation for the intensity dip in the spectrum above T_C and possibly for the softening of the acoustic mode.

On the other hand, the spectra below T_C [Fig. 3(b)] do not show any obvious hardening of the acoustic mode, instead the apparent splitting is observed just below T_C. The intensity of the broad central component in the spectra (between ± 20 GHz) becomes smaller with decreasing temperature from T_C. The spectrum at 21.0 K clearly shows sharp transverse acoustic mode peak, which coexists with the broad central component. Furthermore, the intensity dip seen in the spectra above T_C is not found below T_C. These facts indicate that the coupling between the order parameter and shear acoustic does not exist below the transition temperature. In connection with the coupling between the strain and gradient of polarization, this is likely to be related to the zero gradient of polarization when the polarization is homogeneous in space.

Above T_C, large fluctuations of polarization lead to the dynamic domain states that can be considered as inhomogeneous polarization fluctuation in time. Such dynamic states can possess a large gradient of polarization. This can result in a large coupling between the gradient of polarization and shear acoustic mode, even considering the fact that the coupling strength is proportional to q^2 and q is small in our Brillouin scattering experiment. On the other hand, in the ferroelectric phase below T_C homogeneous polarization is induced, which reduces the gradient of polarization and, as a result, reduces the coupling between the shear acoustic mode and gradient of polarization.

It has been recently reported that $SrTiO_3$ exhibits a rapidly growing, ''giant'' piezoelectric response with decreasing temperature[4] although tetragonal phase possesses inversion symmetry. It is possible that in $SrTi^{18}O_3$ a similar piezoelectric coupling exists and understanding its mechanisms may provide a possible way of analyzing the bilinear coupling between the polarization and shear acoustic mode. Clearly, many further studies are called for to provide a coherent explanation of the softening of shear acoustic mode at T_C and probe possible interesting phenomena in $SrTi^{18}O_3$.

In conclusion, the results of Brillouin scattering measurements performed on $SrTi^{18}O_3$ have revealed new acoustic anomalies near the ferroelectric phase transition at T_C. These interesting features should stimulate further experimental and theoretical efforts needed to clarify their mechanisms. This provides a significant challenge for future studies.

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