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Silent soft mode in hexagonal barium titanate observed by hyper-Raman scattering

Kuon Inoue, Atsushi Hasegawa, and Kenji Watanabe
Research Institute of Applied Electricity, Hokkaido University, Sapporo 060, Japan

Hirotaka Yamaguchi, Hiromoto Uwe, and Tunetaro Sakudo
Institute of Applied Physics, University of Tsukuba, Tsukuba 305, Japan
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A soft optic phonon which is neither Raman nor infrared active has been directly observed for the first time in the higher-symmetry phase above T_a (221.5 K) of hexagonal $BaTiO_3$ by an experiment of hyper-Raman scattering. The underdamped feature of the soft-phonon mode even close to T_a allows one to determine unambiguously both the frequency and the damping constant as a function of temperature. It is found that the soft-mode frequency obeys the Landau-Cochran theory in contrast with the nonclassical behavior below T_a which was previously found by a Raman scattering experiment. Furthermore, the second-harmonic-generation observation indicates that the crystal structure below T_a should be of acentric symmetry, which is closely related with the ferroelastic nature of the phase transition at $T_c = 74$ K.

Recently, two different kinds of phase transitions were observed for hexagonal $BaTiO_3$ (Refs. 1 and 2) that are polymorphs of the cubic-perovskite type. Extensive studies by x-ray analysis,[3] dielectric[4] and elastic[5] measurements, and optical measurements[6] have been done. According to those, the hexagonal crystal shows a second-order phase transition at $T_a = 222$ K from the phase of $P6_3/mmc$ to a different phase. This latter phase is known to be followed by a ferroelectric phase at $T_c = 74$ K. Recently, soft optic phonons were found to exist by an experiment of Raman scattering[7] in the phase below T_a. Judging from the fact that no soft mode was observed above T_a by the Raman scattering, two possibilities concerning it are considered:[7] i.e., either the soft mode is located at the zone center but is Raman forbidden, or it is located at the nonzero point of Brillouin zone other than the center. The alternative may conveniently be discriminated by hyper-Raman spectroscopy. If the former possibility proves to be the case, a silent optic phonon mode will be involved, because no dielectric anomaly was observed[4] at T_a. The present report indicates that this is indeed the case.

The purpose of the present study is to clarify the character of the phase transition at T_a as well as the behavior of the soft phonon above T_a. It is noted that no detailed study of the structural phase transition caused by the silent soft phonon has ever been reported.

The measurement was done by using a standard hyper-Raman spectroscopic system.[8,9] An acousto-optically Q-switched Nd-YAG laser (Nippon Electric Co.) of 1.06-μm wavelength was employed for excitation. Two samples cut from different single crystals of hexagonal $BaTiO_3$, which were grown by a method similar to those used for the previous Raman scattering measurement,[7] were prepared. The sizes of the rectangular parallelepiped samples with the planes perpendicular to the respective crystallographic axes are $1.2\times1.2\times2.5$ mm^3 and $1.8\times2.1\times4.0$ mm^3, respectively. The sample was set either in a cryostat of gas-flow type for measurement below room temperature, or in a small furnace above room temperature. For both cases, the temperature of the sample was kept constant within ±0.5 °C. All hyper-Raman measurements were carried out in the 90° scattering geometry. The scattered light was collected by a lens onto an entrance slit of a single-grating monochromator (Jobin-Yvon, HR-1000) with F number of 6.8 and an inverse wavelength dispersion of 8 Å/mm. The signal was detected with an optical multichannel detector (Tracor-Northern Co., TN-6133) which was cooled below -40 °C by a liquid circulator in order to improve greatly the signal-to-noise ratio. The beam of the laser, the peak power of which was suppressed to be less than 2.5 kW so as not to cause trouble to the sample, was focused on the sample by a lens of $f = 4.8$ cm.

First, we describe the measurement at room temperature. The phase above T_a belongs to the space group of $P6_3/mmc(D_{6h}^4)$. Then, the optic phonon modes at the Brillouin-zone center are classified into

$$5A_{1g}(\mathrm{R})+2A_{2g}(ia)+6B_{1g}(ia)+B_{2g}(ia)+6E_{1g}(\mathrm{R}) +8E_{2g}(\mathrm{R})+A_{1u}(\mathrm{HR})+6A_{2u}(\mathrm{ir,HR})+2B_{1u}(\mathrm{HR}) +6B_{2u}(\mathrm{HR})+8E_{1u}(\mathrm{ir,HR})+7E_{2u}(\mathrm{HR}), \quad (1)$$

where R, ir, and HR in the parentheses refer to the mode allowed in Raman, infrared, and hyper-Raman spectroscopies, respectively. The symbol *ia* represents the mode forbidden in all those spectroscopic methods. A low-frequency mode such as shown in spectrum (c) of Fig. 1 was found with the center frequency of 25 cm^{-1} in the $x(yz,x)z$ configuration, where the first two notations and the last one in the parantheses refer to the polarization directions of incident and scattered lights, respectively. According to the hyper-Raman tensors for the point symmetry D_{6h}, the B_{1u}, E_{1u}, and E_{2u} modes can be observed for this configuration. This spectrum was also observed in the $x(yy,z)y$ configuration, but was not in the $y(zz,z)x$ one, where the A_{2u} and E_{2u} modes, and A_{2u} mode can be observed, respectively. As a consequence, the spectral line

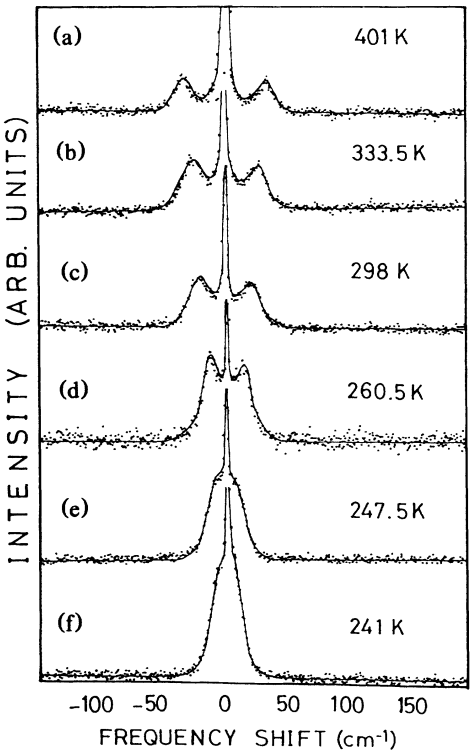

FIG. 1. Variation of the hyper-Raman spectrum due to the soft phonon with temperature in the phase above T_a(221.5 K) of the hexagonal $BaTiO_3$. The upper three spectra from (a) to (c) were observed with a furnace and the others with a cryostat. The sample used in (a) to (c) was different from the one in (d) to (f). Note that the relative vertical scales from (a) to (f) are different from one to another in magnitude. The solid curves are theoretical fits.

was determined to belong to the nonpolar E_{2u} mode which is the so-called silent mode.

This "E_{2u}" mode was found to exhibit remarkable temperature dependence. Examples of those temperature-dependent spectra observed in the $x(yz,x)z$ configuration are shown in Fig. 1. As can be seen there, it turns out that the soft mode remains underdamped down to the temperature very close to T_a. A few comments are given. The upper three spectra and the others were observed with a furnace and a cryostat, respectively. Further, different samples were used in the above two cases. The sample used in spectra (a) to (c) was not a good one so that a rather intense hyper-Rayleigh light located at 0 cm^{-1} was observed. Presumably, the hyper-Rayleigh origin in this case might not be intrinsic but static, arising from the sample portion losing a center of symmetry locally. Furthermore, it is remarked that the signals from (a) to (f) were observed under different experimental conditions, but relative magnitudes were not normalized to each other. As the phase transition temperature T_a is approached from above, the soft-mode signal merges the hyper-Rayleigh or central mode, the intensity of which gradually grows.

The frequency ω_0 and the damping constant Γ of the soft phonon at the respective temperature are readily obtained by analyzing the spectrum. The whole raw spectrum $I(\omega)$ below 50 cm^{-1} was fitted to an equation

$$I(\omega)=A\left[B(\omega)\frac{|\omega|\Gamma}{(\omega^2-\omega_0^2)^2+\omega^2\Gamma^2}+aH(\omega)\right], \tag{2}$$

$$B(\omega)=\begin{cases} n(|\omega|)+1 & \text{for } \omega<0, \\ n(\omega) & \text{for } \omega>0, \end{cases} \tag{3}$$

where a is a constant independent of frequency; the first term in Eq. (2) describes the Stokes and anti-Stokes hyper-Raman components for $\omega<0$ and $\omega>0$, respectively, with the corresponding Bose factor $B(\omega)$, and the second term represents the hyper-Rayleigh component $H(\omega)$. Since the spectral width of the central mode was narrower than the instrumental one, $H(\omega)$ equals the instrumental function of the optical analyzing system. The result of the fitting with three independent adjustable parameters, ω_0, Γ, and a was satisfied at the respective temperature, as is shown in Fig. 1. Variations of the soft-mode frequency and its damping constant with temperature are plotted in Fig. 2. In the above analysis, information about variation of the hyper-Rayleigh component with temperature was also obtained. It was found that the intensity of the hyper-Rayleigh component increases in a divergent manner as T_a is approached from above. The intensity of the central component, on the other hand, is much stronger below T_a than that above T_a. This fact indicates that the phase below T_a should lose a center of inversion[10] and that the origin of the central component is not a scattering light but a coherent one, i.e., the second-harmonic generation (SHG). A plot of the SHG intensity as a function of temperature, as shown in Fig. 3, exhibits a distinct change at a definite temperature, which we define as the phase transition temperature T_a. The absolute

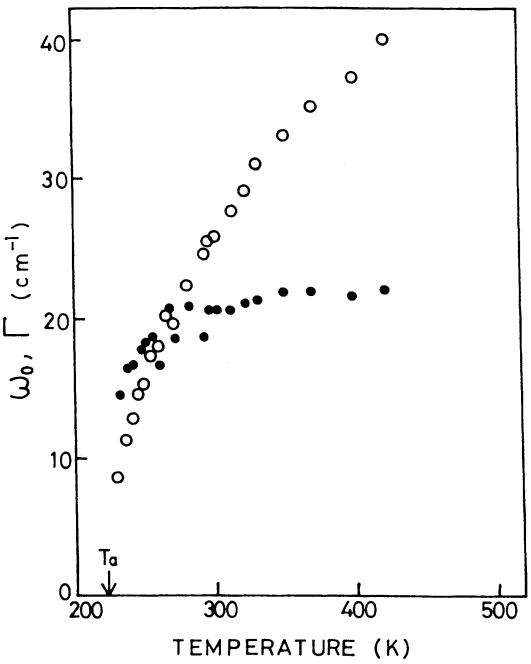

FIG. 2. Variation of the soft-phonon frequency ω_0 (○) and the damping constant Γ (●) with temperature in the phase above T_a (221.5 K) of the hexagonal $BaTiO_3$.

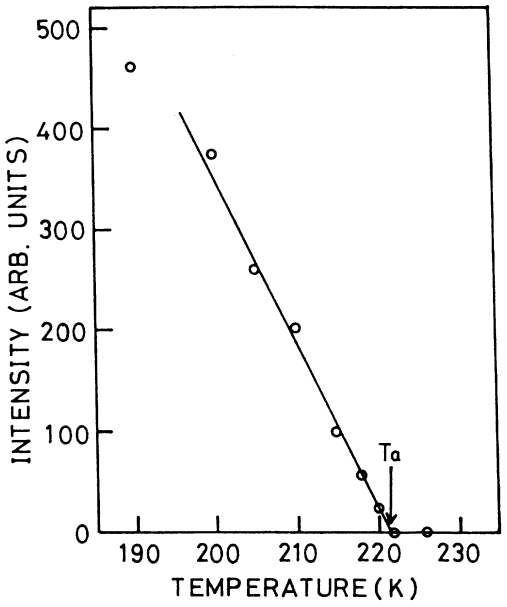

FIG. 3. Variation of the relative intensity of the central component (SHG) as the temperature T_a (221.5 K) is approached from below in the hexagonal $BaTiO_3$. The line is a guide to the eye.

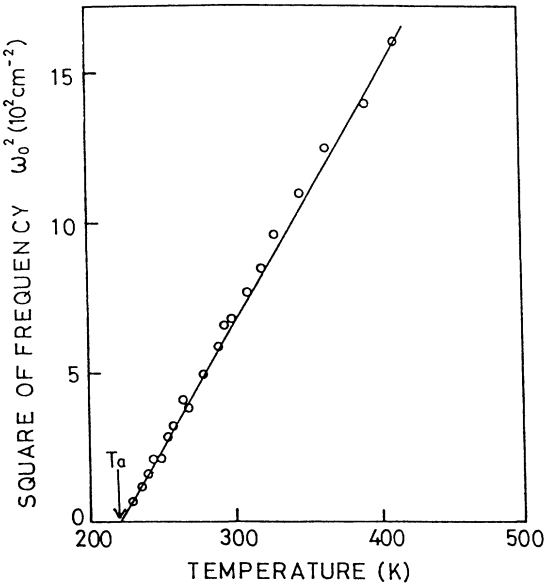

FIG. 4. A plot of the squared soft-phonon frequency vs temperature, indicating that Landau's theory holds in the phase above T_a (221.5 K) of the hexagonal $BaTiO_3$. The straight line is a least-mean-square fit.

temperature was 221.5 ± 0.5 K, which agrees closely with the value determined by Raman measurement.[7] In this connection, it is remarked that the actual temperature in the sample was confirmed to be accurate within ± 3 °C, by inspecting the dependence of the soft-mode frequency on the incident laser power.

The present work might be the first direct observation, as far as we know, of the silent soft phonon at the zone center. As can be seen from Fig. 4, it turns out that the silent soft phonon behaves in an ordinary way, i.e., the soft-phonon frequency obeys, over a rather wide temperature range, the equation $\omega_0(T)^2 = C(T - Ta)^\gamma$, $\gamma = 1$, which holds in the framework of the soft-mode theory by Landau and Cochran, where C is a constant. This result contrasts well with the soft-mode behavior studied by the Raman scattering experiment,[7] where the critical index $\gamma = \frac{2}{3}$ was obeyed. Such tendency at the lower-temperature phase is often reported in several crystals such as $SrTiO_3$ (Ref. 11) and SbSI (Ref. 12) without any adequate explanation. As an example of the phase transition caused by the silent soft mode, we know the only work by neutron scattering on the β quartz where the silent soft optic phonon of B_1 symmetry is believed to be responsible for the α-β phase transition.[13] However, the nature of the overdamped mode hampered to estimate the values of ω_0 and Γ directly from the spectral-line fitting, and only the rough estimate of the values of ω_0 was obtained from the integrated intensity under an assumption. Since an incommensurate phase was recently found to exist[14] in a very narrow temperature range between the α and β phases, and the strong coupling between the soft-optic and acoustic phonons is thought[13,15] to cause the incommensurate phase, the situation in the β quartz should be complicated in comparison with the present simple case.

Prior to the present experiment, whether or not the soft phonon in the phase above T_a is located at the zone center was left undetermined.[7] Now, it has been established that it is the E_{2u} mode located at the zone center. As already described, this fact is consistent with the result of dielectric measurement[4] which does not show any appreciable anomaly at T_a. As for a divergent behavior of the intensity of the hyper-Rayleigh light which is observed as T_a is approached from above, a detailed measurement will be needed including whether or not its origin would be intrinsic. The mode pattern of the present E_{2u} mode will be presented in a forthcoming paper, together with detailed discussion concerning the phase transition mechanism. Finally, on the basis of the present result the symmetry of the intermediate phase below T_a should be $222(D_2)$ or $mm2(C_{2v})$ which lacks an inversion symmetry. This result is consistent with the recent measurement on elastic properties.[5]

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