Soft Acoustic Mode in the Ferroelectric Phase Transition of Hexagonal Barium Titanate

M. Yamaguchi, K. Inoue, and T. Yagi
Research Institute for Electronic Science, Hokkaido University, 060 Sapporo, Japan

Y. Akishige
Faculty of Education, Shimane University, Nishikawatsu-cho, Matsue 690, Japan
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A Brillouin scattering study of the hexagonal modification of barium titanate (h-$BaTiO_3$) was done to elucidate the soft mode behavior in the ferroelectric phase transition at 74 K. Measurements were made in the temperature region $20 < T < 300$ K. A clear softening of the c_{66} shear acoustic mode was found at the phase transition. The squared frequency of the c_{66} mode exhibits a linear dependence on the temperature difference from T_c, both above and below T_c. We conclude from this that the phase transition at T_c is the proper ferroelastic transition with order parameter the elastic strain s_6.

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Barium titanate has two structural polymorphous forms: one is well known and the most extensively investigated ferroelectric perovskite (p-$BaTiO_3$) and the other is the hexagonal modification (h-$BaTiO_3$). The crystal structure of h-$BaTiO_3$ has $6/mmm$ symmetry at room temperature and it differs significantly from the perovskite-type structure in the TiO_6 octahedral arrangement [1]. Both polymorphs undergo a phase transition which contains a ferroelectric phase; however, they have a different series of ferroelectric phase transitions and exhibit different ferroelectric properties from each other.

h-$BaTiO_3$ has a structural phase transition from the hexagonal phase to the orthorhombic 222 phase (phase II) at $T_0 = 222$ K. This phase transition has been understood using the concept of the freezing of the soft E_{2u} silent mode at the zone center [2]. Below T_0, the E_{2u} mode becomes two Raman-active soft optical modes, ω_1 and ω_2. In phase II, h-$BaTiO_3$ still remains paraelectric but it shows piezoelectric properties because of the lack of inversion symmetry. With further decreasing temperature, it undergoes a ferroelectric phase transition at $T_c = 74$ K and exhibits both ferroelectric and ferroelastic properties below T_c (phase III). The mechanism of this phase transition has not been clearly understood up to now. The dielectric constant parallel to the c axis shows an anomaly near T_c and displays Curie-Weiss behavior [3,4]. However, no soft optic mode has been observed by Raman scattering experiments [5]. Only small changes in the frequency of the ω_2 mode have been found around T_c. In addition to this, the elastic strain s_1 measured on a polydomain sample shows an anomaly near 74 K [6]. Unfortunately, due to the existence of domains below T_0, it is impossible to determine each component of the elastic tensor from elastic measurements. The mechanism of the ferroelectric phase transition in h-$BaTiO_3$ is still controversial, and the answer has still not been found to the fundamental question: What is the order parameter for the phase transition at $T_c = 74$ K, the electric polarization P_3, or the elastic strain s_6?

This answer can be found if we study the temperature dependence of the elastic stiffness constant c_{66}, which is known to be different in proper ferroelectric and proper ferroelastic transitions [7]. Brillouin scattering is an extremely powerful tool for these studies, since its high resolution allows very accurate determination of the elastic constant. Thus the character of the phase transition at T_c can be revealed from the results of a Brillouin scattering study. The present study is the first report of a Brillouin scattering study of h-$BaTiO_3$. Though it is impossible to give a detailed discussion of all experimental and theoretical aspects here, we will focus on the experimental results necessary to illustrate the acoustic mode behavior at T_c in order to answer the questions about the fundamental mechanisms of the phase transition at T_c.

Single crystals of hexagonal $BaTiO_3$ were grown from molten $BaTiO_3$; details of the crystal growth were presented previously by one of the authors (Y. A.) in Ref. [4]. The crystal used had the size $3 \times 3 \times 3$ mm^3, with the faces perpendicular to [010], [101], and [10$\bar{1}$] directions. The crystal was annealed at 800 °C for 48 h before the measurement.

The sample was mounted in a closed-cycle He-gas refrigerator and was triply surrounded by superinsulation (Al-coated polyester film) as a radiation shield. We used a temperature controller with a silicon diode sensor. Temperature stability within 0.04 K was achieved during the measurements. In the measurements without a uniaxial stress applied to the sample, the temperature of the crystal was monitored with a Au + Fe (0.07%)–chromel thermocouple attached directly to the sample. Measurements were carried out in the temperature range from 300 to 20 K.

To perform Brillouin scattering, an Ar^+-ion laser operated at $\lambda = 514.5$ nm with a V polarized longitudinal

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single mode was used as a light source. The average incident light power was 50–70 mW. Scattered light was analyzed using a Sandercock-type six-pass tandem Fabry-Pérot (TFP) interferometer with finesse more than 100 [8]. Output light from the interferometer was detected by a photomultiplier (PMT). Spectra presented in this Letter were recorded in a multichannel scaler with 512 channels and were accumulated 500–2000 times with 0.5 sec/channel scans. The PMT signal was also used for finesse maximization of the TFP. When elastic scattering was intense, we included a mechanical shutter in our experimental system in order to eliminate the elastic scattering peak and prevent damage to the PMT. In such a case we used a glass plate to reflect about $\frac{1}{10}$ of the output light from the TFP and direct it into a second PMT for finesse maximization.

As mentioned above, the temperature dependence of the c_{66} mode, which propagates in the direction of the a axis, is necessary to determine the order parameter for the phase transition at T_c. However, the existence of domains below T_0 makes it extremely difficult to obtain the frequency of the c_{66} mode from direct measurements of its Brillouin spectra. As a result of the phase transition from hexagonal to orthorhombic structure, three kinds of domains are formed in phase II. The direction of the a axis of each domain differs by 60° around the c axis [8]. To avoid the effects of these domains, we started the experiments with a weak uniaxial stress along the b^* axis, since it is known that $T_0 = 222$ K at 1 bar is a tricritical point and even a small stress along the b^* axis can induce the monodomain state [9].

Brillouin scattering spectra were observed with several scattering geometries while the area hit by the incident laser beam was changed. No changes in the spectra were observed under the uniaxial stress, thus indicating that a monodomain was formed over the sample below T_0 as a result of the stress applied.

Figures 1(a) and 1(b) show the Brillouin scattering spectra at various temperatures above and below T_c under weak uniaxial stress. Spectra were taken with the right-angle scattering geometry where the acoustic wave vector was parallel to the a axis and the a-c plane was chosen as the scattering plane. The polarizations of the incident and scattered lights were V and $V + H$, respectively. The spectra apparently show softening of the c_{66} mode as T_c is approached from above [Fig. 1(a)] and hardening of the mode below T_c with a new central component [Fig. 1(b)]. This fact strongly suggests that this phase transition is a proper ferroelastic rather than a proper ferroelectric transition, where the acoustic anomaly would be weak. Furthermore, the broad central component is observed separately from the soft mode in the spectra at 70 and 73 K in Fig. 1(b). Though the origin of the central component is not clear at present, presumably it is due to a fluctuation of polarization. However, as this component is not clearly seen in the spectra taken without stress, it might be strongly stress dependent. To clarify the behavior of this component around T_c, further investigation is necessary and will be discussed in future.

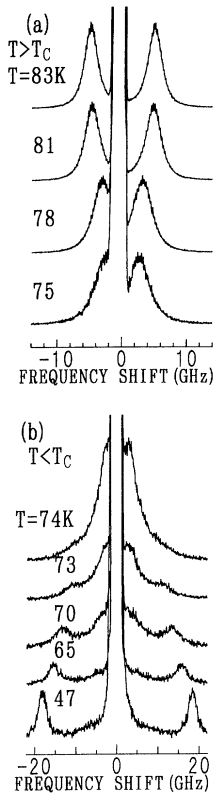

FIG. 1. Brillouin scattering spectra of h-$BaTiO_3$ taken with right angle V-open scattering geometry with weak uniaxial stress (a) above and (b) below T_c, where the q vector is parallel to the a axis and the scattering plane is the a-c plane.

The temperature dependence of the c_{66} mode frequency shifts with weak uniaxial stress observed from phases I to III is shown in Fig. 2(a). A significant anomaly in the frequency shift has been found around T_c and T_0. Before we discuss further the phase transition at T_c, let us briefly mention some important features found for the phase transition at T_0. A downward stepwise jump of the frequency shift is seen at T_0. This change coincides with the mean-field behavior derived in a phenomenological study of the improper ferroelastic phase transition from a centrosymmetric phase to a noncentrosymmetric phase [10]. The frequency shifts just below T_0 are not plotted in Fig. 2 because the central peak also appears around T_0 and the c_{66} mode is merged with the central peak. We concluded that the origin of the central peak is the bilinear coupling between the E_{2u} soft optical mode and the c_{66} acoustic mode below T_0. A detailed analysis of the central peak is important for a description of the nature

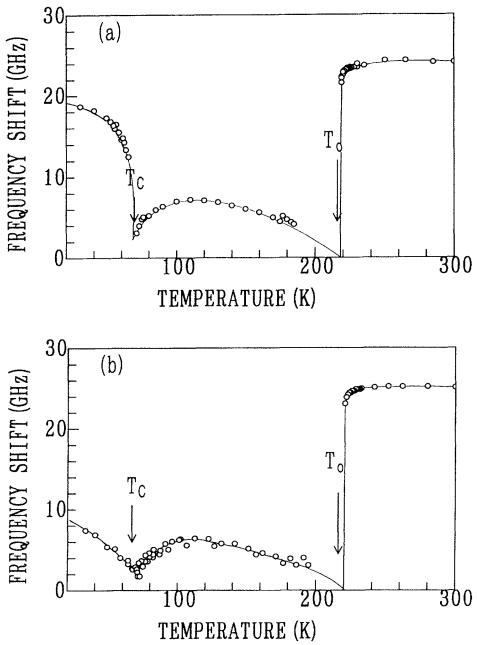

FIG. 2. Temperature dependence of the c_{66} shear acoustic mode frequency shifts observed without (a) and with (b) a small uniaxial stress along the b^* axis. Solid line is a guide to the eyes.

of the phase transition at T_0. This analysis is very lengthy indeed and will be presented separately; in the present Letter we shall focus on the temperature dependence of the frequency shift of the c_{66} acoustic mode. The frequency shift of the c_{66} mode becomes zero at T_0, and it increases with decreasing temperature. Ishibashi *et al.* [11] discussed the temperature dependence of the c_{66} mode in terms of mean-field theory and pointed out that the zero value of c_{66} comes from the symmetry relation of the phase transition at T_0. The agreement between that discussion and the present is quite good around T_0. This strongly suggests mean-field behavior of the elastic constant around T_0, although it is contradictory to Raman scattering results which show nonclassical behavior of the soft mode below T_0 [5].

As the temperature is decreased further from T_0, the c_{66} mode exhibits significant softening, reflecting the existence of the soft acoustic mode in the phase transition at T_c. Once we know the temperature dependence of the c_{66} mode in phase II under small stress, we can unambiguously assign the c_{66} peak without stress by looking for a domain that has a similar frequency shift of the shear acoustic mode. Figure 2(b) shows the temperature dependence of the c_{66} mode observed without any stress on the b^* axis. Our results indicate that the temperature dependence of the c_{66} mode without stress is quite similar to that with small stress, except for the temperature region below T_c. When uniaxial stress is present, the c_{66} mode has a considerably larger frequency below T_c, compared to the case when no stress is applied. This difference in frequency is considered to be due to a transition to domains which have different directions of the crystal axis below T_c.

The squared frequency shift of the c_{66} mode around T_c is plotted in Fig. 3. This squared value of the frequency shift is proportional to the elastic stiffness constant c_{66} when density is assumed constant. The squared frequency near T_c exhibits a linear dependence on the temperature difference from T_c both above and below T_c in the temperature region about 30 K below and 10 K above the transition temperature (Fig. 3), indicating that the index of this soft acoustic mode is $\frac{1}{2}$. Sawada, Udagawa, and Nakamura [7] described the principal difference in the temperature dependence of the elastic constant in proper ferroelastic and proper ferroelectric phase transitions from a noncentrosymmetric phase within the framework of the mean-field theory. While in the proper ferroelastic transition the elastic stiffness constant is proportional to the temperature difference $(T - T_c)$, in the proper ferroelectric transition it varies with temperature as $c_{66} \sim (T - T_c)/(T - T_a)$, where T_a is the Curie-Weiss temperature and T_c is the phase transition temperature [7]. In Fig. 3, the linear dependence of the squared frequency on $(T - T_c)$ near the transition temperature shows the mean-field behavior of the proper ferroelastic phase transition. In Fig. 3, the squared soft mode frequency has not reached zero at the phase transition temperature $T_c = 74$ K; thus a first order phase transition is indicated. However, this small frequency shift at T_c could be thought as the result of the relatively large refractive index of h-$BaTiO_3$, in which case even a slight misalignment of the sample could cause relatively large uncertainty in the results. It is difficult to establish whether or not the squared soft mode frequency dependence in Fig. 3 is discontinuous at T_c. According to the thermal analysis results of Akishige *et al.* [12], no significant anomaly was detected at the transition temperature within the experimental resolution, suggesting that the discontinuity must be very small if it exists. Thus the question about the order of

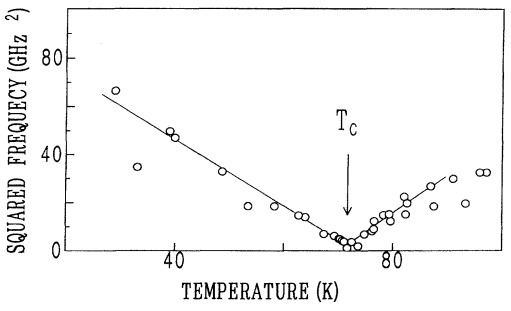

FIG. 3. Temperature dependence of squared frequency of the c_{66} mode near T_c. Solid line is a guide to the eyes.

the transition still remains and the possibility of a second order transition cannot yet be excluded.

We have discussed the soft acoustic mode behavior at the ferroelectric phase transition in h-$BaTiO_3$ in order to determine its character and find the order parameter. A few significant efforts have been previously made to characterize the phase transition at T_c. It was pointed out that Raman scattering experiments of h-$BaTiO_3$ found no soft optic mode around T_c [5]. Furthermore, it was reported that the dielectric anomaly near T_c decreases with increasing uniaxial stress. Both results suggest the ferroelastic character of the phase transition at T_c. The existence of the soft acoustic mode in the ferroelectric phase transition of h-$BaTiO_3$ revealed by the present Brillouin scattering experiment is of great importance for understanding the dynamics of this phase transition. The present result supports the view that the phase transition at T_c is the ferroelastic transition and leads to the conclusion that it is the proper ferroelastic phase transition with the order parameter the elastic strain s_6.

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