Elastic softening and central peaks in BaTiO$_3$ single crystals above the cubic-tetragonal phase-transition temperature

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A strong relaxation mode was observed in the paraelectric phase of barium titanate (BaTiO$_3$) single crystals by Brillouin scattering study and was found to correlate with the softening of the longitudinal acoustic mode and the increase in the hypersonic damping. These observations support the existence of polar precursors and their electrostrictive coupling with the strain caused by the acoustic waves, consistent with former studies evidencing off-centered Ti ions in the high-symmetry cubic phase. A critical slowing down has been clearly observed in the vicinity of the cubic-tetragonal phase transition, indicating order-disorder component contributes to the phase transition of BaTiO$_3$. © *2008 American Institute of Physics.* [DOI: 10.1063/1.2980444]

Barium titanate (BaTiO$_3$) is one of the most extensively studied ferroelectrics characterized by the simple cubic perovskite structure. It shows successive cubic-tetragonal-orthorhombic-rhombohedral phase transitions upon cooling. Originally, a displacive soft-mode concept has been used to explain the nature of the phase transitions of BaTiO$_3$.[1,2] However, infrared measurements revealed an overdamped soft mode at small wavevectors, which levels off near 60 cm^{-1} close to the cubic-tetragonal phase-transition temperature ($T_{C\text{-}T}$) indicating the possibility of a disorder in the paraelectric cubic phase.[3] In addition, the observation of diffuse x-ray scattering,[4] persistent Raman spectra far above $T_{C\text{-}T}$,[5,6] anomalous temperature dependence in the refractive index,[7] and the birefringence[8,9] suggested a formation of pretransitional polar clusters in the paraelectric cubic phase. The microscopic nature of these polar precursors has recently been revealed by x-ray absorption fine structure[10] and nuclear magnetic resonance measurements[11] to be composed of dynamic off- center displacements of Ti ions along eight equivalent ⟨111⟩ directions, consistent with the original eight-site model suggested for the order-disorder component in BaTiO$_3$.[4] However, although the disorder at the *B*-site ions is expected to enhance the ferroelectric instability,[12] exact roles and microscopic natures of displacive and order-disorder components during the phase transition are still controversial. In addition, the relation of two-mode behaviors, recently revealed by a first-principles-based calculation and far-infrared reflectivity measurements,[13] to these two phase-transition components remains far from complete understanding.

Analysis of the acoustic anomalies occurring near the phase transition can be used to get more insights into the nature of the phase-transition process of BaTiO$_3$.[14] Previous acoustic studies on this ferroelectric compound measured in a limited temperature range showed that the longitudinal sound velocity becomes softened on approaching $T_{C\text{-}T}$ from

high-temperature side.[15–19] The anomalous part of the sound velocity has been explained by using different phenomenological approaches,[15,17] and the acoustic absorption was shown to increase upon cooling near $T_{C\text{-}T}$.[16] Moreover, inelastic light scattering technique carried out by Sokolov *et al.*[20] revealed the existence of central peaks (CPs) near $T_{C\text{-}T}$ indicating relaxation modes are related to this phase transition. However, there has been no systematic comparison between the acoustic anomalies and the quasielastic relaxation modes observed in the paraelectric phase of BaTiO$_3$ as well as their relation to the nature of the cubic-tetragonal phase transition, which can now be tackled and discussed in more detail; thanks to the high-resolution tandem Fabry–Pérot interferometer. The purpose of this letter is to report clear correlation between the acoustic anomalies and the temperature evolution of CPs based on the light scattering spectra measured in a widest temperature range up until now.

The BaTiO$_3$ single crystal used in this study was grown by a flux method. It is the same crystal as the one used for local strain analysis.[21] The surface normal of the grown single crystals was prepared to be [001] and the surfaces were polished to optical quality. Typical sample dimensions were $1 \times 1 \times 0.1$ mm^3. Complex dielectric constant was measured using a conventional impedance analyzer (HP 4284A) from which $T_{C\text{-}T}$ was found to be 374 K for the cooling process. A 3+3 pass Sandercock-type tandem Fabry-Pérot interferometer has been used to measure the Brillouin spectra for the laser beam of 532 nm at a backward scattering geometry for observing longitudinal acoustic (LA) waves propagating along the [001] (=[100]) direction in the cubic phase, where $C_{11}(=C_{33})$ elastic constant is probed in the paraelectric phase.

Figures 1(a) and 1(b) show measured Brillouin spectra of the BaTiO$_3$ single crystal in a narrow and a wide spectral ranges, respectively, at selected temperatures. Brillouin spectrum measured at 573 K shown in Fig. 1(a) consists of one Brillouin doublet corresponding to the LA waves propagating along the [001] direction. The sudden appearance of the
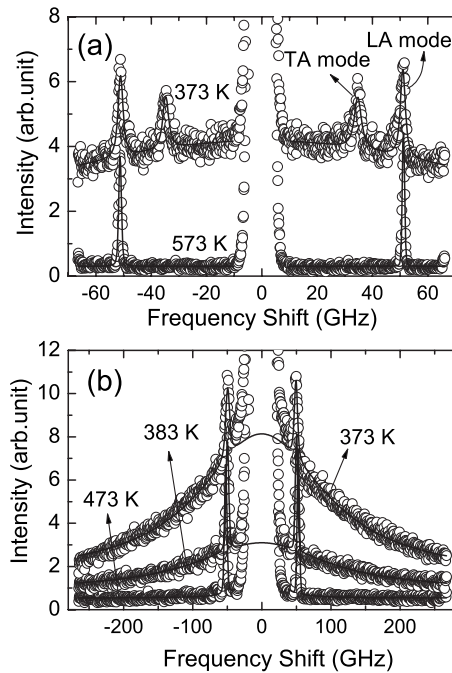
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FIG. 1. Brillouin spectra of BaTiO$_3$ single crystals in (a) a narrow- and (b) a wide-frequency ranges at selected temperatures (open symbols) along with fitted results (solid lines).
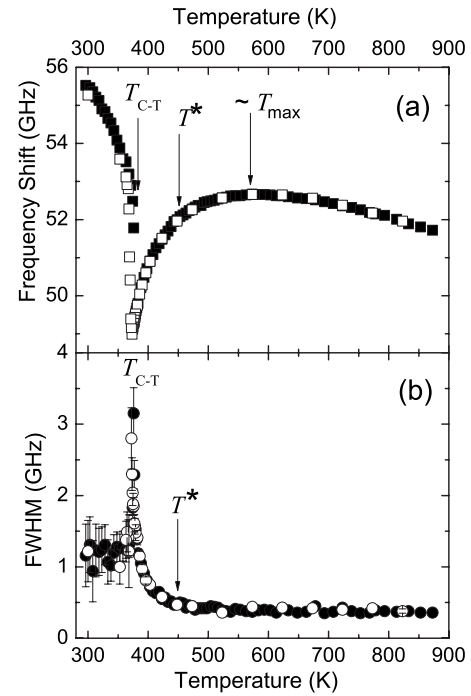

FIG. 2. The temperature dependences of (a) the Brillouin frequency shift and (b) the FWHM of LA waves measured during both heating (solid symbols) and cooling (open symbols) processes.

transverse acoustic mode at 373 K just below T_{C-T} indicates a structural phase transition from cubic to tetragonal phase. The spectrum measured in a wide-frequency range shown in Fig. 1(b) includes a CP component in addition to the phonon contributions, which grows gradually upon cooling below 450 K and shows a drastic change in the intensity at T_{C-T}. The Brillouin doublet has been fitted by the response function of the damped harmonic oscillator, which was approximated by the Lorentzian functional form. The fitted results are shown as solid lines in Fig. 1. The resulting Brillouin shift (ν_B) and the full width at half maximum (FWHM) are shown in Figs. 2(a) and 2(b), respectively, measured during both heating (solid symbols) and cooling (open symbols) processes. The high-temperature side of ν_B above 600 K displays a monotonic increase with decreasing temperature, which can be understood in terms of normal lattice anharmonicity.[22] ν_B reaches a maximum at $T_{max} \simeq T_{C-T} + 200$ K and then becomes softened upon further cooling. In the temperature range above T_{max}, the hypersonic damping represented by FWHM is almost constant without any noticeable change. ν_B displays softening below T_{max} concomitant with gradual increase in the FWHM on approaching T_{C-T}. In particular, the changes in both ν_B and FWHM become more substantial at about 450 K, which will be denoted as T^*. ν_B becomes minimum at T_{C-T}, which coincides with the maximum temperature of the hypersonic damping.

The CP shown in Fig. 1(b) was fitted by using a single Lorentzian function centered at zero frequency superposed on a constant background signal assuming a single Debye relaxation process. The constant background signal was fixed to the value measured at 473 K at which no CP was observed. The inverse of the relaxation time was obtained from the FWHM and is shown Fig. 3(a), and the integrated intensity is plotted in Fig. 3(b). The inverse of the relaxation time shows a linear behavior near T_{C-T}, which signifies that the order-disorder mechanism contributes to the cubic-tetragonal

phase transition of BaTiO$_3$. The relaxation time τ related to the critical slowing down for order-disorder-type phase transition is given by the following formula[23]

$$\frac{1}{\tau} = \frac{T - T_0}{\tau_0 T_0}. \tag{1}$$

The results from the fitting procedure using Eq. (1) in the cubic (temperature range of $T_{C-T} \sim T_{C-T} + 20$ K), and tetrago-
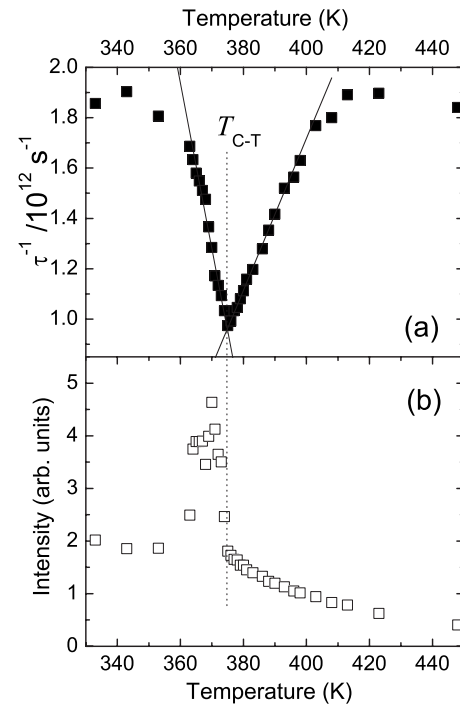

FIG. 3. The temperature dependence of (a) the inverse of the relaxation time estimated from the width of CP and (b) the integrated intensity of CP. The solid lines shown in (a) are best-fitted results by using Eq. (1).

nal (temperature range of $T_{C-T} \sim T_{C-T} - 15$ K) phases are $T_0 = 343$ K ($\tau_0 = 0.09$ ps) and $T_0 = 389$ K ($\tau_0 = 0.04$ ps), respectively. It should be noted that the specific temperature range above T_{C-T}, where critical slowing down is observed, is very similar to the region where relatively large birefringence has been observed.[9] The incomplete slowing down observed near T_{C-T} may partly be due to the first order character of the phase transition and also to the defects included in the crystal.

The temperature dependences of ν_B and FWHM are very similar to those of relaxor ferroelectrics (RFEs) where polar nanoregions (PNRs) play an important role in the formation of complex dynamics RFEs exhibit.[24,25] The deviation of the elastic constant from the normal anharmonic behavior at high temperatures is correlated to the formation of dynamic PNRs at the so-called Burns temperature.[24] As the PNRs become long lived with longer correlation length with decreasing temperature, electrostrictive coupling between the squared polarization of PNRs and the strain caused by the acoustic waves become stronger resulting in the substantial softening of ν_B and the increase in the hypersonic damping. Similar scenario can be applied to the interpretation of the acoustic anomalies observed from BaTiO$_3$. There have been many experimental evidences for the existence of off-centered Ti ions in the paraelectric cubic phase of BaTiO$_3$. These will instantaneously be off-centered along eight equivalent $\langle 111 \rangle$ directions and hop between them on a shorter time scale and may form randomly oriented polar clusters on a longer time scale.[10,11] The polarization fluctuations induced by this disorder is the origin of CP formed at T^* as well as the acoustic anomalies seen as substantial changes in ν_B and the hypersonic damping. It is believed that the same origin is responsible for the appearance of diffuse x-ray scattering,[4] persistent Raman spectra far above T_{C-T},[5,6] anomalous temperature dependence in the refractive index[7] and the birefringence,[8,9] and the observation of broad CP in the Raman spectrum.[20] Moreover, these polar clusters seem to be more correlated with enhanced intercluster interactions below T^* toward T_{C-T} because the acoustic anomalies seen in Fig. 2 are closely correlated to the formation of CP.

However, it is difficult to identify the microscopic nature of the relaxation mode of CP from only the Brillouin scattering study. Recent first-principles-based calculations and far-infrared reflectivity measurements[13] showed that two different overdamped modes exist in the paraelectric phase. The higher-frequency mode was shown to level off above 60 cm^{-1} at all temperatures while the lower-frequency mode softened upon cooling toward T_{C-T}. The characteristic frequency of the latter mode at which the imaginary part of the dielectric function peaks enters into the Brillouin frequency window [approximately ± 600 GHz ($= 20$ cm^{-1}) in the present experiment] near $T \sim T_{C-T} + 80$ K. It should be pointed out that CP began to appear at $T^*(450$ K$) \simeq T_{C-T} + 83$ K in our samples. The susceptibility of heavily overdamped harmonic oscillator is hardly distinguishable from that of the Debye relaxation mode, and the relaxation frequency estimated from the width of CP decreases linearly in almost the same temperature interval above T_{C-T}. It is thus suggested that the origin of CP observed in the paraelectric phase of BaTiO$_3$ is related to the low-frequency overdamped mode revealed by the most recent infrared study.[13]

In conclusion, the present Brillouin scattering study revealed that a strong CP representing a relaxation mode and a significant softening of the phonon frequency of the LA waves are observed and shown to correlate to each other in the paraelectric phase of BaTiO$_3$ single crystals. The Brillouin shift shows deviation from normal anharmonic behavior in the high-temperature range, and it shows a substantial softening below 450 K accompanied by drastic increase in the hypersonic damping as well as the growth of CP. All these observations support the existence of polar precursors that couple to acoustic waves via electrostrictive interactions, consistent with previous studies reporting the existence of disorder due to off-centered Ti ions in the high-symmetry cubic phase. The temperature dependence of the relaxation time estimated from the width of CP shows a critical slowing down indicating the importance of the order-disorder nature during the cubic-tetragonal ferroelectric phase transition in BaTiO$_3$.

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