Precursor dynamics in the ferroelectric phase transition of barium titanate single crystals studied by Brillouin light scattering

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The acoustic anomalies and precursor dynamics of high-quality barium titanate single crystals were investigated by Brillouin light scattering and the birefringence measurements in the paraelectric phase above the cubic-to-tetragonal ferroelectric phase transition temperature (T_c). Two elastic stiffness coefficients C_{11} and C_{44}, the related sound velocities, and their absorption coefficients were determined from T_c to 400 °C for the first time. The longitudinal acoustic (LA) mode showed a substantial softening over a wide temperature range above T_c which was accompanied by a remarkable increase in the acoustic damping as well as growth of central peaks. The broad central peak (CP) exhibited a two-mode and one-mode behavior in the paraelectric and ferroelectric phase, respectively, which was consistent with recent far-infrared reflectivity measurements and first-principle-based calculations [Ponomareva *et al.*, Phys. Rev. B **77**, 012102 (2008)]. The acoustic anomalies and CP behavior were correlated with the anomalous birefringence, piezoelectric effect, and the deviation of the Curie-Weiss law observed from the same crystal. This strongly indicates similarity between the dynamics of polar clusters in typical ferroelectrics and the dynamics of polar nanoregions in relaxors, consistent with recent acoustic emission measurements [Dul'kin *et al.*, Appl. Phys. Lett. **97**, 032903 (2010)]. The relaxation times estimated from the central peak and the LA mode anomalies exhibited similar temperature dependences with comparable orders of magnitude, indicating that the polarization fluctuations due to the precursor polar clusters couples to the LA mode through density fluctuations. All these anomalies share common microscopic origin, correlated Ti off-centered motions forming polar clusters having local symmetry breaking in the paraelectric phase. The existence of the polar clusters were directly evidenced by the temperature evolution of the precise birefringence map. The narrow central peak within ±5 GHz proposed before was not confirmed to exist in the present study.

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I. INTRODUCTION

Barium titanate ($BaTiO_3$, abbreviated as BT) is one of the most archetypal ferroelectrics that have been studied intensively since its discovery in 1943.[1] BT was originally considered to belong to the class of displacive-type ferroelectrics where the instability of the low-lying transverse optic soft mode plays an important role.[2] However, an order-disorder model for BT was already proposed at the early stage of the research on this ferroelectric material.[3] In addition, observation of diffuse x-ray scattering,[4] incomplete softening of the low-frequency soft mode,[5] persistent Raman spectra in the paraelectric cubic phase,[6] and the deviation of the optic index of refraction from the high-temperature linear behavior[7] illustrated order-disorder nature of the phase transition of BT single crystal. Burns and Dacol ascribed the anomalous behavior of the index of refraction to the existence of "precursor order," that is, precursor local polarizations in the paraelectric phase above T_c. These precursor polar clusters are local, noncubic regions having a broken inversion symmetry and a local polarization. They can thus give rise to many anomalous properties above T_c, for example, anomalous behavior of the birefringence observed in the paraelectric phase of BT single crystals.[8,9]

The original diffuse x-ray scattering study[4] suggested that the Ti ions are disordered among eight equivalent ⟨111⟩ sites, and this eight-site model was supported by recent x-ray absorption fine structure(XAFS) study on BT.[10] The disorder at the B-site ions is expected to enhance the ferroelectric instability.[11] The relaxational hopping motions of these Ti ions between equivalent sites have been investigated and discussed via various experimental methods such as soft pulsed x-ray speckle measurements,[12] photon correlation spectroscopy study,[13] and Raman and Brillouin light scattering techniques.[14,15] The soft pulsed x-ray speckle measurements[12] and photon correlation spectroscopy study[13] revealed that the cluster dynamics can become longer up to 100 ps and a few tens of microseconds, respectively. The Brillouin light scattering study[15] carried out on flux-grown BT single crystals showed that the acoustic phonons exhibit anomalous changes concomitant with the appearance of quasielastic central peak (CP) on approaching T_c in the paraelectric phase.

Today, it is widely accepted that the displacive and order-disorder components coexist in the ferroelectric phase transition of barium titanate.[16] NMR (nuclear magnetic resonance) study on this material revealed that three tetragonal distortions induced by displacive soft mode exist in the paraelectric phase in addition to the dynamic Ti disorder.[17,18] Two dynamic time scales were suggested from this coexistence, that is, fast $\langle 111 \rangle$ hopping of Ti ions and slow 90° flipping of tetragonal nanodomains on a much longer time scale. Namikawa *et al.* attributed their observation of the precursor dynamics to the Ti hopping motions[12] and suggested a possible existence of narrow CP component in the giga-Hertz range, consistent with the observation by Sokoloff *et al.*[14] Recently, Ponomareva *et al.* reported a dielectric response of BT single crystal in the tera-Hertz range by using far-infrared reflectivity measurements and revealed two different overdamped modes.[19] The high-frequency mode stays in the range of 60–100 cm^{-1} while the low-frequency mode softens toward T_c. This two-mode behavior was confirmed in the first-principle-based calculation results carried out by the same group.[19]

In spite of all previous studies on this important ferroelectric material, a detailed microscopic picture of displacive and order-disorder components and their exact role during the phase transition remain still unresolved. In this context, we determined to revisit the elastic properties of high-quality BT single crystals based on which we may get more insights into the precursor dynamics of polar clusters related with the order-disorder nature of the ferroelectric phase transition. In previous Brillouin scattering study on flux-grown BT single crystals,[15] it was found that the longitudinal acoustic (LA) mode frequency and its damping factor exhibited substantial changes in the paraelectric phase. These acoustic anomalies were accompanied by the excitation of strong CP. The relaxation time estimated from the width of CP was found to increase toward T_c, indicating a slowing down behavior of the relevant dynamics. The appearance of an order parameter and its interaction with elastic strain caused by acoustic waves are usually the main origin of acoustic anomalies observed during structural phase transitions. The order-parameter fluctuations due to relaxation processes of precursor clusters are expected to contribute to anomalous changes in both real and imaginary parts of the complex elastic constants.

The present contribution can be differentiated from the previous study in many aspects. First, this paper reports on high-quality BT single crystals grown by top-seeded solution growth (TSSG) method whose cubic-tetragonal phase transition temperature (T_c) is about 130 °C. This study is thus a complementary work to the previous one carried out on flux-grown BT single crystals.[15] However, the spectral range used to record the inelastic light scattering spectrum was extended to ±700 GHz by which more accurate spectral features in both narrow and broad frequency ranges could be obtained. Second, there have been many experimental results on the same crystal such as piezoelectricity,[20] nonlinear properties,[21] and birefringence[9] in the paraelectric phase. Therefore, systematic comparisons between these physical properties could become possible. Special attention was paid to the relaxor-like behavior recently proposed based on acoustic emission measurement on BT[22] in order to discuss similarities and differences between typical ferroelectrics and relaxors. Third, the lower limit of the spectrum was extended down to ±1 GHz in order to check out whether narrow CP, reported in previous Brillouin study[14] and suggested by Namikawa to exist in the giga-Hertz frequency range,[12] really exists or not. Fourth, elastic properties of reduced BT single crystal were investigated and compared to those of pure BT single crystal. The effect of oxygen vacancies on the polar cluster dynamics may be discussed accordingly.

II. EXPERIMENT

The BT single crystals used in the present study were grown by TSSG method in air from a standard solution with an excess of TiO_2. The obtained crystals were cut to obtain (100)-oriented platelets, which were polished to optical quality. The reduced BT single crystal, abbreviated as R-BT, was post-growth annealed in a reducing 90% CO_2 + 10% CO atmosphere at 1000 °C. A micro-Brillouin scattering system with a (3 + 3) pass Sandercock-type tandem Fabry-Perot interferometer was used to measure the Brillouin spectra of BT single crystals at a backward scattering geometry with a free spectral range of 75 GHz for LA mode, 400 GHz for CP, and 12 GHz for narrow CP measurements. A diode pumped solid state laser at the wavelength of 532 nm was used as an excitation light source. The sample was placed inside a cryostat cell (Linkam, THMS600) and the temperature was changed from 400 °C to room temperature with a minimum temperature interval of 1 °C. In the present backward scattering geometry, only the LA mode propagating along the $\langle 100 \rangle$ direction is allowed, but a leakage signal of the transverse acoustic (TA) mode can be seen due to the aperture broadening effect caused by the finite solid angle of the objective lens of the micro-Brillouin spectrometer.[23] Thanks to this leaked signal of TA mode, the temperature dependence of the related sound velocity and the elastic stiffness coefficient C_{44} could be obtained in the paraelectric phase.

In order to corroborate the existence of polar clusters and find their spatial distribution, the birefringence measurements were performed by means of an Oxford Cryosystems Metripol Birefringence Imaging System (Metripol). The sample was held by a high precision Linkam TMSG600 temperature stage combined with a birefringence imaging system. Details of this automated optical technique are described in Ref. 24.

III. RESULTS AND DISCUSSION

A. Acoustic modes

Figure 1(a) shows a part of the measured Brillouin spectra at a few selected temperatures. The spectrum at 400 °C, which is far above T_c, exhibits a strong LA mode at about 53 GHz and a weak TA mode at ~42 GHz, which is attributed to a leakage signal due to aperture broadening effect mentioned above. When the temperature decreases across T_c, additional TA mode appears at about 37 GHz. Figure 1(b) displays the spectra of R-BT single crystals, which exhibit qualitatively similar behaviors as pure BT crystals do. These spectra were fitted by using a superposition of a response function of damped harmonic oscillators, from which the Brillouin frequency shift (ν_B) and the full width at half maximum (FWHM) of each mode could be obtained. Figure 2 shows the temperature

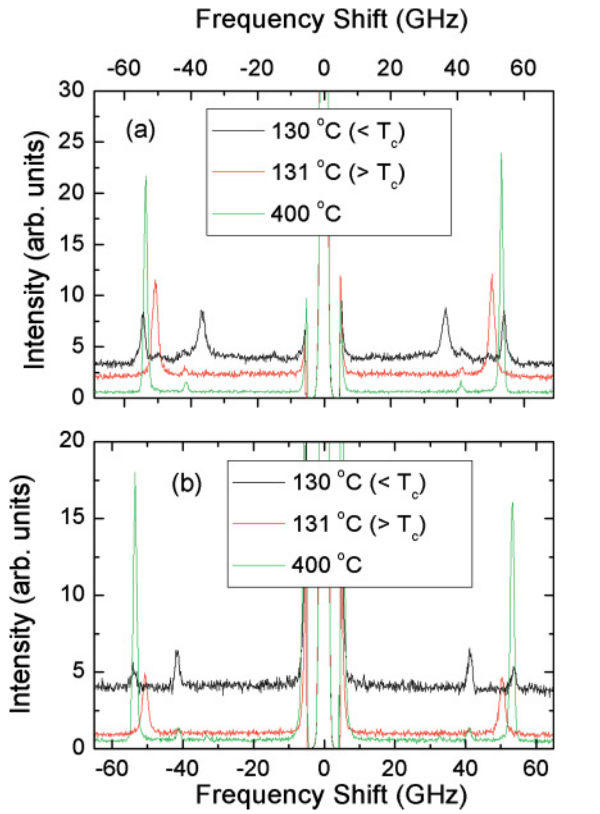

FIG. 1. (Color online) Brillouin spectra at three temperatures of (a) BT and (b) R-BT single crystals.

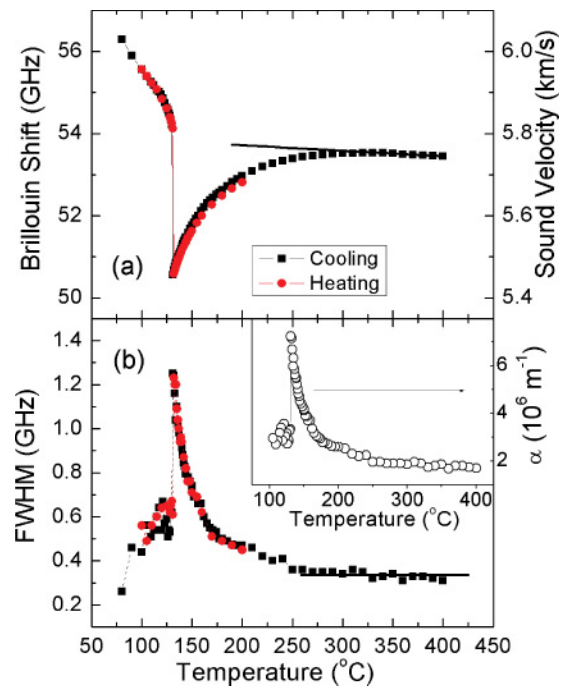

FIG. 2. (Color online) Temperature dependence of (a) the Brillouin shift of the LA mode and (b) the FWHM of the LA mode of BT single crystal. (Inset: The temperature dependence of the attenuation coefficient.)

dependence of ν_B and FWHM of BT single crystals. Figure 3 shows the same data for R-BT single crystals. The sound velocity V and the attenuation coefficient α can be calculated from ν_B and FWHM (denoted as Γ_B) as follows:

$$V = \frac{\lambda \nu_B}{2n}, \tag{1}$$

$$\alpha = \pi \Gamma_B / V. \tag{2}$$

In these equations, λ and n are the wavelength of the laser light (532 nm in the present case) and the refractive index at λ. The refractive index n of BT single crystals at 200 °C in the paraelectric phase reported by Burns *et al.*[7] was used to derive the refractive index at the wavelength of 532 nm to be 2.48. The calculated sound velocities are proportional to ν_B and thus shown on the right ordinate of Figs. 2(a) and 3(a). α is plotted in the insets of Figs. 2(b) and 3(b). The temperature dependence of n was neglected in this calculation. The temperature variation of n in the range from T_c till 400 °C is about 0.0055,[7] which overestimates V by about 0.2% at the highest temperature.

The elastic stiffness coefficients C_{11} and C_{44} can be obtained from the sound velocity and the density ρ according to the following equations:

$$C_{11} = \rho V_{\mathrm{LA}}^2, \tag{3}$$

$$C_{44} = \rho V_{\mathrm{TA}}^2, \tag{4}$$

V_{LA} and V_{TA} denote the LA and TA sound velocities, respectively. The temperature dependence of the density was calculated based on the reported lattice constant of BT in the cubic phase by Shebanov.[25] The temperature dependences of C_{11} and C_{44} in the paraelectric phase are shown in Fig. 4 for both single crystals.

The LA mode behaviors of these two single crystals share common characteristics. First, the LA mode frequency is almost constant above 300 °C. The maximum temperature of ν_B is very similar to that of the flux-grown BT single crystal.[15] The degree of softening of V_{LA} of the BT single crystal near T_c is consistent with the result obtained by ultrasonic measurements.[26] Second, ν_B of the LA mode decreases and FWHM of this mode increases substantially upon cooling below 180 °C. This indicates the LA waves are strongly coupled to other degrees of freedom resulting in the remarkable damping as well as softening. The attenuation coefficient α of the LA mode is less than 2×10^6 m^{-1} at temperatures above 250 °C, but it increases substantially upon cooling and reaches more than 6×10^6 m^{-1} near T_c. The sharp discontinuity in both ν_B and FWHM (and thus V and α) reflects the structural phase transition from cubic to tetragonal phases of BT single crystals. The thermal hysteresis in T_c between the cooling and heating processes indicates the first-order character of the ferroelectric phase transition. These remarkable changes in the LA mode properties are in contrast to the temperature dependences of TA mode and C_{44}, which do not show any substantial change in the paraelectric phase, consistent with previous ultrasonic study.[26] Among the three eigenvalues (that is, $C_{11} + 2C_{12}$, $C_{11} - C_{12}$, and C_{44}) for the elastic constant matrix in the cubic phase, $C_{11} - C_{12}$ and C_{44} correspond to the tetragonal (or orthorhombic) and rhombohedral distortion, respectively. The substantial softening of C_{11}, which may reflect in part the critical behavior of the eigenmode $C_{11} - C_{12}$, seems to be consistent with the NMR results that tetragonal distortions

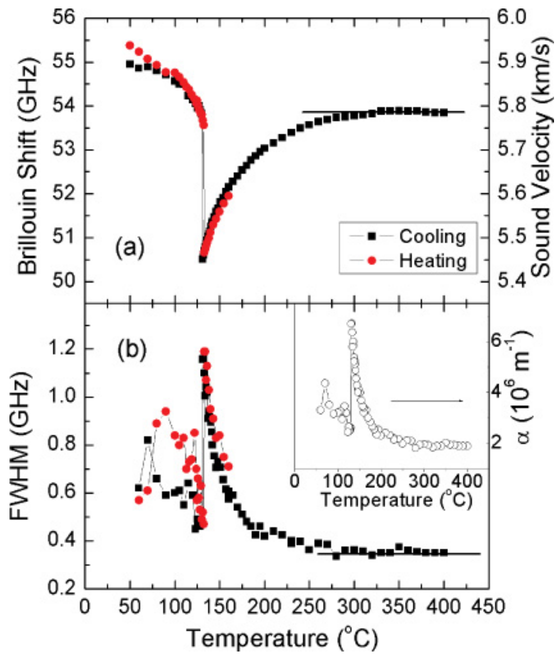

FIG. 3. (Color online) Temperature dependence of (a) the Brillouin shift of the LA mode and (b) the FWHM of the LA mode of R-BT single crystal. (Inset: The temperature dependence of the attenuation coefficient.)

are induced by displacive soft mode in the paraelectric phase.[18]

In case of normal solids, the Brillouin frequency shift proportional to the sound velocity increases monotonically upon cooling and becomes saturated near 0 K. This temperature dependence can be explained based on normal lattice anharmonicity.[27] However, ν_B of BT single crystals deviates from this normal behavior at temperatures far above T_c. According to the first-principle calculations by Geneste,[28] the local free energy in the paraelectric phase of BT begins to exhibit eight minima along the ⟨111⟩ directions at $\sim(T_c + 400)\,^\circ$C. This suggests that the deviation of ν_B from the normal anharmonic behavior is due to the formation of off-center dipoles and their electrostrictive coupling to the LA waves.

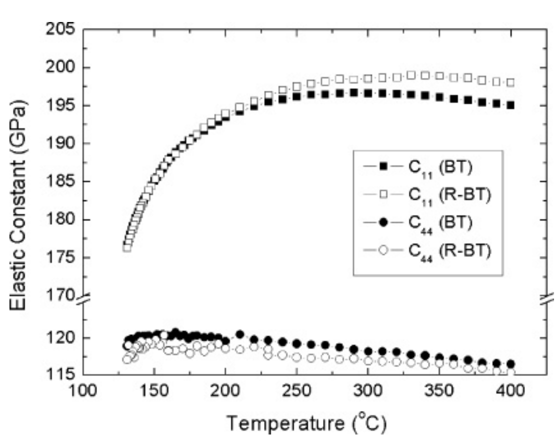

FIG. 4. The temperature dependence of the elastic stiffness coefficients C_{11} and C_{44} in the paraelectric phase.

B. Central peaks

1. *Broad central peak*

Figures 5(a) and 5(b) show the temperature dependence of CP of the BT single crystal above and below T_c, respectively. Figure 6 shows the same data of the R-BT single crystal. The frequency range investigated in this study (−700 to +700 GHz) corresponds to ±23.3 cm^{-1}. At temperatures above 300 °C in the paraelectric phase, the light scattering spectrum is almost flat and does not show any significant change during temperature variation. However, we can notice some mild slope from the spectrum. As temperature decreases, the CP grows and its half width becomes narrower. The intensity and the spectral shape of CP suddenly change at T_c, below which CP intensity decreases upon further cooling.

The microscopic origin of the strong CP observed from BT crystals has been ascribed to the off-centered motions of Ti ions in the oxygen octahedra.[15] The polarization fluctuations induced by the relaxational Ti motions have been considered to induce the quasielastic CP observed from many BT-based perovskite ferroelectrics. In this case, the spectral feature can be explained by using the response function of a single Debye relaxor or superposition of several relaxors. In previous studies,[15,29] the CP observed in the paraelectric phase measured in a limited frequency range could be fitted by using a single Debye function. However, the CP data shown in Fig. 5(a), of which the frequency range is much wider than before, could not be fitted by using one Debye function. It indicates that the quasielastic CP in the paraelectric phase of BT consists of, at least, two relaxation (or overdamped)

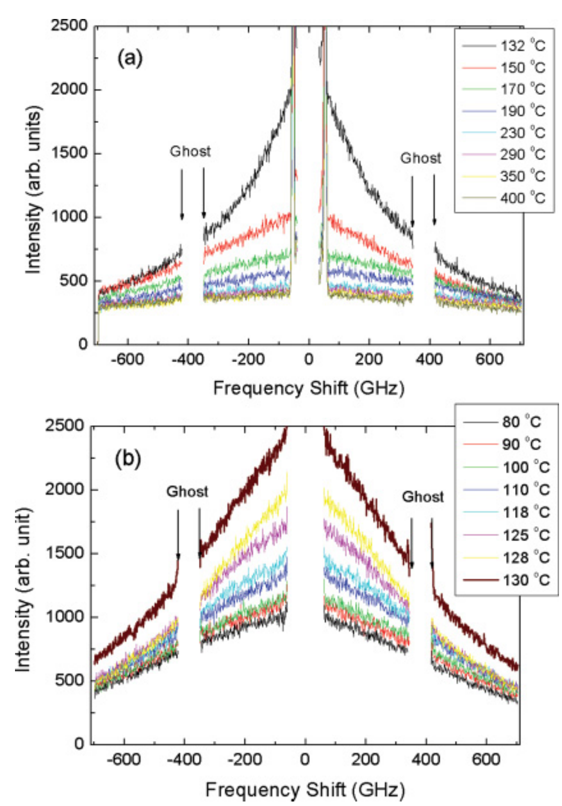

FIG. 5. (Color online) The CP spectra of BT single crystal in the (a) paraelectric phase and (b) ferroelectric phase.

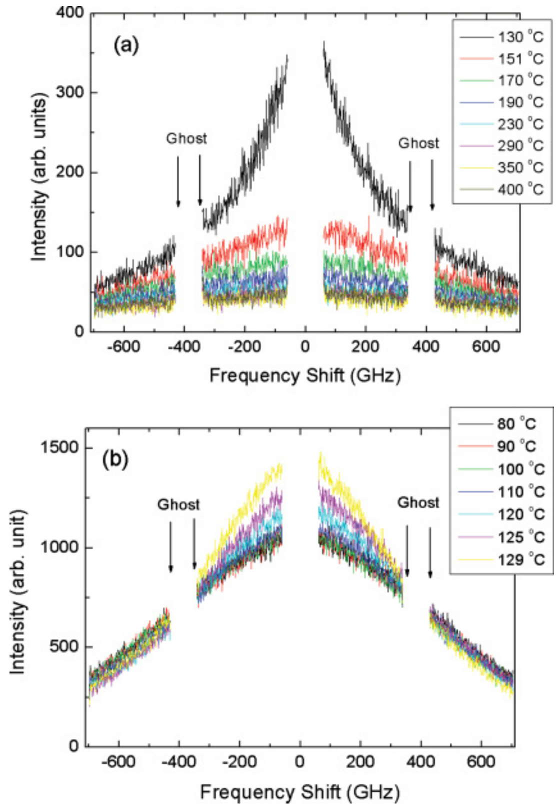

FIG. 6. (Color online) The CP spectra of R-BT single crystal in the (a) paraelectric phase and (b) ferroelectric phase.

processes. On the other hand, the CP in the ferroelectric phase could be explained perfectly based on a single-Debye form. These results are consistent with recent tera-Hertz spectroscopic study and the first-principle calculation that show one-mode behavior in the ferroelectric phase and two-mode behavior in the paraelectric phase.[19] According to this study, the mode frequency of the fast process is insensitive to temperature and is on the order of 100 cm^{-1} (more than 80 cm^{-1}). In this case, the fast mode is expected to contribute to almost constant background signal in the present Brillouin frequency window. Therefore, the broad background spectrum measured at the highest temperature (400 °C) was fixed to be constant (as an unchanging, high-frequency mode in the Brillouin frequency window), and the excess CP spectrum measured at lower temperatures was fitted by using one Lorentzian function centered at zero frequency. This approach can be justified by the fact that the light scattering spectrum does not show any noticeable changes in the temperature range of 300–400 °C.

Figure 7 exhibits the temperature dependence of the FWHM of the broad CP, which is proportional to the inverse relaxation time τ_{CP}^{-1}, of two single crystals. $(\pi\tau_{\text{CP}})^{-1}$ (=FWHM) decreases linearly as temperature approaches T_c indicating a slowing down behavior of the relevant relaxation process. The linear part of $(\pi\tau_{\text{CP}})^{-1}$ near T_c shown in Fig. 7 was fitted by using the following equation:

$$\frac{1}{\pi\tau_{\text{CP}}} = \frac{1}{\pi\tau_0}\frac{T - T_0}{T_0}. \tag{5}$$

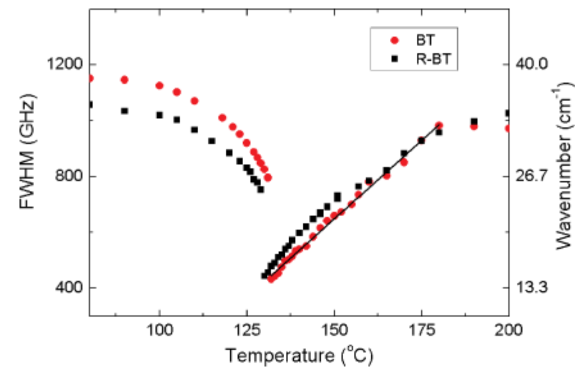

FIG. 7. (Color online) The FWHM of CP as a function of temperature. The solid line is the best-fitted result for BT single crystals obtained by using Eq. (5).

In this equation, τ_0 and T_0 are fitting parameters. The best-fitted result for BT is shown as a solid line in Fig. 7 and the obtained parameters of both crystals are shown in Table I. This equation may be considered as a convenient approach for describing the slowing down process of the related relaxation process giving rise to the formation of CP. τ_{CP}^{-1} of R-BT single crystal is comparable to that of τ_{CP}^{-1} of BT single crystal. This result might indicate that the dynamics of polar clusters is similar in both crystals even when oxygen vacancies are introduced in BT single crystals. Finally, we would like to point out that the relaxation frequency of BT single crystals obtained in the ferroelectirc phase is similar to the values determined by tera-Hertz spectroscopy recently.[30]

2. The existence of narrow central peak

Sokoloff *et al.* investigated BT single crystals by inelastic light scattering and reported that a narrow CP was observed from A-symmetry spectra within ± 5 GHz above T_c.[14] Namikawa *et al.* found the maximum relaxation time of polar clusters to be about 90 ps and suggested a similar CP in a narrow spectral range.[12] In this respect, it would be interesting to revisit the narrow spectral region by high-resolution Brillouin spectroscopy in order to find out whether or not narrow CP really exists and to discuss its microscopic origin if it appears.

Figure 8 shows Brillouin spectra of BT single crystal in a narrow spectral range. We can clearly see low-frequency contributions within ±5 GHz. However, this low-frequency spectrum exhibits a maximum at a nonzero frequency and is thus not CP, that is, not relaxation-type but resonance-type contribution. It was found from temperature investigation that these narrow doublets are barely temperature dependent and appear in both paraelectric and ferroelectric phases with similar spectral shapes. When the sample was inclined with

TABLE I. The best-fitted parameters of BT and R-BT single crystals by using Eq. (5).

Crystal	Fitted T range (°C)	$(\pi\tau_0)^{-1}$ (GHz)	T_0 (°C)
BT	132–180	1037 ± 26	92.3 ± 1.9
R-BT	130–140	1586 ± 42	101.5 ± 4.7

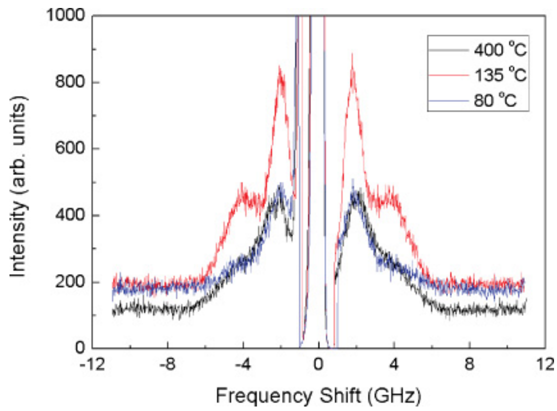

FIG. 8. (Color online) The light scattering spectrum in a narrow frequency range of BT single crystal.

respect to the incident laser beam, the peak positions were found to be sensitive to the inclination angle. Considering these results, we tentatively suggest that the low-frequency doublets may be related to near-forward-scattered light by acoustic modes due to the specular-reflected laser beam from the bottom surface of the BT single crystal or contributions from surface acoustic waves. However, the damping of surface acoustic modes is usually small, and thus the former scenario seems to be more plausible. More thorough investigation is necessary to reveal microscopic origin of these low-frequency doublets.

In short, narrow CP of BT in its paraelectric phase suggested in previous studies[12,14] was not confirmed in the present study. The collective flipping motion of Ti ions is reflected in the wide CP discussed in the previous section. The transition time between the tetragonal nanodomains, suggested by NMR study,[18] is too long to be probed in the present frequency window. The absence of narrow CP also seems to be consistent with previous dielectric studies that did not reveal any significant dispersion in the microwave range, as reviewed by Petzelt.[31] The narrow CP which Sokoloff *et al.* observed is probably part of the low-frequency doublets which we observed from the present study.

C. Discussion

In this section the acoustic anomalies and CP behaviors will be compared to each other and also to other properties of BT single crystals. It is clear that the appearance and growth of CP is correlated to the substantial softening and increasing damping of LA mode in both single crystals. It was suggested from various experiments (for example, NMR study[17,18]) that the off-center motions of Ti ions are correlated and form polar clusters in which off-center dipoles align in the same direction and flip together. Theoretical studies also support the formation of polar clusters with broken symmetry above T_c.[16,28] The relaxation time of these polar clusters becomes longer upon approaching T_c.[12,13] The decrease in τ_{CP}^{-1} of CP reflects this slowing down behavior.

The relaxation behavior exhibited by CP is due to the polarization fluctuations of precursor polar clusters. Since their correlation length is expected to become large on approaching T_c, it is reasonable that their relaxation time τ_{CP} increases upon

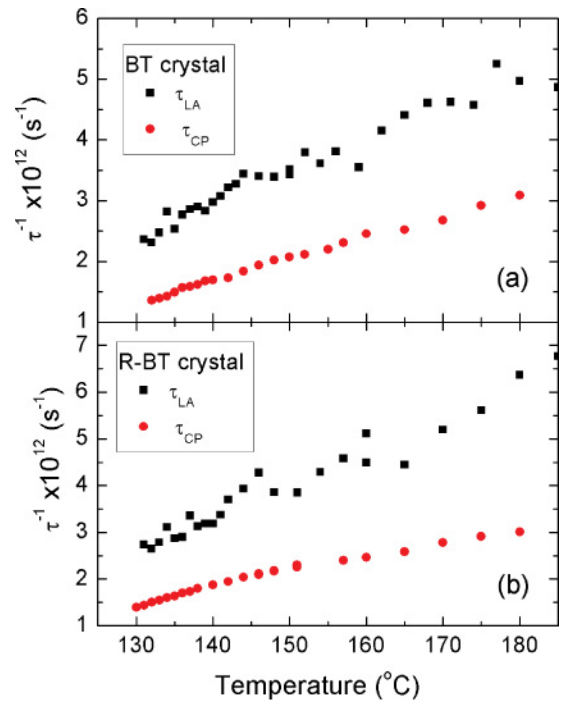

FIG. 9. (Color online) The inverse of relaxation times obtained from CP and LA modes for (a) BT and (b) R-BT siingle crystals.

cooling as shown in Fig. 7. These polar clusters can interact with the acoustic phonons, in particular, the LA modes via electrostrictive and/or linear coupling between the polarization and the strain caused by the acoustic waves.[32] The maximum size of polar clusters was estimated to be in the range between 200 nm and 1 μm near T_c as was revealed by means of photon correlation spectroscopy[13] and a picosecond soft x-ray laser speckle technique.[12] These large and long-lived polar clusters might be related to some extended static defects that are always believed to exist in perovskite system (see the discussions below). The relaxation times of these large polar clusters are much larger than the values estimated from the CP width shown in Fig. 9. This means the precursor clusters may have some size distribution and thus the distribution of relaxation times. Because of increasing correlation length and a long relaxation time of slow polar clusters near T_c, a piezoelectric effect is expected in the paraelectric phase and was indeed shown to exist.[20] Since these large polar clusters may be treated as static objects to acoustic waves in the giga-Hertz range, it would be justifiable to rely on a Landau-Khalatnikov-like approach for analyzing the relaxation time of the relevant intracluster relaxation process coupled to the LA waves.[29,33] According to this approach, the relaxation time τ_{LA} can be determined as follows:[33,34]

$$\tau_{\mathrm{LA}} = \frac{\Gamma_B - \Gamma_\infty}{2\pi\left(\nu_\infty^2 - \nu_B^2\right)}. \tag{6}$$

In this equation, ν_∞ is an unrelaxed, high-frequency limiting Brillouin shift which can be obtained from the linear region at high temperatures, and Γ_∞ is the background damping and is estimated to be the average FWHM of the flat region at high temperatures. ν_∞ and Γ_∞ are shown as solid lines in Figs. 2 and 3. The temperature dependence of τ_{LA} of both single crystals is shown in Fig. 9 and compared to that determined from CP shown in Fig. 7. The temperature dependence of τ_{LA} is similar to τ_{CP} in both crystals. The orders of magnitude of τ_{LA} and τ_{CP} are also comparable and belong to the subpicosecond region. This result clearly suggests that the relaxation process that causes quasielastic CP also induces the LA mode anomalies. The density fluctuations of the LA waves are strongly coupled to the polarization of polar clusters of which the flipping motions cause CP behavior. τ_{LA} and τ_{CP} shown in Fig. 9 are similar to the time scale of Ti hopping motions obtained by molecular dynamic simulations.[28,35] In addition, relaxation frequency of BT single crystal in the ferroelectirc phase is very similar to the values determined by tera-Hertz spectroscopy.[30] The similarity of the CP parameters in this study and previous far-infrared and tera-Hertz spectroscpies[19,30] is interesting and noteworthy, and seems to support its microscopic picture as due to the collective hopping of the off-centered Ti ions. However, mainly the LA mode and the corresponding CP were studied due to the backscattering geometry. The LA mode displacement driven by C_{11} elastic constant is in principle coupled to the square of the order parameter due to its full symmetry in the long-wavelength approximation and therefore is expected to reveal a weaker critical behavior than the ferroelectric CP seen in the tera-Hertz spectra.[19,30]

The formation and growth of precursor polar and noncentrosymmetric clusters influence not only acoustic waves but also other properties. Figure 10 shows the temperature dependences of the FWHM of the LA mode and the birefringence data (Δn) (Ref. 9) obtained from the same single crystal measured on cooling. The intensity of CP is shown in the inset for comparison. It is clear that these data sets are strongly correlated to one another. Δn and Γ_B exhibit sudden increase at about 180 °C around which the CP intensity begins to increase substantially. The temperature ranges over which these three properties change remarkably are almost the same. When the size of polar clusters increases on approaching T_c, these clusters contribute to the birefringence

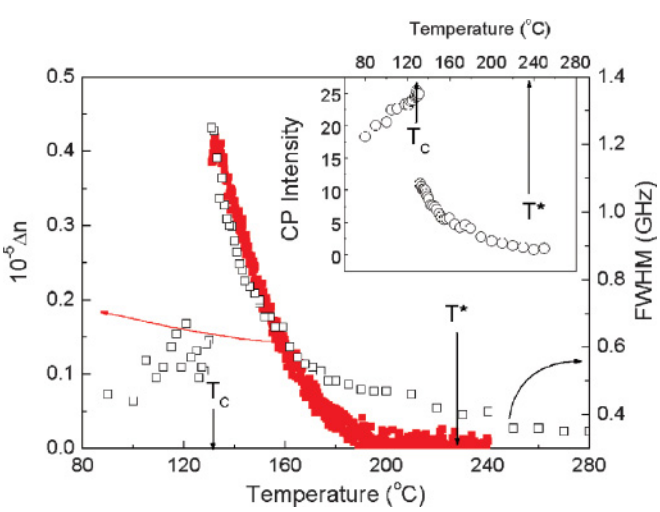

FIG. 10. (Color online) The temperature dependences of the birefringence[9] and the FWHM of the LA mode of BT single crystal. The inset shows the temperature dependence of the CP intensity of BT single crystal.

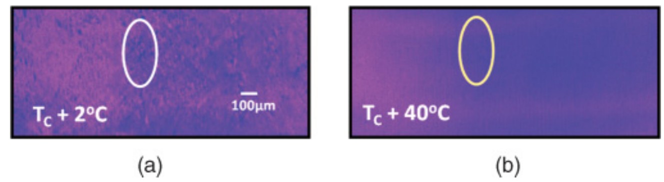

FIG. 11. (Color online) Birefringence Δn measured on heating and presented for two temperatures for pure barium titanate single crystal. Stable polar clusters are visible close to T_c (inside the ellipse) and disappear far above T_c.

due to their noncentrosymmetric nature, their relaxation time increases, and they shorten the lifetime of LA phonons due to order-parameter fluctuations.[32] Moreover, it was shown that these precursor clusters give rise to a piezoelectric effect and make the real part of the complex dielectric constant deviate from the Curie-Weiss law in similar temperature ranges above T_c.[20]

In order to corroborate the existence of polar clusters, a systematic birefringence map was investigated, and Fig. 11 shows the measurement result. Figures 11(a) and 11(b) represent examples of birefringence map for the BT crystal at two selected temperatures. Difference in Δn values in these experimental images can be seen using false color technique (here, the pink color corresponds to $\Delta n = 0$). The polar clusters have been recognized as dots. Close to T_c [Fig. 11(a)] on the background of inhomogeneous Δn distributions, stable regions of cigar-like shape and of size of microns are clearly visible inside the ellipse. Far above T_c, that is, above 170 °C, these regions disappear [Fig. 11(b)]. This is a direct proof for the existence of stable polar clusters in a quite wide temperature range above T_c. According to theoretical predictions by Bussmann-Holder *et al.*,[16] a universal behavior is proposed. While the distinction between displacive and order-disorder-type ferroelectrics has been attributed to the depth of the local double-well potential, it was shown that precursor dynamics are always present and that this is independent of the shape and the depth of the double-well potential. Both dynamics coexist, exhibiting different length and time scales. The displacive mechanism is related with the long wavelength for the optic ferroelectric mode (tera-Hertz frequencies) and the order-disorder mechanism related to acoustic mode (mega-Hertz–giga-hertz) in a few lattice constants. Far above T_c a coexistence of order-disorder and displacive phase transition mechanisms leads to the appearance of stable precursor clusters. When the temperature reaches about twice the transition temperature, their dimensions start to grow to be doubled at $T/T_c = 1.5$. Approaching T_c from the high temperature side they are growing rapidly, reaching at $T/T_c = 1.1$ several lattice constants. All this happens in a temperature range of the order of 10–30 °C. It means that the pretransitional local dynamics occur far above T_c. This theoretical approach describes the investigated BT single crystals well. Taking into account the value of T_c equal to 405 K (= 132 °C), the temperature window $\Delta T = (1.1 \times T_c) - T_c = (1.1 \times 405) - 405$ K $= 40$ K. All anomalies described in this paper have in fact been observed in this temperature range.

As it was already discussed in Ref. 9, the appearance of micrometer-sized inhomogeneity (polar clusters, precursor domains) above T_c is an intrinsic effect based on the short wavelength structural instability that is related to the long wavelength polar soft mode and driven by the temperature dependent fluctuating dipole moment.[16] The temperature evolution of this interdependence of the structural and polar soft mode could be responsible for the $\Delta n(T)$ dependences reported in Ref. 9. However, one cannot exclude the possibility of the influence of some defects (mainly related to oxygen vacancies arising during crystal growth) which influence the behavior close to T_c and may break the cubic symmetry statically. It may be, for example, stacking faults, the existence of which has clearly been revealed in $SrTiO_3$.[36] On the other hand, various methods like high-resolution transmission electron microscopy, x-ray photoelectron spectroscopy, and atomic force microscopy have provided evidence that extended defects, such as dislocations and shear planes, can also appear in perovskites. Similar kinds of defects were observed in in $SrTiO_3$, $KNbO_3$, and $KTaO_3$.[37] Around these faults, which are difficult to remove by thermal rejuvenation, the local mechanical and electrical stresses are created. These stresses may cause that the structural instability (reported by Bussmann-Holder *et al.*[16]) transforms into much larger and strongly pinned polar regions above T_c observed in birefringence experiments [Fig. 11(a)]. A proof for this is also a fact that the piezoelectric signal, observed above T_c for nonpoled $BaTiO_3$ single crystals,[21] has disappeared just at a temperature at which stable polar regions disappear [Fig. 11(b)].

The above acoustic results suggest that in some aspects the precursor phenomena in the paraelectric phase of BT single crystals are similar to the dynamics of polar nanoregions (PNRs) of ferroelectric relaxors.[38] Recently, acoustic emission measurements carried out on BT single crystal revealed two characteristic temperatures ($T^* \sim 230\,^\circ$C and $T_d \sim 280\,^\circ$C) where strong acoustic emission signals were observed in addition to T_c.[22] T_d was interpreted to be a Burns-like temperature where polar clusters begin to form, similar to the formation of PNRs in relaxor ferroelectrics. On the other hand, T^* was correlated to be the temperature at which local, cooperative freezing occurs in polar clusters. A similar characteristic temperature was also observed in relaxor ferroelectrics.[39,40] The temperature region where Δn and Γ_B exhibit substantial increase is not coincident with T^* but certainly below it. However, T^* ($\sim$230 °C) is the approximate temperature below which the CP begins to grow from the background signal (i.e., high-frequency mode) as shown in Fig. 5(a). Therefore, if some kind of local freezing occurs in the polar clusters, it will make the dynamics of these clusters become more sluggish and enter into the Brillouin frequency window. The deviation of the dielectric constant from the Curie-Weiss law observed in similar temperature range[20] can also be understood in the same context. This kind of deviation is commonly observed from ferroelectric relaxors.[38] In case of relaxors, the deviation occurs at the Burns temperature at which PNRs appear. In case of BT, the deviation of the dielectric constant from the Curie-Weiss law occurs at 170–180 °C below which the birefringence and the acoustic attenuation increase remarkably. The rapid growth in the size of polar clusters may bring about dipolar couplings between clusters that may induce changes in the dielectric behavior. The present study indicates all these anomalies share a common microscopic origin, correlated Ti off-centered motions forming polar clusters having local symmetry breaking in the paraelectric phase.

IV. CONCLUSION

In this study, the inelastic light scattering spectrum of high-quality BT single crystals was investigated over wide frequency and temperature ranges in order to analyze the dynamics of precursor polar clusters. The anomalous changes in the acoustic properties such as LA mode and CP were examined and compared to other properties obtained from the same single crystals. Major findings can be summarized as follows.

(1) The sound velocities and the related elastic constants (C_{11} and C_{44}) of the LA and TA modes propagating along the $\langle 100\rangle$ direction in the paraelectric phase were obtained in the widest temperature range ever measured. The LA mode (and C_{11}) showed anomalous changes upon approaching T_c while the changes in the TA mode frequency (and C_{44}) are very small, consistent with previous ultrasonic measurements.[26]

(2) The LA mode frequency showed a substantial softening and the acoustic attenuation displayed a marked increase on approaching T_c in the paraelectric phase. This was accompanied by the growth of CP that exhibited a critical slowing down behavior. The relaxation process represented by CP showed a two-mode and one-mode behavior in the paraelectric and ferroelectric phases, respectively, consistent with recent first-principle-based calculations and IR reflectivity measurements.[19] The relaxation times obtained from CP and LA mode behaviors of BT single crystals were consistent with each other, indicating the formation of CP and the acoustic anomalies of LA mode were caused by the same origin, that is, the correlated hopping motions of Ti ions in polar clusters.

(3) The acoustic anomalies and CP behavior were correlated with the anomalous birefringence, piezoelectric effect, and the deviation of the Curie-Weiss law observed from the same single crystal.[9,20] All these results could be explained by the existence of polar clusters and their growth with longer correlation length in a certain temperature range above T_c. This was demonstrated by the temperature evolution of the highly precise birefringence map. This seems to be related to the recent[22] acoustic emission results and the suggestion for the characteristic temperature T^* at which local freezing occurs in the polar clusters since the CP began to increase below the same temperature.

(4) The narrow CP within $\pm$5 GHz, which was suggested by light scattering[14] and soft pulsed x-ray speckle measurements,[12] was not confirmed in the present study. Instead of relaxational CP, resonance-type Brillouin doublets were observed in a narrow spectral range, which was sensitive to the inclination angle of the sample and thus tentatively attributed to near-forward scattering or surface excitation.

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