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Effect of electric field on elastic properties of $BaTiO_3$ single crystals: a micro-Brillouin scattering study

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The analysis of local polar clusters formed by random fields in ferroelectrics is of technical and fundamental importance in understanding piezoelectricity. The temperature and electric field dependences of elastic properties and the ferroelectric phase transition have been investigated in (100)-oriented $BaTiO_3$ single crystals by micro-Brillouin scattering. In the field cooling process, LA phonons are scattered by polar clusters. As a result, the LA phonon frequency increases as compared with that of the zero-field cooling process. Under the application of an external electric field along the [100] direction in the tetragonal ferroelectric phase, a complete 90° domain switching is accomplished. Under the electric field, abrupt changes in the frequency shift and FWHM of the LA phonons in the paraelectric cubic phase indicate the occurrence of a phase transition from the cubic to the tetragonal phase. An *E–T* phase diagram has been proposed from the field-induced phase transition.

1. Introduction

In the last several decades, ferroelectric materials with perovskite structures have been widely used in transducing and sensing applications due to their classic electromechanical coupling constant along certain crystallographic axes. The prototypical ferroelectrics such as barium titanate ($BaTiO_3$, abbreviated as BT) are some of the most widely studied ferroelectric materials that undergo successive phase transitions from a paraelectric cubic phase to ferroelectric tetragonal, orthorhombic, and rhombohedral phases. In spite of extensive studies over decades, the nature of ferroelectric phase transitions—in particular, order–disorder versus displacive-type—in BT single crystals is still a controversial matter. Displacive-type phase transitions have been observed in BT[1,2] from the condensation of soft phonon modes, although they are not simply compatible with a purely displacive character. Furthermore, the existence of an order–disorder nature of phase transitions has been confirmed by means of several experiments and theories.[3–7] Order–disorder phase transitions in BT single crystals were proposed by Takahasi[4] and Comes[8] et al., who considered the off-centering of Ti ions along eight equivalent [111] directions inside a cubic matrix with a non-zero local dipole moment. Off-centering at B-site cations is expected to increase ferroelectric instability.[4,8–11] Nowadays, it is widely believed that both the order–disorder and displacive components coexist in the ferroelectric phase transition in BT single crystals. Although the order–disorder phase transition is shown in Ref. 10, details on the nature of the phase transition mechanism are not discussed. In the paraelectric phase above the Curie temperature, T_C, the deviation of the refractive index from the high-temperature linear behavior was observed by Burns and Dacol, who ascribed it to the existence of precursor local polarization.[12,13] These precursor polar clusters in the paraelectric phase are local and noncubic and have no inversion symmetry and a local polarization. These local polar clusters appear a few hundred degrees above T_C, the so-called Burns temperature (T_B). Therefore, temperatures above T_C give rise to so many anomalous properties in the paraelectric phase of BT single crystals.[14] A lot of typical phenomena related to the relaxation dynamics of local polar clusters, namely significant softening of the LA frequency,[14–16] deviations from the Curie–Weiss law for the permittivity,[17] first-order Raman spectra[18] and deviation from the linear temperature dependence of the refractive index,[12,13] have been observed in BT single crystals.

Understanding the role of domain switching in ferroelectrics has great technological relevance for the optimization of devices based on ferroelectric materials. To enhance the piezoelectric response, the domain structure can be configured by the application of an electric field and mechanical stress. A group of unit cells constitute ferroelectric domains with the same orientation as spontaneous polarization. Under the application of an electric field and/or mechanical stress, domain switching occurs via movement of domain walls and nucleation of new domains. Prior investigation on ferroelectrics demonstrates that domain switching is usually accomplished by inhomogeneous domain nucleation followed by forward and sidewise domain wall motions.[19] In BT single crystals, two types of domains can nucleate under the application of an electric field: 180° domains with spontaneous polarization anti-parallel to each other which minimizes depolarization fields and 90° domains with polarization perpendicular to each other which minimizes strain via the formation of twins.[20] The domain switching mechanism can induce mechanical stress and electric fields which may lead to the failure behavior of ferroelectric materials. Therefore, it is essential to investigate the field-induced domain switching process for the applications and development of ferroelectric materials.

BT single crystals have been the subject of many studies for more than 50 years. Although great meaningful results have been explored in relation to BT, there is a significant lack of understanding of some decisive properties concerning electric field dependence on elastic anomaly and domain switching which must be attained to unlock the full potential of BT for possible technological applications. Exploration of the above-mentioned physical properties of BT single crystals with temperature and electric field constitutes the prime motivation of the present work. So far, there has been limited discussion on the electric field dependence of acoustic

anomalies in the paraelectric cubic phase and/or in the ferroelectric tetragonal phase. In addition, the electric field dependence of phase transitions in BT is an intriguing and interesting phenomenon under discussion. Based on the above-mentioned discussion, in the current study, the micro-Brillouin scattering technique has been applied to explore the effect of the electric field on acoustic properties and dynamic polar clusters. The domain switching behavior and electric field dependence of phase transitions are also reported. The detailed and novel results presented in this study have yielded valuable information regarding prospective applications of BT in the future.

2. Experimental

A (100)-oriented plate of BT single crystals was bought from MTI Company with dimensions of 5×5 mm^2 and a thickness of 1 mm which was polished to optical quality for measurements. To measure the Brillouin scattering spectra in backward scattering geometry, we used a micro-Brillouin scattering system with a $3+3$ pass Sandercock-type tandem Fabry–Pérot interferometer (JRS TEP-1).[21] A single-frequency diode pump solid-state laser with a wavelength of 532 nm and a power of about 100 mW was used as an exciting source. The mirror space was set at 2 mm with a free spectral range of 75 GHz. The sample was placed inside a cryostat cell (Linkam, THMS600) with a stability of ±0.1 K and the temperature was changed from 593 K to room temperature with a minimum temperature interval of 1 K. To observe the effect of the electric field, the two opposite surfaces of the crystals were coated with silver paste along the [100] direction and gold contact wires were attached to the electrodes. Before the start of each measurement, the electrodes of the sample were short-circuited for 10 min at a high enough temperature to remove any kind of memory effect of the electric field retained from previous measurements.

3. Results and discussion

The measured Brillouin scattering spectra of the BT single crystals at 398 and 403 K under zero-field cooling (ZFC) and field cooling (FC) processes are shown in Figs. 1(a) and 1(b), respectively. It is remarkable that at 403 K, the Brillouin scattering spectrum consists of one LA mode and a weak central peak (CP). It is widely accepted that the existence of a CP in Brillouin scattering spectra is due to the presence of a random field created by the off-centered motion of Ti ions in the oxygen octahedra.[14,22] The polarization fluctuations induced by the relaxational Ti motions have been thought to induce the quasielastic CPs observed from many BT-based ferroelectrics. To observe the effect of electric fields, we applied a 1 kV cm^{-1} electric field at a higher temperature and then the spectra were taken in the FC process. It is seen from Fig. 1(b) that in the FC process, the CP disappears. Therefore, it can be stated that the electric field reduces the effect of random fields which results in the decrease of intensity of CPs in Brillouin scattering spectra. A TA mode is also noticed below T_C (~402 K), which clearly reflects the appearance of a ferroelectric tetragonal phase.

For quantitative analysis, each of the Brillouin spectra was fitted by a Lorentzian function convoluted by a Gaussian instrumental function from which the frequency shift (υ_{LA})

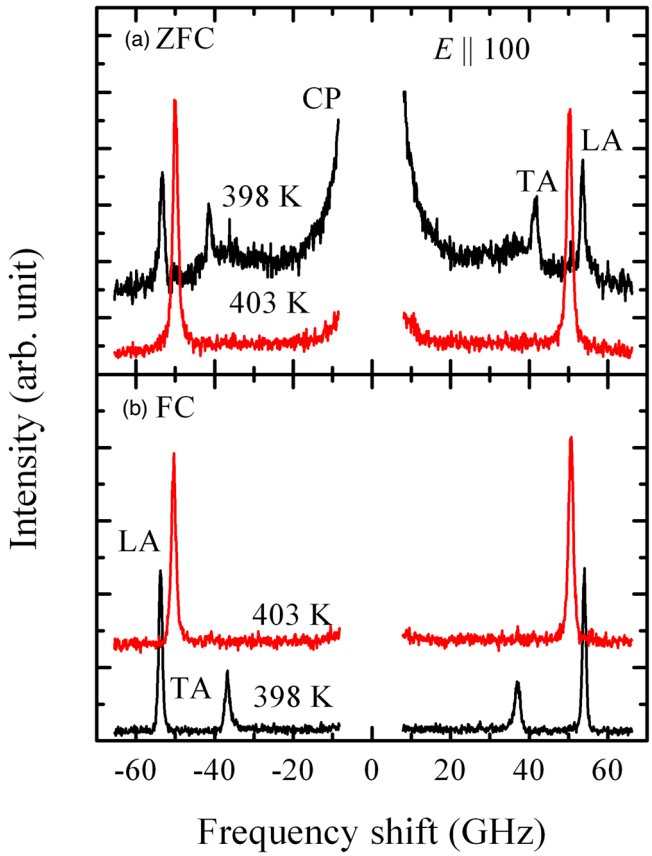

Fig. 1. (Color online) Brillouin spectra of a 100-BT single crystal in (a) ZFC and (b) FC processes at 398 and 403 K.[10,16]

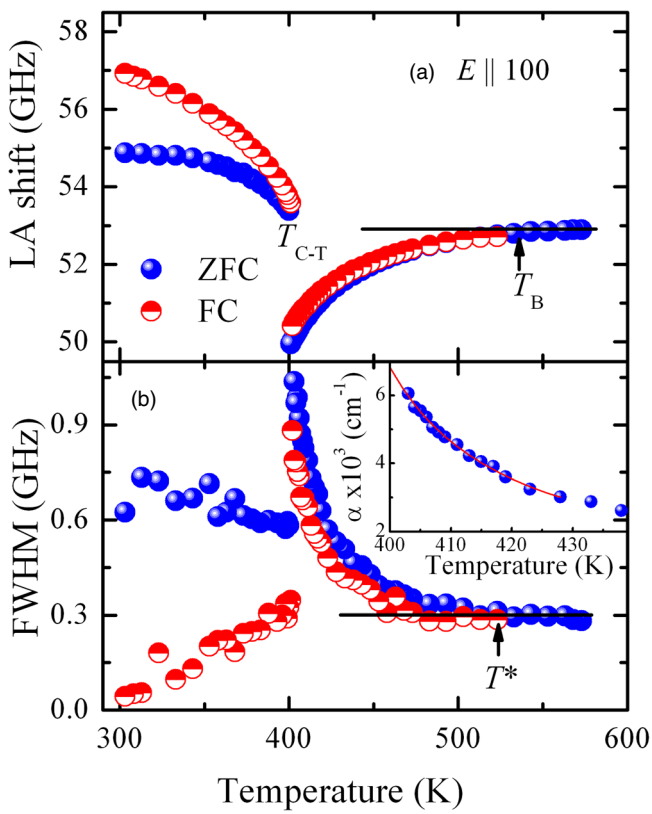

Fig. 2. (Color online) The temperature dependences of the (a) frequency shift (υ_{LA}) and (b) FWHM (Γ_{LA}) of the LA phonon mode of 100-BT single crystals measured in ZFC (blue solid symbols) and FC (red half-filled symbols) processes. The solid line in the inset of (b) is the best-fitted line for the order–disorder transition.[10,16]

and the FWHM (Γ_{LA}) of each mode could be obtained. The temperature dependences of the υ_{LA} and FWHM of the LA phonon under the ZFC and FC processes are shown in Figs. 2(a) and 2(b), respectively. In ZFC, both υ_{LA} and Γ_{LA} show a sharp discontinuity at around 402 K suggesting a first-order phase transition from cubic to tetragonal phase. The elastic constant (related to υ_{LA}) starts to deviate from its normal anharmonic behavior at around 533 K. This indicates that the LA phonon mode is strongly coupled with other degrees of freedom resulting in significant damping as well as in softening. We ascribe this temperature to the formation of dynamic polar clusters and it is assigned as T_B. In Fig. 2(b), in ZFC, the sound attenuation (related to Γ_{LA}) of the LA mode starts to increase rapidly toward T_C at around 503 K, where the permanent polar clusters appear and which is called the intermediate temperature, T^*. The two measured characteristic temperatures are somewhat different from previously reported results obtained by Brillouin scattering.[14] The changes of these two characteristic temperatures can be due to the quality of the sample because the previous studies observed T_C at around 373 K which is not equal to the true T_C in BT single crystals. Interestingly, recent acoustic emission measurements have also revealed these two characteristic temperatures which are very close to the present results.[23] A similar characteristic temperature was also observed in relaxor ferroelectrics.[22,24] To discuss the nature of ferroelectric phase transitions in BT crystals, the sound attenuation was calculated from the sound velocity using the following formula:

$$V_{LA} = \frac{\lambda \upsilon_{LA}}{2n}, \ \alpha_{LA} = \frac{\pi \Gamma_{LA}}{V_{LA}}$$

where λ and n are the wavelength of the laser light (532 nm) and the refractive index at λ. The sound attenuation in the inset of Fig. 2(b) was fitted with the following power law predicted by Levanyuk et al.[25] just above 25 K from T_C:

$$\alpha_{LA} = \alpha_1 (T - T_0)^{-m}.$$

Here, T_0 is the extrapolated Curie temperature which is not equal to T_C. The value of T_0 was determined from the fitting parameters of the temperature dependence of sound velocity. The best-fitted result is shown by a red solid line in the inset of Fig. 2(b). It is predicted that the value of the critical exponent m is 1.5 for order–disorder phase transitions. A fairly good consistency between the observed data and fitting parameters was obtained with the exponent $m = 1.47 \pm 0.22$ suggesting the order–disorder nature of the phase transition in BT. This type of phase transition was also observed from different experiments.[3–7,14]

In BT, local polar clusters can be created by weak random fields. Under the FC process, a remarkable difference is observed between υ_{LA} and Γ_{LA} in both the cubic and tetragonal phases. It is already known that in BT crystals, in the cubic phase Ti ions fluctuate along eight equivalent [111] directions. Therefore, due to the externally applied electric field along the [100] direction, the density of static/dynamic polar clusters decreases which is expected to weaken the scattering of LA phonons by the polar clusters, resulting in a higher frequency shift and a lower damping of LA phonons. A significant change of υ_{LA} and Γ_{LA} below T_C is observed. This is due to the complete suppression of random fields by cooling in an external electric field from a high-temperature region, which forms macro-domains in the ferroelectric phase. On the other hand, the large differences in υ_{LA} and Γ_{LA} between the ZFC and FC processes in the tetragonal phase indicate transformation from the ferroelectric [100] direction to the [001] direction.

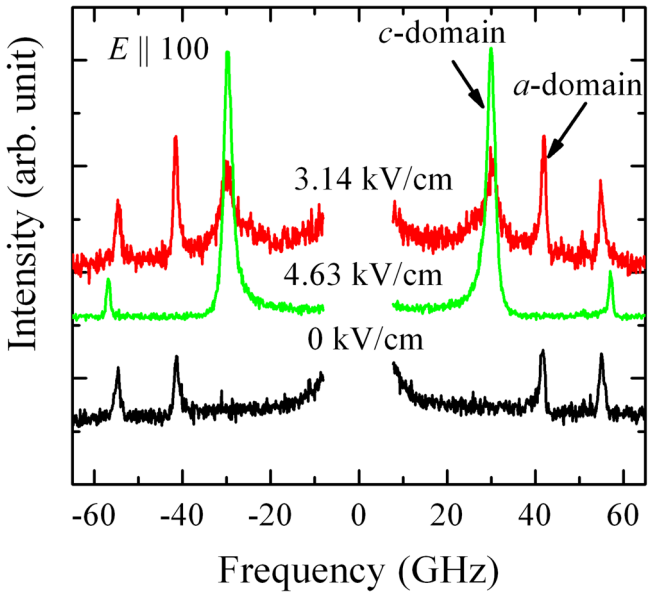

Fig. 3. (Color online) Brillouin spectra of 100-BT single crystals in the ferroelectric tetragonal phase at selected electric fields at 303 K.[16]

In the tetragonal phase, the behavior of LA and TA phonon frequency shifts as a function of the electric field was investigated at 303 K and some spectra at selected temperatures are shown in Fig. 3. From Fig. 4, it is seen that with an increasing electric field, υ_{LA} and Γ_{LA} show a sudden jump at around 3.9 kV cm^{-1} which indicates the change of sound velocity from the [100] to the [001] direction.

It is quite interesting to discuss the results obtained for the TA phonon mode as shown in Fig. 5. For convenience, we define the domains with polarization vectors along the [100] and [001] directions as a- and c-domains, respectively. Since we have measured and analyzed the [100]-oriented plate at the backscattering geometry, before applying the electric field, we observed only a-domains. At around 2.94 kV cm^{-1}

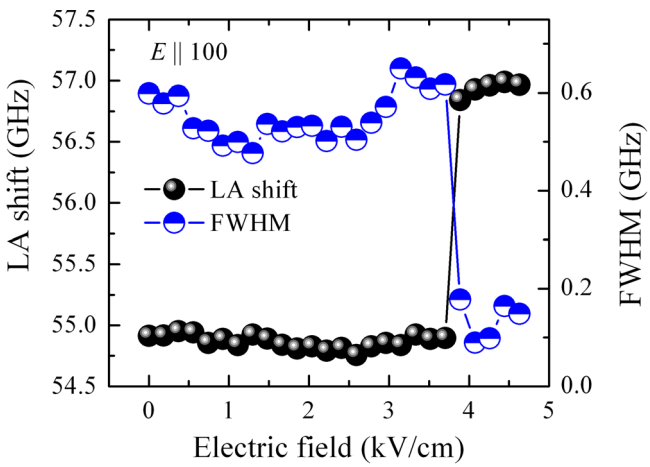

Fig. 4. (Color online) Electric field dependence of the frequency shift and FWHM of LA phonons in the ferroelectric tetragonal phase at 303 K of a 100-BT single crystal.[16]

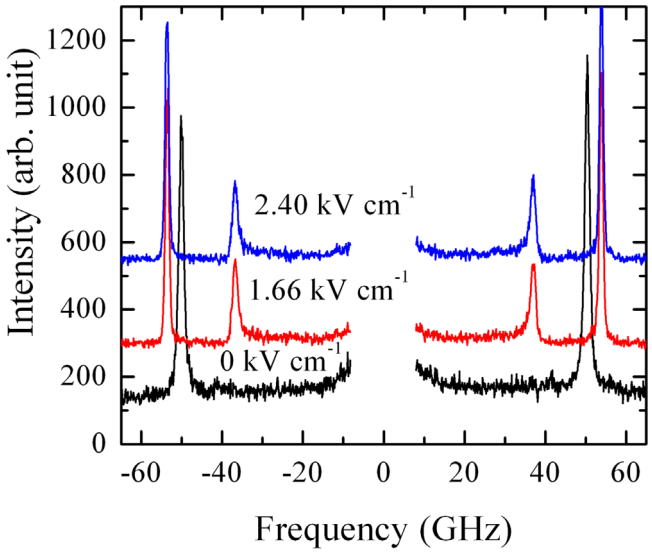

Fig. 5. (Color online) Electric field dependence of the (a) frequency shift and (b) intensity of TA phonons in the ferroelectric tetragonal phase at 303 K of a 100-BT single crystal.

electric field, a new TA mode at around 30 GHz begins to appear with low intensity and it persists up to 3.9 kV cm^{-1}. The new TA mode indicates the appearance of *c*-domains. Therefore, from 2.94 kV cm^{-1} to 3.9 kV cm^{-1}, both domains coexist in BT single crystals. In addition, the intensity of the new TA mode gradually increases with an increasing electric field which indicates that the *a*-domains are beginning to transform into *c*-domains. The intensity of the new TA mode reaches its maximum and saturates at 3.9 kV cm^{-1}, suggesting that all of the polarization switching has been completed. Therefore, at around 3.9 kV cm^{-1}, the 90° domain switching is completed. It is pertinent to note that the LA mode shows sudden changes while the TA mode changes gradually. Therefore, the TA mode seems to play the role of a "soft transverse acoustic mode" during the domain switching process. The coercive field, $E_c = 5$ kV cm^{-1}, for 90° domain switching in BT crystals has been measured by Li et al.[26] However, in their study, they used thin wafer specimens; therefore, differences in the coercive field could have existed. Meanwhile, using two sets of typical Landau coefficients, they also calculated the electric field versus stress diagram. According to their diagram, when the value of E_c is corrected for stress, because Pramanick et al. reported that compressive stresses in multidomain BT crystals are typically on the order of a few tens of megapascals,[27] then the value of $E_c \sim 3.9$ kV cm^{-1} seems reasonable in BT crystals.

Figure 6 shows the Brillouin scattering spectra of BT single crystals in the paraelectric cubic phase at selected electric fields above T_C. At zero electric field, there is no TA mode that reflects the cubic phase of BT single crystals according to the selection rules. Following Landau theory, the electric field–temperature (*E*–*T*) phase diagram has been calculated by Iwata et al.[28] It was reported that the applied electric field in a paraelectric cubic phase along the [100] direction causes a change of the phase from cubic to tetragonal.[28] Figure 7 shows the field dependence of υ_{LA} and Γ_{LA} at 405 K (cubic phase). As the value of the applied electric field approaches 2.7 kV cm^{-1}, υ_{LA} and Γ_{LA} abruptly

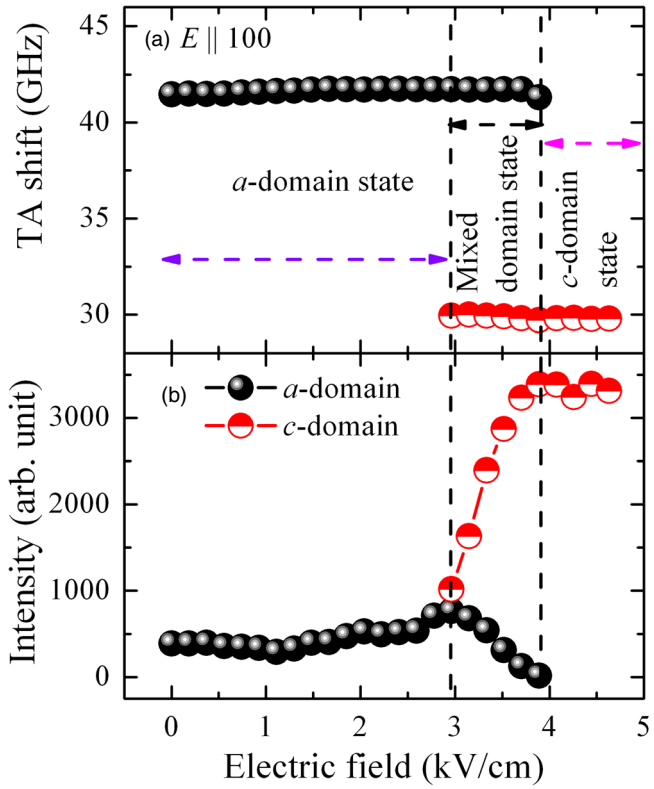

Fig. 6. (Color online) Brillouin scattering spectra of 100-BT single crystals at selected electric fields above T_C.[16]

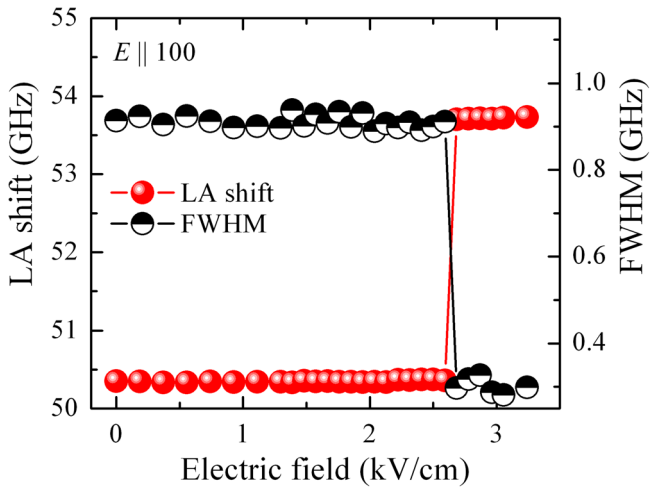

Fig. 7. (Color online) Electric field dependence of frequency shift and damping of LA phonons at 405 K of 100-BT single crystal.[16]

jump which indicates a structural phase transition from the paraelectric cubic to the ferroelectric tetragonal phase. From the field-induced paraelectric-to-ferroelectric phase transition, an *E*–*T* phase diagram has been proposed which is shown in Fig. 8. The proposed *E*–*T* phase diagram is in good agreement with previously reported field-induced polarization measurements.[29] Recently, Novak et al. also reported an *E*–*T* phase diagram above the transition temperature for BT crystals and proposed that below 5.4 kV cm^{-1} the transition weakly depends on the applied electric field.[30] However, the present experimental results and polarization measurements[29] confirm that below 5.4 kV cm^{-1}, a cubic-to-tetragonal phase transition above T_C is possible.

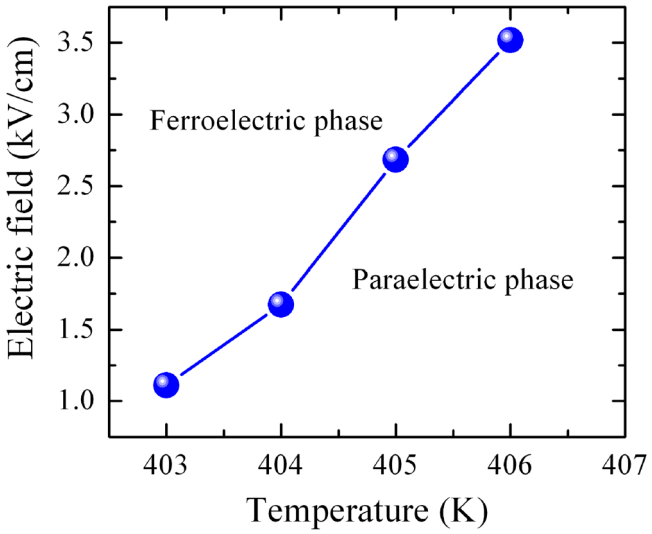

Fig. 8. (Color online) The *E*–*T* phase diagram measured in the paraelectric cubic phase in the case of a 100-BT single crystal.[16)]

4. Conclusions

The effects of temperature and applied electric fields on the elastic properties of BT single crystals with weak random fields were studied by Brillouin scattering measurement. In the vicinity of the cubic-to-tetragonal phase transition, $T_C \sim 402$ K, a significant softening of υ_{LA} and Γ_{LA} was observed. Under the field cooling process, an increase in υ_{LA} and a decrease in Γ_{LA} were found due to a reduced density of twin domain walls and static/dynamic polar clusters. The order–disorder nature of the ferroelectric phase transition was confirmed near T_C from the analysis of the temperature dependence of sound attenuation by a theoretical model. At 303 K, a complete 90° domain switching process was noticed which could be very helpful in the field of ferroelectric materials for deep understanding of the domain switching mechanism. From the field-induced phase transition measurement in the paraelectric cubic phase, an *E*–*T* phase diagram was proposed.

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