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# Precursor polar clusters in the paraelectric phase of ferroelectric $\text{Ba}_{0.80}\text{Ca}_{0.20}\text{TiO}_3$ single crystals studied by Brillouin light scattering

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## Abstract

A strong relaxation mode was observed in the gigahertz frequency window in the paraelectric phase of  $\text{Ba}_{0.80}\text{Ca}_{0.20}\text{TiO}_3$  single crystals by using Brillouin light scattering. The appearance and growth of this relaxation mode were accompanied by substantial softening of the longitudinal acoustic mode as well as a remarkable increase in the hypersonic damping. Similar to  $\text{BaTiO}_3$ , the temperature dependence of the relaxation time of  $\text{Ba}_{0.80}\text{Ca}_{0.20}\text{TiO}_3$  displayed a slowing-down behavior near the Curie temperature, indicating the order–disorder nature of the paraelectric–ferroelectric phase transition in this substance. The dynamics of precursor polar clusters observed in this work was discussed in relation with recent theoretical studies and found to be consistent with their predictions.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

The high-temperature phase of perovskite ferroelectrics has attracted a great deal of attention during the past half-century from the viewpoint of the nature of their paraelectric–ferroelectric phase transition, i.e. displacive versus order–disorder scenarios.  $\text{BaTiO}_3$  has been noted as a textbook substance and studied intensively for more than half a century. Originally,  $\text{BaTiO}_3$  had been regarded as a typical displacive-type ferroelectrics [1, 2]. However, an order–disorder model for  $\text{BaTiO}_3$  was already proposed at the early stage of the study on this substance [3]. Later, it was found by infrared measurements that the overdamped soft mode leveled off close to  $60\text{ cm}^{-1}$  near the cubic–tetragonal phase transition without complete softening [4]. In addition, observations of diffuse x-ray scattering [5] and persistent Raman spectra [6]

in the paraelectric phase indicated the order–disorder nature of the phase transition of  $\text{BaTiO}_3$ . Moreover, the existence of precursor polar clusters in the paraelectric phase was supported by many experiments such as the measurements of the index of refraction [7], the birefringence [8, 9], quasielastic central peaks by Raman and Brillouin scattering [10, 11], speckle intensities by a pulsed x-ray laser technique [12], etc.

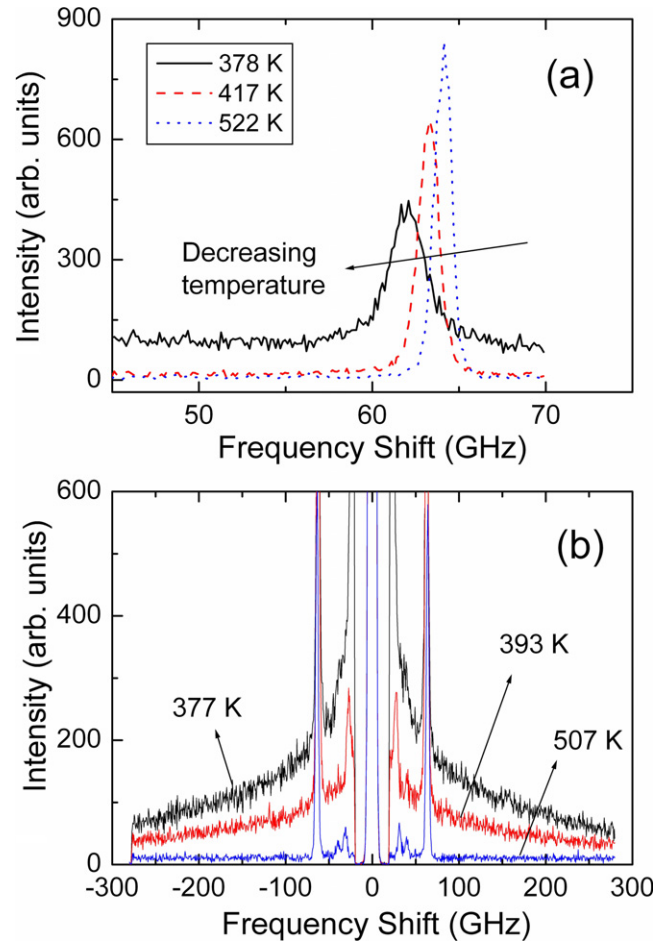
It is now well understood that the cubic–tetragonal ferroelectric phase transition of  $\text{BaTiO}_3$  is of both displacive and order–disorder type [13–16]. Recent nuclear magnetic resonance experiments showed both dynamic disorder related to off-center Ti sites and displacive-induced deformation of the unit cell in the tetragonal nanodomains in the paraelectric phase [14]. Additional relaxation modes in addition to the partially soft lattice mode were revealed by Brillouin scattering [11] and terahertz spectroscopy [15]. From the

theoretical point of view, the displacive dynamics was shown to coexist with order–disorder dynamics in a wide temperature range in the framework of the polarizability model [16]. However, a more detailed microscopic picture about the correlation between displacive and order–disorder components in the paraelectric phase of BaTiO<sub>3</sub> is necessary for complete understanding of the precursor dynamics and the ferroelectric phase transition occurring in this prototype ferroelectric material.

The dynamics of the Ti cations in the oxygen octahedra and associated anharmonicity with a multi-well potential are a very important factor for understanding the order–disorder nature of the cubic–tetragonal phase transition of BaTiO<sub>3</sub> [17]. In this sense, modification of precursor dynamics in the paraelectric phase by substitution of cations may be one way to get more insight into the phase transition dynamics of BaTiO<sub>3</sub>. For example, it was shown that the polarization fluctuations in the paraelectric phase could be enhanced in KF-substituted BaTiO<sub>3</sub> single crystals [18]. The substitution of Ba ions by nonstereochemical Ca ions is an effective way of stabilizing the tetragonal phase at low temperatures. Moreover, it was suggested that smaller Ca<sup>2+</sup> ions than Ba<sup>2+</sup> may form additional polarization components cooperative with Ti–O distortion [19]. This off-center displacement of Ca ions is considered to stabilize the ferroelectric tetragonal phase. It would thus be interesting to investigate the effect of this additional polarization component due to the small Ca ions at the Ba site on the dynamics of precursor polar clusters and the order–disorder nature of the ferroelectric phase transition of BaTiO<sub>3</sub>. The present work is devoted to the investigation of the precursor dynamics of Ca-substituted BaTiO<sub>3</sub> and comparison of it with pure BaTiO<sub>3</sub> by using the Brillouin light scattering technique. Both acoustic modes and central peaks in the gigahertz frequency range were investigated in a wide temperature range, from which a slowing-down behavior was clearly observed.

## 2. Experiment

Perovskite Ba<sub>0.80</sub>Ca<sub>0.20</sub>TiO<sub>3</sub> single crystals were grown by using the optical floating-zone method. The crystals showed a yellow color, were cut into platelet shapes and polished to optical quality. The composition ratio of Ba to Ca was measured on the sample surface by using energy-dispersive x-ray spectroscopy. The ferroelectric phase transition temperature from the cubic to the tetragonal phase ( $T_{C-T}$ ) was confirmed to be  $\sim 376$  K by using both dielectric spectroscopy and polarizing microscopy. The Brillouin spectrum was measured by using a tandem Fabry–Perot interferometer. Different free spectral ranges (FSRs) were used to cover a wide frequency range from 1 to 280 GHz. A single-mode diode-pumped solid state laser (DPSS532) operating at a wavelength of 532 nm and a power of  $\sim 100$  mW was used to excite the sample at a backward scattering geometry. A microscope (Olympus BH-2) combined with a temperature controller (Linkam, THMS 600) was used to monitor the sample surface and to control the temperature. Before starting the measurement, the sample was annealed at 700 K for



**Figure 1.** The temperature dependence of the Brillouin spectra (a) in a narrow and (b) in a wide frequency range.

1 h to release any remaining stress that might have been generated during crystal growth and sample preparation. All the measurements were carried out during the cooling process.

## 3. Results and discussion

Figure 1(a) shows the temperature dependence of selected Brillouin spectra corresponding to the longitudinal acoustic (LA) mode which is allowed at the backward scattering geometry.  $\nu_B$  decreases and  $\Gamma_B$  increases as the temperature is reduced. In addition, an additional broad contribution can be seen from the spectrum measured at 378 K, which is part of a broad central peak (CP) existing in a wider frequency window. A larger FSR of 300 GHz than that used for observing the LA mode was adopted in order to investigate the spectral features of CP. Some of the measured spectra are shown in figure 1(b). At high temperatures above 500 K, no CP is seen. The CP grows and its half-width decreases on lowering the temperature, similar to the case of pure BaTiO<sub>3</sub> [11].

The Brillouin frequency shift  $\nu_B$  and the full width at half-maximum (FWHM)  $\Gamma_B$  were obtained via the following fitting procedure. The spectral response of phonon modes as a function of frequency ( $\nu$ ) is usually modeled by the response

function of the damped harmonic oscillator having the form

$$I(\nu) \propto \frac{\nu_B^2 \Gamma_B}{(\nu^2 - \nu_B^2)^2 + \nu^2 \Gamma_B^2}. \quad (1)$$

If  $\nu_B$  is much larger than  $\Gamma_B$  as is usual, the above form is well approximated by a Lorentzian function as

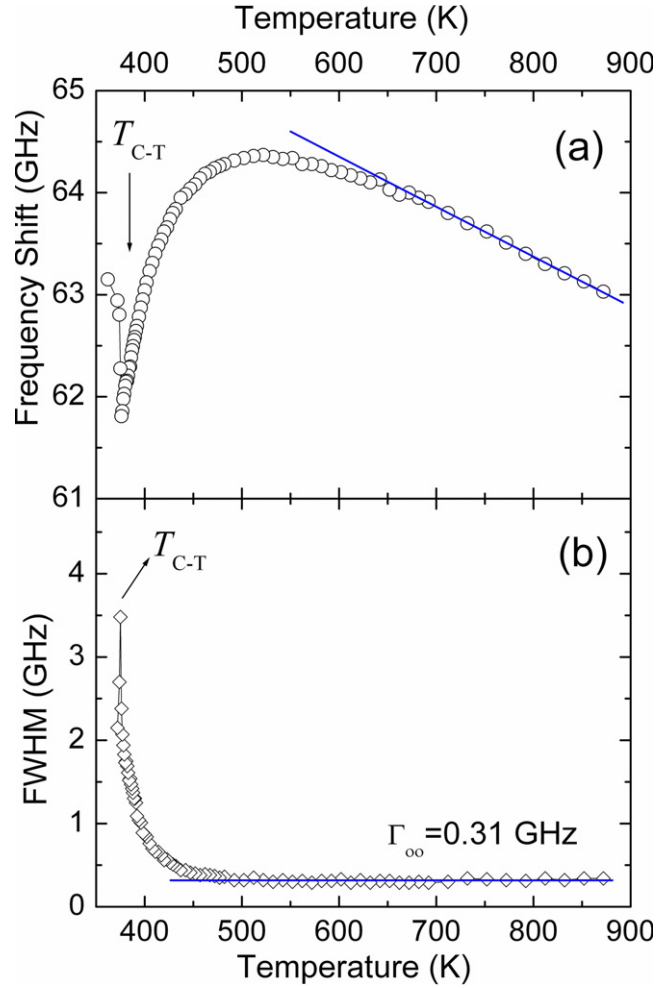
$$I(\nu) = I_0 \frac{\Gamma_B/4}{(\nu - \nu_B)^2 + \Gamma_B^2/4}, \quad (2)$$

where  $I_0$  is a proportional constant. The measured spectrum  $I$  as a function of frequency  $\nu$  was fitted by using (2) convoluted by the Gaussian instrumental function of the interferometer.

The derived  $\nu_B$  and  $\Gamma_B$  are shown in figures 2(a) and (b), respectively, as a function of temperature.  $\nu_B$  displays a linearly decreasing behavior above 650 K, consistent with the prediction from the theory based on normal lattice anharmonicity. The temperature dependence of elastic constants of normal solids that do not exhibit a phase transition can be explained by using a simple model based on normal lattice anharmonicity in the quasiharmonic approximation. Varshni and Lakkad functions have been proposed and used to explain the temperature dependence of the elastic constant of some oxides in a wide temperature range [20]. These models predict a linear negative slope in  $\nu_B$  at high temperatures and an asymptotic behavior toward zero slopes upon cooling to 0 K. The data of  $\nu_B$  above 650 K of BaTiO<sub>3</sub> reflects this normal anharmonicity. This linear part above 650 K was fitted to obtain the limiting high-frequency Brillouin shift, which will be denoted as  $\nu_\infty$ . The solid line in figure 2(a) shows the fitted result of  $\nu_\infty(T) = 67.29 - 0.0049 \times T$  (K).

$\nu_B$  begins to deviate from the high-temperature linearity at about 650 K, displays a maximum at  $\sim 500$  K and then exhibits a significant softening upon cooling toward  $T_{C-T}$ . This characteristic temperature ( $\sim 650$  K) is similar to the ones around which  $\nu_B$  of BaTiO<sub>3</sub> and KF-substituted BaTiO<sub>3</sub> single crystals begin to deviate from their high-temperature linearity. These results indicate a common existence of some dynamic degrees of freedom which couple to the LA waves. These degrees of freedom are under the influence of the strain field caused by acoustic waves and then react back on the elastic system, resulting in the softening of the elastic constant. The anomalous behavior of  $\nu_B$  and thus of the corresponding elastic constant is assumed to be a consequence of the interaction between the strain and the order parameter fluctuations in this system.

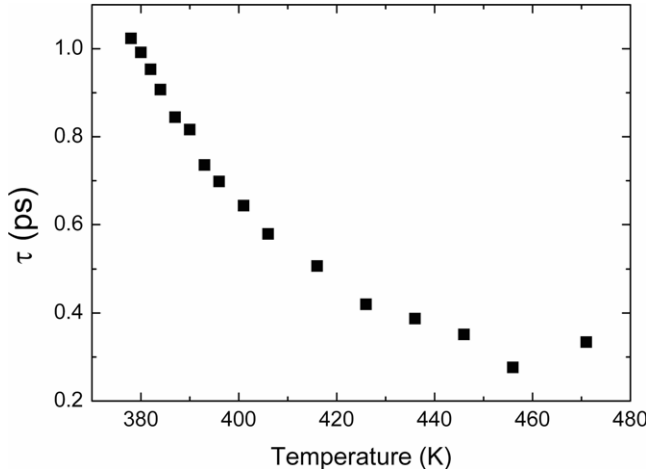
Burns and Dacol reported a temperature dependence of the optical index of refraction  $n(T)$  of several BaTiO<sub>3</sub> single crystals [7]. They found in all crystals that  $n(T)$  deviates from the high-temperature linearity at about 580 K and ascribed this observation to the formation of ‘local regions of polarization’ in the paraelectric phase. In addition, Geneste suggested that the local free-energy landscape related to the Ti motion changes at about  $T_{C-T} + 400$  K [17]. According to his molecular dynamics simulation, the free energy has its minimum at the center of the local mode above  $T_{C-T} + 400$  K while it exhibits eight minima along the  $\langle 111 \rangle$  directions between  $T_{C-T}$  and  $T_{C-T} + 400$  K. This result demonstrates



**Figure 2.** The temperature dependence of (a) the Brillouin frequency shift and (b) the full width at half-maximum.

the existence of local polarization fluctuations due to off-centered motions of Ti ions up to very high temperatures in the paraelectric cubic phase of BaTiO<sub>3</sub>. Therefore, the most plausible explanation for the onset of the deviation of  $\nu_B$  from high-temperature linearity occurring at 600–700 K, observed in both BaTiO<sub>3</sub> and Ba<sub>0.80</sub>Ca<sub>0.20</sub>TiO<sub>3</sub> single crystals, is the formation of off-centered motions of Ti ions, their short-range correlations and their coupling to the acoustic waves. As the paraelectric phase is non-piezoelectric, this coupling is quadratic in polarization and the fluctuation mechanism gives rise to a downward dip in the sound velocity.

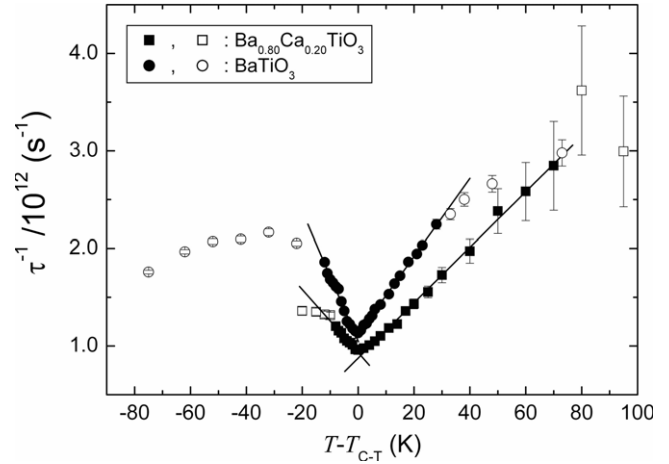
The softening of  $\nu_B$  becomes more substantial below  $\sim 450$  K and displays a minimum at  $T_{C-T}$ . On the other hand,  $\Gamma_B$  shows a constant value of  $\sim 0.31$  GHz ( $\Gamma_\infty$ ) in a wide temperature range from 870 to  $\sim 450$  K. It begins to increase from  $\Gamma_\infty$  at about 450 K ( $\sim T_{C-T} + 70$  K) and grows remarkably upon cooling, reaching  $\sim 3.5$  GHz near  $T_{C-T}$ .  $\Gamma_B$  becomes a maximum at  $T_{C-T}$ . The acoustic attenuation in the cubic phase with  $\langle P \rangle = 0$  is exclusively due to fluctuation damping. There are other theoretical and experimental evidences for the existence of polar clusters in a limited temperature range above  $T_{C-T}$ . Bussmann-Holder *et al* showed via their theoretical calculation that the onset of precursor



**Figure 3.** The temperature dependence of the relaxation time estimated from the half-width of central peaks.

dynamics begins at about 75 K above the actual ferroelectric phase transition [16]. Anomalous birefringence was observed up to 30 K above  $T_{C-T}$  and was attributed to the existence of polar clusters connected with correlated motions of off-centered Ti ions [9]. However, these suggested characteristic temperatures are much lower than those proposed by Burns and Dacol ( $\sim 580$  K) and Geneste ( $T_{C-T} + 400$  K). Our Brillouin data of both BaTiO<sub>3</sub> and Ba<sub>0.80</sub>Ca<sub>0.20</sub>TiO<sub>3</sub> exhibit two characteristic temperatures associated with two acoustic anomalies, the onset of softening of  $\nu_B$  at high temperatures and the remarkable increase in the attenuation reflected in the temperature variation of  $\Gamma_B$ . We therefore suggest that the temperature evolution of polar clusters in the paraelectric phase of BaTiO<sub>3</sub> and Ba<sub>0.80</sub>Ca<sub>0.20</sub>TiO<sub>3</sub> can be characterized by two characteristic temperatures. The first one is the high temperature (located in 600–700 K) at which off-center motions of Ti ions set in. Below the temperature of  $\sim T_{C-T} + 70$  K, the Ti jumps between off-center sites are more correlated and longer lived, resulting in larger correlations and higher fluctuation damping than at higher temperatures. The coupling between LA waves and polar clusters will be enhanced as Ti jumps are more correlated. As the size of polar clusters increases, their characteristic relaxation frequency will move to the Brillouin frequency window (a few tens of gigahertz) resulting in enhanced coupling with LA waves. This suggestion may be justified by correlating the acoustic behaviors with the formation of CP in the paraelectric phase.

CP appears at about 470 K and grows substantially on approaching  $T_{C-T}$ . CP was fitted by using a single Lorentzian function centered at zero frequency to obtain its FWHM  $\Delta\Gamma_{CP}$ . The corresponding relaxation time is obtained via  $\tau = 1/(\pi\Delta\Gamma_{CP})$ . The obtained temperature dependence of the relaxation time is shown in figure 3.  $\tau$  is of the order of picoseconds and rapidly grows toward  $T_{C-T}$ . If we plot  $\tau^{-1}$  as a function of temperature with respect to  $T_{C-T}$ , we get the result shown in figure 4. Similar to BaTiO<sub>3</sub>,  $\tau^{-1}$  of Ba<sub>0.80</sub>Ca<sub>0.20</sub>TiO<sub>3</sub> shows a linear behavior at temperatures near  $T_{C-T}$ . The same data from pure BaTiO<sub>3</sub> [11] are also shown for comparison. This kind of temperature dependence



**Figure 4.** The inverse of the relaxation time of both BaTiO<sub>3</sub> (circles) and Ba<sub>0.80</sub>Ca<sub>0.20</sub>TiO<sub>3</sub> (squares) single crystals along with the best-fitted results (solid lines) by using (3). The open symbols were not included in the fitting procedure.

is typical in order–disorder type phase transitions. Therefore,  $\tau^{-1}$  of Ba<sub>0.80</sub>Ca<sub>0.20</sub>TiO<sub>3</sub> was fitted by using the following equation [21]:

$$\frac{1}{\tau} = \frac{1}{\tau_0} \left( \frac{T - T_0}{T_0} \right). \quad (3)$$

In figure 4, open symbols were not included in the fitting procedure. The results from the fitting procedure by using (3) in the cubic (temperature range of  $T_{C-T} \sim T_{C-T} + 70$  K), and tetragonal (temperature range of  $T_{C-T} \sim T_{C-T} - 8$  K) phases are  $T_0 = 345$  K ( $\tau_0^{-1} = 9.8 \times 10^{12}$  s<sup>-1</sup>) and  $T_0 = 404$  K ( $\tau_0^{-1} = 1.31 \times 10^{13}$  s<sup>-1</sup>), respectively. The obtained parameters for both BaTiO<sub>3</sub> and Ba<sub>0.80</sub>Ca<sub>0.20</sub>TiO<sub>3</sub> are shown in table 1. Regarding the parameters of BaTiO<sub>3</sub>, the data of CP in [11] was reanalyzed without assuming any constant background in the fitting procedure considering the negligible dark current of the photomultiplier tube used in the experiment. As can be seen from figure 4, the temperature dependence of  $\tau^{-1}$  is well explained by (3). This suggests a slowing-down behavior of the dynamics of polar regions. It is very interesting that the temperature region where CP appears and  $\tau^{-1}$  satisfies the linear slowing-down behavior is almost the same as that where  $\Gamma_B$  exhibits a remarkable increase from the background damping shown in figure 2(b). We believe this nice correlation supports the suggestion that the off-center Ti ions, formed at much higher temperature, are more correlated at an additional characteristic temperature resulting in the formation of polar clusters having increased size as well as longer lifetime. At this temperature, larger polarization fluctuations, and thus larger coupling between the LA waves and the order parameter, are expected. The formation of CP along with the slowing-down behavior is also correlated with this additional temperature.

The correlation length of polarization fluctuations becomes very large near the Curie point. The size of precursor clusters was measured to be about 200 nm by means of photon correlation spectroscopy [22] and about 1  $\mu$ m by means of a picosecond soft x-ray laser speckle technique [23], much larger than the acoustic wavelength. Moreover, the

**Table 1.** Best-fitted results for the temperature dependence of the relaxation time of  $\text{Ba}_{0.80}\text{Ca}_{0.20}\text{TiO}_3$  and  $\text{BaTiO}_3$  single crystals in both paraelectric and ferroelectric phases by using (3).

Crystal	Phase	$\Delta T$ used for fitting	$1/\tau_0$ ( $\text{s}^{-1}$ )	$T_0$ (K)
$\text{Ba}_{0.80}\text{Ca}_{0.20}\text{TiO}_3$	Paraelectric	$T_{C-T} \sim T_{C-T} + 70$ K	$9.8 \times 10^{12}$	345
	Ferroelectric	$T_{C-T} \sim T_{C-T} - 8$ K	$1.31 \times 10^{13}$	404
$\text{BaTiO}_3$ <sup>a</sup>	Paraelectric	$T_{C-T} \sim T_{C-T} + 28$ K	$1.38 \times 10^{13}$	347
	Ferroelectric	$T_{C-T} \sim T_{C-T} - 11$ K	$2.59 \times 10^{13}$	392

<sup>a</sup> CP data were taken from [11] and reanalyzed as described in the text.

relaxation time of precursor clusters can be as large as several microseconds [22] near  $T_{C-T}$ . In this case, large precursor polar clusters may be treated as static objects for acoustic waves, and the linear coupling between intracluster polarization and the strain should appear, giving rise to acoustic mode softening and Landau–Khalatnikov-like damping, which we really observe in the temperature range close to and above  $T_{C-T}$ . This suggestion is consistent with the observation of the induced piezoelectric effect in the paraelectric phase of  $\text{BaTiO}_3$  single crystals, which was ascribed to the existence of polar regions [24].

Similar to  $\text{BaTiO}_3$ , the slowing down of  $\text{Ba}_{0.80}\text{Ca}_{0.20}\text{TiO}_3$  is incomplete, which may be attributable to the first-order character of the phase transition and/or to the disordered distribution of the perovskite A-site and/or to defects included in the crystal. One difference between  $\text{BaTiO}_3$  and  $\text{Ba}_{0.80}\text{Ca}_{0.20}\text{TiO}_3$  is that the temperature range where  $\tau^{-1}$  follows the slowing-down behavior is larger in  $\text{Ba}_{0.80}\text{Ca}_{0.20}\text{TiO}_3$  than in  $\text{BaTiO}_3$ . It was suggested that off-center displacement of Ca ions may comprise an additional polarization component which will be cooperative with Ti–O distortion [19]. This component may induce enhanced polarization fluctuation in the paraelectric phase of  $\text{Ba}_{0.80}\text{Ca}_{0.20}\text{TiO}_3$ . On the other hand, the change in  $\tau^{-1}$  of  $\text{Ba}_{0.80}\text{Ca}_{0.20}\text{TiO}_3$  as a function of temperature is rather gradual compared to that of  $\text{BaTiO}_3$  and  $\tau^{-1}$  near  $T_{C-T}$  seems to deviate slightly from the linear behavior predicted by (3). These may be due to the compositional disorder introduced by random substitution of Ca ions at the Ba site.

There is seemingly an apparent analogy between  $\text{BaTiO}_3/\text{Ba}_{0.80}\text{Ca}_{0.20}\text{TiO}_3$  and ferroelectric relaxors such as  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (PMN). Relaxors exhibit gradual softening of  $\nu_B$  in a wide temperature range too, indicating a formation of polar nanoregions (PNRs) [25]. The temperature evolution of PNRs is correlated with anomalous changes in the elastic constant and the hypersonic attenuation as well as the formation of CP [26]. In addition, the temperature evolution of dynamics of PNRs in relaxors is also characterized by two characteristic temperatures, i.e. a so-called Burns temperature where PNRs appear and an additional temperature at which PNRs become more correlated and longer lived to form quasi-static PNRs [27, 28]. However, the temperature dependence of the relaxation time associated with the dynamics of PNRs does not follow the critical slowing-down behavior in general [29, 30]. This may be due to the strong disordered nature inherent to the relaxor which prevents it from realizing a ferroelectric long-range order at low temperatures. However, critical slowing down may be observed in such relaxors which

display ferroelectric long-range order at low temperatures due to enhanced ferroelectric interactions by, for example, increasing  $\text{PbTiO}_3$  (PT) content in PMN-PT [31, 32].

#### 4. Conclusion

Acoustic properties and phase transition behaviors of  $\text{Ba}_{0.80}\text{Ca}_{0.20}\text{TiO}_3$  were investigated in a wide temperature range of 300–880 K by using micro-Brillouin spectroscopy. The observed anomalous acoustic behaviors indicated two characteristic temperatures associated with the dynamics of precursor polar clusters, consistent with recent theoretical predictions and calculation results for  $\text{BaTiO}_3$ . Firstly, the longitudinal acoustic phonon mode showed an onset of softening of the Brillouin frequency shift at about 650 K, which is very similar to the temperature where the free energy begins to exhibit eight minima along the  $\langle 111 \rangle$  directions of the oxygen octahedral predicted by Geneste [17]. Secondly, the hypersonic attenuation began to increase remarkably and the quasielastic central peak appeared at about 450–480 K, which is similar to the theoretical prediction below which precursor dynamics set in [16]. Combining these two results, we suggest that observed acoustic anomalies are related to the dynamics of precursor polar clusters that exhibits a two-step temperature evolution: off-center motions of Ti ions set in at about 650 K and then they become correlated substantially with longer lifetimes at about 450 K in  $\text{Ba}_{0.80}\text{Ca}_{0.20}\text{TiO}_3$ . The former seems to affect the onset of softening of LA modes while the latter should be responsible for the significant increase in the acoustic attenuation and the growth of the central peak. This scenario is equally applicable to  $\text{BaTiO}_3$  [11]. Compared to  $\text{BaTiO}_3$ , the temperature region where slowing-down behavior was observed became larger in the paraelectric phase of  $\text{Ba}_{0.80}\text{Ca}_{0.20}\text{TiO}_3$ , which may be attributable to the off-center displacement of Ca ions and the resulting additional polarization component that is expected to be cooperative with Ti–O distortion.

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