

## Order-disorder nature of ferroelectric BaTi<sub>2</sub>O<sub>5</sub>

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Ferroelectric single crystals of BaTi<sub>2</sub>O<sub>5</sub> have been studied in detail by Raman and high-resolution micro-Brillouin scattering with a focus on the central component of the relaxation mode over a wide temperature range (20–600 °C). A relaxation mode has been clearly observed in these single crystals. The temperature dependences of the relaxation time and integrated intensity of the relaxation mode are well reproduced by the extended semiclassical tunneling model. The ferroelectric phase transition shows, at least near the vicinity of  $T_c$ , an order-disorder nature. Our results indicate that the spontaneous polarization mainly resulted from the dynamic disorder of the Ti ions in the octahedra along the polar  $b$  axis of BaTi<sub>2</sub>O<sub>5</sub>. © 2005 American Institute of Physics. [DOI: 10.1063/1.1880442]

Lead-based ferroelectric materials with perovskite structure, lead zirconium titanate (PZT) and lead magnesium niobate-lead titanate (PMN-PT), exhibit good ferroelectric and piezoelectric properties, and thus are widely used as electromechanical devices. However, lead may affect the natural environment. The development of lead-free ferroelectric materials is required from the viewpoint of environmental problems. Barium titanate (BaTiO<sub>3</sub>) is a good candidate for a lead-free ferroelectric material. Usually A- and B-site dopants have been used to modify the electrical properties of BaTiO<sub>3</sub>. In this way, either or both the Curie temperature  $T_c$  and the nature of a phase transition may be modified and sometimes lead to a diffuse phase transition-type behavior.<sup>1</sup> Statton<sup>2</sup> grew single crystals of barium dititanate (BaTi<sub>2</sub>O<sub>5</sub>) together with BaTi<sub>2</sub>O<sub>3</sub>, BaTi<sub>4</sub>O<sub>9</sub>, and Ba<sub>2</sub>TiO<sub>4</sub> to investigate the binary system of BaO–TiO<sub>2</sub> in the 1950s. Harrison<sup>3</sup> and Tillmanns<sup>4</sup> determined that its crystal system is monoclinic with space group C<sub>2h</sub>. Very recently, Akishige *et al.*<sup>5,6</sup> found ferroelectricity in this single crystal. The crystal system of the ferroelectric phase is monoclinic with space group C2 and has a spontaneous polarization of 7 μC cm<sup>-2</sup> along the  $b$  axis. The unit-cell parameters are  $a=16.91$  Å,  $b=3.94$  Å,  $c=9.49$  Å, and  $\beta=103.0^\circ$ . Dielectric measurements show that the ferroelectric BaTi<sub>2</sub>O<sub>5</sub> crystal grown in a reducing air shows a diffuse phase transition at around  $T_c\sim 430$  °C. The crystal grown in air shows a sharp dielectric anomaly reaching 30 000 at  $T_c\sim 479$  °C. Kimura *et al.*<sup>7</sup> shows the displacement of Ti atoms in the one of the Ti sites is mainly responsible for the ferroelectricity. Furthermore, ferroelectricity of this single crystal was confirmed and explained using first-principle calculation.<sup>8</sup> However, except dielectric measurements, minimal information is available regarding the physical properties and dynamics of the ferroelectric phase transition of this material. To clarify the origin of ferroelectricity, an important point is to know whether this transition is primarily of displacive or of order-disorder type.<sup>9</sup>

To understand the phase transition mechanism at  $T_c$  and lattice dynamics, it is useful to apply an inelastic light scattering technique. Since, frequency shifts and full width at half maximum (FWHM) of the optical and acoustical modes are very sensitive to phase transitions and also low frequency, relaxation phenomena can be directly observed by this method. Here, we report on the normal modes and central peak of BaTi<sub>2</sub>O<sub>5</sub> single crystals by the Raman and Brillouin light scattering technique.

Needlelike crystals of BaTi<sub>2</sub>O<sub>5</sub> were grown by rapidly cooling fine powders of BaTiO<sub>3</sub> and TiO<sub>2</sub> as starting materials. The consequent mixing ratio is BaO:TiO<sub>2</sub>=33:67. Crystal growth was performed in air ambient. Details of the growth conditions have been reported elsewhere.<sup>5,6</sup> Raman scattering is excited using a diode-pumped solid-state laser at a wavelength of 532 nm and a power of about 100 mW. The signal was analyzed by a triple-grating spectrometer of additive dispersion (Jobin Yvon T64000). The spectral resolution was about 2 cm<sup>-1</sup>. The Brillouin scattering spectra were measured using a (3+3) tandem Fabry–Perot interferometer of high contrast, combined with an optical microscope (OLYMPUS BH-2). A conventional photon-counting system and a multichannel analyzer were used to detect and average the signal. A single-frequency Ar<sup>+</sup>-ion laser with a wavelength of 514.5 nm and power of 100 mW was used to excite the sample. In both methods, backward scattering geometry was employed. A cryostat cell (THMS 600) with temperatures varying from –190 °C to 600 °C and with a stability of ±0.1 °C was used for temperature variation.

The temperature dependence of the Raman spectra of a BaTi<sub>2</sub>O<sub>5</sub> single crystal measured in  $a(b,b+c)\bar{a}$  geometry from 8 cm<sup>-1</sup> to 120 cm<sup>-1</sup> is shown in Fig. 1. No soft mode was observed. The lowest mode appeared at 80 cm<sup>-1</sup> at room temperature where indicated by arrows. Although, the mode frequency of this lowest mode does not show clear softening, it shows broadening approaching  $T_c$  then disappears. A typical Brillouin spectra with a free spectral range (FSR) of 100 GHz and a scan range of 1.5 FSR on a (100) plane at selected temperatures are shown in Fig. 2. Both methods, in

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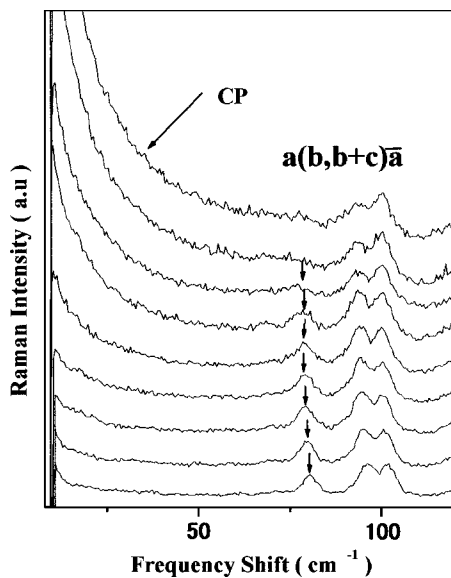


FIG. 1. Low-frequency Raman spectra in  $\text{BaTi}_2\text{O}_5$  obtained between  $8 \text{ cm}^{-1}$  and  $120 \text{ cm}^{-1}$  at temperatures 500, 440, 380, 320, 260, 200, 140, 80, and  $20^\circ\text{C}$ , from top to the bottom. The arrows indicate the lowest mode observed at  $80 \text{ cm}^{-1}$  at room temperature. CP indicates central peak.

In addition to the usual phonon features, such as normal modes determined by selection rules, a relaxation mode has been clearly observed in  $\text{BaTi}_2\text{O}_5$  crystals. Upon heating, a central peak appears around  $300^\circ\text{C}$  and shows marked temperature dependence. The intensity of the central peak increases markedly as the temperature approaches  $T_c$  from both above and below. The spectral analysis on Brillouin spectra was carried out using the convolution of a Lorentzian spectral function with a Gaussian broadening function. The temperature dependences of elastic stiffness constant  $c_{66}$  obtained from frequency shifts and FWHM for the transverse acoustic (TA) mode are shown in the inset of Fig. 3. One anomaly is clearly observed at  $T_c = 470^\circ\text{C}$  from both  $c_{66}$  and FWHM of the TA mode. The transition temperature reported here is in good agreement with those obtained by dielectric measurements for  $\text{BaTi}_2\text{O}_5$  of the same sample.<sup>5</sup> The elastic stiffness constant  $c_{66}$  shows a softening upon approaching  $T_c$  from below. However, above  $T_c$ , it does not show any clear temperature dependence. The interesting part is above  $T_c$ , where

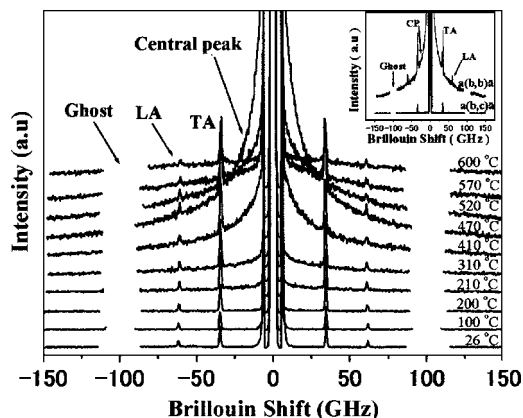


FIG. 2. Brillouin spectra obtained with FSR of  $100 \text{ GHz}$  and scan range of  $\pm 1.5 \text{ FSR}$  at temperatures 600, 570, 520, 470, 410, 350, 310, 200, 100, and  $26^\circ\text{C}$ , respectively, from the top to the bottom. LA: longitudinal acoustic mode. TA: transverse acoustic mode. Inset: Polarization dependence of Brillouin spectra of  $\text{BaTi}_2\text{O}_5$  at  $410^\circ\text{C}$ .

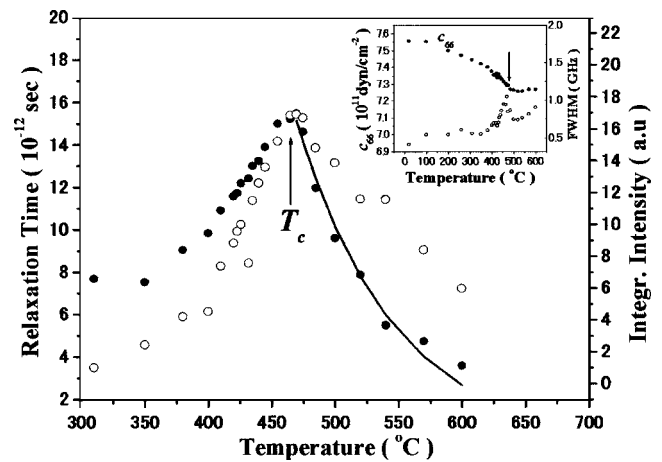


FIG. 3. The temperature dependence of the integrated intensity (open circle) and the relaxation time  $\tau$  (dark circle) of the relaxation mode of  $\mathbf{q} \parallel a$ . Solid line is the fit of the relaxation times using the tunneling model, with  $1/\tau_0 = 670 \text{ cm}^{-1}$ ,  $\Delta V = 821 \text{ cm}^{-1}$ . Inset: Elastic stiffness constants  $c_{66}$  (dark circle) and FWHM (open circles) for the TA mode. The arrow indicates the phase transition temperature  $T_c$ .

we can still see the hypersonic damping. This observation correlated with the appearance of a central peak, as shown in Fig. 2. Here, we will focus on the properties of the relaxation mode; The acoustic properties will be published separately.

When the relaxation occurs in the ionic motion, the spectral response  $S(\omega)$  is usually well described by the Debye relaxation in the high-temperature approximation.

$$S(\omega) = \chi''(\omega)[n(\omega) + 1] \propto \frac{1}{1 + \omega^2 \tau^2}, \quad (1)$$

where  $S(\omega)$  is approximated by a Lorentzian centered at zero-frequency shift with a half width at half maximum equal to the inverse of the relaxation time  $\tau$ .

The obtained intensity of the central peak and the relaxation time are shown in Fig. 3. It can be noted that the anomalies are observed in both intensity and relaxation time at around  $470^\circ\text{C}$ , which is the same temperature as the anomalies of the acoustic anomalies shown in Fig. 2. The relaxation time slows down and the central peak intensity increases markedly when temperature approaches  $T_c$  from above and below. However, the rate of slowing down is different above and below  $T_c$ . Point symmetry of  $\text{BaTi}_2\text{O}_5$  at room temperature is monoclinic  $C_2$ ;  $a(b,b)\bar{a}$  scattering geometry relates to A(y)-symmetry excitation, which involves ionic motion parallel to the polar axis, and  $a(b,c)\bar{a}$  scattering relates to B(x,z)-symmetry excitations, which involve ionic motion in a plane perpendicular to the polar axis. Brillouin scattering spectra observed in the above two scattering geometries at  $410^\circ\text{C}$  is shown in the inset of Fig. 2. In  $a(b,b)\bar{a}$  scattering geometry, we can see the strong central component. However, in  $a(b,c)\bar{a}$  geometry, the strong broad central component disappeared, indicating that the central peak has an A(y) symmetry connected to the dynamic disorder of the Ti ions in the octahedra along the polar  $b$  axis of  $\text{BaTi}_2\text{O}_5$ . This kind of collective motion of Ti ions may be the origin of ferroelectricity in  $\text{BaTi}_2\text{O}_5$ .

The presence of the central peak is direct evidence that a relaxation mechanism takes place in  $\text{BaTi}_2\text{O}_5$  and that the relaxation modes play a key role in the lattice dynamics. Concerning relaxation modes in Brillouin or Raman scatter-

ing, there are different origins, static or dynamic. The most important distinction of the origin of the central peak, whether static or dynamic, is the spectral width. The static origin gives rise to a narrow and temperature-independent central peak, while the dynamic origin results in a relatively broad and temperature-dependent central peak. The finer distinctions among various dynamic mechanisms, such as entropy and phonon density fluctuations, degenerate electronic levels, phasons, ion hopping, precursor clusters, and tunneling, are its temperature, symmetry, and wave vector dependence.<sup>10–16</sup>

Similar central peak features that we observed in BaTi<sub>2</sub>O<sub>5</sub> have been reported in several classical pure and mixed perovskite compounds, such as KNbO<sub>3</sub>, BaTiO<sub>3</sub>, and KTa<sub>1-x</sub>Nb<sub>x</sub>O<sub>3</sub> in a Raman scattering study.<sup>16,17</sup> Their central peaks have Lorentzian-type shapes centered at the zero-frequency shift that is indicative of a Debye relaxation. The width of the central peaks is temperature dependent, as predicted by the semiclassical model which was first used to explain the dielectric properties and anomalous of the A<sub>1</sub> [transverse optical (TO)] mode in BaTiO<sub>3</sub>.<sup>18</sup> Later, it was extended to explain the relaxation modes in some relaxor ferroelectrics.<sup>19,20</sup> In this semiclassical model, the thermally excited B ions tunnel through the top of a barrier between the two sites in the eight-site potential which describes a set of off-center positions for the B ions in every perovskite unit cell. The average relaxation time  $\tau$  in this set of sites can be written as

$$\tau = \tau_0 \exp\left(\frac{\Delta V - kT}{kT_0}\right), \quad (2)$$

where  $\Delta V = V_0 - E$  is the difference between the height of the barrier and the B-ion zero-point energy.  $E = kT$  is the average B-ion energy.

$$kT_0 = \hbar/2\pi\sqrt{\alpha/m_b}, \quad (3)$$

is related to the mass  $m_b$  of B ions and curvature  $\alpha$  of the top of the potential barrier. The quantity  $\tau_0^{-1}$  is a tunneling “attempt” frequency, and a typical physically plausible value for this quantity is several hundred wave numbers. We have attempted to fit the temperature-dependence behavior of the broad central peak in BaTi<sub>2</sub>O<sub>5</sub> using Eq. (3) with a physically reasonable attempt frequency  $1/\tau_0 = 670 \text{ cm}^{-1}$ . These fitting results are shown as a solid line in Fig. 3. The fitting yields  $\Delta V = 821 \text{ cm}^{-1}$  and  $kT_0 = 52 \text{ cm}^{-1}$ . A main assumption of this tunneling modeling is that, in the case of BaTi<sub>2</sub>O<sub>5</sub> single crystal, the Ti ion in the oxygen octahedra located at the one of the minima of a double-well potential is thermally excited to just below the top of the potential barrier and tunnels from that level to the another potential minima. Since  $T_c = 470 \text{ }^\circ\text{C}$  is equivalent to the thermal energy of  $516 \text{ cm}^{-1}$ ,  $\Delta V = 821 \text{ cm}^{-1} \sim 909 \text{ }^\circ\text{C}$  is physically reasonable for a thermally excited relaxation process and consistent with the tunneling model for our Brillouin data in which the thermally excited Ti ions have energies just below the top of the barrier and then tunnel through the barrier. As defined earlier,  $kT_0 \sim \sqrt{\alpha}$ ,  $kT_0$  determines the curvature center of the barrier. A relatively small value ( $kT_0 = 52 \text{ cm}^{-1}$ ) implies that the barrier

width broadens rapidly below the top of the barrier. Therefore, small changes in the thermal energy of Ti ions give rise to large changes in the size of the barrier width through which it must tunnel. This model explains the strong temperature dependence of the relaxation time observed in the high-temperature phase. As noted in Fig. 3, the relaxation time also shows a rather strong temperature dependence below  $T_c$ , but slightly weaker than that above  $T_c$ . For ferroelectrics, spontaneous polarization appears just below  $T_c$ , so that the double-well potential along the polar axis shows a strong asymmetric line shape. For a BaTi<sub>2</sub>O<sub>5</sub> single crystal below  $T_c$ , the asymmetric line shape of the double-well potential resulting from spontaneous polarization suppresses the temperature dependence behavior of the Ti ions under tunneling.

In conclusion, a relaxation mode was observed in the Raman and Brillouin scattering spectra of ferroelectric BaTi<sub>2</sub>O<sub>5</sub> single crystals. These central peaks have line shapes of Debye relaxation. The temperature dependence of the relaxation time and integrated intensity of the central peak are consistent with the extended semiclassical tunneling model in which the off-center Ti ion in the octahedra tunnels between two sites of a double-well potential. The ferroelectric phase transition shows, at least near the vicinity of  $T_c$ , an order-disorder nature. It seems that the spontaneous polarization mainly resulted from the dynamic disorder of the Ti ions in the octahedra along the polar  $b$  axis of BaTi<sub>2</sub>O<sub>5</sub>.

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