Proceedings of Symposium on Ultrasonic Electronics, Vol. 36 (2015)
5-7 November, 2015

Angle-resolved polarized Raman scattering from $BaTiO_3$ crystals

$BaTiO_3$結晶の角度分解偏光ラマン散乱

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1. Introduction

One of the ferroelectric perovskites, barium titanate $BaTiO_3$, has broad applications in capacitors, thermistors, and sensors. The useful properties are dependent on temperature and closely related with the phase transitions. $BaTiO_3$ has rhombohedral (R), orthorhombic (O), tetragonal (T), and cubic (C) phases. However, micro- and mesoscopic pictures of these phases and phase transitions are still uncertain. One important picture in history is the displacive model, in which microscopic Ti-ion shift from the center of oxygen-octahedron agrees with the polar axis: Ti-ion is at the center in C (1b site), while Ti-ion displaces to <100> in T, <110> in O, and <111> in R, respectively [1]. Although various properties of $BaTiO_3$ have been understood well on the basis of this simple model, inconsistencies of experimental results from the model have been apparent. For example, i) the diffuse x-ray scattering observed in C, T, and O phases. ii) second harmonic generation signal (SHG) appears even in C phase. iii) x-ray fine structure and nuclear magnetic resonance indicate that Ti-ion displaces <111> in all phases. iv) first-order Raman scattering appears in C phase. Here, i)- iv) are not expected by the displacive model. The appearance of SHG and Raman scattering are never allowed in the microscopic structure with inversion symmetry.

In order to explain these experimental results inconsistent with the displacive model, temporal disorders due to the Ti-ion-hopping in eight-site (8g site with x=0.5+δ, where δ denotes the deviation from the center of oxygen-octahedron) have been considered as microscopic dipoles and ferroelectricity is induced by their interaction. In other words, Ti-ions are always located in one of eight minima along <111>-direction for all phases, and the average position of Ti-ions determines the macroscopic polarization. The Ti-ion-hopping picture is called order-disorder eight-site model. In this framework, correlated regions several nanometers wide are necessary to be taken into account to explain the entropy changes at phase transitions [2-3].

From the view point of Raman scattering, Lambert, *et al*. explained the origin to be disorder on the basis of order-disorder eight-site model [4-5]. On the other hand, Barbosa, *et al*. attributed it to second-order process on the basis of the displacive model [6]. Even though the origin is still in controversy, Raman scattering from $BaTiO_3$ is widely used to evaluate the materials properties in applications for convenience. To understand $BaTiO_3$ more clearly and to apply Raman scattering from $BaTiO_3$ for evaluating electric components in the next generation, at the present stage, it is necessary to answer i) whether the Raman scattering is first-order or second-one, and ii) whether phonon mode or relaxation is related with the phase transitions. In order to solve these questions, angle-resolved polarized Raman scattering from $BaTiO_3$ was measured in the present study.

2. Experimental

Figure 1(a) shows the schematic diagram of the micro-Raman scattering experimental setup. A $BaTiO_3$ crystal with [100]-surface was put inside the temperature controlled stages on the *xyz* mapping stage installed in the microscope. Linearly polarized incident light traveled to the sample through a polarization rotation device equipped with a broadband half-waveplate [7]. When the polarization direc-tion of incident light is inclined θ/2 with respect to the optical axis of the waveplate, the waveplate rotates polarization plane of incidence θ degree as shown in FIG. 1(b). On the other hand, the polarization direction of scattering light, propagating in opposite direction of incident light, is rotated by -θ degree. Thus, θ-directed incident light was focused on the sample and light was scattered according to the Raman polarizability. Thus, angle-resolved polarized Raman spectroscopy rotate the polarization without rotaing the specimen. This method enable us to measure the angle dependence with changing atmospheres such as temperature and pressure. The strong elastic scattering is eliminated by two volume Bragg gratings so called "ultra narrow-band notch fil-ters". Volume Bragg grating contains periodic variation in

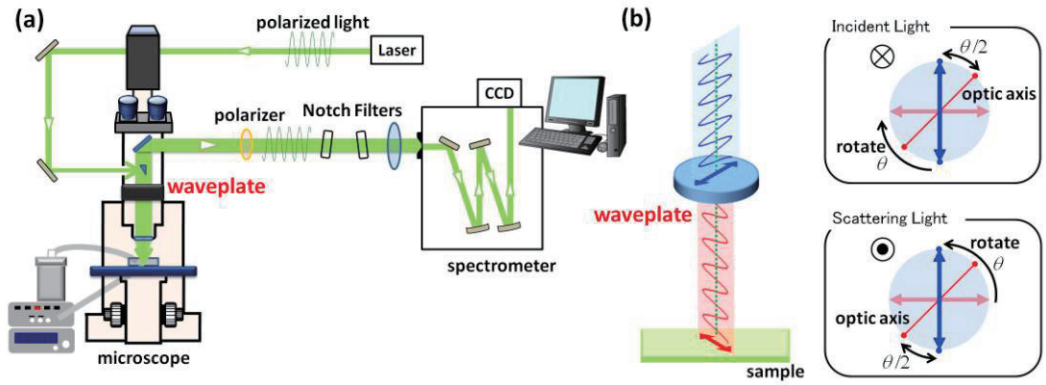

FIG 1. (a) Schematic diagram of the experimental setup. A sample is irradiated to incident light on the *xyz* mapping stage. To rotate polarization of incident and scattering light, a half-waveplate which rotation mechanism is under computer control is installed in the microscope. The strong elastic scattering is eliminated by ultra narrow-band notch filters. The Raman scattering is dispersed by a single-monochromator and is detected using a CCD. (b) Polarization rotation through a half-waveplate.

the refractive index, which generates a dielectric mirror for one specific wavelength. The inelastic scattering light was dispersed by a single-monochromator and the dispersed component was detected using a charge coupled device.

3. Results and Discussion

Figure 2 (above) shows the Raman spectra at 600 K at various polarization angles. Because T_C of $BaTiO_3$ is 400 K, 600 K is in the paraelectric C phase and is enough high to vanish the ferroelectric phase. By measuring both Stokes- and anti-Stokes-Raman scattering, we confirmed for one peak at 200 cm^{-1} that ratio of the peak intensity between Stokes- and anti-Stokes-Raman scattering obeys the first-order process (Bose factor). Thus, we attribute peaks at 200 and 500 cm^{-1} to be first-order Raman scattering. The appearance of first-order Raman scattering is prohibited in C phase without disorder, our experimental result supports the order-disorder eight-site model.

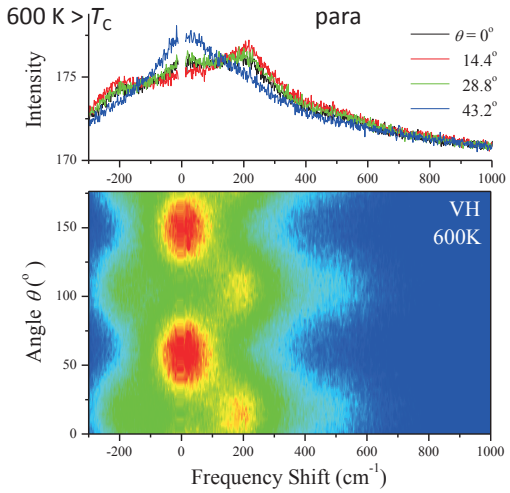

FIG. 2 Raman spectra of $BaTiO_3$ at 600 K in the backscattering geometry on (001) plane crystal. The angle denotes polarization direction of incident light. [100]-direction corresponds to 12°, while [010]-direction corresponds to 102°.

Contour map in FIG. 2 (below) shows that quasi-elastic scattering and phonon peaks depend on polarization-angle of the incident light. The dependence is well-explained on the assumption of the existence of disorder with the point group *R*3*m*. Thus, we conclude that Raman scattering of $BaTiO_3$ in the paraelectric phase is from the inhomogeneous structure with *R*3*m*.

Similar contour maps were acquired at various temperatures (not shown). The results show apparent narrowing of the quasi-elastic scattering, i.e. critical slowing down, with approaching T_C from high temperature, which also supports the appearance of polar disorders related with the order-disorder eight-site model.

Acknowledgment

This research was supported by JSPS KAKENHI (Grant No. 26790040 and 25400329) and by Murata Science Foundation.

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