7C, 15B1/2010G697, 2012G738

X-ray Raman Scattering Study of Structural Phase Transition of Ferroelectric $BaTiO_3$

Ryusuke Oura[1], Yusuke Sasaki[1], Masaya Mikami[1], Nobuo Nakajima[2], Shunsuke Nozawa[3], Toshiaki Iwazumi[4] and Yasuhisa Tezuka[1]*
[1]Grad. Sch. of Sci. and Tech., Hirosaki Univ., 3 Bunkiyo-cho, Hirosaki, 036-8561, Japan
[2]Grad. Sch. of Sci., Hiroshima Univ., 1-3-1 Kagamiyama, Higashi-Hiroshima 739-8526, Japan
[3]Photon Factory, Inst. of Mats. Struct. Sci., 1-1 Oho, Tsukuba 305-0801, Japan
[4]Grad. Sch. of Eng., Osaka Pref. Univ., Sakai 599-8531, Japan

1 Introduction

$BaTiO_3$ (BTO) is one of the typical ferroelectric materials having perovskite structure and undergoes ferroelectric phase transition at T_C (~120ºC) from tetragonal ferroelectric phase to cubic paraelectric phase. The cations (nominally Ti^{4+}, Ba^{2+}) are displaced along the c-axis relative to the anion (O^{2-}) site and spontaneous polarization is developed along the c-axis at room temperature. Though the BTO is classified into displacement type phase transition in general, the mechanism of the transition has not been elucidated fully yet, because the hybridization between Ti and O affects strongly [1]. We have reported X-ray Raman scattering (XRS) spectra of BTO observed under excitation at around the Ti *K* absorption edge, which showed anisotropic electronic structure of unoccupied Ti 3*d* state at room temperature [2]. In this study, azimuth dependence of the XRS was observed to investigate the anisotropy in high temperature paraelectric phase.

2 Experiment

The XRS and Ti *K* XAS experiments were performed at beamline BL7C. Single crystal BTO(100) having single domain was used in this study. A sample holder that can rotate the sample around c-axis at high temperature was installed to the x-ray emission spectrometer (ESCARGOT). Temperature were raised gradually from room temperature to about 150°C via T_C.

3 Results and Discussion

Figure 1 shows Ti *K* XAS spectra of paraelectric BTO(100) at 150°C observed by partial photon yield (PPY) method that detect the emission around the Ti *Kα* fluorescence peak. Inset shows entire XAS spectrum, while main panel shows pre-edge structures. It is known the pre-edge structures are overlapping between electric dipole (ED) and quadrupole (EQ) transition peaks, both of which are split into t_{2g} and e_g states by ligand field [3]. In the figure, both the XAS spectra excited along c-axis (E//c) and b-axis (E//b) are shown. There is no significant difference between these spectra, though the XAS spectra showed clear anisotropy in ferroelectric phase. The XRS measurement was observed under excitation energy just below Ti *K* absorption edge (4965.5eV) as denoted by the arrow in the figure.

Figure 2 shows azimuth dependence of XRS spectra of BTO(100) at 150°C, where the XRS spectra of E//b and

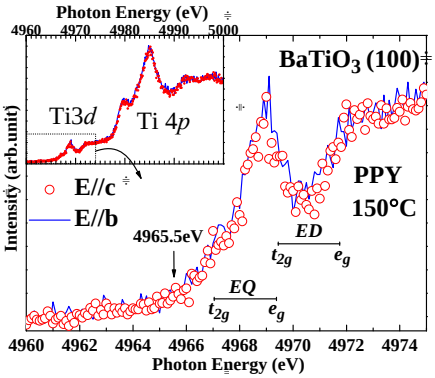

Fig.1 XAS spectra of paraelectric BTO(100) observed by partial photon yield method (inset) and pre-edge structures (main).

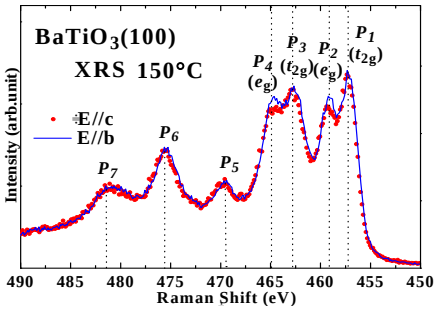

Fig.2 Azimuth dependence of XRS spectra of paraelectric BTO(100).

E//c are shown. The low energy four peaks (P_1~P_4) are the XRS by Ti $\underline{2p}3d$ and the high energy three peaks (P_5~P_7) are the XRS by Ti $\underline{2p}4p$ excitations, where underline denote core-hole, which reflect unoccupied Ti 3*d* and Ti 4*p* density-of-states, respectively [4]. The XRS spectra, which showed clear anisotropy at e_g peaks in ferroelectric phase [2], changed to isotropic gradually with increased temperature. Fig. 2 shows the spectra at paraelectric phase, but it still shows small anisotropy at e_g peaks (P_2, P_4). The result suggests that there is a residual anisotropy of Ti 3*d* state in paraelectric phase and the phase transition of BTO includes order-disorder aspects.

References

[1] R.E. Cohen, Nature **358**, 136 (1992).
[2] Y. Tezuka, et al., PF Act. Rep. 2010, #28, 92(2011)
[3] T. Uozumi, et al., Europhys. Lett. **18**, 85 (1992).
[4] Y. Tezuka, et al., PF Act. Rep. 2006, #24, 69(2007).
* tezuka@cc.hirosaki-u.ac.jp