

Anisotropic Electronic Structure of Ferroelectric BaTiO₃ Measured by X-ray Raman Scattering

Yasuhisa TEZUKA*¹, Nobuo NAKAJIMA², Hitoshi OSAWA³, Shunsuke NOZAWA⁴,
Toshiaki IWAZUMI⁵, Yasuhito ISOZUMI⁶

¹Grad. Sch. of Sci. and Tech., Hirosaki Univ., 3 Bunkyo-cho, Hirosaki, 036-8561, Japan

²Grad. Sch. of Sci., Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima 739-8526, Japan

³JASRI/SPring-8, Kouto 1-1-1, Sayo-cho, Hyogo 679-5198, Japan

⁴JST/ERATO, 1-1 Oho, Tsukuba 305-0801, Japan

⁵Photon Factory, Institute of Materials Structure Science, 1-1 Oho, Tsukuba 305-0801, Japan

⁶Radioisotope Research Center, Kyoto University, Kyoto 606-8501, Japan

Introduction

X-ray Raman scattering (XRS) spectra of ferroelectric BaTiO₃ (BTO) were observed under excitation at around the Ti *K* absorption edge. BTO undergoes ferroelectric phase transition at about 120°C from tetragonal ferroelectric phase to cubic paraelectric phase. The mechanism of the phase transition is still under discussion, because the hybridization between Ti and O affect to it strongly [1]. In this study, unoccupied Ti 3*d* state was observed by XRS of Ti 2*p*3*d* excitation, where underline denotes core hole.

Experimental

The XRS and Ti *K* XAS experiments were performed at beamlines BL7C and BL15B1. X-ray emission spectra having an energy centered at the Ti *K*α fluorescence lines (*K*α₁=4510.84 and *K*α₂=4504.86 eV) were observed. The energy resolution for both the Ti *K* XAS and XRS measurements was about 1 eV for 5 keV photon.

Commercially obtained powder and single domain crystals of BTO(100) were used. Resonant XRS spectra of powder sample were observed in detail, and the azimuth dependence of the XRS spectra was observed for the single crystal. BTO has a perovskite structure. Cations (nominally Ti⁴⁺, Ba²⁺) are displaced along the *c*-axis relative to the anion (O²⁻) site, then spontaneous polarization (*P*_s) is produced along the *c*-axis.

Results and Discussions

Figure 1 shows Ti *K* XAS spectrum of powdered BTO. Inset shows entire XAS spectrum, while the main panel shows pre-edge structure overlapping electric dipole (ED) and quadrupole (EQ) transitions, both of which are split into *t*_{2g} and *e*_g states by the ligand field. Excitation energies of XRS measurements are denoted by the position of the vertical bars and numbers.

Figure 2 shows azimuth dependence of XRS spectra of single crystal BTO(100). The XRS spectra in the configuration E//*b* and E//*c* are shown. Seven Raman peaks (*P*₁ - *P*₇) were observed. In the previous XRS study of TiO₂, the *P*₁ - *P*₄ were assigned to the unoccupied Ti 3*d* state, while *P*₅ - *P*₇ were assigned to unoccupied Ti 4*p* state. The *P*₁ and *P*₂ correspond to core-exciton of Ti 2*p*_{3/2}3*d*(*t*_{2g}) and Ti 2*p*_{3/2}3*d*(*e*_g), respectively, while the *P*₃,

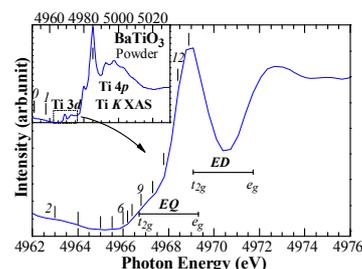


Fig.1. Ti *K* XAS spectrum of BTO. Inset shows entire XAS spectrum. Main panel shows pre-edge structure overlapping electric dipole (ED) and quadrupole (EQ) transitions, both of which are split into *t*_{2g} and *e*_g states by the ligand field.

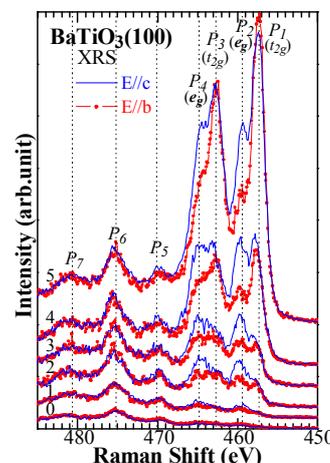


Fig.2. Azimuth dependence of XRS spectra of single crystal BTO(100). The XRS spectra in the configuration E//*b* (dot and line) and E//*c* (solid line) are shown.

and *P*₄ correspond to Ti 2*p*_{1/2}3*d*(*t*_{2g}) and Ti 2*p*_{1/2}3*d*(*e*_g), respectively. The *e*_g states have orbits along the Ti-O bonds, while *t*_{2g} states have orbits pointing between two Ti-O bonds. The result suggests anisotropy of Ti 3*d* state concerning to the spontaneous polarization direction. The XRS would reveal the effect of the hybridization to the ferroelectric phase transition.

References

[1] R.E. Cohen, Nature 358, 136 (1992).

* tezuka@cc.hirosaki-u.ac.jp