BL-7C/2019G591

Temperature dependence of resonant X-ray Raman scattering of $SrTiO_3$.

Yasuhisa Tezuka[1*], Masanori Shimamura[1], Shunsuke Nozawa[2], and Toshiaki Iwazumi[3]

[1] Grad. Sch. of Sci. and Tech., Hirosaki Univ., Hirosaki, Aomori 036-8561, Japan
[2] Photon Factory, Inst. of Mats. Struct. Sci., Tsukuba, Ibaraki 305-0801, japan
[3] Grad. Sch. of Eng., Osaka Pref. Univ., Sakai, Osaka 599-8531, Japan

Perovskite $SrTiO_3$ (STO) is known to maintain paraelectricity until absolute zero, while it has giant dielectric constant of $\varepsilon \sim 2\times10^4$ in quantum paraelectric phase under 10 K [1]. On the other hand, another perovskite $BaTiO_3$ undergoes ferroelectric phase transition at about 400 K, which is affected by the hybridization between Ti and O [2]. In this study, to understand the electronic state of STO, resonant X-ray Raman scattering (XRS) by Ti2*p*3*d* and Ti2*p*4*p* excitations (underline means core-hole) [3] and their temperature dependence were measured around the Ti *K* absorption edge.

In this study, single crystal of STO(100) was used. XRS spectra were measured using X-ray emission spectrometer (Escargot) at BL-7C of Photon Factory. The scattered photons were dispersed by Ge (400) crystal and detected using a multi-channel proportional counter (PSPC). The total energy resolution is about 1 eV. A helium circulation refrigerator was used for low temperature measurements. Using a thermal shield, lowest temperature of 13K was obtained.

Figure 1 shows Ti *K* absorption spectrum of STO(100) measured by a partial photon yield (PPY) method that measures the total X-ray emission detected in XRS measurements around Ti *Kα* fluorescence energy. The main structure reflects unoccupied Ti 4*p* state, while pre-edge structure reflects unoccupied Ti 3*d* state. The pre-edge structure splits into t_{2g} and e_g peaks under crystal field of O_h symmetry, and further splits to electric dipole (ED) and electric quadrupole (EQ) structures under core hole potential [4]. XRS spectra were measured under EQ excitations shown by vertical bars in the figure.

Figure 2 shows temperature dependence of resonant XRS spectra of STO(100). The emission spectra are plotted against the energy loss from the excitation energy (Raman shift), and three sets of the resonant XRS spectra at RT (red), 80K (green) and 13K (blue) are superimposed. Here, t_{2g} and e_g peaks of Ti 3*d* state, which reflect crystal field splitting under O_h symmetry, are observed in both L_{III} and L_{II} spectrum. These spectra show temperature dependence under Ti 3*d* resonant condition, where the e_g peak changes its intensity more than the t_{2g} peak. Since the e_g orbit is directed to O-ion and participate in Ti-O bonding, the result indicates change of Ti-O hybridization with changing temperature. The spectrum change at very low temperature suggests the relation between electronic structure and quantum paraelectricity.

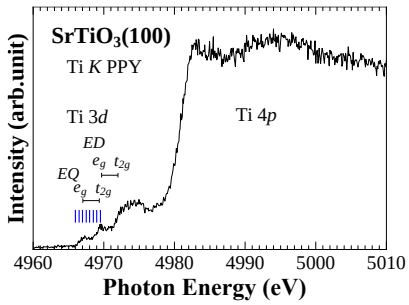

Fig.1: Ti *K* XAFS spectrum of $SrTiO_3$(100) measured by PPY method. Electric quadruole transition Ti 1*s*→3*d* was observed at pre-edge region. Vertical bars denote excitaion energies in XRS measurements.

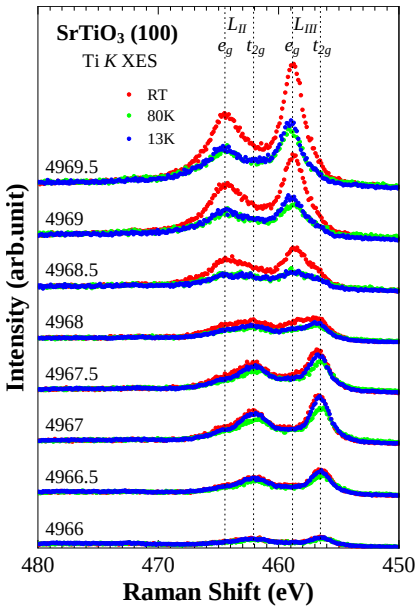

Fig.2: Temperature dependence of Ti *K* resonant XRS spectra of $SrTiO_3$(100). Excitations from Ti 2*p* core to unoccupied Ti 3*d* state were observed. Red: RT, Green: 80K, Blue: 13K. Numbers beside each spectrum denote excitation energies.

[1] K.A. Müller and H. Burkard, Phys. Rev. B**19**, 3593 (1979).
[2] Y. Tezuka, *et al*., Phys. Rev. B**104**, 235148 (2021).
[3] Y. Tezuka, *et al*., J. Phys. Soc. Jpn. **83**, 014707 (2014).
[4] T. Uozumi, *et al*., Europhys. Lett. **18**, 85 (1992).
*tezuka@hirosaki-u.ac.jp