Polarization dependent Ti 2p resonant X-ray Raman Scattering Study of CaCu$_3$Ti$_4$O$_{12}$

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1. Introduction
CaCu$_3$Ti$_4$O$_{12}$ (CCTO) is an A-site ordered perovskite (AA′B$_2$O$_{12}$). A-site of the perovskite structure (ABO$_3$) is held by Ca and Cu in the ratio of 1:3, thus the TiO$_6$ cluster in CCTO is tilted. The CCTO shows a huge dielectric constant ($\varepsilon$~10$^6$) in a wide temperature range including room temperature, while the dielectric constant decreases rapidly at about 100K [1]. Since CCTO does not undergo structural phase transitions at the dielectric anomaly temperature, it is important to study the electronic structure to explain the dielectric anomaly. X-ray Raman scattering (XRS) is suitable to measure the electronic structure in insulator, because the XRS is a photon-in/photon-out technique. We have reported resonant X-ray scattering study in the energy range of Ti $K$, Cu $K$ [2,3] and Cu 2p region [4]. In this study, XRS study in Ti 2p region and its polarization dependence are reported.

2. Experiment
In this study, a single crystal CCTO(100) made by floating zone method was used. The experiments were performed using a soft X-ray emission spectrometer at beamline BL-13A. Polarization dependent Resonant X-ray emission spectra (XES) were measured. Scattering to horizontal direction with angle of 90° was observed. Then, polarized and depolarized spectra were measured by using vertically and horizontally polarized SR beams, respectively [5].

3. Results and Discussions
Figure 1 shows the Ti 2p XAS spectrum of CCTO (100) measured by partial photon yield (PPY) and total electron yield (TEY) method. Structures caused by spin-orbit splitting of Ti 2p core level and crystal field splitting of unoccupied Ti 3d state were observed. The vertical bars indicate excitation energy in the XES measurement. Figure 2 shows the polarization dependence of the CCTO(100). Polarized (dot) and depolarized (line) spectra are shown. XES spectra are plotted against energy loss (Raman shift), thus the fluorescence peaks change these energies with changing excitation energy. Raman scattering peaks are observed at about 7.0 and 14.0 eV, both of which shows polarization dependence. The peak at 7.0 eV is caused by non-bonding state, while the peak at 14.0 eV is caused by bonding state [5]. Temperature dependence of these excitations would give us important information about dielectric anomaly in CCTO.

References