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Temperature Dependent Electronic Structure of A-site Ordered Perovskite $CaCu_3Ti_4O_{12}$

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1 Introduction

$CaCu_3Ti_4O_{12}$(CCTO) has A-site ordered perovskite structure ($A'A_3B_4O_{12}$). One of the four A-site (Cu) in the perovskite structure (ABO_3) is replaced by Ca-ion, so that the TiO_6 cluster in CCTO is tilted from crystallographic axis. CCTO exhibits a huge dielectric constant of $\varepsilon \sim 10^4$ in the temperature range of 100 to 600 K, while the dielectric constant decreases suddenly below about 100 K without a structural phase transition [1]. Since CCTO does not undergo structural phase transitions on the dielectric anomaly, it is important to study the electronic structure to understand the dielectric properties. In this study, resonant X-ray Raman scattering (XRS) [2-4] of CCTO was measured. Core excitations such as $\underline{2p}3d$ and $\underline{2p}4p$, where underline denote a hole state, were observed. These spectra reflect unoccupied density-of-states. Temperature dependent XRS spectra were observed at Cu *K* absorption edge.

2 Experiment

Single crystal CCTO (100) was used in this experiment. The XRS spectra were measured using X-ray emission spectrometer (Escargot) at beamline BL-7C of Photon Factory. XRS measurements were carried out at temperatures of 15, 30, 80 and 120 K as well as room temperature. 80 and 120 K are below and just above the dielectric anomaly temperature, respectively. Helium circulation cryostat was used in these measurements.

3 Results and Discussion

Figure 1 shows the Cu *K* XAS spectrum of CCTO (100) measured by partial photon yield (PPY) method. Cu 3*d* states were observed at the pre-edge region, while the main structure shows Cu 4*p* state. The vertical bar denotes excitation energy in the XRS measurement.

Figure 2 shows the temperature dependent XRS spectra of CCTO (100) excited at 8980.2 eV. X-ray Emission spectra are plotted against energy loss (Raman shift). Four XRS peaks were observed with each core level of Cu $2p_{3/2}$ and $2p_{1/2}$. The P_1 and P_2 are originated from Cu $\underline{2p}3d$ excitations, while the P_3 and P_4 are originated from Cu $\underline{2p}4p$ excitations. These spectra were normalized with P_3 peak intensity that reflects 4*p* state and does not change with excitation energy and temperature. The temperature dependence measurements show that the intensity of P_1 (P_1') decreases around 100K, then it increases again at low temperature. Since the XRS spectra reflect the unoccupied density of states, the result shows increase of Cu 3*d* state around dielectric anomaly temperature. Other hand, Ti 3*d* peak was observed decreasing continually with decreasing temperature in Ti *K* XRS measurements. These results suggest the relation between electronic state and dielectric properties.

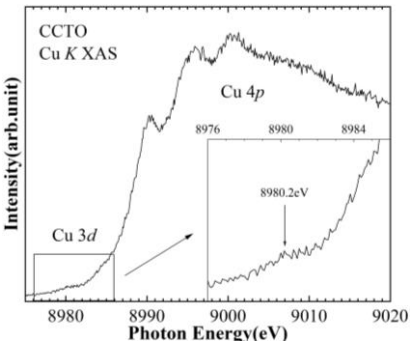

Fig.1: Cu *K* XAS spectrum of CCTO (100). The vertical bars indicate the excitation energy of the XRS measurement.

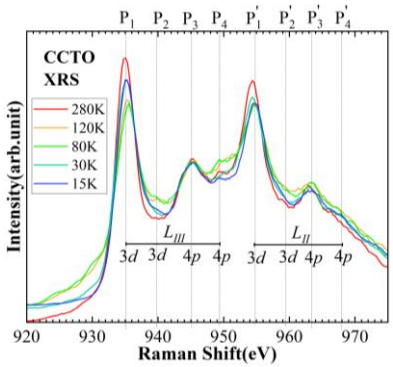

Fig.2: Temperature dependence of the Cu *K* resonant X-ray Raman scattering spectra of CCTO (100) excited at 8980.2 eV.

References

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