

Temperature Dependent Electronic Structure Study of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ by means of X-ray Raman Scattering

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1 Introduction

A-site ordered perovskite $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) has attracted much attention recently, because it shows a giant dielectric constant ($\sim 10^4$) over a wide temperature range from about 100 to 600K. Furthermore, the dielectric constant decreases to one-hundredth at the temperature below about 100K without structural phase transition [1]. To clarify the nature of the anomalous dielectric property, electronic structure of CCTO should be investigated. X-ray Raman scattering (XRS) is an effective method studying electronic state of insulator material, since it uses photons in both excitation and detection. It has been reported the XRS by core excitation reflects unoccupied density-of-state [2]. The XRS spectra observed at Ti *K* and Cu *K* edge were reported [2, 3]. In each spectra, scatterings by $\underline{2p}3d$ and $\underline{2p}4p$ core-excitations were observed, where underline denote a core-hole state. We have reported XRS results of polycrystalline CCTO and its temperature dependence [4]. In this article, temperature dependent XRS spectra of single crystal CCTO observed at Cu *K* edge are reported.

2 Experiment

In this study, single crystal CCTO(100) and (111) were used. The XRS spectra were observed using X-ray emission spectrometer (ESCARGOT) at beamline BL-7C. Scattered photons were analyzed using crystals Ge(444) and (400) in the measurements on Cu *K* and Ti *K* edge, respectively. One-dimensional multi-channel proportional counter was used to detect the dispersed photons. The energy resolution of XRS measurement was about 1 eV.

3 Results and Discussion

In this study, the XRS spectra of single crystal (100) and (111) were observed at both Ti *K* and Cu *K* absorption edge. Azimuth dependence and temperature dependence were observed in these samples.

Figure 1 shows the temperature dependence of XRS spectra of CCTO(100) observed at the Cu *K* absorption edge. The polarization of excitation photon was aligned to the [110] axis, in which direction oxygen ion is located. The spectra are plotted against energy-loss from excitation energy (Raman shift). The XRS spectra observed at 45K (circles) and 300K (line) are shown. These spectra were excited at the energy just below the Cu *K* absorption edge, where quadrupole transition to Cu *3d* state is observed, so that these are the Cu *3d* resonant XRS spectra.

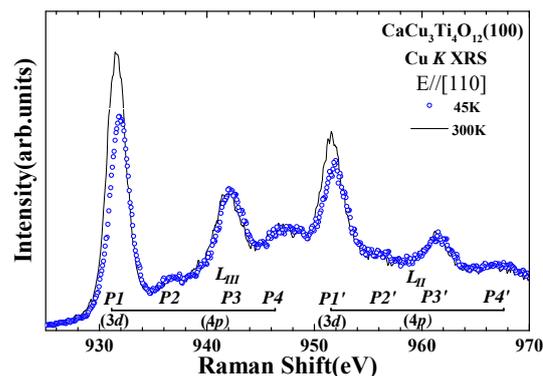


Fig.1: XRS spectra of CCTO(100) observed at Cu *K* absorption edge. Spectra at 300K (line) and 45K (dot) are shown.

The figure shows the excitation from Cu $2p_{3/2}(L_{III})$ and $2p_{1/2}(L_{II})$ core state, both of which shows unoccupied Cu *3d* and *4p* states. The peaks *P1* and *P1'* are caused by the excitation of Cu $\underline{2p}3d$, while the other peaks are caused by the excitation of Cu $\underline{2p}4p$. The *3d* peaks (*P1* and *P1'*) become weak at low temperature, while the *4p* structure does not change. Similar peaks with *P1* and *P1'* have been observed in the several divalent Cu-compounds [5] and these are supposed to reflect $3d^9$ state. Thus, the temperature dependence of Cu *3d* peak in this study suggests the increasing of the electron in Cu *3d* state at low temperature. It would be caused by increasing hybridization between Cu and O ions.

Recently, temperature dependence of XRS were observed in detail and showed drastic decrease of Cu *3d* peak intensity at about 100K. The result suggests close relation between dielectric constant and electronic state. However, CCTO shows complicated variety on azimuth angle. Further experiments and investigations would reveal the electronic state of CCTO.

References

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