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Electronic Structure Study of $CaCu_3Ti_4O_{12}$ by means of X-ray Raman Scattering.

Yasuhisa Tezuka[1*], Masaya Mikami[1], Yuto Yokouchi[1], Hojun Im[1], Takao Watanabe[1],
Shunsuke Nozawa[2], Nobuo Nakajima[3], Toshiaki Iwazumi[4]
[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 Sci., Hiroshima Univ., Higashi-Hiroshima, Hiroshima 739-8526, Japan
[4]Grad. Sch. of Eng., Osaka Pref. Univ., Sakai, Osaka 599-8531, Japan

1 Introduction

A-site substituted perovskite $CaCu_3Ti_4O_{12}$ (CCTO) have recently attracted much attention due to their high dielectric constant (~10^5) over a wide temperature range from 100 to 600 K [1]. The dielectric constant decreases abruptly at about 90 K in two orders without structural phase transition. To understand such anomalous dielectric behavior, electronic structure should be investigated in detail. X-ray Raman scattering (XRS) study is suitable technique to investigate such an insulator material. The XRS results have been reported on Ti *K* edge of Ti-compounds and showed scattering by Ti $\underline{2p}3d$ and $\underline{2p}4p$ core-excitations where underlines show core-hole [2]. In this study, both measurements at the Ti *K* and Cu *K* absorption edge of CCTO were performed. The Ti *K* measurement shows similar results with Ti-compound. In this report, the Cu *K* measurements are described.

2 Experiment

The XRS and Cu *K* XAS experiments were performed at beamlines BL7C. X-ray emission spectra having an energy centred at the Cu *Kα* fluorescence lines ($K\alpha_1$= 8,047.78 and $K\alpha_2$=8,027.83 eV) were observed. The spectrum changes continuously from *Kα* fluorescence to XRS when the excitation energies are changed from above to below the absorption edge. The fluorescence peaks have constant emission energies, while each XRS peak has each constant loss-energy from the excitation energy (Raman shift). The energy resolution for the Cu *K* XAS and XRS measurements were about 2 and 3 eV for 8 keV photon, respectively. The polycrystalline CCTO was prepared by a solid state reaction. The single phase of samples was confirmed by X-ray diffraction pattern.

3 Results and Discussion

Figure 1 shows comparison of several spectra of CCTO. Fig. 1(a) and 1(e) show Cu 2*p* and 1*s* X-ray absorption spectra (XAS), which reflect Cu 3*d* and 4*p* density-of-state, respectively. The spectrum (e) was plotted in relative energy in which incident photon energies were subtracted by a binding energy of Cu 1*s* (8979 eV), so that the zero energy roughly corresponds to Fermi energy. In the Cu *K* XAS spectrum, it is known that Cu 3*d* state is observed at the pre-edge. The XRS measurements were performed with several excitation energies in the pre-edge region and characteristic spectra were shown in the figure. Each excitation-energy is shown by arrows. The spectrum (d) is a non-resonant (normal) XRS excited far below absorption edge and shows Cu 4*p* state because of selection rules of light scattering. It shows similar spectrum with the Cu *K* XAS, then the spectrum (d), as well as (b) and (c), is plotted so that the peaks coincide with those of Cu *K* XAS. The spectrum (b) is resonant XRS spectra excited just below the absorption edge, where the Cu 3*d* absorption is observed by quadrupole transition, and shows corresponding peaks with the Cu 2*p* XAS spectrum. These peaks should correspond to the Cu 3*d* states. The assignments of the P_1~P_7 in the figure are based upon the XRS of Ti-compounds [2]. The spectrum (c) is also a resonant XRS spectrum excited by the energy corresponding to the peak below absorption edge. Strong peaks (*) are observed in the spectrum. Such peaks are known to be observed in divalent Cu-compounds such as CuO [3]. These peaks could not be corresponded to a band structure and seem to be excitonic state. These peaks should be studied further in many-body schemes.

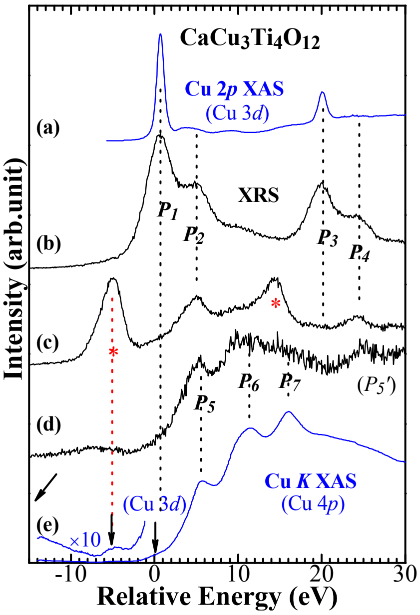

Fig. 1: Comparison of several spectra of CCTO. (a) Cu 2*p* XAS. (b), (c), (d) XRS spectra. (e) Cu *K* XAS.

References

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