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

Yuto Yokouchi[1*], Masaya Mikami[1], Hojun Im[1], Takao Watanabe[1], Shunsuke Nozawa[2], Nobuo Nakajima[3], Toshiaki Iwazumi[4], Yasuhisa Tezuka[1**]

[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 ordered perovskite $CaCu_3Ti_4O_{12}$ (CCTO) has attracted much attention recently, because it shows a giant dielectric constant (~10^5) over a wide temperature range from about 100 to 600K and the dielectric constant decreases to one-hundredth without structural phase transition at the temperature under about 100K [1]. To clarify the nature of the anomalous dielectrics, electronic structure of CCTO should be investigated. Since X-ray Raman scattering (XRS) uses photons in both excitation and detection, it is effective in the study of electronic state of an insulator material. The results of XRS on Ti *K* edge of several Ti-oxides have been reported and showed scattering by Ti 2*p*3*d* and 2*p*4*d* core-excitations where underlines denote a core-hole [2]. The results on Cu *K* edge were also reported on CCTO [3]. In this study, XRS spectra of CCTO on both Ti *K* and Cu *K* edge were observed at low temperature and room temperature (RT).

2 Experiment

The polycrystalline sample of CCTO was used in this study. The XRS spectra were observed using X-ray emission spectrometer (ESCARGOT) at beamline BL-7C. Scattered photons were analyzed using crystals Ge(400) and Ge(444) in the measurements on Ti *K* and Cu *K* edge, respectively. A 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

Figure 1 is a comparison between the Ti *K* resonant XRS spectra of CCTO observed at RT and 20K. The XRS spectra are plotted against energy-loss from excitation (Raman shift). These spectra were excited at an energy just below the Ti 3*d* structure of Ti *K* absorption edge. We have reported that the P1~P4 are caused by the excitation of Ti 2*p*3*d*, while the P5~P7 are caused by the excitation of Ti 2*p*4*p* [2]. The 3*d* peaks are split by ligand-field and spin-orbit interaction as shown in the figure. The figure shows the whole 3*d* structure becomes weak at 20K, while the 4*p* structure does not change. Since the XRS spectra reflect the density-of-state of unoccupied Ti 3*d* state, this result suggests the electron numbers in Ti 3*d* state increase at low temperature.

Figure 2 is a comparison between the Cu *K* resonant XRS spectra of CCTO observed at RT and 30K. The figure shows the peaks at about 930 and 950 eV (*) become weak at 30K. Since these peaks are specific peak

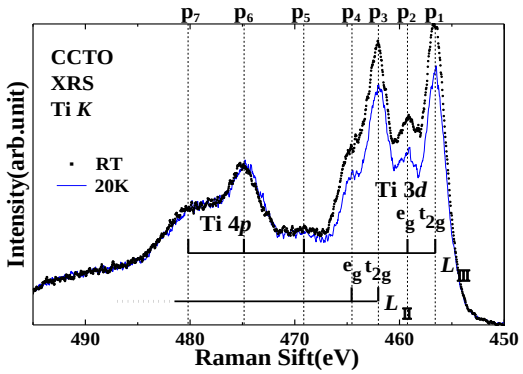

Fig. 1: Ti *K* resonant XRS spectra of CCTO observed at RT (dot) and 20K (line).

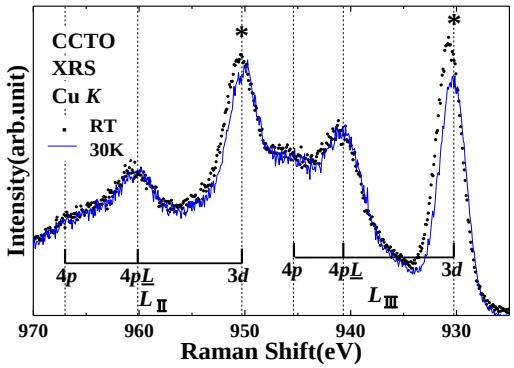

Fig. 2: Cu *K* resonant XRS spectra of CCTO observed at RT (dot) and 30K (line).

in XRS of the divalent Cu-compounds [4], these peaks should reflect the unoccupied Cu 3*d* state. This result suggests the electron numbers in Cu 3*d* state increase at low temperature.

In this study, increase of electron numbers at low temperature was observed in both Ti 3*d* and Cu 3*d* state. Though the results in this study cannot be connected to dielectric constant directly, XRS measurement would have possibility to clarify the origin of the anomalous dielectric constant.

References

[1] A.P. Ramirez, et al., Solid State Commun., 115, 217 (2000).
[2] Y. Tezuka, et al., J. Phys. Soc. Jpn. 83, 014707 (2014).
[3] Y. Tezuka, et al., PF Activity Report #31, 323 (2014)
[4] G. Döring, et al., Phys. Rev. B70, 085115 (2004).

* h14ms213@hirosaki-u.ac.jp
** tezuka@hirosaki-u.ac.jp