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Temperature Dependent O *K* Resonant X-ray Emission Spectra of $CaCu_3Ti_4O_{12}$

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1 Introduction

A-site ordered perovskite $CaCu_3Ti_4O_{12}$ (CCTO) has attached much attention recently, because it shows a giant dielectric constant (~10^4) over wide temperature range from about 100 to 600 K and the dielectric constant decreases to one-hundredth without structural phase transition at the temperature under about 100 K [1]. To clarify the nature of the dielectric anomalies, it is important to investigate electronic structure of CCTO.

The CCTO was studied by X-ray Raman scattering (XRS) study, which observes core excitation like $\underline{2p}3d$ and $\underline{2p}4d$, where underline denote core hole [2]. The results of XRS on Cu *K* edge have been reported [3]. Temperature dependent XRS study showed increasing both Ti 3*d* and Cu 3*d* state at low temperature [4]. In this study, O *K* resonant X-ray emission (XE) spectra of CCTO were observed.

2 Experiment

Single crystal CCTO(100) made by floating zone method was used in this study. XRS spectra were observed using soft X-ray emission spectrometer at beamline BL-16A. Vertically polarized light was used and scattering spectra in polarized configuration [5] were observed. The energy resolution of XRS measurement was about 1.0 eV.

3 Results and Discussion

Figure 1 shows O *K* XAS spectra of CCTO(100) measured by partial photon yield method (O *K* emission intensity). Temperature dependence of the XAS was observed. Line and circles show the spectra at RT and 85K, respectively. No distinct difference was observed in these spectra. XE spectra were observed under excitations in this energy range. Vertical bars with numbers denote the excitation energies in XRS measurements.

Figure 2 shows temperature dependence of O *K* resonant XE spectra of CCTO(100). Line and circles show the spectra at RT and 85K, respectively. Resonantly enhanced fluorescence peaks were observed at about 523 and 526 eV, while a weak Raman peak was observed at about 2 eV lower than elastic peak as shown by vertical bars (2, 3). The fluorescence peaks show clear temperature dependence at O *K* resonance (3~7), while the fluorescence peak does not show the dependence at high excitation energy (11). These peaks are originated from O 2*p* state that hybridized with both Ti 3*d* and Cu 3*d* states. The temperature dependence results show decrease of O 2*p* state at low temperature, suggesting charge transfer to Ti 3*d* and Cu 3*d* state. More detailed study of O *K* XES would reveal the nature of charge transfer in CCTO.

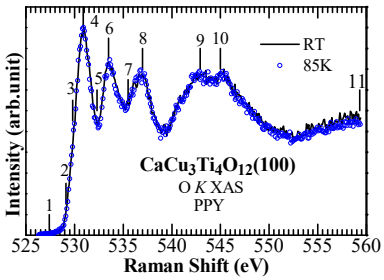

Fig. 1: Temperature dependence of O *K* XAS spectra of CCTO(100). Line: RT, circles: 85K. Vertical bars denote excitation energies of XE measurements.

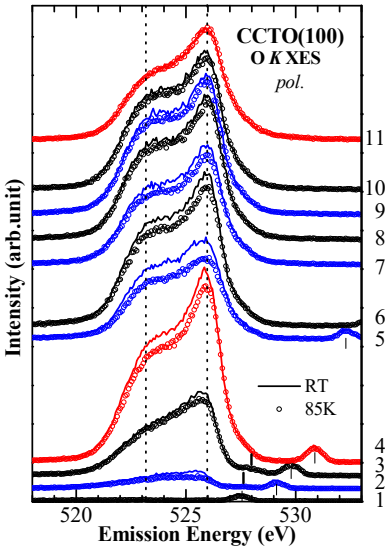

Fig. 2: Temperature Dependence of O *K* resonant XE spectra of CCTO(100). Line: RT, circles: 85K. Thin and bold vertical bars denote elastic and Raman scattering peaks, respectively. Numbers beside spectra denote excitation energies in Fig. 1.

References

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