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Polarization dependent Ti 2*p* resonant X-ray Raman Scattering of $CaCu_3Ti_4O_{12}$

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1. Introduction

The A-site ordered perovskite $CaCu_3Ti_4O_{12}$ (CCTO) exhibits a giant dielectric constant (~10^4) over a wide temperature range (100–600 K), which decreases by two orders of magnitude below 100 K without any structural phase transition [1]. The origin of this anomalous behaviour remains unclear. To gain into this unique property of CCTO, its electronic structure must be investigated. X-ray Raman scattering (XRS), a photon-in/photon-out technique, is well suited for probing the electronic structure of insulating materials. We have previously reported resonant XRS studies in the energy ranges corresponding to the Ti *K,* Cu *K* [2-4] and Cu 2*p* core levels [5]. In this study, we report polarization-dependent XRS measurements in the Ti 2*p* region.

2. Experiment

A polycrystalline CCTO sample was prepared by conventional solid state reaction techniques. To enable polarization-dependent measurements, an isotropic sample was required. The experiments were conducted using a soft X-ray emission spectrometer at beamline BL-13A. Polarization-dependent resonant X-ray emission spectra (XES) were measured. The scattering was observed in the horizontal direction at a 90° angle. Polarized and depolarized spectra were obtained using vertically and horizontally polarized synchrotron radiation (SR) beams, respectively [6].

3. Results and Discussions

Figure 1(a) shows the polarization-dependent Ti 2*p* X-ray absorption spectra (XAS) of CCTO measured using the partial photon yield (PPY) method. The polarized (solid line) and depolarized (circles) spectra are shown. The main peaks correspond to unoccupied Ti 3*d* states. The vertical bars indicate the excitation energies used in the XES measurement. Since second-order light from the beamline was not filtered out, the Cu 2*p* core states were also excited above approximately 464 eV as shown in Fig. 1(a).

Figure 1(b) shows the polarization-dependent X-ray Raman scattering (XRS) of CCTO. The polarized (solid line) and depolarized (circles) spectra are plotted as a function of energy loss (Raman shift), meaning that the positions of fluorescence peaks shift with changes in excitation energy. The Peaks marked by vertical bars correspond to fluorescence features with constant emission energy. Elastic scatterings were observed at 0 eV, while several peaks showing clear polarization dependence were detected. Due to the spectrometer's disperses second-order light, Cu 2*p* emission features appear in the spectra. The peaks indicated by arrows are attributed to charge transfer (CT) excitations involving Cu states. Other peaks at 3.0, 6.5, and 13.8 eV arise from CT excitations involving Ti

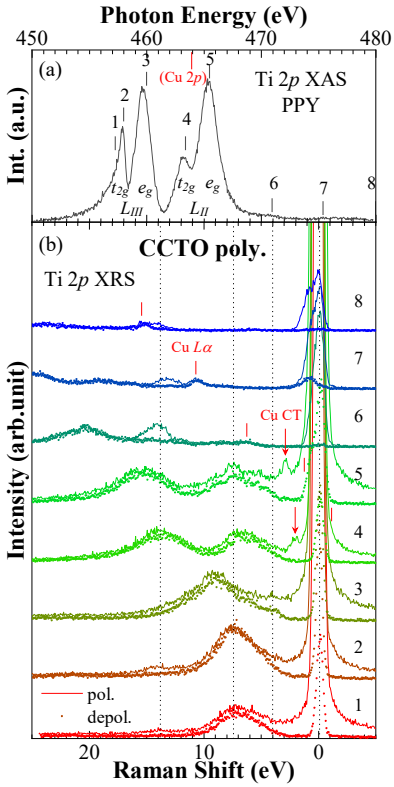

Fig.1: (a) Polarization-dependent Ti 2*p* X-ray absorption spectra (XAS) of CCTO measured using the partial photon yield (PPY) method. Vertical bars indicate the excitation energies in the X-ray emission spectroscopy (XES) measurements. (b) Polarization-dependence of the Ti 2*p* resonant XES of CCTO. Solid lines represent the polarized spectra; open circles represent the depolarized spectra.

states [6]. The presence of such high-energy excitations suggests strong electron correlation in CCTO. To clarify the origin of these features, detailed polarization-dependent XRS studies are necessary. Additionally, temperature-dependent XRS measurement could provide critical information regarding the dielectric anomaly in CCTO.

References

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