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Electronic Structure Study of nano-particle Anatase (TiO_2) by means of X-ray Raman Scattering

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1 Introduction

Anatase titanium-dioxide (TiO_2) exhibits larger photocatalytic activity than other polymorphs; rutile and brookite. The electronic structure should be investigated to make clear the nature of TiO_2. We have reported X-ray Raman scattering (XRS) of several Ti-oxides [1] and anatase [2] excited around Ti *K* absorption edge. In this study, we investigated electronic structure of nano-particle anatase and its doping-effect with Co^{2+}.

2 Experiment

Nano-particle anatase was made by thermal decomposition method. The structure and particle size (~5nm) were confirmed by X-ray diffraction and transmission electron microscope methods, respectively. XRS spectra were observed using X-ray emission spectrometer (ESCARGOT) at beamline BL-7C. Scattered photon was analyzed using Ge(400) and detected by one-dimensional multi-channel proportional counter. The energy resolution of XRS measurements was about 1eV for 5keV photon. In this experiment, XRS spectra were excited at 4963.0 eV that is just below Ti *K* absorption edge where Ti 3*d* state was observed via quadrupole transition [1].

3 Results and Discussion

Figure 1 shows XRS spectra of two kinds of anatase which have different particle-sizes. The XRS spectra are plotted against energy-loss from excitation (Raman shift). These samples were made in different growth time; longer growth-time results larger particle-size. We have reported that four peaks on the right correspond to the excitation of Ti 2*p*3*d*, while three peaks on the left correspond to the excitation of Ti 2*p*4*p*, where underline denote core-hole [1]. The Ti 2*p*3*d* peaks are split by ligand-field and spin-orbit interaction as shown in the figure. The figure shows the whole 3*d* peaks become weak in larger sample, while 4*p* peaks does not change. Since the XRS spectra reflect unoccupied 3*d* state, the intensity change suggests increase of 3*d*-electron numbers. Usually, crystal of TiO_2 has rutile structure at RT and anatase undergoes a transition to rutile phase when annealed at high temperature, while nano-particle TiO_2 has anatase structure. The fact means that bond strength become tighter with increasing particle size. The result in this study suggests increasing of hybridization between Ti and O with increasing particle-size.

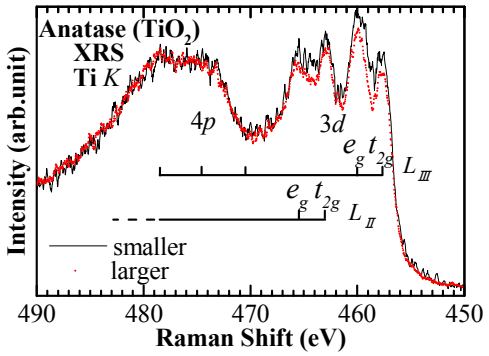

Fig.1 Size dependence of XRS spectra of nano-particle anatase. Line: smaller size, Dot: larger size.

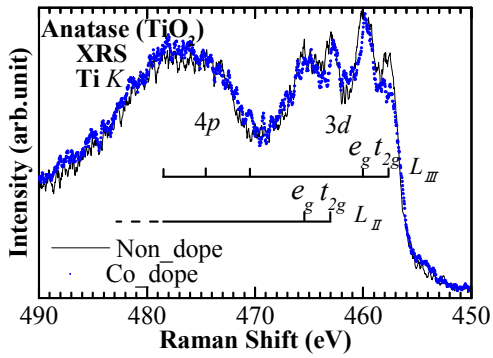

Fig.2. Doping-effect of XRS spectra of nano-particle anatase; Line: non-doped, Dot: Co-doped.

Figure 2 shows doping-effects of XRS spectra. Black line shows XRS of non-doped sample that is same with smaller sample in Fig. 1, while blue dot shows XRS of doped samples with about 8% Co. The figure shows the t_{2g} peaks of L_{III} excitation become weak in doped sample, while the t_{2g} peaks of L_{II} excitation does not change very much. The Co ion is thought to be Co^{2+} and electrons are doped in the anatase. Usually, the doped electron enters in lowest levels of unoccupied state. The result seems to be consistent roughly to the doping effect. Multiple scattering effects might affect in the L_{II} scattering.

References

[1] Y. Tezuka, et al., J. Phys. Soc. Jpn. **83** (2014) 014707
[2] Y. Tezuka, et al., PF Activity Report #29, 138 (2011); #31, 325(2014).

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