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 3d 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$p^3d$, while three peaks on the left correspond to the excitation of Ti 2$p^4p$, where underline denote core-hole [1]. The Ti 2$p^3d$ 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.

References
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