

## Polarization dependence of soft-x-ray Raman scattering of $\text{Ti}_2\text{O}_3$

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### Introduction

$\text{Ti}_2\text{O}_3$  is known to be the typical MH type semiconductors that have narrow band gap ( $E_{\text{gap}} < 0.1$  eV) in the insulator phase, which has one  $3d$  electron nominally. It is known that the Ti  $3d$  components are strongly mixed in the O  $2p$  state [1]. Early TM compounds including Ti compounds have attracted the interest of researchers because of their strong hybridization energies. Many body effects are observed in these compounds [2-4].

### Experimental

SXE spectra were obtained at beamline BL-2C in Photon Factory, KEK. A soft X-ray monochromator consisting of a Rowland type grazing-incidence monochromator with a 5-m spherical grating (1200 lines/mm) [5] was used. The energy resolution of SXE spectroscopy (SXES) and XAS measurements was about 0.4 and 0.1 eV at 450 eV, respectively.

Powdered  $\text{Ti}_2\text{O}_3$  was measured in this experiment.  $\text{Ti}_2\text{O}_3$  has a corundum structure with a trigonal Bravais lattice. The structure includes the  $\text{TiO}_6$  octahedron. In  $O_h$  symmetry, the  $3d$  state is split into a lower  $t_{2g}$  and a higher  $e_g$  state by a crystal field. The  $\text{TiO}_6$  cluster in the corundum structure is distorted. Therefore, the  $t_{2g}$  state is split further into  $a_{1g}$  and  $e_g$  states.

### Results and Discussions

Figure 1 shows the XAS spectrum of  $\text{Ti}_2\text{O}_3$ . The XAS spectrum shows four main peaks and two satellites. The two lower peaks ( $L_{III}$ ) in the main structure originate from the excitation of Ti  $2p_{3/2}$  electrons, while the two higher peaks ( $L_{II}$ ) originate from the excitation of Ti  $2p_{1/2}$  electrons. Each structure is split into two peaks by the crystal field. The satellites are assigned to the CT satellite.

Figure 2 shows the polarization dependence of resonant Raman spectra of  $\text{Ti}_2\text{O}_3$ , which are plotted against the energy shift from elastic scattering energy. Numbers beside the spectra correspond to the numbers in Fig.1. Vertical bars indicate Ti  $3d \rightarrow 2p_{3/2}$  fluorescence. The lower energy peak corresponds to the Ti  $3d$  state just below the Fermi energy, while the higher energy peak corresponds to the Ti  $3d$  state mixed with the O  $2p$  state.

The spectra observed in a polarized configuration show the elastic peak at 0 eV, while the spectra in depolarized configuration do not show the elastic peak. The peak near 0 eV in the depolarized spectrum 4 is not elastic peak, but a fluorescence peak, since it has finite energy shift from 0 eV.

On the other hand, two Raman peaks are observed at about 1.0 and 3.0 eV, indicated by dotted lines in Fig. 2. These peaks are thought to originate in the  $d-d$  excitation. Since the  $t_{2g}$  state is split into  $a_{1g}$  and  $e_g$  states in a trigonal symmetry, several  $d-d$  excitations would be possible.

These results are in contrast to that of  $\text{TiO}_2$  [4], in which several CT excitations are observed at 5-13 eV but no  $d-d$  excitation is observed. The  $3d$  electron just below the Fermi energy considerably affects the resonant SXE spectra.

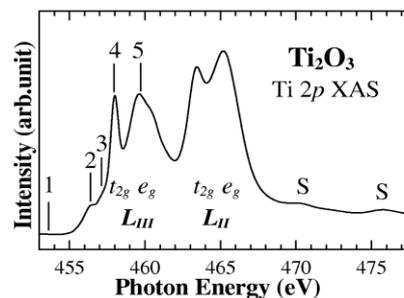


Fig.1 Ti  $2p$  X-ray absorption spectrum of  $\text{Ti}_2\text{O}_3$ . Vertical bars indicate excitation energies in the SXES measurements.

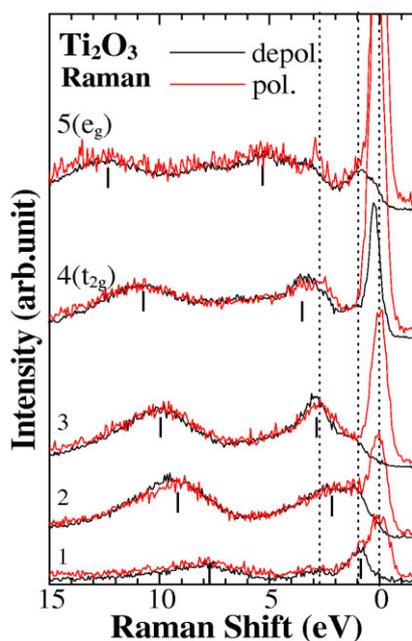


Fig.2 Polarization dependence of Raman spectra of  $\text{Ti}_2\text{O}_3$ . The vertical dotted line at 0 eV indicates the Fermi energy and the others indicate the Raman peaks. Vertical bars indicate Ti  $3d \rightarrow 2p$  fluorescence.

### References

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