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Contour Plot of Soft X-ray Raman Scattering of Ti_2O_3

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Introduction

Ti_2O_3 is known to be a typical MH type semiconductor having narrow band gap (< 0.1 eV), which has one 3*d* electron nominally. It is known that the Ti 3*d* states are strongly hybridized with the O 2*p* state. The Ti compounds have attracted the interest of researchers because of their strong hybridization energies, resulting many-body effects in high energy spectra [1, 2].

Recently, soft x-ray emission (SXE) spectrometer at BL2c was improved [3]. The beamline monochromator and undulator gap became controllable by the computer of SXE system. Unlimited numbers of SXE spectra can be observed continuously and automatically. In this experiment, SXES spectra of Ti_2O_3 were observed in detail.

Experimental

Powdered Ti_2O_3 was measured in this experiment. Ti_2O_3 has corundum structure with trigonal Bravais lattice, including TiO_6 octahedron. In O_h approximation, the 3*d* state is split into t_{2g} and e_g state by ligand field. Since the TiO_6 cluster in the corundum structure is trigonally distorted, the t_{2g} state is split further into a_{1g} and e_g states.

SXE spectrometer at BL2c was used in polarized configuration. The incident slit width of spectrometer is set to 10 μm corresponding to about 0.3 eV resolution.

Results and Discussions

Figure 1(a) shows XAS spectra of Ti_2O_3 measured by total electron yield method. The main structure originates from Ti 2*p* → 3*d* transition. The Ti 2*p* core level is split into $2p_{3/2}$ and $2p_{1/2}$ levels by spin-orbit interaction and the unoccupied Ti 3*d* state is split into t_{2g} and e_g states by crystal field (O_h approximation). Charge transfer (CT) satellites (S) were observed at about 13 eV above each main structure. SXES spectra were observed under excitations around the absorption edge.

Figure 1(b) shows contour plot of resonant SXES spectra of Ti_2O_3. About hundred spectra of SXES were observed with changing excitation energies and these were plotted to the contour graph. The figure is plotted by emission energy in ordinate and by excitation energy in abscissa. The excitation energies are corresponding to the abscissa of XAS spectrum. If the excitation energy is higher than absorption edge, Ti *L* fluorescence lines ($L\alpha_{1,2}$: Ti $3d \rightarrow 2p_{3/2}$, $L\beta_1$: Ti $3d \rightarrow 2p_{1/2}$) are observed having same emission energies, which are indicated by horizontal dotted lines in the figure. Both $L\alpha_{1,2}$ and $L\beta_1$ have two components as shown in the figure. High and low energy components originate from localized Ti 3*d* state near Fermi level and Ti 3*d* state hybridizing with O 2*p* state, respectively [2,3]. On the other hand, x-ray scattering was observed by excitation around the absorption edge. The oblique line at lowest part is elastic scattering, while x-ray Raman scattering (XRS) was observed as shown by oblique dotted line. Lower line corresponds to *d-d* excitation, while upper line corresponds to CT excitation. The *d-d* excitations were not observed in TiO_2 that has no 3*d* electron nominally.

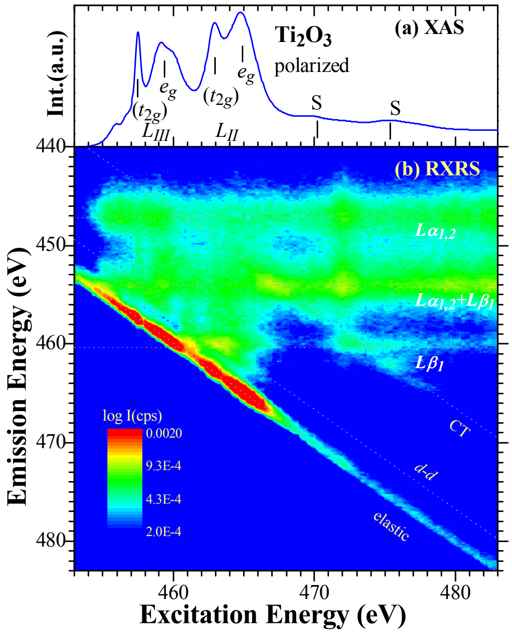

Fig.1. (a) XAS spectra of Ti_2O_3 by means of total electron yield method. (b) Contour plot (log scale) of resonant XES spectra of Ti_2O_3 plotted by emission energy in ordinate and by excitation energy in abscissa. Ti *L* fluorescence energies are indicated by horizontal dotted lines. A lowest oblique line shows elastic scattering and the other oblique dotted lines shows XRS peak.

References

[1] T. Uozumi, et al., J. Phys. Soc. Jpn., 65, 1150 (1996).
[2] Y. Tezuka et al., J. Phys. Soc. Jpn. 65, 312 (1996).
[3] Y. Tezuka, et al., PF Activity Report 2007 #25 Part B, 96 (2008); *ibid* 2008 #26 Part B, 84 (2009)

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