

Contour Plot of Soft X-ray Raman Scattering of TiO₂

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Introduction

Recently, improvement of Soft x-ray emission (SXE) spectrometer at BL2c was reported [1]. Further improvement in the measurement system is reported, here. The computer of beamline monochromator as well as the computer of undulator became controllable by the computer of SXE system. SXE observations are processed continuously and automatically using parameter list made by the experimenter.

We measured soft x-ray emission spectra (SXES) of TiO₂ (001) using the SXE measurement system.

Experimental

A commercially obtained single crystal TiO₂ was used. The crystal has rutile structure (D_{4h} symmetry) and (001) surface was used in this experiment. TiO₂ is a nominally $3d^0$ system and it has wide band gap (~3 eV).

SXE spectrometer at BL2c was used in polarized configuration [1]. Incident angle of irradiation is selected to 10° (grazing) to avoid a strong elastic scattering. The incident slit width of spectrometer is set to rather wide (30 μm) corresponding to about 0.7 eV resolution to get enough intensity for measurement of many spectra.

Results and Discussions

Figure 1(a) shows XAS spectra of TiO₂ measured by total electron yield method. The main structure originates from Ti $2p \rightarrow 3d$ transition. The Ti $2p$ core level splits to $2p_{3/2}$ and $2p_{1/2}$ levels by spin-orbit interaction and the unoccupied Ti $3d$ state splits to t_{2g} and e_g state by crystal field (O_h approximation). Charge transfer (CT) satellites (S) are observed at about 13 eV above each main structure. SXES spectra were observed by photon energies in the XAS spectra.

Figure 1(b) shows contour plot of resonant SXES spectra of TiO₂. 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 correspond 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. The Ti $3d$ state originates from hybridization with O $2p$ state, regardless of the $3d^0$ system. On the other hand, resonant x-ray scattering was observed by excitation around the

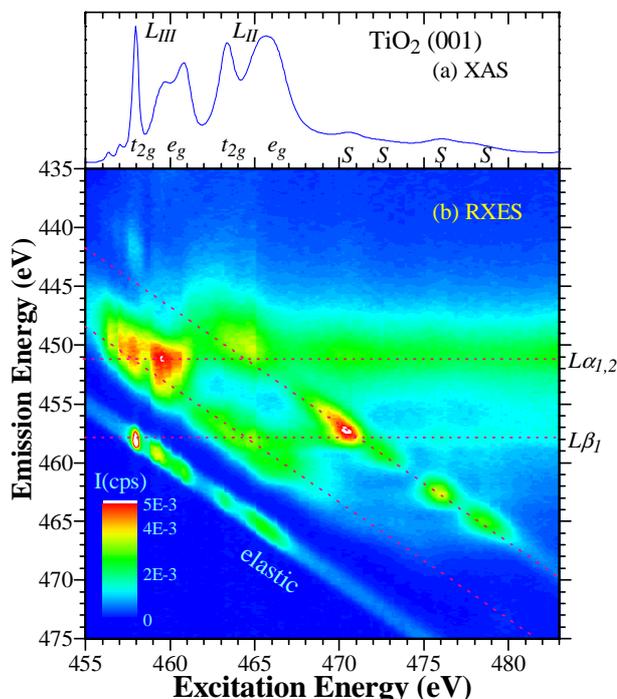


Fig.1. (a) XAS spectra of TiO₂ (001) by means of total electron yield method. (b) Contour plot (log scale) of resonant XES spectra of TiO₂ (001) plotted by emission energy in ordinate and by excitation energy in abscissa. Ti L fluorescence energies are indicated by horizontal dotted lines. A lowest oblique line is elastic scattering and oblique dotted lines show XRS peak.

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 non-bonding $3d$ state, while upper line corresponds to $3d^1\bar{L}$ (CT) state, where \bar{L} denote ligand hole. Strong resonance was observed at the crossing points of the fluorescence and XRS. The CT state is also enhanced at excitation energy corresponding to CT satellite of XAS. However, the resonant spectra shows more complicated change. The origin of these peaks should be studied in detail.

References

- [1] Y. Tezuka, et al., PF Activity Report 2007 #25 Part B, 96 (2008)
- [2] Y. Harada, et al., J. Synchrotron Rad. 5, 1013 (1998).
- [3] Y. Harada, et al., Phys. Rev. B61, 12854 (2000).

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