

Site-specific photoelectron spectroscopy of FeTiO₃ by resonant x-ray excitations

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Introduction

Hematite (α -Fe₂O₃) – ilmenite (FeTiO₃) solid solution system is one of the candidates for novel magnetic semiconductors at room temperature [1]. The electronic structures of Fe_{2-x}Ti_xO₃ are generally considered as the mixed valence states between Fe²⁺ and Fe³⁺ if the nominal valence states of Ti are assumed to 4+. However our systematic study of high-resolution x-ray fluorescence spectra of various titanium oxides suggested that the valence states of Ti ions in FeTiO₃ seemed to have some Ti³⁺ characters [2]. In order to clarify the real electronic structures of FeTiO₃ we tried to obtain the site-specific valence-band spectra by means of the resonant x-ray photoelectron spectroscopy (XPS).

Experimental

The RXPS measurements of FeTiO₃ bulk crystals were performed at the beam line BL11D of KEK-PF. Before the measurements the sample surface was filed in vacuum (6×10^{-10} Torr) to obtain the clean surface. The incident photon energy for resonant XPS was determined from the Ti L_{ii,iii} and Fe L_{ii,iii} x-ray absorption spectra of FeTiO₃ to measure the secondary electron emission yields. The RXPS were measured at room temperature by using a hemispherical electron analyzer (Scienta SES-200) with the pass energy of 10 eV. Because of the low photon flux of BL11D, it took two days to obtain one spectrum.

Results and discussion

Fig. 1 shows the x-ray absorption spectra of FeTiO₃ for both Ti L_{ii,iii}- and Fe L_{ii,iii}-edges. The photon energies in a horizontal axis are nominal values without the energy calibration. For the Ti 2p-3d resonant XPS, nominal photon energies of 447 and 453 eV were applied to obtain the off- and on-resonant condition, respectively. While for the Fe 2p-3d resonant XPS, nominal photon energies of 707 and 712 eV were applied as well.

Fig. 2 shows the XPS valence-band spectra of FeTiO₃ as a function of the incident photon energy. The spectrum using the high-energy excitation source (hv=4,750 eV) obtained at a beam line BL15XU of SPring-8 is also indicated for the comparison. The high-energy excitation spectrum clearly indicated the detailed structures in the valence-band including the weak intensity close to the Fermi level. However the statistics and energy-resolutions of the obtained on- and off-resonant XPS spectra were considerably wrong. The details in the valence-band were completely missing. A well adjusted x-ray source and an

electron analyzer are required to obtain the useful high-resolution valence-band spectra.

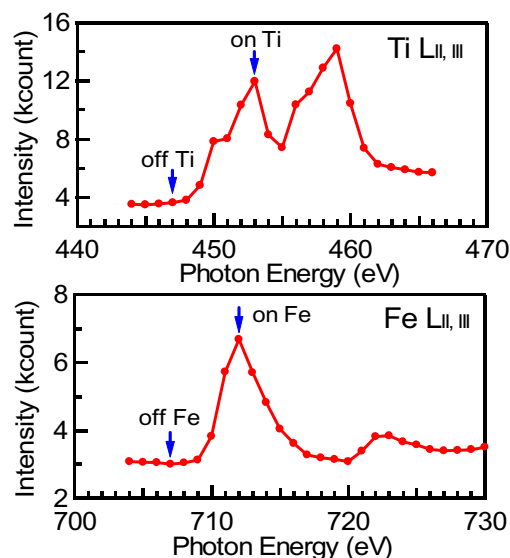


Fig. 1. X-ray absorption spectra of FeTiO₃.

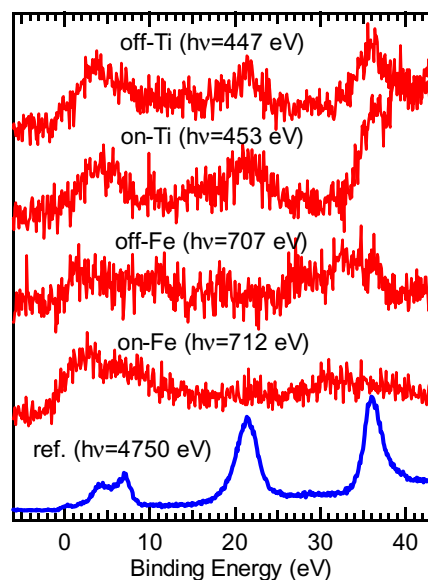


Fig.2. Resonant XPS valence-band spectra of FeTiO₃.

References

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- [2] T. Fujii, et al., Nanotechnology in SPring-8, 2004B, in press.

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