

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

Tatsuo FUJII*, Yusuke TAKADA, Miki YAMASHITA, Makoto NAKANISHI, Jun TAKADA,
Dept. Applied Chemistry, Okayama Univ., Okayama 700-8530, Japan

Introduction

The valence states of cations in ilmenite (FeTiO₃) are nominally considered as Fe²⁺ and Ti⁴⁺. However the observed Fe²⁺→Ti⁴⁺ charge transfer energies in minerals are very small [1]. 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 at room temperature, we tried to obtain the site-specific valence-band spectra by means of the Ti 2p→3d resonance photoemission spectroscopy (RPES).

Experimental

The RPES measurements of FeTiO₃ bulk crystals were performed at the beam line BL11D of KEK-PF. Before the measurements the sintered FeTiO₃ sample was broken in vacuum (6×10⁻¹⁰ Torr) to obtain the clean surface. The incident photon energy for RPES was determined from the Ti L_{II,III} x-ray absorption spectrum (XAS) by means of the secondary electron emission yields. The on- and off-resonance RPES were measured at room temperature by using a hemispherical electron analyzer (Scienta SES-200) with the pass energy of 75 eV.

Results and discussion

Fig. 1 shows the Ti L_{II,III} XAS spectrum of FeTiO₃. The photon energies in a horizontal axis are nominal values without the energy calibration. According the XAS spectrum, nominal photon energies of 447 and 453 eV were adopted to obtain the off- and on-resonant RPES spectra, respectively.

Fig. 2 shows the valence-band spectra of FeTiO₃ at on- and off-resonance conditions. It was already known that the valence-band spectra were mainly composed by the Fe 3d and O 2p levels. The Ti 3d levels had small contributions to the valence-band spectra because of no 3d electrons in Ti⁴⁺ ions. However the on-resonance spectrum clearly showed additional two intensities in the valence-band. The intensity marked for "B" in the deep valence-band was generally assigned to the bonding states for the O 2p - Ti 3d molecular orbital levels, as well as TiO₂, etc. Besides, in the shallow level, the intensity marked for "A" also appeared. This second intensity was never observed in the conventional Ti⁴⁺ compositions, and was characteristic only for FeTiO₃.

Fig. 3 shows the energy diagrams calculated by the DV-X α method using a FeTiO₉¹²⁻ cluster. The ones suggested the formation of Fe 3d - Ti 3d hybridization. Ti⁴⁺ ions in FeTiO₃ had relatively large 3d electron populations than the conventional Ti⁴⁺ compounds.

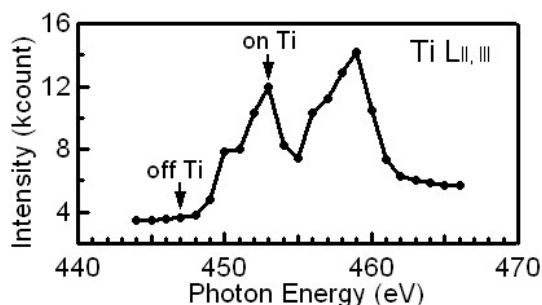


Fig. 1. Ti L_{II,III} XAS for FeTiO₃.

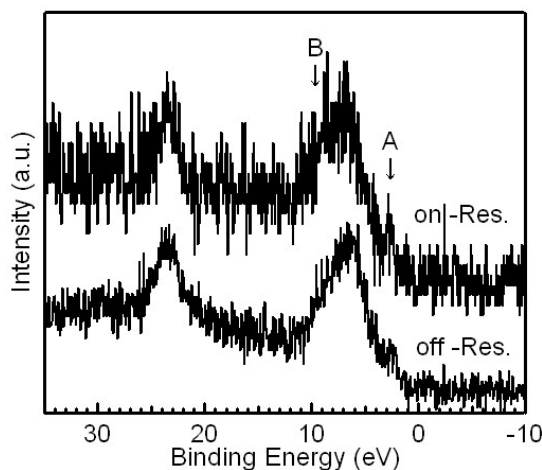


Fig.2. On- and off-resonance RPES for FeTiO₃.

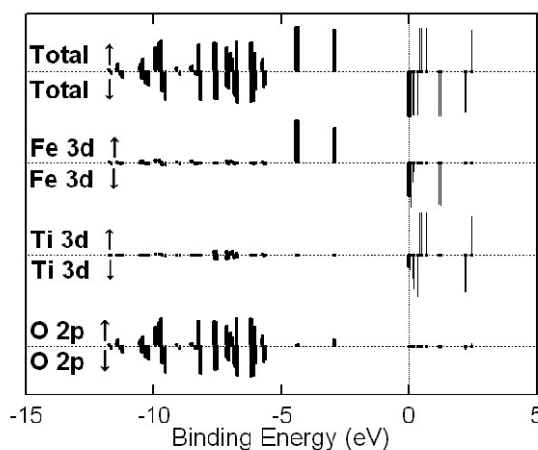


Fig.3. Energy diagrams by DV-X α calculation.

References

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- [2] T. Fujii, et al., Nanotechnology in SPring-8, **5**, 32 (2004).

* tfujii@cc.okayama-u.ac.jp