Electronic structures of hematite-ilmenite solid solutions by photoelectron spectroscopy

*T. FUJII[1] (8764), M. KAYANO[1] (8778), Y. TAKADA[1] (8771), M. YAMASHITA[1](13847), Y. ITO[2](3629)
A. M. Vlaicu[3] (3630), M. KIMURA[3] (2011), H. YOSHIKAWA[3] (1407), and S. FUKUSHIMA[3] (4198)

1) Department of Applied Chemistry, Faculty of Engineering, Okayama Univ., Okayama 700-8530 Japan
2) Institute for Chemical Research, Kyoto Univ., Uji, Kyoto 611-0011 Japan
3) Harima Office, National Institute of Material Science, 1-1-1 Mikazuki, Sayo-Gun Hyogo 679-5148 Japan

Thin films of the hematite-ilmenite solid solution (α-Fe_2O_3-$FeTiO_3$) are one of the candidates for novel magnetic semiconductors at room temperature. The electronic structures of α-Fe_2O_3-$FeTiO_3$ are generally considered as the mixed valence states between Fe^{2+} and Fe^{3+} due to the substitution of Fe^{3+} for Ti^{4+}. The nominal valence states of Ti are fixed to 4+. However our recent high-resolution X-ray fluorescence spectroscopy study of various titanium oxides suggested that the Ti $K\alpha$ peak profiles of $FeTiO_3$ were slightly different form those of other Ti^{4+} compounds and were better to assign to have some Ti^{3+} characters. In order to clarify the real electronic structures of α-Fe_2O_3-$FeTiO_3$ we did the systematic study of high-energy X-ray photoelectron spectroscopy (XPS) of various titanium oxides.

The high-energy XPS measurements were performed at BL15XU in Spring-8. The hemispherical electron energy analyzer can detect the large kinetic energy photoelectrons up to 4800eV. Thus the incident X-ray energy was selected to 4750eV to obtain the XPS valence band spectra clearly. The binding energy calibration of all XPS spectra was done by the C 1s spectra (284.6 eV).

Fig.1 shows the Ti 2p core-level spectra of $MgTiO_3$, $NiTiO_3$ and $FeTiO_3$ bulk powders and a $FeTiO_3$ single crystal. Each oxide has an isomorphic structure with $FeTiO_3$ (ilmenite structure). The Ti ions occupy octahedral sites of the hcp oxygen sublattice. The chemical shifts of all samples are nearly consistent with each other. However their Ti $2p_{3/2}$ peak width seems to be influenced by the coexisting cations. One of the possibilities of the Ti $2p_{3/2}$ peak broadening is due to the

multiplet splitting of d^1 (Ti^{3+}) components.

Fig.2 shows valence band spectra of various Ti oxides. The characteristic features of these spectra appeared at the valence band edge. Only the $FeTiO_3$ has shallow peak close to the Fermi level. This peak is assigned mainly to the Fe^{2+} 3d levels but the 3d levels in Ti^{3+} should appear at the same energy region. Our XPS results support the formation of the Ti^{3+}-like states in $FeTiO_3$.
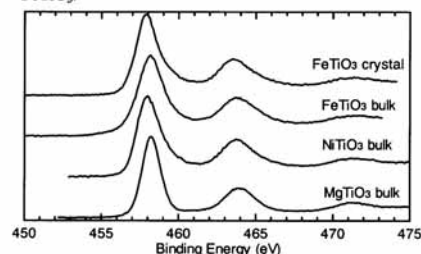

Fig. 1   Ti 2p core-level XPS spectra of various Ti oxides with the ilmenite structure.
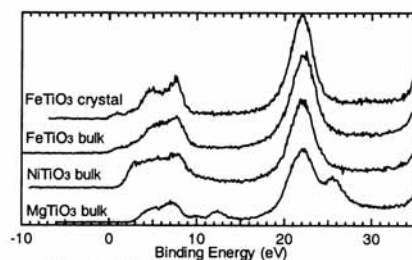

Fig. 2   Valence band XPS spectra of various Ti oxides with the ilmenite structure.

Elucidation of the mechanism of the luminescence in the oxides containing Ti^{3+} fabricated by nanoscale technology

*T. TERASHIMA[1](13329), R. KANDA[1](13330), S. SAKAKURA[1](13258),
H. OOHASHI[1](4847), T. TOCHIO[1](4007), Y. ITO[1](3629),
A. M. VLAICU[2](3630), and S. FUKUSHIMA[2](4198)

1) Institute for Chemical Research, Kyoto Univ., Uji, Kyoto 611-0011 Japan
2) Harima Office, National Institute of Material Science, 1-1-1 Mikazuki, Sayo-Gun Hyogo 679-5148 Japan

Fluorescence measurements have been performed in reduced thin film of $SrTiO_3$ fabricated with Ar^+ ion irradiation. A luminescence with life time of ~10 n sec has been observed using He – Cd laser (~325 nm), whose behavior may be accounted for by Ti^{3+} ascribed to the reduction. Connection with a super Coster-Kronig transition in Ti is demonstrated.

The Ti $K\beta_{1,3}$ fluorescence lines for Ti oxides are usually accompanied by weak lines appearing at around 4945 and 4960 eV. These lines are nominally assigned to $K\beta_{2,5}$ and are explained as the transition from 3d-derived valence band hybridized orbitals to an 1s core-hole. Therefore, peak profiles of $K\beta_{2,5}$ lines should be very sensitive to the change of valence states of Ti ions. If an additional electron hole was created in the 3s or 3p orbital besides the 1s core hole, the population of the 3d electrons could be decreased due to the 3s(3p)-3d3d super Coster-Kronig transition. And the decreased 3d electrons can influence the $K\beta_{2,5}$ peak profiles.

Ti $K\beta$ fluorescence spectra of reduced powder $SrTiO_3$ were measured using a Johann-type high-resolution spectrometer at BL15XU in SPring-8. Figure 1 shows Ti $K\beta$ fluorescence spectra for

$SrTiO_3$ measured at different excitation energies. We investigated whether the $K\beta_{2,5}$ peak profiles were influenced by the change of the 3d electron using Mercury lamp which has energies more than a energy gap of $SrTiO_3$. In Fig. 1, the Ti $K\beta_{2,5}$ profiles at same energy with lamp on/off are different with each other, and those at different energies with lamp on are also different with each other. The super Coster-Kronig transition and valence electron excitation by a lamp may result in the difference. We need further measurement and analysis in order to elucidate the mechanism on the luminescence in reduced $SrTiO_3$.
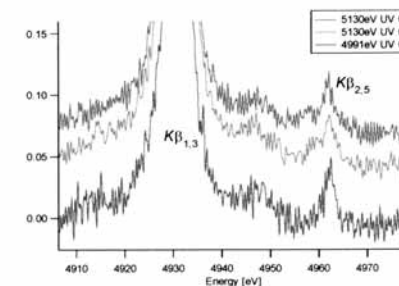

Fig. 1 High-resolution Ti $K\beta$ spectra of $SrTiO_3$