Electronic Structure of Ilmenite and Ilmenite-Hematite Solid Solution Using Hard X-Ray Photoemission Spectroscopy

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Abstract

We have conducted hard X-ray photoemission spectroscopy on FeTiO₃ and FeTiO₃₋ₓFe₂O₃ solid solution in order to examine the electronic structure and electrical conduction mechanism of the compounds. The valence band spectrum of FeTiO₃₋ₓFe₂O₃ solid solution manifests a clear peak shift compared to FeTiO₃, indicating that the electronic structure of FeTiO₃₋ₓFe₂O₃ solid solution consists of strongly mixed Fe 3d and O 2p components and that the electron correlation of the Fe 3d components is varied by the formation of solid solution between FeTiO₃ and α–Fe₂O₃. We propose that insulating FeTiO₃ is converted into semiconductor via this mechanism by the formation of FeTiO₃₋ₓFe₂O₃ solid solution, and the electron transfer between Fe²⁺ and Fe³⁺ in C-plane dominantly contributes to the electrical conduction in FeTiO₃₋ₓFe₂O₃ solid solution.

Key Words: Spintronics, Electron correlation, Electronic structure

I. INTRODUCTION

Transition-metal oxides with strongly correlated electrons have been intensively investigated in the field of solid-state physics [1]. Some of them have the degrees of freedom both in charge and spin, which correlate to each other and enable the control of electrical conduction by external magnetic field. This phenomenon is an essential principle for spintronics devices and has been widely observed in many transition-metal oxides such as La₁₋ₓSrₓMnO₃ [2]. A solid solution of ilmenite (FeTiO₃) with hematite (α–Fe₂O₃) is considered to be one of promising materials for spintronics applications. Both FeTiO₃ and α–Fe₂O₃ have a corundum-based structure where oxide ions are arranged into a distorted hexagonal close-packed structure, and thus the system forms a complete solid solution xFeTiO₃·(1−x)Fe₂O₃ (0 < x < 1). For an ordered phase of the solid solution where alternating Ti-rich and Fe-only cation layers stack along the c-axis direction, an antiparallel coupling of magnetic moments between adjacent cation layers results in ferrimagnetism although both end members are antiferromagnetic. The Curie temperature can be above room temperature for x < 0.73 [3].

For the electrical properties of FeTiO₃₋ₓFe₂O₃ solid solution, it is known that the conduction type can be controlled as either p- or n-type by simply changing the composition [4]. In the present study, we suggest that the carrier transfer occurs between Fe²⁺ and Fe³⁺ when Fe²⁺ and Ti⁴⁺ in FeTiO₃ are mixed with Fe³⁺ in α–Fe₂O₃. When x < 0.73 (n-type carrier), the carrier is considered to be an extra electron at Fe²⁺. On the other hand, an extra positive hole at Fe³⁺ is considered to be a carrier in the range of x > 0.73 (p-type carrier) where FeTiO₃ is a host material. Despite the above suggestion, the electronic structure of FeTiO₃₋ₓFe₂O₃ solid solution has not been experimentally clarified yet. The information on the electronic structure is important in understanding the electrical conduction mechanism of FeTiO₃₋ₓFe₂O₃ solid solution. In this study, we carried out hard X-ray photoemission spectroscopy (HX-PES) on FeTiO₃ and xFeTiO₃·(1−x)Fe₂O₃ (x = 0.6 and 0.8) in order to reveal the electronic structure and electrical conduction mechanism for FeTiO₃₋ₓFe₂O₃ solid solution.

II. EXPERIMENTAL

Bulk FeTiO₃ specimen was prepared by conventional solid-state reaction. α–Fe₂O₃ (Kojundo Chemical Laboratory Co. Ltd., purity: 99.99%) and TiO₂ (Kojundo Chemical Laboratory Co. Ltd., purity: 99.9%) powders were mixed thoroughly with alumina mortar and pestle and the resultant mixture was heated in air at 900 °C for 12 h. The mixture was reground and pressed into a pellet. The pellet was sintered in an alumina tube furnace in CO + CO₂ (CO = 40%) atmosphere at 1300 °C for 24 h. Thin films with 0.6FeTiO₃·0.4Fe₂O₃ and 0.8FeTiO₃·0.2Fe₂O₃ compositions were grown on α–Al₂O₃ (0001) single crystal substrates by a pulsed laser deposition method using KrF excimer laser (λ = 248 nm, 2 Hz, 2 J/cm). The substrate temperature and oxygen partial pressure during the deposition were kept at 700 °C and 1.0 × 10⁻³ Pa, respectively. The film thickness was evaluated to be about 70 nm using a surface profiler. Hereafter, FeTiO₃, 0.8FeTiO₃·0.2Fe₂O₃ and 0.6FeTiO₃·0.4Fe₂O₃ samples are denoted as “x = 1”, “x = 0.8” and “x = 0.6”, respectively. The HX-PES measurements were carried out at BL47XU beam-line of SPring-8 (photon energy is 7.94 keV) at room
temperature. The total energy resolution was set at 250.06 meV. The take-off angle of photoelectrons was set at 87º to reduce the effect of surface contamination on the HX-PES spectrum. The obtained spectra shifted by a surface charging effect were calibrated using C 1s peak position (binding energy: 284.6 eV [5]).

III. RESULTS AND DISCUSSION

Fe 2p core-level HX-PES spectra are shown in Fig. 1. The Fe3+ component increases whereas the Fe2+ component decreases, as the molar ratio of α–Fe2O3 in the solid solution increases. Because FeTiO3 and α–Fe2O3 are nominally described as Fe2+Ti4+O3 and α–Fe3+2O3, the observed behavior in the molar ratio of Fe3+/Fe2+ is reasonable. On the other hand, there is no difference among three Ti 2p spectra (not shown); they dominantly consist of Ti4+ component, which means that Ti ions are still present as tetravalent state even in the FeTiO3–Fe2O3 solid solution. Figure 2 shows the valence band spectra of those samples. In contrast to Fe 2p and Ti 2p core-level spectra, the peak position shift was observed in the valence band spectra, as indicated by arrows in Fig. 2.

In contrast to FeTiO3–Fe2O3 solid solution, some theoretical studies have been performed to reveal the electronic structure and electrical conduction mechanism for FeTiO3. The molecular-orbital calculation by Sherman [6] suggests that Fe 3d state splits into lower Fe 3d α-state overlapping with O 2p band and higher Fe 3d β-state by the intra-atomic exchange energy, and that Fe2+ + Ti4+ → Fe3+ + Ti3+ charge transfer is considered to occur by exciting an electron from 16α1 orbital (Fe t2g) to 17α1 orbital (Ti t2g). Therefore, the experimental spectra for FeTiO3 and FeTiO3–Fe2O3 solid solution indicate that the valence structure of these materials consists of strongly mixed Fe 3d and O 2p component. However, the peak corresponding to the Fe 3d β-state shifts toward the lower binding energy as the molar ratio of FeTiO3, x, decreases from 1 to 0.6. We consider that the peak shift observed for the three samples is due to the shift in Fe 3d components corresponding to the variation in the electron correlation caused by the formation of solid solution between FeTiO3 and α–Fe2O3 and that the peak shift toward the lower binding energy in the valence band HX-PES spectra (Fig. 2) corresponds to the narrowing of the Mott-Hubbard gap. A similar peak shift in valence band spectra was reported by Takaobushi et al. for Fe3−xMxO4 (M

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Fig. 1  Fe 2p core-level spectra for FeTiO3 (x = 1, black line), 0.8FeTiO3·0.2Fe2O3 (x = 0.8, red line) and 0.6FeTiO3·0.4Fe2O3 (x = 0.6, blue line). The components ascribed to Fe2+ and Fe3+ are indicated by broken lines.

Fig. 2  The valence band spectra for FeTiO3 (x = 1, black line), 0.8FeTiO3·0.2Fe2O3 (x = 0.8, red line) and 0.6FeTiO3·0.4Fe2O3 (x = 0.6, blue line). The peaks indicated by arrows correspond to the Fe 3d β-state.
observed in the valence band spectra, as indicated by arrows in Fig. 2. FeTiO₃ is converted into semiconductor via this mechanism by the formation of FeTiO₃ structure and electrical conduction mechanism for FeTiO₃. The molecular-orbital calculation by Sherman [6] suggests that p

Fe 2⁺ reduce the effect of surface contamination on the HX-PES spectrum. The obtained spectra shifted by a surface charging solution indicate that the valence structure of these materials consists of strongly mixed Fe 3⁺. As mentioned above, FeTiO₃–Fe₂O₃ solid solution has alternating Ti-rich and Fe-only cation layers, stacking along the c-axis direction. The Fe ions in one cation layer are ferromagnetically coupled, whereas the adjacent two cation layers are antiferromagnetically coupled; these interactions result in the ferrimagnetism of FeTiO₃–Fe₂O₃ solid solution. As for the direction of the electrical conduction in FeTiO₃–Fe₂O₃ solid solution, it was experimentally revealed that the electrical conduction is easier to occur within the C-plane rather than along the c-axis direction of the solid solution [8]. We consider that the anisotropic electrical conduction is due to a preferential electron transfer between Fe²⁺ and Fe³⁺ within the C-plane rather than along the c-axis direction, reflecting the anisotropic magnetic coupling in FeTiO₃–Fe₂O₃ solid solution. In FeTiO₃, all Fe ions are present as Fe³⁺, leading to electrons localized on their own Fe³⁺ (3d⁸) site where one electron already exists in the Fe β-state t₂g orbital. Hence, electrons transfer between Fe²⁺ and Ti⁴⁺ (3d⁶) in the c-axis direction. In FeTiO₃–Fe₂O₃ solid solution, however, Fe³⁺ (3d⁶) somewhat reduces the electron localization and the electron transfer is thought to occur within a ferromagnetically coupled Fe²⁺ and Fe³⁺ layer.

IV. CONCLUSION

We have conducted the HX-PES measurements on FeTiO₃ and xFeTiO₃(1−x)Fe₂O₃ (x = 0.6 and 0.8) in order to clarify the electronic structure and electrical conduction mechanism for FeTiO₃–Fe₂O₃ solid solution. The valence band structure of FeTiO₃ and FeTiO₃–Fe₂O₃ solid solution indicates that the electronic structure of FeTiO₃–Fe₂O₃ solid solution also consists of strongly mixed Fe 3d and O 2p components. A peak shift is observed in the valence band spectra of those compounds, whereas such a shift was not observed in the Fe 2p and Ti 2p core-level spectra. We consider that the observed peak shift is due to the variation in the electron correlation of Fe 3d components caused by the formation of solid solution of FeTiO₃ with α–Fe₂O₃. The intermixture of Fe²⁺ and Fe³⁺ reduces the electric correlation, and electron transfer between Fe²⁺ and Fe³⁺ occurs easily within the C-plane of FeTiO₃. We propose that insulating FeTiO₃ is converted into semiconductor via this mechanism by the formation of FeTiO₃–Fe₂O₃ solid solution, and the electron transfer between Fe²⁺ and Fe³⁺ in C-plane is the dominant electrical conduction mechanism in FeTiO₃–Fe₂O₃ solid solution rather than that between Fe²⁺ and Ti⁴⁺ along c-axis, which is considered to be a dominant electrical conduction mechanism in FeTiO₃.

ACKNOWLEDGMENTS

The HX-PES experiments on BL47XU at SPring-8 were performed with the approval of the JASRI (Proposal Nos. 2009B1742, 2010A1652, and 2010B1705). The authors thank E. Ikenaga for his assistance in the HX-PES measurements. This research was financially supported by Grants-in-Aids for Scientific Research (B) (No. 22360273) and Challenging Exploratory Research (No. 23655198) from MEXT.

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