

Electronic states of infinite-layer $\text{Sr}_{1-x}\text{Eu}_x\text{FeO}_{2+\delta}$ thin films studied by X-ray photoemission and absorption spectroscopies

Akira CHIKAMATSU*^{1,2}, Toshiya MATSUYAMA¹, Tsukasa KATAYAMA¹,
Yasushi HIROSE^{1,2,3}, Hiroshi KUMIGASHIRA⁴, Masaharu OSHIMA⁵,
Tomoteru FUKUMURA^{1,2}, Tetsuya HASEGAWA^{1,2,3}

¹Department of Chemistry, The University of Tokyo, Tokyo 113-0033, Japan

²CREST, Japan Science and Technology Agency (JST), Tokyo 113-0033, Japan

³Kanagawa Academy of Science and Technology (KAST), Kawasaki 213-0012, Japan

⁴Institute of Materials Structure Science, KEK, Tsukuba 305-0801, Japan

⁵Department of Applied Chemistry, The University of Tokyo, Tokyo 113-8656, Japan

1 Introduction

SrFeO_2 has attracted much attention because it is an isostructural analog of an infinite-layer cuprate, SrCuO_2 , which exhibits high transition-temperature superconductivity by carrier doping [1]. SrFeO_2 shows an antiferromagnetic insulator with a high Néel temperature of $T_N = 473$ K, and has tetragonal unit cells with a lattice constant of $a = 0.3991$ nm and $c = 0.3475$ nm [1]. We recently demonstrated that electron carriers can be doped into SrFeO_2 by Eu substituting for Sr sites in the form of epitaxial thin film [2]. The $\text{Sr}_{0.9}\text{Eu}_{0.1}\text{FeO}_{2+\delta}$ film exhibited as low as ~ 0.15 Ωcm at room temperature, which was approximately four orders of magnitude lower than that of undoped SrFeO_2 , and showed semiconducting behavior [2]. In this study, we measured the core-level spectra of $\text{Sr}_{1-x}\text{Eu}_x\text{FeO}_{2+\delta}$ films by X-ray photoemission (XPS) and absorption (XAS) spectroscopies to investigate the valences of the Fe and Eu ions in them.

2 Experiment

Epitaxial thin films of $\text{Sr}_{1-x}\text{Eu}_x\text{FeO}_{2+\delta}$ with $x = 0, 0.05, 0.10, 0.15,$ and 0.20 were fabricated on SrTiO_3 (001) substrates by combining pulsed laser deposition method with solid-phase reduction using CaH_2 at 280 °C for 24 hours. The typical thickness of the films was ~ 150 nm. The valences of the Fe and Eu ions were evaluated by Fe $2p$ core-level XPS spectra and XAS spectra near the Eu M -edge at beamline 2C of the Photon Factory, KEK. The Fermi levels of the samples were referred to that of Au foil in electrical contact with the samples. The XAS spectra were measured by the total-electron-yield method.

3 Results and Discussion

Figure 1(a) shows the Fe $2p$ core-level XPS spectra of the $\text{Sr}_{1-x}\text{Eu}_x\text{FeO}_{2+\delta}$ films. Each spectrum is characterized by a Fe $2p^{1/2}$ -Fe $2p^{3/2}$ doublet and a weak satellite located at a binding energy of ~ 715 eV between the doublet peaks. It is known that the position of the Fe $2p$ satellite is very sensitive to the oxidation state of Fe. By comparing Fig. 1(a) with the Fe $2p$ XPS spectra of the SrFeO_2 and $\text{SrFeO}_{2.5}$ films [3], we determined the valences of the Fe ions in all compositions of the $\text{Sr}_{1-x}\text{Eu}_x\text{FeO}_{2+\delta}$ films to be divalent, irrespective of Eu contents. Figure 1(b) shows

the XAS spectra near the Eu M -edge in the $\text{Sr}_{1-x}\text{Eu}_x\text{FeO}_{2+\delta}$ films. As seen in Fig. 1(b), each spectrum has peaks at photon energies of ~ 1127 eV, ~ 1132 eV, and ~ 1136 eV in the Eu M_5 -edge. It also has peaks at ~ 1160 eV and ~ 1163 eV, and a shoulder at ~ 1158 eV in the Eu M_4 -edge. These spectra are completely similar to the calculated $3d-4f$ XAS spectra for Eu^{3+} ions as reported previously [4]. Therefore, the valences of Eu in the $\text{Sr}_{1-x}\text{Eu}_x\text{FeO}_{2+\delta}$ films are essentially trivalent, irrespective of Eu contents. These results imply that the electron carriers in $\text{Sr}_{1-x}\text{Eu}_x\text{FeO}_{2+\delta}$ are supplied by Eu^{3+} ions substituting for Sr^{2+} sites, corresponding to the negative Hall coefficients of the $\text{Sr}_{1-x}\text{Eu}_x\text{FeO}_{2+\delta}$ films [2]. Considering charge neutrality of $\text{Sr}_{1-x}\text{Eu}_x\text{FeO}_{2+\delta}$, it is suggested that excess oxygen atoms δ are incorporated between FeO_2 sheets with increasing Eu contents.

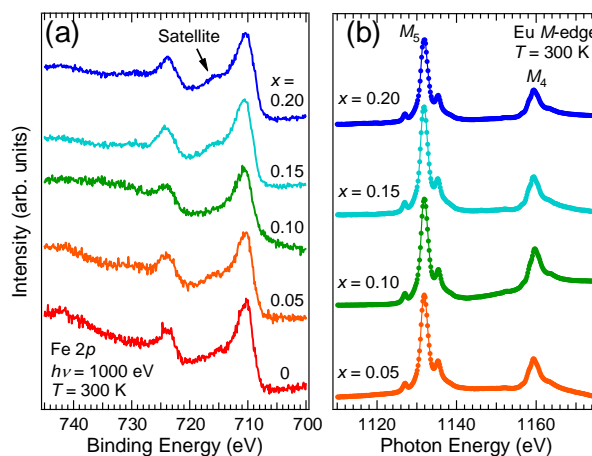


Fig. 1. (a) Fe $2p$ XPS spectra and (b) XAS spectra near the Eu M -edge in the $\text{Sr}_{1-x}\text{Eu}_x\text{FeO}_{2+\delta}$ thin films.

References

- [1] Y. Tsujimoto, et al., *Nature* **450**, 1062 (2007).
 - [2] T. Matsuyama, et al., *Appl. Phys. Express* **4**, 013001 (2011).
 - [3] A. Chikamatsu, et al., *J. Electron Spectrosc. Relat. Phenom.*, **184**, 547 (2012).
 - [4] T. Kinoshita, et al., *J. Phys. Soc. Jpn.* **71**, 148 (2002).
- * chikamatsu@chem.s.u-tokyo.ac.jp