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Elucidation of Fe Electronic Structure in Ba-Doped Bismuth Iron Oxyfluoride Thin Films Using X-ray Spectroscopy

Akiko KAMIGAITO,[1,*] Masaki KOBAYASHI,[2] Kenta AMEMIYA,[3]
Hiroshi KUMIGASHIRA,[4] and Akira CHIKAMATSU[1]
[1]Department of Chemistry, Faculty of Science, Ochanomizu University,
2-1-1 Otsuka, Bunkyo-ku, Tokyo 112-8610, Japan
High Energy Research Organization,
[2]Center for Spintronics Research Network, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku,
Tokyo 113-8656, Japan
[3]Institute of Materials Structure Science, High Energy Accelerator Research Organization,
1-1 Oho, Tsukuba, Ibaraki 305-0801, Japan
[4]Institute of Multidisciplinary Research for Advanced Materials, Tohoku University,
2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

1 Introduction

Multiferroic materials such as $BiFeO_3$ (BFO) have attracted attention because of the unique property of having both ferroelectricity and magnetic order. BFO exhibits multiferroic properties at room temperature and has a large ferroelectric polarization of ~100 μC/cm^2 [1], which originates from the alignment of the 6s^2 lone electron pairs of Bi^{3+} [2]. However, its *R*3*c* structure poses challenges for deterministic ferroelectric switching required for practical multifunctionality, because multiple switching pathways among eight equivalent [111] directions of FE polarization can compete [3]. Therefore, Ba- and F- co-doping to BFO have attempted to obtain the *P*4*mm* structure, which is more suitable for switching.

Recently, Ba- and F-codoped BFO ($Bi_{1-x}Ba_xFeO_{3-x}F_x$) has been reported to adopt a tetragonal *P*4*mm* structure with large polar distortions in polycrystalline form and exhibit magnetic order at room temperature [4]. Our previous work demonstrated the successful fabrication of single-crystalline thin films of $Bi_{1-x}Ba_xFeO_{3-x}F_x$ (x = 0.2, 0.3) and confirmed that these films exhibit ferroelectricity and magnetic order at 300 K [5]. Despite these advances, the effects of fluorine doping on the electronic structures and magnetic interactions in Ba- and F-codoped BFO remain insufficiently understood. In particular, a detailed comparison of the electronic states associated with the magnetic Fe ions has not been conducted between Ba-only-doped BFO thin films and films codoped with Ba and F.

In this study, we investigated the effects of Ba- and F-codoping on the magnetic properties of $Bi_{0.8}Ba_{0.2}FeO_{2.9}$ and $Bi_{0.8}Ba_{0.2}FeO_{2.8}F_{0.2}$ thin films (denoted as Ba:BFO and (Ba,F):BFO respectively) using X-ray spectroscopy.

2 Experiment

Epitaxial thin films of Ba:BFO and (Ba,F):BFO were grown on 0.5 wt% Nb doped $SrTiO_3$ (100) by combining pulsed laser deposition with a topochemical fluorination process using polyvinylidene difluoride at 200 °C for 12 h in Ar gas flow. The typical thickness of the films was set to ~130 nm.

The tetragonal structure of the Ba:BFO and (Ba,F)BFO thin film was confirmed by reciprocal space mapping. The valence-band X-ray photoemission spectroscopy (XPS) and Fe L-edge X-ray absorption spectroscopy (XAS) measurements were performed at the BL-2A MUSASHI beamline of the KEK Photon Factory synchrotron facility. The XPS spectra were acquired at 300 K using a VG SCIENTA SES-2002 electron-energy analyzer with an energy resolution of ~300 meV at 709 eV and an energy step size of 50 meV. The XAS were collected with an energy resolution of ~200 meV. The binding energy was calibrated to the Fermi level of an *in situ* evaporated Au foil electrically connected to the sample and was further referenced to the C 1s peak (step size: 50 meV) at 284.2 eV. X-ray magnetic circular dichroism (XMCD) measurements were conducted at 300 K using a vector-magnet XMCD apparatus with circularly polarized soft X-rays at the BL-16A [6,7] beamline of the Photon Factory, KEK, under a magnetic field of 5 T. The circularly polarized light propagated parallel to the magnetic field and was incident normal to the sample surface. The Fe L-edge XAS and XMCD spectra were collected in the total-electron-yield mode. The XMCD spectra around 710 eV (L3 edge) were collected with an energy resolution of ~200 meV.

3 Results and Discussion

First, we discuss the valence bands of Ba:BFO and (Ba,F):BFO. The valence band of Ba:BFO consists of O 2p, Fe 3d, and Bi 6s states, whereas F 2p states are additionally present in (Ba,F):BFO [5]. To clarify the contribution of Fe—the magnetic element in both Ba:BFO and (Ba,F):BFO thin films—to the valence band, Fe 2p–3d resonant photoemission spectroscopy measurements were performed. Figure 1(a) shows the Fe 2p–3d resonant XPS spectra of the two films obtained at 709 eV, where the strongest resonance was exhibited. The Fe-resonant spectra of both samples display nearly identical spectral

shapes, with distinct peaks at ~2 and ~6 eV, suggesting that the electronic state of Fe remains essentially unchanged upon fluorine incorporation. In contrast, Figure 1(b) shows the antiresonant XPS spectra of the two films obtained at 704 eV, at which the Fe-derived contribution to the valence band becomes minimal. Clear differences are evident between the spectra of the two films. The electronic states near ~7 eV after fluorination can be attributed to F 2p states. The states in the 2–6 eV region also exhibit distinct modifications. These results suggest that fluorination affects the O 2p and Bi 6s states that constitute the valence band, rather than Fe 2p states.

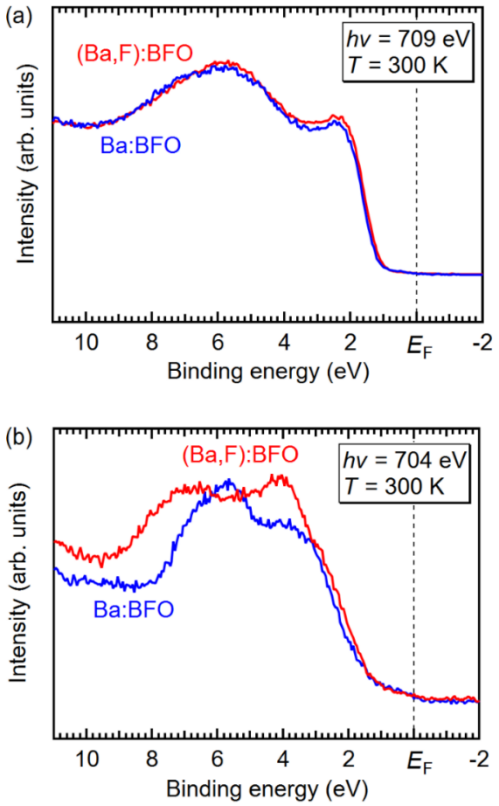

Fig. 1: Fe 2p–3d XPS spectra of Ba:BFO and (Ba,F):BFO thin films: (a) resonant spectra measured at 709 eV and (b) antiresonant spectra measured at 704 eV. All spectra were normalized to the photon flux of the incident beam.

To directly examine how the contribution of Fe to the magnetic properties changes upon fluorination, XMCD measurements were performed. Figures 2(a) and 2(c) show the XAS spectra of the Ba:BFO and (Ba,F):BFO thin films, respectively, obtained at 300 K around the Fe $L_{2,3}$ absorption edges. Here, μ^+ and μ^- denote the absorption coefficients for photon helicity parallel and antiparallel to the majority spin direction of Fe 3d states, respectively. The spectra were normalized to the intensity above the absorption edge, after subtraction of a constant background below the absorption edge. A small but clearly discernible difference is observed between μ^+ and μ^-. From the shape of the XAS spectra, Fe was determined to be trivalent in both films. Figures 2(b) and 2(d) show the XMCD spectra ($\Delta\mu = \mu^+ - \mu^-$) of the Ba:BFO and (Ba,F):BFO thin films measured at 300 K. In both samples, clear XMCD signals appear at 708–710 eV in the Fe L_3-edge region, confirming that the films exhibit ferromagnetism at 300 K. Comparison with previously reported XMCD spectra of various iron compounds [8] enables assignment of the observed features: the peaks in both spectra at 708 and 710 eV correspond to Fe^{3+} ions in octahedral (O_h) sites. Therefore, the XMCD analysis further confirms that the magnetic state of iron is identical in both Ba:BFO and (Ba,F):BFO thin films, indicating that fluorination does not alter the iron magnetic state.

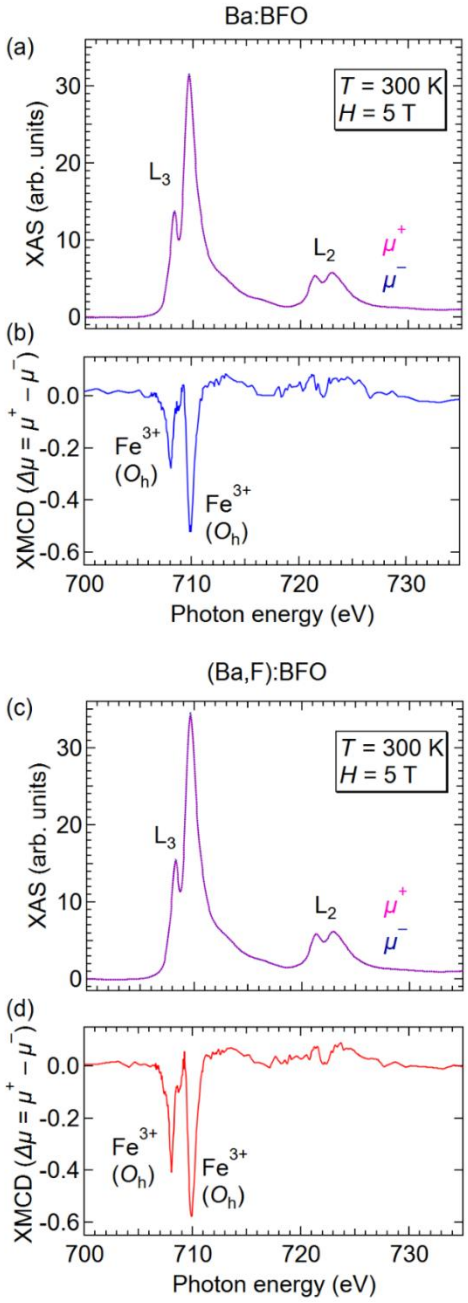

Fig. 2: (a), (c) XAS spectra of Ba:BFO and (Ba,F):BFO thin films measured at 300 K around the Fe $L_{2,3}$ absorption edges. The spectra were normalized to the intensities below and above the absorption edges. (b), (d) XMCD spectra ($\Delta\mu = \mu^+ - \mu^-$) at the Fe $L_{2,3}$ absorption edges for Ba:BFO and (Ba,F):BFO thin films.

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* g2570606@edu.cc.ocha.ac.jp