In situ electronic structure investigation of Mn doped BiFeO₃ thin films

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Abstract. The electronic structure of BiFe₁₋ₓMnₓO₃ (₀ ≤ x ≤ ₀.₃) thin films has been investigated by in situ near edge X-ray absorption fine structure (NEXAFS) and photoemission spectroscopy. Fe ions are found to be trivalent for the whole range of x in BiFe₁₋ₓMnₓO₃ and a hybridization between the Fe 3d and O 2p states is decreased by increasing Mn concentration. Charge transfer multiplet (CTM) calculation is used to understand the experimental results of the Fe L-edge spectra. The experimental results plus the CTM calculation show the hybridization degree between the transition metal 3d and O 2p states are critical for the multiferroic properties of underlying systems.

1. Introduction
Multiferroics are multifunctional materials that simultaneously possess ferroelectric, ferromagnetic and ferroelastic ordering. This kind of materials has been studied broadly and enthusiastically in recent years due to their potential application in spintronics, high temperature sensors, visible light photocatalyst[1] and memory storage systems. As ABO₃ perovskite counterparts, rhombohedral BiFeO₃ (BFO) has attracted much attention due to both magnetic and ferroelectric orderings at ambient conditions (antiferromagnetic below the Neel temperature Tₑ ≈ 370 °C, ferroelectric below the Curie temperature Tₑ ≈ 825 °C[2]).

Investigations of multiferroic BFO bulk and thin films[3, 4] focus on a high remnant polarization and magnetization behavior. Proper substrates[5], controlling films thickness[6], and A or B site cation substitutions in the lattice[7, 8] were used to improve these properties. However, the origin of enhanced physical properties is still controversial, especially enhanced magnetization by cation substitution. In this work, we have investigated electronic structures of BiFe₁₋ₓMnₓO₃ (₀ ≤ x ≤ ₀.₃) (BFMO) thin films by employing in situ photoemission spectroscopy (PES) and near edge X-ray absorption fine structure (NEXAFS) spectroscopy. Charge transfer multiplet (CTM) calculation[9] was performed to simulate the Fe L-edge NEXAFS data.

2. Experiment
The BiFe₁₋ₓMnₓO₃ (₀ ≤ x ≤ ₀.₃) films were prepared on the Pt(111)/TiO₂/SiO₂/Si(100) substrates by pulsed laser deposition (PLD) and studied by in situ PES system at 4B9B beam line of the Beijing Synchrotron Radiation Facility (BSRF). The detailed method of sample preparation and investigation of structural, morphological and magnetic properties were reported in elsewhere[10]. The Fe L-edge NEXAFS and PES experiments in the soft X-ray range of the BFMO samples were carried out in situ at 4B9B beam line of the BSRF with total electron yield (TEY) detection mode. After the in situ measurements, the films were taken out for Fe K-edge hard X-ray NEXAFS measurements at 4B9A XRD/SAXS beam line. The Fe K-edge NEXAFS spectra of all samples were made in total fluorescence yield (TFY) mode and the resolution of the monochromator was about 3–4eV in the...
energy ranges which used for Fe K-edge. The simulation of experimentally observed Fe L-edge NEXAFS spectra of BFMO films were carried out by charge transfer multiplet for X-ray absorption spectroscopy (CTM4XAS) program that was developed by E. Stavitski and F.M.F.de Groot[11].

3. Result and Discussion

3.1 Photoemission spectra

Figure 1 illustrates wide scan PES spectra of the BFMO films at $h\nu=900$eV, including the main photoemission peaks of constituent elements in the system. The core-level photoemission peaks and Auger lines of Bi, Fe, Mn and O atoms are dominant. Absence of the C 1s signal at $\sim285$eV indicates that the surface is free from contamination, since the measurements are carried out in situ in high vacuum. The binding energy in the spectra are calibrated by Pt 4f peak from substrate. The corresponding characteristic core-level photoemission peaks and Auger peaks are labeled on the spectra of BiFe$_{1-x}$Mn$_x$O$_3$ ($x=0.1,0.2,0.3$) films. It is obvious that the characteristic peaks of undoped BFO films are the same as that of doped samples, except the signal of Mn.

![Figure 1](image)

Figure 1. PES survey spectra of BiFe$_{1-x}$Mn$_x$O$_3$ ($0 \leq x \leq 0.3$) thin films on Pt (111)/TiO$_2$/SiO$_2$/Si (100) substrate.

3.2 Fe K-edge NEXAFS spectra

In order to obtain oxidation state of Fe and influence of Mn doping in internal region of the films, we have performed hard X-ray NEXAFS (NEXAFS is also called X-ray Absorption Near Edge Structure, XANES. However, some researchers used the term NEXAFS for soft x-ray absorption spectra and XANES for hard x-ray absorption spectra. Here, we totally used the same term NEXAFS for both Fe L and K-edge measurement on BFMO thin films. The probing depth of hard X-ray NEXAFS spectroscopy is much larger than that of soft X-ray PES in section 3.1 and could detect the deeper region of thin films under the surface.

Figure 2 shows the Fe K-edge NEXAFS spectra of BFMO films, which are similar to that of Fe$_2$O$_3$[12], except the intensity difference of the three peaks labeled with A, B and C. It implicates
that all the Fe ions in the deeper region of thin films are also in trivalent state. That also proves the valence state of Fe ions in entire region of thin films is not changed by Mn doping [10]. Dongeun et al. [13] reported that peak A corresponds to the 1s-3d electric quadrupole-forbidden transition, peak B appeared as a shoulder peak is caused by the shakedown process in which 2p electron in ligand (here the ligand is oxygen) 2p band partially transfer to the Fe 3d orbitals, so called ligand to metal charge transfer process. Peak C is dipole allowed transition to unoccupied 4p orbital. Intensities of peak B and C are more sensitive to Mn doping than peak A and increased by increasing of Mn doping amount. As is well known, the BFO is a charge transfer type insulator and assume to be Fe \( 3d^5 + Fe \ 3d^6 \ \overset{L}{\underset{\text{L represents the ligand hole state O 2p}}{\text{mixed states derived by the hybridization of Fe 3d with O 2p states}}.}

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\begin{align*}
\text{main causes of the current observation at the Fe K-edge, in a self-consistent way with an decreased hybridization strength between Fe 3d- O 2p states. This is clearly seen affirmatively through the below Fe L-edge NEXAFS measurement results and CTM simulation.}
\end{align*}
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\begin{align*}
\text{Figure 2. Fe K-edge NEXAFS spectra of BiFe}_{1-x}\text{Mn}_x\text{O}_3 (0 \leq x \leq 0.3) thin films as a function of Mn content x.}
\end{align*}
\]

3.3 Fe L-edge NEXAFS spectra and CTM simulation

To investigate the influence of Mn doping on unoccupied Fe 3d states of BFMO systems, we have carried out the Fe L-edge NEXAFS spectra of the samples and also simulated the experimental spectra by CTM program. Figure 3(a) shows the normalized NEXAFS spectra of Fe L-edge for the BFMO \((0 \leq x \leq 0.3)\) films. It involves the excitation from the Fe 2p state to an unoccupied Fe 3d state. There is a strong overlap between the core wave function and the valence wave function. Spin-orbit coupling effects make Fe L-edge absorption spectra split into \(L_1\) and \(L_2\) structures, which further split into lower-lying \(t_{2g}\) and higher-lying \(e_{g}\) (where \(\downarrow\) denotes the minority spin states) states because of the octahedral
crystal ligand field effects. The energy difference between $t_{2g}\downarrow$ and $e_{g}\downarrow$ states for both $L_3$ and $L_4$ levels is about 1.4eV, in corresponding to the crystal field splitting energy, $10Dq$. We have reported the influence of Mn doping on the valence states of Fe ions and relative intensity of $t_{2g}\downarrow$ and $e_{g}\downarrow$ states[10]. Here, we will discuss the simulation of spectraby CTM calculation in detail. Figure 3(b) shows the simulation curves for the absorption spectra in Figure 3(a). Atomic multiplet model is chosen, and different crystal field splitting ($10Dq$) and charge transfer energy ($\Delta$) are used. $10Dq$ varies from 1.0 to 1.8eV to get the best fitting curves (the simulation with the other value of $10Dq$ is not shown here). When $10Dq$ is around 1.65eV for all the doped films, the calculation and experiment curves match very well. Especially, the same fit parameter, $10Dq$, gives the best fitting results, which indicates that B site doping in ABO$_3$ perovskite has less influence on the octahedral crystal field.

![Diagram](image)

Figure 3. (a) Fe L-edge NEXAFS spectra of BiFe$_{1-x}$Mn$_x$O$_3$ (0 $\leq$ $x$ $\leq$ 0.3) thin films. (b) calculated spectra of Fe L-edge with various value of charge transfer energy ($\Delta$).

The other fitting parameter, $\Delta$, are 2.0, 2.5, 2.8, and 3.3eV for $x$=0, 0.1, 0.2 and 0.3, respectively. Charge transfer effects refer to charge fluctuations in the initial and final states. In the charge transfer multiplet model[14], the charge transfer energy $\Delta$ is defined as the energy difference between the lowest states of the 3d5 and Fe 3d6 configuration. It is found that $\Delta$ decreases with Mn doping increasing, which suggests the portion of Fe 3d6 in the Fe 3d5 + Fe 3d6 mixed state decreasing. It is equal to decreasing of hybridization between Fe 3d and O 2p states. In a word, Mn doping in BFMO systems can modify the charge transfer effect between Fe 3d orbital and the O 2p ligand orbitals. The Fe K-edge NEXAFS spectra and Fe L-edge CTM simulation also prove that Mn doping could induce the variation of hybridization interactions and further change the electron density of state (DOS) distribution between Fe-O and Mn-O pairs.

4. Conclusion

PES and NEXAFS spectroscopy in the soft and hard photon energy range have been used to study
BiFe_{1-x}Mn_xO_3 thin films with x=0, 0.1, 0.2 and 0.3. The Fe K, L-edge NEXAFS spectra reveals that the valence state of Fe ions remains +3 under all of the doping conditions. Combined with Fe L-edge CTM simulation, it can be concluded that Mn doping in BFMO systems modified the charge transfer effect between Fe 3d orbital and the O 2p ligand orbitals. In conclusion, increasing Mn doping can increase the charge transfer energy, decrease the portion of Fe 3d^6 L in Fe 3d^5 + Fe 3d^6 L mixed state, and decrease the hybridization between Fe 3d and O 2p states.

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