

## Comparison between conductive and insulating cobalt-ferrite thin films with perpendicular magnetic anisotropy studied by XMCD

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Spinel-type cobalt ferrites [CoFe<sub>2</sub>O<sub>4</sub> (CFO)] have been investigated for a long time for magnetic applications as magnetic insulators in the forms of bulk, powder, and thin films. They have an inverse spinel structure in AB<sub>2</sub>O<sub>4</sub> chemical formulation, with Fe<sup>3+</sup> at the tetragonal A-site (T<sub>d</sub>) and Fe<sup>3+</sup> and Co<sup>2+</sup> at the octahedral B-site (O<sub>h</sub>). Recent developments in spintronics boost the application of thin CFO films stacked with other nonmagnetic and magnetic layers, which are, for example, utilized as spin-filtering tunnel barriers. There are some reports that CFO (001) films exhibit perpendicular magnetic anisotropy (PMA) under tensile epitaxial strain [1]. The PMA in CFO films is thought to originate from Co<sup>2+</sup> (3d<sup>7</sup>) at the octahedral B-site (O<sub>h</sub>) in the tetragonally distorted inverse spinel structure. For the charge neutrality, the formal valence states are recognized as Co<sup>2+</sup> (O<sub>h</sub>), Fe<sup>3+</sup> (O<sub>h</sub>), and Fe<sup>3+</sup> (T<sub>d</sub>) in stoichiometric CFO films. However, the substitution of Co<sup>2+</sup> by Fe<sup>2+</sup> promotes the formation of Fe<sup>2+</sup> (O<sub>h</sub>) sites, which induces the conductive properties in CFO films. The conductivity in CFO (C-CFO) films would arise depending on the compositions due to the formation of Fe<sup>2+</sup> states through Co<sup>2+</sup> → Fe<sup>2+</sup> substitution, which is regarded as an approach to magnetite Fe<sub>3</sub>O<sub>4</sub>. On the other hand, insulative CFO (I-CFO) can be grown by Co<sup>2+</sup> → Fe<sub>2/3</sub><sup>3+</sup>□<sub>1/3</sub> (□ = cation vacancies) substitution, which is an approach to insulative maghemite γ-Fe<sub>2</sub>O<sub>3</sub>.

In spite of applications of both C-CFO and I-CFO films in the spintronics researches, the characterizations of both CFOs have not been performed until now [2,3]. Here, we aim to establish the selective film growth methods between I-CFO and C-CFO films with PMA and discuss the origin of conductive properties from the results of transport measurements and site-specific magnetic spectroscopies of XMCD.

Samples were grown on MgO (001) substrates by a pulsed laser deposition (PLD) method using source materials with different powder compositions. The source materials for I-CFO were prepared by mixing CoFe<sub>2</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub> powder, and those for C-CFO, were by mixing CoFe<sub>2</sub>O<sub>4</sub> and α-Fe powder.

X-ray absorption spectroscopy (XAS) and XMCD were performed at BL-7A in the Photon Factory at the High Energy Accelerator Research Organization (KEK-PF). For the XAS and XMCD measurements, the photon helicity was fixed, and a magnetic field of ±1.2 T was applied parallel along the incident polarized soft x-ray beam, to obtain signals defined as m+

and m-spectra. The total electron yield (TEY) mode was adopted, and all measurements were performed at room temperature.

Figure 1 shows the XAS and XMCD of C-CFO and I-CFO for Fe and Co L-edges with different Co compositions. The Fe and Co intensities are plotted in the same vertical scales because XAS roughly provides the Fe and Co compositions. XAS and XMCD line shapes for the Fe L-edges show distinctive features with differential line shapes due to the three kinds of Fe states (Fe<sup>3+</sup> in O<sub>h</sub>, Fe<sup>3+</sup> in T<sub>d</sub>, and Fe<sup>2+</sup> in O<sub>h</sub>). For the Fe L-edges, although the difference in XAS is small, clear differential XMCD line shapes are detected. The Fe<sup>3+</sup> state with T<sub>d</sub> symmetry exhibits the opposite XMCD sign, which is common for the spinel ferrite compounds. The Fe<sup>2+</sup> component at 708.0 eV decreases in high Co compositions. In the case of Fe<sub>3</sub>O<sub>4</sub>, the Fe<sup>2+</sup> component is more enhanced. Therefore, the conductive properties are related to the amounts of Fe<sup>2+</sup> states, whose quantitative analysis is performed by using the ligand-field-multiplet calculation [4].

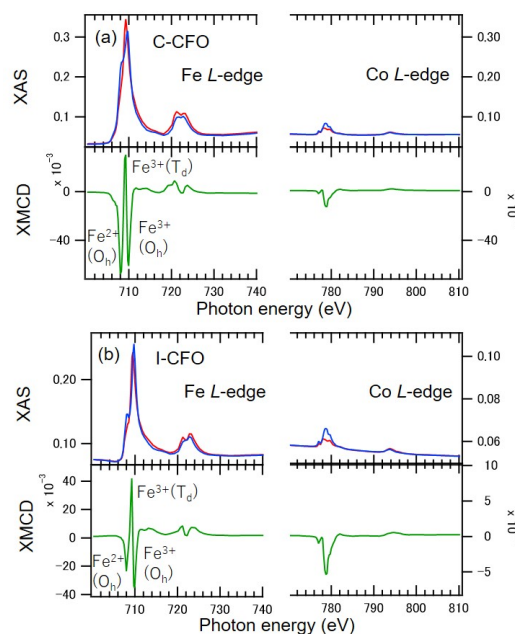


Fig. 1, XAS and XMCD of (a) conductive Co<sub>0.23</sub>Fe<sub>2.77</sub>O<sub>4</sub> and (b) insulative Co<sub>0.23</sub>Fe<sub>2.77</sub>O<sub>4</sub>.

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