

## Structural and Magnetic Properties of Thin-film ScFeO<sub>3</sub>

Kwang Joo Kim<sup>1</sup>, Jongho Park<sup>1</sup>, and Jae Yun Park<sup>2\*</sup>

<sup>1</sup>Department of Physics, Konkuk University, Seoul 05029, Korea

<sup>2</sup>Department of Materials Science and Engineering, Incheon National University, Incheon 22012, Korea

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Structural and magnetic properties of ScFeO<sub>3</sub> compound were investigated by X-ray diffraction (XRD), X-ray photoelectron spectroscopy, and vibrating sample magnetometry (VSM) in comparison with those of Fe<sub>2</sub>O<sub>3</sub> and Sc<sub>2</sub>O<sub>3</sub>. The specimens were prepared as thin films under identical sol-gel deposition process. The XRD data indicated that the ScFeO<sub>3</sub> specimen have cubic bixbyite structure, identical to that of the Sc<sub>2</sub>O<sub>3</sub> specimen but different from that of the Fe<sub>2</sub>O<sub>3</sub> specimen (rhombohedral). The estimated lattice constant of ScFeO<sub>3</sub> is smaller than that of Sc<sub>2</sub>O<sub>3</sub> by 2.9 %. According to the VSM data, the ScFeO<sub>3</sub> specimen showed a magnetic hysteresis curve that is alike in shape to that of the Fe<sub>2</sub>O<sub>3</sub> specimen with the saturation magnetization of the former (2.6 emu/cm<sup>3</sup>) being smaller by 30 % than that of the latter (3.7 emu/cm<sup>3</sup>). The observed small magnetization in ScFeO<sub>3</sub> implies an antiferromagnetic spin alignment of neighboring Fe<sup>3+</sup> ions with canted spin magnetic moment.

**Keywords :** bixbyite, thin film, canted spin, magnetic properties

### 1. Introduction

There has been a good deal of attention on ABO<sub>3</sub>-type compounds, not only for practical applications but also for fundamental solid-state physics. Some of ABO<sub>3</sub>-type transition-metal (T-M) oxides are known to have perovskite structure with interesting ferroelectric and superconducting properties. As one of such ABO<sub>3</sub>-type T-M oxides, ScFeO<sub>3</sub> is in the middle of two binary ends, Sc<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>.

Sc<sub>2</sub>O<sub>3</sub> crystallizes in a cubic bixbyite (Mn<sub>2</sub>O<sub>3</sub>) structure [1, 2] where Sc<sup>3+</sup> ions are located at the body center of a cube with six O<sup>2-</sup> ions occupying its corners. The Sc<sup>3+</sup> ions can occupy two different body-centered sites along (110) direction, denoted by C<sub>2</sub> (24d) and S<sub>8</sub> (8b) [2]. The two sites differ by the locations of two oxygen vacancies out of eight cube corners. On the other hand, Fe<sub>2</sub>O<sub>3</sub> is known to have various crystal structures such as α-Fe<sub>2</sub>O<sub>3</sub> (rhombohedral), β-Fe<sub>2</sub>O<sub>3</sub> (bixbyite), γ-Fe<sub>2</sub>O<sub>3</sub> (spinel), and ε-Fe<sub>2</sub>O<sub>3</sub> (orthorhombic) [3-5]. As in Fe<sub>2</sub>O<sub>3</sub>, ScFeO<sub>3</sub> is known to exist in various crystal structures such as orthorhombic, rhombohedral, and bixbyite [6, 7].

In this work, structural and magnetic properties of

ScFeO<sub>3</sub> compound are investigated in comparison with those of Sc<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>. The specimens were prepared as thin films under identical sol-gel process. The structural properties of the specimen were investigated by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The magnetic hysteresis curves of the specimens were investigated by vibrating sample magnetometry (VSM).

Sc atom (atomic number = 21) has [Ar] 4s<sup>2</sup> 3d<sup>1</sup> electronic configuration, while Fe atom (atomic number = 26) has [Ar] 4s<sup>2</sup> 3d<sup>6</sup> electronic configuration. Thus, when the cations in ScFeO<sub>3</sub> have valence of +3, Fe<sup>3+</sup> has half-filled 3d states (3d<sup>5</sup>), while Sc<sup>3+</sup> has no 3d electron. With high-spin Fe<sup>3+</sup> ions in either C<sub>2</sub> or S<sub>8</sub> sites, bixbyite ScFeO<sub>3</sub> might have interesting magnetic properties. The magnetic properties of the ScFeO<sub>3</sub> specimen were analyzed in comparison with those of the Fe<sub>2</sub>O<sub>3</sub> specimen.

### 2. Experimental

ScFeO<sub>3</sub> specimens were prepared as thin films through a sol-gel deposition process. Precursor solution was prepared by dissolving Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and Sc(NO<sub>3</sub>)<sub>3</sub>·xH<sub>2</sub>O together in 2-methoxyethanol and ethanolamine at 170 °C. Spin-coating of the precursor solution was done on Si(100) substrate rotating 3000 rpm for 20 s, followed by

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\*Corresponding author: Tel: +82-32-835-8271

Fax: +82-32-835-0778, e-mail: [pjy@inu.ac.kr](mailto:pjy@inu.ac.kr)

heating at 300 °C for 5 min. This process was repeated to increase the thickness of the gel film. Post-annealing of the gel film was done at 800 °C for 4 h in air to obtain solid-state thin-film specimen. Thin-film  $\text{Sc}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  specimens were also prepared under the same sol-gel process for comparing structural and magnetic properties with  $\text{ScFeO}_3$ . All specimens have thicknesses in the 500-600 nm range observed by scanning electron microscopy.

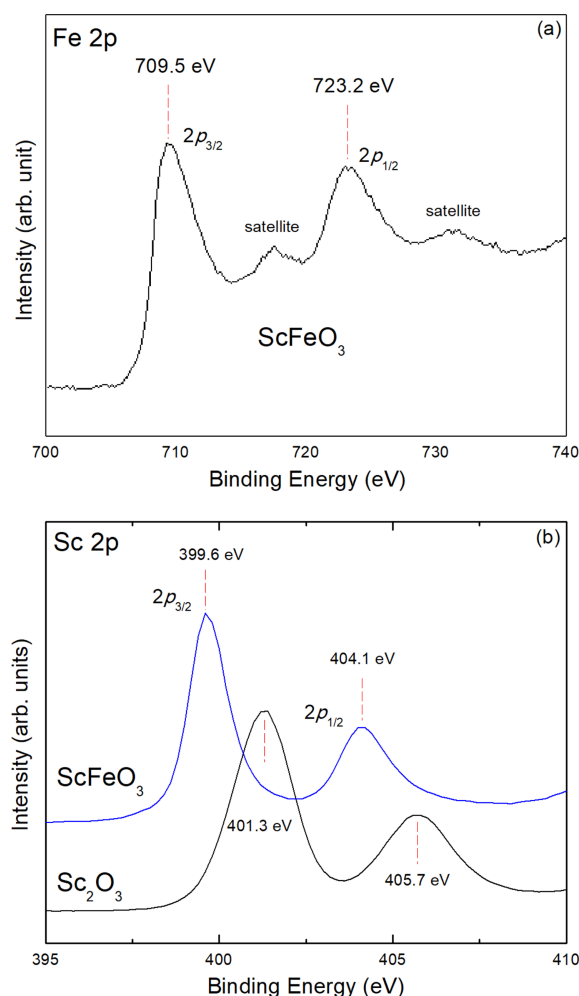
The crystal structure of the specimen was investigated by using XRD ( $\text{Cu } K_\alpha$  line, wavelength = 0.15418 nm) under a grazing-incidence geometry with fixed X-ray incidence angle ( $4^\circ$ ) from the specimen plane. XPS measurements were performed using  $\text{Al } K_\alpha$  line (photon energy = 1486.7 eV) for confirming ionic valences of Sc and Fe ions in the compound. Magnetic hysteresis curves of the specimens were obtained from VSM measurements under external magnetic field applied parallel to the film's plane and varied in the  $\pm 15$  kOe range.

### 3. Results and Discussion

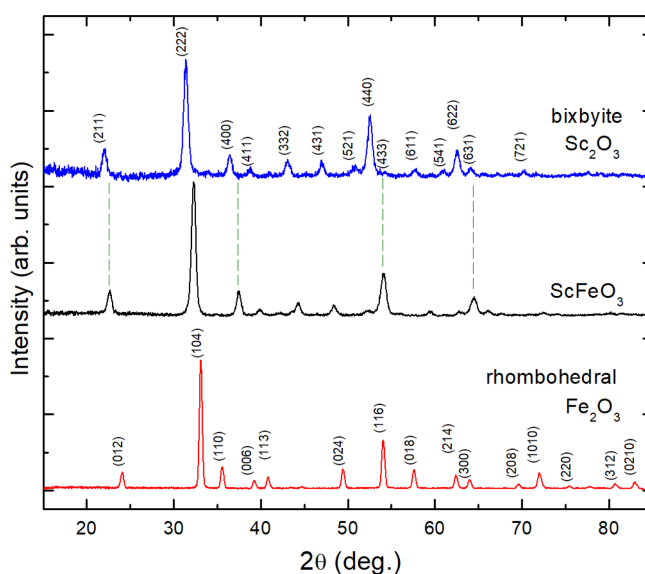
The existence of Fe ion in  $\text{ScFeO}_3$  can be identified by XPS on Fe 2*p* electrons. As shown in Fig. 1(a), the binding-energy (B-E) peaks of  $2p_{3/2}$  and  $2p_{1/2}$  electrons of Fe ions in the  $\text{ScFeO}_3$  specimen are located at 709.5 and 723.2 eV, respectively. The observed 2*p* spin-orbit (s-o) splitting of 13.7 eV implies that the Fe ions have valence of +3 [6]. The satellites are attributable to energy loss of the 2*p* photoelectrons due to their interactions with spin-polarized 3*d* electrons in the Fe ion. In Fig. 1(b), the s-o splitting of 4.4 eV between  $2p_{3/2}$  (401.3 eV) and  $2p_{1/2}$  (405.7 eV) peaks for Sc 2*p* electrons of  $\text{Sc}_2\text{O}_3$  implies the existence of  $\text{Sc}^{3+}$  ions [6]. For  $\text{ScFeO}_3$ , the observed s-o splitting is consistent with that of  $\text{Sc}_2\text{O}_3$ , but the  $2p_{3/2}$  (399.6 eV) and  $2p_{1/2}$  (404.1 eV) peaks are shifted to low energies by  $\sim 1.7$  eV compared to those of  $\text{Sc}_2\text{O}_3$ . Such low-energy shift is attributable to changes of local bonding environment for  $\text{Sc}^{3+}$  ion due to the  $\text{Fe}^{3+}$  substitution.

In Fig. 2, XRD pattern of the  $\text{ScFeO}_3$  specimen is exhibited in comparison with those of  $\text{Sc}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ . The  $\text{ScFeO}_3$  specimen shows the same (cubic bixbyite) crystal structure as that of the  $\text{Sc}_2\text{O}_3$  specimen [1, 2]. On the other hand, the  $\text{Fe}_2\text{O}_3$  specimen shows a different XRD pattern compared to  $\text{ScFeO}_3$  and  $\text{Sc}_2\text{O}_3$ . The XRD pattern implies that the  $\text{Fe}_2\text{O}_3$  specimen has rhombohedral structure ( $\alpha\text{-Fe}_2\text{O}_3$ ) [3, 4].

The peaks in the XRD pattern of the  $\text{ScFeO}_3$  specimen are seen to shift to higher angles from the corresponding ones of the  $\text{Sc}_2\text{O}_3$  specimen, indicating that the lattice constant ( $a_0$ ) of the former is smaller than that of the latter. The estimated  $a_0$  of the  $\text{ScFeO}_3$  specimen is 0.954



**Fig. 1.** (Color online) X-ray photoelectron spectra of (a) Fe 2*p* electrons and (b) Sc 2*p* electrons of  $\text{ScFeO}_3$  specimen.



**Fig. 2.** (Color online) X-ray diffraction pattern of  $\text{ScFeO}_3$  specimen compared to those of  $\text{Sc}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  specimens.

nm, while that of the  $\text{Sc}_2\text{O}_3$  specimen is 0.982 nm.  $\text{Sc}_2\text{O}_3$  is known to be isostructural to  $\text{Y}_2\text{O}_3$  ( $a_0 = 1.081$  nm) [8] with the difference in  $a_0$  being primarily ascribed to the difference in ionic radius [9] between  $\text{Sc}^{3+}$  (0.0745 nm) and  $\text{Y}^{3+}$  (0.09 nm) at the octahedral sites. Thus, the smaller  $a_0$  of  $\text{ScFeO}_3$  compared to  $\text{Sc}_2\text{O}_3$  is partly attributable to the difference in ionic radius between  $\text{Sc}^{3+}$  and high-spin  $\text{Fe}^{3+}$  (0.0645 nm). Due to an ambient nature of the present sol-gel synthetic condition for the  $\text{ScFeO}_3$  film, random distribution of  $\text{Sc}^{3+}$  and  $\text{Fe}^{3+}$  among the  $\text{C}_2$  and  $\text{S}_8$  sites is expected. The present XRD data are not in agreement with the prediction of a theoretical energy-band structure calculation [10], in which  $\text{ScFeO}_3$  crystal prefers to be non-cubic structure, such as orthorhombic and rhombohedral.

In Fig. 3, magnetic hysteresis loop of the  $\text{ScFeO}_3$  specimen measured by using VSM at room temperature is shown in comparison with that of the  $\text{Fe}_2\text{O}_3$  specimen. The  $\text{Sc}_2\text{O}_3$  specimen had a diamagnetic behavior. The observed saturation magnetization ( $M_S$ ) of the  $\text{Fe}_2\text{O}_3$  specimen is  $3.7$  emu/cm<sup>3</sup>, while for the  $\text{ScFeO}_3$  specimen it is reduced to  $2.6$  emu/cm<sup>3</sup>. For the remanence  $M_r$ , the  $\text{Fe}_2\text{O}_3$  specimen shows  $1.2$  emu/cm<sup>3</sup> (32% of  $M_S$ ), while the  $\text{ScFeO}_3$  specimen shows  $0.7$  emu/cm<sup>3</sup> (27 % of  $M_S$ ). On the other hand, the coercivity of the  $\text{ScFeO}_3$  specimen is quite close to that of the  $\text{Fe}_2\text{O}_3$  specimen, 0.6 kOe. The magnetizations observable from  $\text{ScFeO}_3$  and  $\text{Fe}_2\text{O}_3$  are primarily ascribed to net magnetic moment derivable from magnetic interactions among high-spin  $\text{Fe}^{3+}$  ions in the compounds. Such small magnetizations observed for both  $\text{ScFeO}_3$  and  $\text{Fe}_2\text{O}_3$  are interpreted as primarily due to antiferromagnetic alignment of neighboring  $\text{Fe}^{3+}$  ions [10,

11].

According to the result of a theoretical calculation of the degree of spin canting in antiferromagnetic  $\text{ScFeO}_3$  [10], the canting angle was estimated to be  $0.48^\circ$ , where it is  $180^\circ$  for ferromagnetic spin alignment. The magnetic moment of high-spin  $\text{Fe}^{3+}$  ion is  $5 \mu_B$ . Thus, antiferromagnetic  $\text{ScFeO}_3$  has net magnetic moment of  $1.3 \times 10^{-2} \mu_B$  per formula-unit (f-u). Considering the unit-cell volume of the  $\text{ScFeO}_3$  specimen,  $(0.954 \text{ nm})^3$ , that contains eight  $\text{Fe}^{3+}$  ions and  $1 \mu_B = 9.27 \times 10^{-21}$  emu, the observed  $M_S$  ( $= 2.6$  emu/cm<sup>3</sup>) for the  $\text{ScFeO}_3$  specimen corresponds to  $3.0 \times 10^{-2} \mu_B/\text{f-u}$  of the bixbyite lattice. The experimental result is seen to be in qualitative agreement with the theoretical prediction on spin-canted antiferromagnetic  $\text{ScFeO}_3$  compound.

## 4. Conclusions

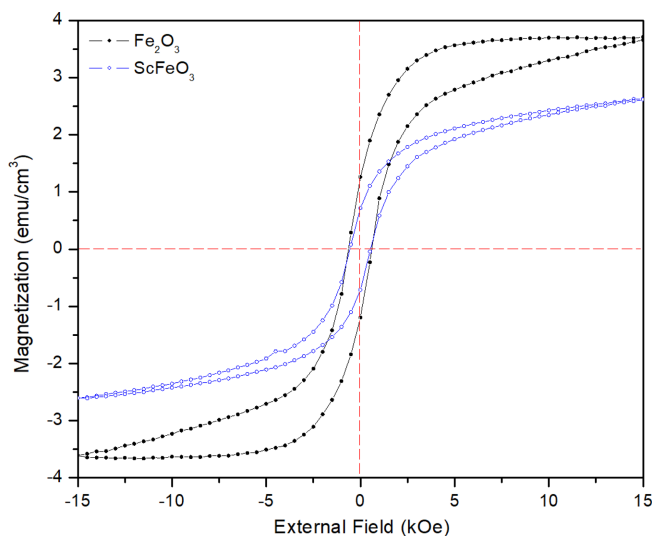
According to XRD analysis,  $\text{ScFeO}_3$  compound maintains the bixbyite crystal structure of  $\text{Sc}_2\text{O}_3$ . The lattice constant of the bixbyite structure is reduced by 2.9 % due to the replacement of Sc by Fe.  $\text{ScFeO}_3$  exhibits a similar magnetic hysteresis behavior to  $\text{Fe}_2\text{O}_3$  with the value of  $M_S$  ( $= 2.6$  emu/cm<sup>3</sup>) being smaller by 30 % than that of  $\text{Fe}_2\text{O}_3$ . The observed small magnetization in  $\text{ScFeO}_3$  can be understood in terms of an antiferromagnetic ordering between neighboring  $\text{Fe}^{3+}$  ions with canted spin.

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**Fig. 3.** (Color online) Magnetic hysteresis loops of  $\text{ScFeO}_3$  and  $\text{Fe}_2\text{O}_3$  specimens.

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