

## X-ray absorption spectroscopy of defect-induced ferromagnetism: (Fe,Co) co-doped SnO<sub>2</sub>

Jun OKABAYASHI<sup>\*1</sup>, Kiyoshi NOMURA<sup>2</sup>, Shin KONO<sup>3</sup>, and Yasuhiro YAMADA<sup>3</sup>

<sup>1</sup>Research Center for Spectrochemistry, The University of Tokyo, 113-0033, Japan

<sup>2</sup>Department of Applied Chemistry, The University of Tokyo, 113-8656, Japan

<sup>3</sup>Department of Chemistry, Tokyo University of Science, 162-8601, Japan

### Introduction

We have reported that SnO<sub>2</sub> doped with Fe ions shows ferromagnetism in room temperature [1]. It is known that 1% Co doping into SnO<sub>2</sub> shows the ferromagnetism although the magnetization decreases with the increase of the Co doping rate [2]. On the other hand, the increase of Fe doping rate induces the large magnetization [1, 3]. We have recently found that SnO<sub>2</sub> co-doped with dilute Fe and Co ions enhanced the magnetization. In order to clarify the origin of the ferromagnetism, we have to determine the electronic structures of Fe and Co ions in SnO<sub>2</sub> explicitly. In this motivation, x-ray absorption spectroscopy (XAS) and Mössbauer spectroscopy were employed.

### Manuscript preparation

Fe and Co co-doped SnO<sub>2</sub> samples were synthesized by a sol-gel method. 0.1 M of SnCl<sub>2</sub> · H<sub>2</sub>O, and 0.01 M of Fe and Co salts were dissolved by using citric acid and HCl. Each solution was mixed together with ethylene glycol for the nominal compositions. These solutions were condensed at 80 °C, calcinated at 250 °C for 2 hours, and annealed at 550 °C for 0.5 hours. After milling samples, the samples were finally annealed at 550 °C for 3 hours. The magnetization was measured by vibrating sample magnetization (VSM) at room temperature, XAS was performed at KEK-PF BL-7A (Research Centre for Spectrochemistry, The University of Tokyo).

### Results and discussion

X-ray diffraction (XRD) patterns of all samples corresponded to the rutile-type crystalline structure of SnO<sub>2</sub>. No other phases were observed within the detectable limit in XRD patterns.

VSM revealed the hysteresis loop at room temperature. Largest saturation magnetization was observed at 1 % Fe and 1 % Co co-doped case. Here, we note that pure SnO<sub>2</sub> is a diamagnetic material and that the only Fe or Co doped SnO<sub>2</sub> showed no clear hysteresis loop at room temperature. It suggests that the co-doping of Fe and Co in SnO<sub>2</sub> was effective for the ferromagnetic ordering as compared with single doping.

Figure 1 shows the XAS of Co *L*-edge in Fe and Co co-doped SnO<sub>2</sub>. XAS of spinel-type ferromagnetic CoFe<sub>2</sub>O<sub>4</sub> ferrite (Co<sup>2+</sup>) and FeCo<sub>2</sub>O<sub>4</sub> (Co<sup>3+</sup>) synthesized by sol-gel method are also shown as references. We found that the Co<sup>2+</sup> electronic structure is formed in Fe

and Co co-doped SnO<sub>2</sub> from the comparison with the Co<sup>2+</sup> spectral lineshape in CoFe<sub>2</sub>O<sub>4</sub>. Since the Fe *L*-edge regions overlap with the dominant Sn 3p core levels, clear absorption signals of Fe were not detected. Mössbauer spectroscopy was used for the observation of the local environment of Fe ions [4]. From the isomer shift and quadrupole splitting values, we conclude that the Fe<sup>3+</sup> states are dominant in Fe and Co co-doped SnO<sub>2</sub>.

Considering the above results, we suggest that the double-exchange interaction occurs through long chains of oxygen and tin atoms between diluted Fe<sup>3+</sup> and Co<sup>2+</sup> ions. From the charge neutrality conditions: Co<sup>2+</sup> + V<sub>O</sub><sup>2-</sup> + 2Sn<sup>4+</sup> ↔ Co<sup>2+</sup> + 2Sn<sup>3+</sup> and Fe<sup>3+</sup> + 1/2V<sub>O</sub><sup>2-</sup> + Sn<sup>4+</sup> ↔ Fe<sup>3+</sup> + Sn<sup>3+</sup> (V<sub>O</sub> is oxygen vacancy), it is considered that not only the electrons from oxygen vacancies but also the elusive Sn carriers also mediate ferromagnetic interaction.

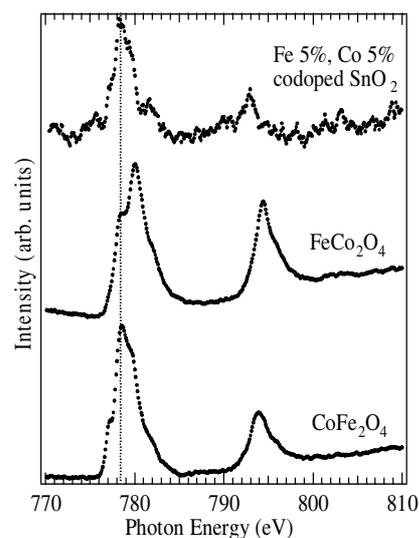


Fig. 1: Co *L*-edge x-ray absorption spectra of (Fe,Co)-codoped SnO<sub>2</sub>, FeCo<sub>2</sub>O<sub>4</sub>, and CoFe<sub>2</sub>O<sub>4</sub>.

### References

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\* jun@chem.s.u-tokyo.ac.jp