

X-ray absorption spectroscopy of defect-induced ferromagnetism: (Fe,Co) co-doped SnO₂

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Introduction

We have reported that SnO₂ doped with Fe ions shows ferromagnetism in room temperature [1]. It is known that 1% Co doping into SnO₂ 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 SnO₂ 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 SnO₂ explicitly. In this motivation, x-ray absorption spectroscopy (XAS) and Mössbauer spectroscopy were employed.

Manuscript preparation

Fe and Co co-doped SnO₂ samples were synthesized by a sol-gel method. 0.1 M of SnCl₂ · H₂O, 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 SnO₂. 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 SnO₂ is a diamagnetic material and that the only Fe or Co doped SnO₂ showed no clear hysteresis loop at room temperature. It suggests that the co-doping of Fe and Co in SnO₂ 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 SnO₂. XAS of spinel-type ferromagnetic CoFe₂O₄ ferrite (Co²⁺) and FeCo₂O₄ (Co³⁺) synthesized by sol-gel method are also shown as references. We found that the Co²⁺ electronic structure is formed in Fe

and Co co-doped SnO₂ from the comparison with the Co²⁺ spectral lineshape in CoFe₂O₄. 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 Fe³⁺ states are dominant in Fe and Co co-doped SnO₂.

Considering the above results, we suggest that the double-exchange interaction occurs through long chains of oxygen and tin atoms between diluted Fe³⁺ and Co²⁺ ions. From the charge neutrality conditions: Co²⁺ + V_O²⁻ + 2Sn⁴⁺ ↔ Co²⁺ + 2Sn³⁺ and Fe³⁺ + 1/2V_O²⁻ + Sn⁴⁺ ↔ Fe³⁺ + Sn³⁺ (V_O is oxygen vacancy), it is considered that not only the electrons from oxygen vacancies but also the elusive Sn carriers also mediate ferromagnetic interaction.

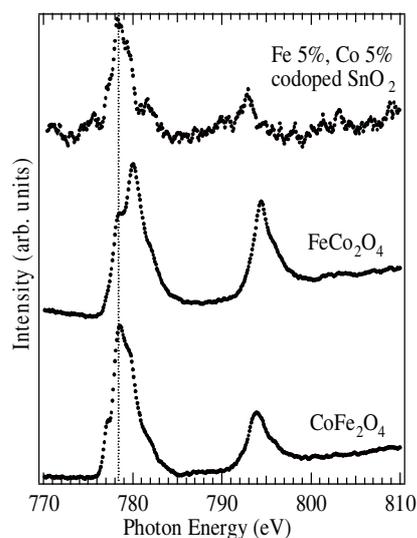


Fig. 1: Co *L*-edge x-ray absorption spectra of (Fe,Co)-codoped SnO₂, FeCo₂O₄, and CoFe₂O₄.

References

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