

Magnetic and electronic structures of two kinds of transition-metal co-doped SnO₂Jun Okabayashi^{1,*} Shin Kono^{1,2}, and Kiyoshi Nomura²¹Research Center for Spectrochemistry, The University of Tokyo 113-0033, Japan²Department of Applied Chemistry, The University of Tokyo 113-8656, Japan

1 Introduction

Since the discovery of Co-ion doped TiO₂ diluted magnetic oxides (DMO), room-temperature ferromagnetism in DMOs has opened up a new research field for spintronic applications combining the functionalities of transparency and chemical sensitivity in host oxide materials such as TiO₂, ZnO, and SnO₂. In the doped DMOs, magnetic interaction between the diluted transition metal (TM) ions mediated by oxygen vacancies is also attractive from the perspective of fundamental physics. The physical origin for room-temperature ferromagnetism in DMOs is still debated, although magnetic polaron formation and defect-induced exchange interaction are proposed. Thus, in order to investigate the mechanism for room temperature ferromagnetism, the electronic structures have to be determined explicitly. Recently, we discovered two kinds of TM co-doping enables to tune the magnetic properties at room temperature [1-3]. Here, we aim to discuss not only the synthesis of dilutely Fe–Ni co-doped SnO₂ nanoparticles but also the electronic and magnetic properties [3].

2 Experiment

TM co-doped SnO₂ samples were synthesized by a sol-gel method. 0.1 M of SnCl₂ · H₂O, and 0.01 M of TM 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).

3 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 2 % Ni co-doped case. Here, we note that pure SnO₂ is a diamagnetic material and that the only Fe or Ni doped SnO₂ showed no clear hysteresis loop at room temperature. It suggests that the co-doping of Fe and Ni in SnO₂ was effective for the ferromagnetic ordering as compared with single doping.

The valence states of Ni were determined by XAS. Figure 1 shows the X-ray absorption spectra of the Ni L-edge region in Fe–Ni co-doped SnO₂. Spectra of Ni²⁺ in NiO and Ni-ferrite (NiFe₂O₄) are shown too as references. The line shapes of the references are similar to those in a previous report. The spectrum of Fe–Ni co-doped SnO₂ remains unchanged for all concentrations [3]. Therefore, we confirm that Ni²⁺ valence states are dominant in Fe–Ni co-doped SnO₂. Furthermore, we note that the Fe L-edge cannot be detected by the XAS since the Fe L-edge regions overlap with the M_{4,5}-edge absorption peaks.

The electronic and magnetic properties of Fe ions are also discussed using Mössbauer spectrometry. The isomer shift values revealed the Fe³⁺ states for Fe and Ni co-doped SnO₂.

Although the model of defect-induced ferromagnetism is proposed for the single-ion doping [4], the enhancement of magnetization in co-doping cannot be explained within that model. The double-exchange-like mechanism through the carrier kinetics between electrons in TMs accompanying the self-carrier doping must be considered.

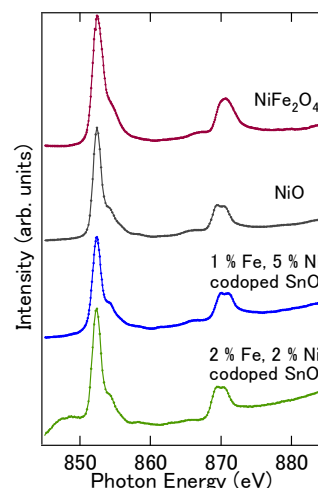


Fig. 1: X-ray absorption spectra of Fe–Ni co-doped SnO₂. As references, spectra of NiO and Ni-ferrite are also shown.

References

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