

Magnetic and Mössbauer studies of Fe and Co co-doped SnO₂

Shin Kono · Kiyoshi Nomura · Yasuhiro Yamada ·
Jun Okabayashi

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Abstract 1–5% Fe and 1% Co co-doped SnO₂ samples were synthesized by sol-gel method. Their magnetization increased with increasing crystal size of rutile SnO₂. Their Mössbauer spectra contain a broad sextet, magnetic relaxation components, and paramagnetic doublet peaks for less than 3% Fe doping. The sextet of α -Fe₂O₃ was observed instead of magnetic relaxation peaks for Fe doping of above 4%. The broad sextet and relaxation components may be related to the magnetic properties of Fe and Co co-doped SnO₂.

Keywords Fe and Co co-doped SnO₂ · Diluted magnetic semiconductors · Mössbauer spectroscopy

1 Introduction

The wide-band-gap oxide semiconductor SnO₂ is a well-known transparent material that is used in gas sensors [1]. Since the discovery of Co-ion-doped TiO₂ in 2001 [2], transition metal (TM) doped oxide semiconductors with spin-related functionalities have been attracting attention for use as room-temperature diluted magnetic semiconductors. Fe-ion-doped SnO₂ [3–5] and Co-ion-doped SnO₂ [6] have been fabricated by sol-gel method [4–6] and pulsed laser deposition [3]. However, their

S. Kono · Y. Yamada
Department of Chemistry, Tokyo University of Science, 162-8601, Tokyo, Japan

K. Nomura (✉)
School of Engineering, The University of Tokyo, Hongo 7-3-1, Bunkyo-ku,
113-8656, Tokyo, Japan
e-mail: k-nomura@t-adm.t.u-tokyo.ac.jp

J. Okabayashi
Research Center for Spectrochemistry, The University of Tokyo, 113-0033, Tokyo, Japan

magnetic properties vary depending on the growth conditions. The presence of oxygen vacancies has been found to be essential for ferromagnetic ordering. Detailed investigations are needed to determine the ferromagnetism mechanism. Coey et al. proposed a model in which defect-induced magnetism occurs between TM ions via oxygen vacancies [7, 8]. The next step in studying SnO₂-based diluted magnetic semiconductors requires controlling the saturation magnetization (M_s) and coercive field (H_c) by the TM concentrations. With this goal in mind, we have focused on TM co-doped SnO₂. Nomura et al. have observed the enhanced magnetization by co-doping Co and Fe into SnO₂ and investigated the dependence of the magnetization on the Co concentration for 1% Fe-ion doping [9].

This study is to investigate the effect of the Fe-ion concentration on the magnetism of Fe and Co co-doped SnO₂.

2 Experimental

SnO₂ powders co-doped with 1–5% Fe and 1% Co were prepared by sol-gel method. SnCl₂·2H₂O and metallic Fe and Co were dissolved in citric acid, HCl, and ethylene glycol. These solutions were condensed at 80°C and calcined at 250°C for 2 h. The black shiny gels obtained were oxidized at 550°C in air for 0.5 h and then annealed at 550°C for 3.5 h after milling. The obtained powders became brownish white in color with increasing TM concentration.

The crystal structures were determined by x-ray diffraction (XRD) using Cu K_α x-rays. The magnetic properties at room temperature were measured using a vibrating sample magnetometer (VSM). X-ray absorption spectroscopy (XAS) was performed at BL-7A, Photon Factory, High-energy Accelerator Organization to investigate the valence states of the Co ions. ⁵⁷Fe Mössbauer spectra were obtained at room temperature in transmission geometry using a ⁵⁷Co (Cr) source and the Doppler velocity was calibrated using α -Fe.

3 Results and discussion

Almost all the XRD patterns obtained for SnO₂ doped with 1–5% Fe and 1% Co reveal rutile-type SnO₂ (lattice parameters: $a = 4.74 \text{ \AA}$, $c = 3.19 \text{ \AA}$). No XRD peaks corresponding to other phases (hematite) were detected. Figure 1a shows VSM results measured at room temperature. M_s increases with increasing Fe concentration, reaching a maximum at 4% Fe and 1% Co; when the Fe concentration is increased to 5% Fe, M_s decreases and H_c increases. This enhancement in M_s occurs only in Fe and Co co-doped samples; it was not observed in samples with single ions. Crystal sizes were estimated from the line width of (110) XRD peaks using the Scherrer's formula. The relationship between the crystal size and magnetization is plotted in Fig. 1b. M_s increases with increasing crystal size. The enhancement of M_s originates from the large crystal size.

Figure 2a shows Mössbauer spectra of 1–5% Fe and 1% Co co-doped SnO₂. The spectra were fitted by two kinds of doublets originated from quadrupole splitting (QS). Fe³⁺ ionic states are revealed by isomer shift value of 0.3 mm/s. The D1 and D2 components are defined as the small and large QS, respectively. The D1 (0.8 mm/s)

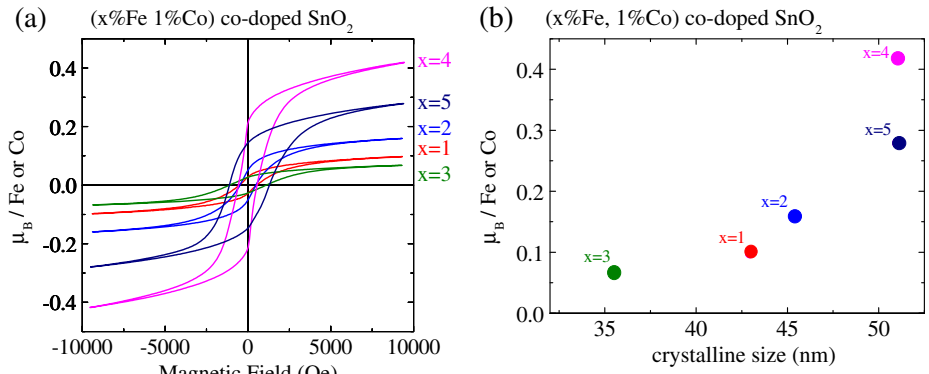


Fig. 1 **a** Magnetization curves obtained by VSM for $x\%$ Fe and 1% Co co-doped SnO₂. **b** Crystal sizes of SnO₂ estimated by XRD versus saturation magnetization by VSM

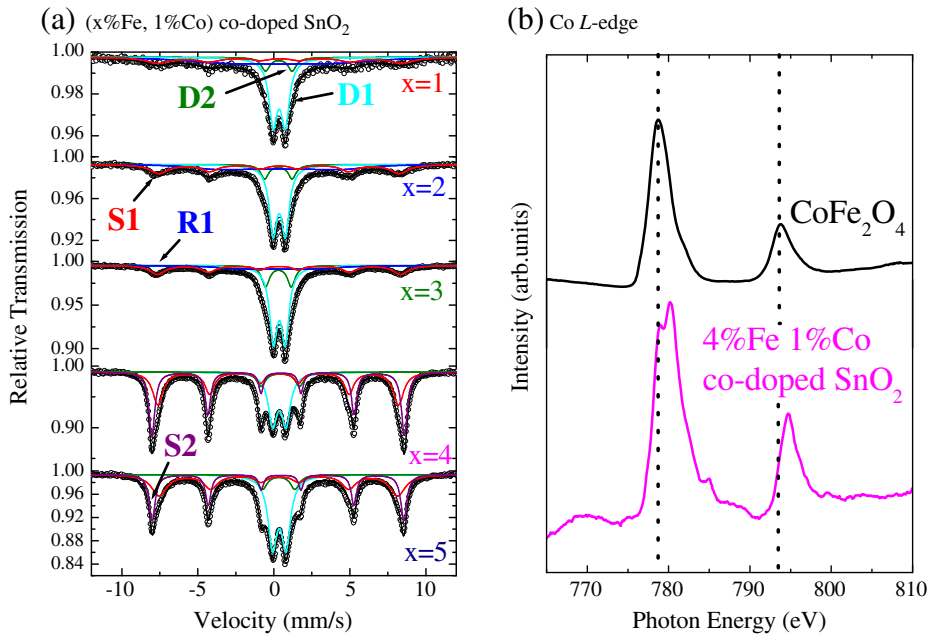


Fig. 2 **a** Mössbauer spectra of $x\%$ Fe and 1% Co co-doped SnO₂. **b** Co *L*-edge XAS 4%Fe and 1%Co co-doped SnO₂ and that of Co-ferrite

originates from Fe³⁺ ions substituted in the Sn site and that the D2 (1.8 mm/s) comes from Fe³⁺ ions near many defects (oxygen vacancies). The intensity ratio D2/D1 increases with increasing Fe concentration, which suggests that the amount of oxygen vacancies increases with increasing TM doping. A sextet component (S1) and a broad magnetic relaxation component (R1) are also observed in the Mössbauer spectra. The broad R1 component originates from spin fluctuations within the relaxation time of 10⁻⁷ s in Mössbauer effect. With increasing Fe concentration, S1 with a hyperfine

field of 49 T increases while R1 decreases. The spectral weights are considered to transfer from R1 to S1 components with increasing Fe concentration. On the other hand, a S2 component with a hyperfine field of 51 T appears, while the R1 component is greatly diminished. The Mössbauer parameters of the S2 component are quite similar to those of hematite [10], suggesting that α -Fe₂O₃ segregation occurs at more than 4% Fe and 1% Co co-doping. Since excess Fe ions contribute to nanoparticle formation, it is considered that α -Fe₂O₃ can be segregated over the solubility limit.

Figure 2b shows the XAS spectra of the Co *L*-edge region for Fe and Co co-doped SnO₂ and Co ferrite (CoFe₂O₄). Since CoFe₂O₄ is assumed to contain the Co²⁺ state, the line shapes of Fe and Co co-doped SnO₂ cannot be explained by only Co²⁺ states. The additional peaks observed at higher photon energies originate from Co³⁺ states [11]. All the samples have very similar XAS spectra. Therefore, Co²⁺/Co³⁺ mixing states are dominant.

We discuss the relationship between the magnetization and Mössbauer spectra. First, R1 and S1 components are considered to be due to spin fluctuation and spin ordering of the doped Fe ions, respectively. The suppression of R1 with increasing Fe concentration may be related to the increase of the magnetic impurity phases or hematite. Therefore, the sample up to 3% Fe and 1% Co seems to be single phase. Second, co-doping enhances M_s so that it can be used to tune the magnetic properties. It may originate from the exchange interaction between Fe³⁺ and Co²⁺/Co³⁺ ions via oxygen vacancies. Another possible cause is the formation of CoFe₂O₄. The Mössbauer spectrum of Co-ferrite (CoFe₂O₄) has been also fitted by two sextet peaks based on the assumption that there are two kinds of Fe sites in the spinel structure [12, 13]. For Fe-ion doping over the stoichiometric CoFe₂O₄, α -Fe₂O₃ compound may be segregated at doping higher than 4% Fe. The ferromagnetism mechanisms of enhanced M_s in the co-doping samples (less than 3% Fe doping) without the formation of precipitated compounds should be clarified further. Antiferromagnetic interaction between TM ions might be considered for more than 3% Fe doping. Defect-induced ferromagnetism models [7] have been proposed for single-ion doped cases. However, these models cannot explain the enhancement in M_s observed in co-doped samples. A double-exchange-like mechanism through carrier kinetics between Fe³⁺ (*d*⁵) and Co²⁺ (*d*⁷) electrons may give rise to the enhanced M_s .

4 Conclusion

Fe and Co co-doped SnO₂ synthesized by sol-gel method. Fe and Co co-doping was found to enhance the magnetization. Mössbauer spectra revealed that the magnetic relaxation and sextet components may result from diluted magnetism for less than 3% Fe doping. However, the magnetic enhancement for 4% Fe and 1% Co doping may be mainly due to Co ferrite formed with hematite precipitation.

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