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Magnetic and electronic structures of Fe and Mn co-doped SnO_2

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1 Introduction

Since the discovery of Co-ion doped TiO_2 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 TiO_2, ZnO, and SnO_2. 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. We aim to discuss not only the synthesis of dilutely Fe–Mn co-doped SnO_2 nanoparticles but also the electronic and magnetic properties [1].

2 Experiment

Fe and Mn co-doped SnO_2 samples were synthesized by a sol-gel method. 0.1 M of $SnCl_2 \cdot H_2O$, and 0.01 M of Fe and Mn 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 Spectroschemistry, The University of Tokyo).

3 Results and Discussion

X-ray diffraction (XRD) patterns of all samples corresponded to the rutile-type crystalline structure of SnO_2. 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 % Mn co-doped case. Here, we note that pure SnO_2 is a diamagnetic material and that the only Fe or Mn doped SnO_2 showed no clear hysteresis loop at room temperature. It suggests that the co-doping of Fe and Mn in SnO_2 was effective for the ferromagnetic ordering as compared with single doping.

The valence states of Mn were determined by XAS. Figure 1 shows the X-ray absorption spectra of the Mn L-edge region in Fe–Mn co-doped SnO_2. Spectra of Mn^{4+} in MnO_2, Mn^{3+} in Mn_2O_3 and Mn_3O_4, and Mn^{2+} in MnO are shown too as references. The shape of the peak at higher photon energy depends on the higher valence states of Mn ions. The line shapes of the references are similar to those in a previous report. The spectrum of Fe–Mn co-doped SnO_2 remains unchanged for all concentrations. Therefore, we confirm that Mn^{2+}/Mn^{3+} mixed valence states are dominant in Fe–Mn co-doped SnO_2. 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 Fe^{3+} states for Fe and Mn co-doped SnO_2.

Although the model of defect-induced ferromagnetism is proposed for the single-ion doping [2], the enhancement of magnetization in co-doping cannot be explained within that model. The double-exchange-like mechanism through the carrier kinetics between Fe^{3+} (d^5) and Mn^{3+} (d^4) electrons accompanying the self-carrier doping must be considered.

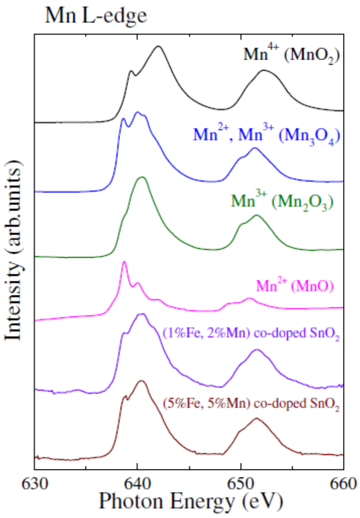

Fig. 1: X-ray absorption spectra of Fe–Mn co-doped SnO_2. As references, spectra of MnO_2, Mn_3O_4, Mn_2O_3, and MnO are also shown.

References

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