Mössbauer and x-ray absorption studies in Fe and V co-doped SnO$_2$

Jun Okabayashi · Shin Kono · Yasuhiro Yamada · Kiyoshi Nomura

Abstract Ferromagnetic nanoparticles of iron and vanadium co-doped SnO$_2$ were synthesized by a sol-gel method. Fe and V co-doped SnO$_2$ enhanced the magnetization, which showed the maximum saturation magnetization ($M_s$) at 1 % of Fe and 1 % of V co-doping. With further increasing the amounts of Fe and V co-doping into SnO$_2$ host, the $M_s$ decreased. Chemical states of vanadium ions were deduced as V$^{5+}$ states by x-ray absorption spectroscopy. Mössbauer spectrometry revealed that the intensities of sextet components are related to the $M_s$, which indicates that small amounts of Fe and V co-doping is effective to enhance $M_s$.

Keywords Diluted magnetism · Mössbauer spectrometry · Magnetization · Co-doping

1 Introduction

SnO$_2$ wide-gap semiconductors doped with transition-metals have been interesting due to their room-temperature ferromagnetism, transparency, and chemical sensitivity for future spin-related devices [1, 2]. There are several reports for transition
metal (TM) doping into oxide semiconductors such as SnO₂, ZnO, and TiO₂, which show room-temperature ferromagnetism even by doping of the dilute TMs with less than a few percentages. However, the physical origin for room-temperature ferromagnetism in diluted magnetic oxides through the oxygen vacancies is still debated at this moment. Fe doping into SnO₂ has been investigated toward the fabrication of new kinds of diluted magnetic oxides through oxygen vacancies [1, 2]. Vanadium doping into SnO₂ also becomes one of candidates for diluted magnetic oxides due to the smaller ionic radius of V ion (V⁴⁺, 0.58 Å, V⁵⁺, 0.54 Å) than that of Sn ion (Sn⁴⁺, 0.69 Å), which is expected to substitute to Sn site in host SnO₂ [3–8]. Active catalytic behaviors of V doped SnO₂ have also reported [9, 10]. Recent studies suggest that the co-doping of different TM ions is effective to enhance the saturation magnetization (Mₛ) such as Fe and Co co-doping [11, 12] or Fe and Mn co-doping [13]. With this motivation, we focus on Fe and V co-doping into SnO₂ in order to elucidate each advantage of two TM elements. Both Fe and V co-doping into SnO₂ enables us to tune the magnetic properties as ferromagnetic oxides.

In this paper, we aim to synthesize Fe and V co-doped SnO₂ nanoparticles and to discuss the electronic and magnetic properties by Mössbauer spectrometry and x-ray absorption spectroscopy (XAS) for understanding the origin for ferromagnetism.

2 Experimental

Fe and V co-doped SnO₂ samples with various concentrations of Fe and V ions were synthesized by a sol-gel method. SnCl₂·2H₂O of 0.1 M, enriched ⁵⁷Fe chlorides and vanadyl chloride (VOCl₃) of 0.01 M solutions with citric acid and HCl were mixed together with ethylene glycol according to the nominal compositions. These solutions were condensed at about 80 °C, calcinated at 250 °C for 2 h, and finally annealed at 550 °C for 2 h. As a reference, V oxide calcinated in the air conditions for V₂O₅ particles is also prepared.

Nanoparticles obtained were evaluated by x-ray diffraction (XRD) and transmission electron microscope (TEM) for the determination of lattice constants and crystalline sizes, respectively. Magnetic properties were investigated by vibrating sample magnetometer (VSM) at room temperature. Electronic and magnetic properties of doped TMs were studied by XAS and Mössbauer spectrometry. XAS were performed at BL-7A, in High-energy accelerator organization, Photon Factory (KEK-PF). Mössbauer spectrometry was performed using the radiation from ⁵⁷Co source. Doppler velocity was calibrated using α-Fe.

3 Results and discussion

First, we performed a thermogravimetric analysis to determine the thermal decomposition of the precursor powders. As the temperature is increased from room temperature to 550 °C, approximately 65 % weight loss was observed due to the removal of the precursor as shown in Fig. 1. However, above 550 °C, no further weight loss was observed, suggesting that the calcination at 550 °C is enough for these sol-gel synthesized materials. Therefore, the calcination temperature of 550 °C is adopted for the fabrication of Fe and V co-doped SnO₂.
Mössbauer and x-ray absorption studies in Fe and V

**Fig. 1** Thermogravimetric analysis for 1 % Fe and 1 % V co-doped SnO$_2$

![Thermogravimetric analysis](image)

![Graph](image)

**Fig. 2** a X-ray diffraction patterns for Fe and V co-doped SnO$_2$. b TEM image of 1 % Fe and 1 % V co-doped SnO$_2$

![X-ray diffraction patterns](image)

![TEM image](image)

XRD patterns of Fe and V co-doped SnO$_2$ shown in Fig. 2a correspond to the rutile-type crystalline structure ($P4_2/mnm$) of SnO$_2$. No secondary phases were observed within the detection limit in XRD up to 5 % Fe and 5 % V concentrations. The lattice parameters of SnO$_2$ are $a = 0.475$ nm and $c = 0.320$ nm. Crystalline sizes were estimated to be approximately 30 nm from the analysis of XRD line widths using Scherrer’s formula. Figure 2b shows the TEM image of 1 % Fe and 1 % V co-doped SnO$_2$ nanoparticles. Uniform particle diameters of 20–30 nm were observed, and the particle sizes are consistent with those determined using XRD.
The VSM data of Fe and V co-doped SnO$_2$ with different concentrations measured at room temperature are shown in Fig. 3. The diamagnetic behavior is observed for pure SnO$_2$. The 1 % Fe single doping and 1 % V single doping into SnO$_2$ do not show clear hysteresis loops at room temperature. For both Fe and V co-doped SnO$_2$, the 1 % Fe and 1 % V co-doping into SnO$_2$ exhibits maximum $M_s$ as shown in Fig. 3a and b. With increasing the V concentration further, the $M_s$ is suppressed and coercive field increases. In the case of 5 % Fe and V co-doped case, hysteresis behavior cannot be observed. This tendency is quite different from the previous studies in Fe and Co co-doped SnO$_2$ cases [11, 12]. The reason why $M_s$ decrease at high concentrations of Fe and V might correspond to the short-rage interaction between Fe and V through the oxygen vacancies. We note that the possible precipitates such as $\alpha$-Fe$_2$O$_3$ (hematite), V$_2$O$_5$, and Fe-V compound alloy are antiferromagnetic compounds. Although another possible candidates of $\alpha$-Fe$_2$O$_3$ (hematite) behave as weak ferromagnets, $M_s$ decreases with increasing Fe concentration. Therefore, simple $\alpha$-Fe$_2$O$_3$ formation cannot explain the changes of $M_s$.

Figure 4 shows the Mössbauer spectra of Fe and V co-doped SnO$_2$. The shifts of center of gravity in doublet (isomer shift; IS) and the splitting width between doublets (quadrupole splitting; QS) are originated from the electron density and the electric field gradient around the nucleus of $^{57}$Fe, respectively. The parameters of IS = 0.3 mm/s are consistent with Fe$^{3+}$ high spin states. Two kinds of QS components (D1 and D2) are used for the fitting in all cases. D1 with QS = 0.8 mm/s is assumed to be due to Fe ion substituting into the Sn sites. D2 is clearly seen in the small shoulder of main doublets. The D2 components with QS = 1.7 mm/s are related to the Fe states in the vicinity of the oxygen vacancies [11, 12]. The sextet peaks with hyperfine field of 51 T, observed in the Mössbauer spectrum of 1 % V and 1 % Fe co-doped SnO$_2$, may be considered as hematite-like clusters from Mössbauer parameters. First, in Fig. 4a, Fe concentrations are fixed to 1 %. With increasing V concentrations, sextet intensities are suppressed. Second, in the doping of both 2 % of Fe and V co-doping cases as shown in Fig. 4b, sextet peaks become broad, which suggests that higher concentrations of Fe and V suppress the simple formation of hematite. Broadening of sextet might be related to the increase of coercive field in VSM results. Furthermore, for both 5 % co-doping, sextet peaks are suppressed completely. This tendency is consistent with the suppression in $M_s$. It suggests that the segregations of ordered...
Mössbauer and x-ray absorption studies in Fe and V

Fe or ferromagnetic Fe oxides are negligible. V doping clearly modulates the single Fe-ion doping effects.

X-ray absorption spectra of V L-edges are shown in Fig. 5. Spectrum of V$_2$O$_5$ is also presented. Two peaks of 521 and 527.5 eV correspond to 2p$_{3/2}$ and 2p$_{1/2}$ peaks, respectively. Fine structures appear at lower photon energies in V$_2$O$_5$, while broadened line shapes are observed in Fe and V co-doped cases. In the region above 530 eV, O K-edge absorption and related pre-edge spectra are overlapped. XAS spectra of V$_x$O$_y$ by the reduction of oxygen also show similar line shapes [14]. Therefore, the simple V$_2$O$_5$ segregation is not plausible for the Fe and V co-doped SnO$_2$.

Here, we discuss the relationship between VSM and Mössbauer spectra of Fe and V co-doped SnO$_2$. Similar tendency between them reveals that Fe ions contribute to ferromagnetic ordering. In both 1 % Fe and V co-doping, distorted hematite-like ferromagnetic clusters, which are not detected by XRD, are formed. This is promoted by V doping, since without V co-doping hematite clusters are not segregated at 1 % Fe doping. Interestingly, with increasing co-doping concentrations up to 2 % of both Fe and V ions, broad sextet components are related to the increase of coercive field, which can be explained by the smaller size distribution of distorted hematite-like ferromagnetic clusters promoted by V ions. However, in both 5 % co-doping, magnetic ordering between Fe ions are completely suppressed by V doping, meaning the nonexistence of spin-ordered hematite. The suppression of ferromagnetism in higher concentrations of Fe and V may be explained by the superparamagnetic behavior. This tendency is quite different from the case of Fe and Co co-doping into SnO$_2$ [11, 12]. One of the reasons is that V$^{5+}$ states compensate the oxygen vacancies and then disturb the magnetic ordering between Fe ions. Therefore, V ions...
can enhance the $M_s$ only when the doping is low. Another reason is the formations of Sn doped Fe$_2$O$_3$ and Sn doped V$_2$O$_5$. Broadening in the line shapes of V L-edge XAS might suggest the intermixing of Sn ions.

4 Conclusions

Fe and V co-doped SnO$_2$ were synthesized by a sol-gel method. Fe and V co-doping enhanced the $M_s$, which showed the maximum $M_s$ at 1% of V and 1% of Fe co-doping. With further increasing the amounts of V and Fe co-doping into SnO$_2$ host, the $M_s$ decreased. Chemical states of vanadium ions were deduced as V$^{5+}$ states by XAS. Mössbauer spectrometry revealed that the intensity of sextet components is related to the $M_s$, which indicates that small amounts of Fe and V co-doping is effective to enhance $M_s$.

Acknowledgements This study was partially supported by The Murata Foundation and Nippon Sheet Glass Foundation for Materials Science and Engineering. XAS was performed under Project 2011G657 at the Institute of Materials Structure Science in KEK.

References

Mössbauer and x-ray absorption studies in Fe and V