

Mössbauer and x-ray absorption studies in Fe and V co-doped SnO₂

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Abstract Ferromagnetic nanoparticles of iron and vanadium co-doped SnO₂ were synthesized by a sol-gel method. Fe and V co-doped SnO₂ 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 SnO₂ host, the M_s decreased. Chemical states of vanadium ions were deduced as V⁵⁺ 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

SnO₂ 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

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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 (M_s) 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

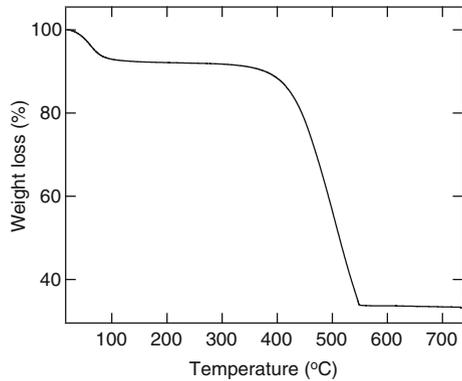
Fe and V co-doped SnO₂ samples with various concentrations of Fe and V ions were synthesized by a sol-gel method. SnCl₂·2H₂O of 0.1 M, enriched ⁵⁷Fe chlorides and vanadyl chloride (VOCl₃) of 0.01 M solutions with citric acid and HCl were mixed together with ethylene glycol according to the nominal compositions. 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.

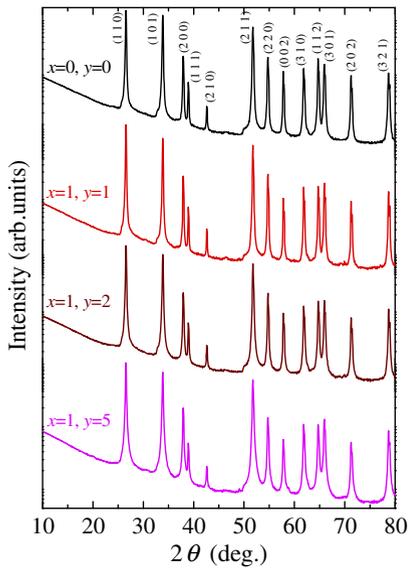
3 Results and discussion

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.

Fig. 1 Thermogravimetric analysis for 1 % Fe and 1 % V co-doped SnO₂



(a) ($x\%$ Fe, $y\%$ V) co-doped SnO₂



(b)

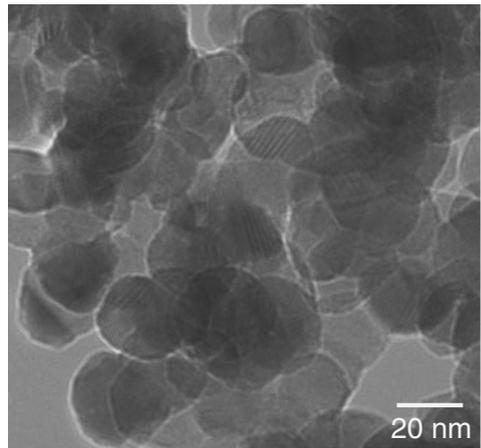


Fig. 2 **a** X-ray diffraction patterns for Fe and V co-doped SnO₂. **b** TEM image of 1 % Fe and 1 % V co-doped SnO₂

XRD patterns of Fe and V co-doped SnO₂ shown in Fig. 2a correspond to the rutile-type crystalline structure ($P4_2/mnm$) of SnO₂. No secondary phases were observed within the detection limit in XRD up to 5 % Fe and 5 % V concentrations. The lattice parameters of SnO₂ 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 SnO₂ nanoparticles. Uniform particle diameters of 20–30 nm were observed, and the particle sizes are consistent with those determined using XRD.

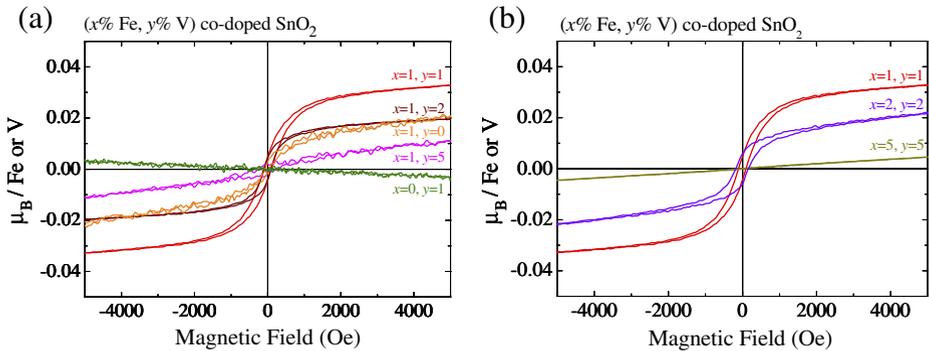


Fig. 3 Magnetization curves of Fe and V co-doped SnO_2 obtained by VSM

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-range interaction between Fe and V through the oxygen vacancies. We note that the possible precipitates such as $\alpha\text{-Fe}_2\text{O}_3$ (hematite), V_2O_5 , and Fe-V compound alloy are antiferromagnetic compounds. Although another possible candidates of $\alpha\text{-Fe}_2\text{O}_3$ (hematite) behave as weak ferromagnets, M_s decreases with increasing Fe concentration. Therefore, simple $\alpha\text{-Fe}_2\text{O}_3$ 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

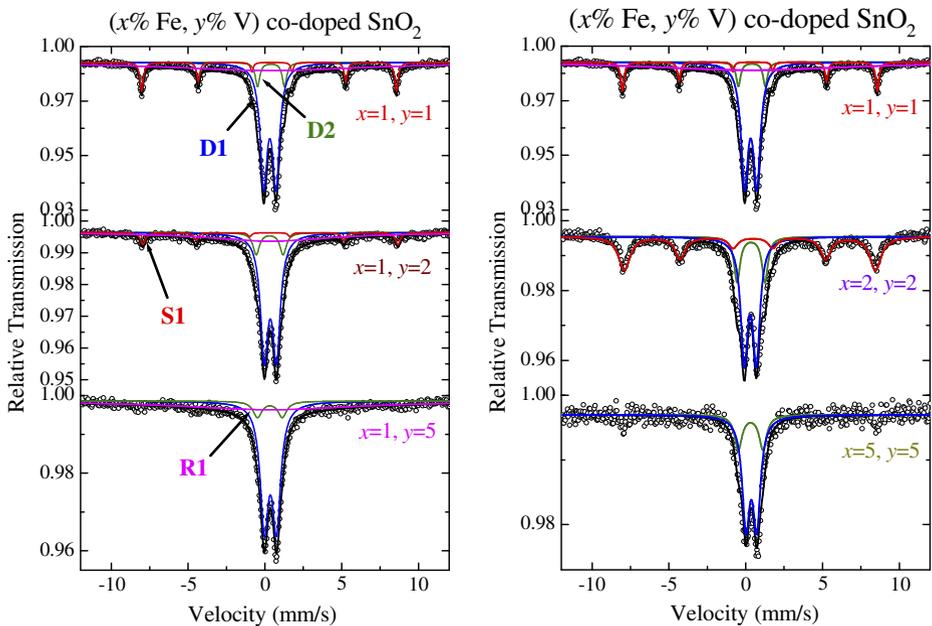


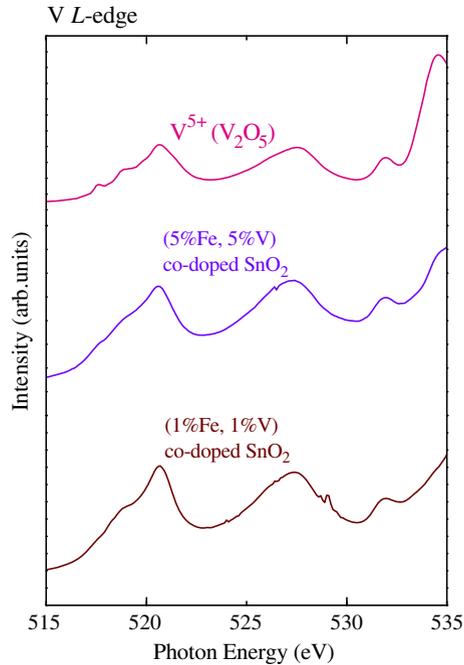
Fig. 4 Mössbauer spectra of Fe–V co-doped SnO₂. Fitting results for D1, D2, S1 components are also shown

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 V₂O₅ 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 V₂O₅, 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_xO_y by the reduction of oxygen also show similar line shapes [14]. Therefore, the simple V₂O₅ segregation is not plausible for the Fe and V co-doped SnO₂.

Here, we discuss the relationship between VSM and Mössbauer spectra of Fe and V co-doped SnO₂. 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 SnO₂ [11, 12]. One of the reasons is that V⁵⁺ states compensate the oxygen vacancies and then disturb the magnetic ordering between Fe ions. Therefore, V ions

Fig. 5 X-ray absorption spectra of Fe–V co-doped SnO₂. As references, spectrum of V₂O₅ is also shown



can enhance the M_s only when the doping is low. Another reason is the formations of Sn doped Fe₂O₃ and Sn doped V₂O₅. Broadening in the line shapes of V L-edge XAS might suggest the intermixing of Sn ions.

4 Conclusions

Fe and V co-doped SnO₂ 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 SnO₂ host, the M_s decreased. Chemical states of vanadium ions were deduced as V⁵⁺ 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 .

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