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Dilute Magnetism and Mössbauer Study of Nanoscaled SnO$_2$ Co-Doped with Fe, Co, and Sb, Prepared by Sol-Gel Method

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Abstract. SnO$_2$-based oxides doped with $^{57}$Fe, prepared by a sol-gel method, are reviewed, and Sb doping effect on (Fe,Co)-doped SnO$_2$ and Fe doping effect on (Sb,Co)-doped SnO$_2$ were investigated. The crystalline grains of SnO$_2$ were grown and the magnetic properties were improved in the doping range of 3–5 at.% of Sb. It was found that the intensity of magnetic broad sextet in Mössbauer spectra correlates with the saturation magnetization for 3 at.% Sb-, 1 at.% Co- and several at.% Fe-doped SnO$_2$. When the doping exceeds 3 at.% of Fe, hematite ($\alpha$-Fe$_2$O$_3$) clusters were produced in addition to maghemite ($\gamma$-Fe$_2$O$_3$)-like clusters or defects inducing ferromagnetism. The origins of the dilute ferromagnetism are discussed.

Keywords: SnO$_2$, Fe, Co, and Sb doping, sol-gel method, thermal decomposition, dilute ferromagnetic oxide, $^{57}$Fe Mössbauer spectroscopy

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INTRODUCTION

Semiconductors with wide band gap energy are supposed to show a ferromagnetic behavior at room temperature when doped with the magnetic ions, and are expected to be applied as components in new nanodevices for spintronics [1]. Transparent oxide semiconductors such as TiO$_2$, ZnO, and SnO$_2$ have the band gap energy of larger than 3.0 eV, and the effect of doping of magnetic ions (e.g., Fe, Co, and Mn ions) at low concentrations have been studied by many researchers [2,3]. Dilute ferromagnetic oxides have Curie temperatures far above 300 K. Conventional superexchange or double-exchange interactions cannot produce a long-range magnetic order at concentrations of magnetic cations of a few percent [4]. This study contains both the application-related and fundamental issues, such as what is the origin of room-temperature ferromagnetism, why low-concentration doping of magnetic ions induces a magnetic moment enlargement, and how the impurity magnetic ions exist in oxide semiconductors, e.g., it is clustered or dispersed.

We have prepared the powders and films of SnO$_2$ doped with $^{57}$Fe ions because $^{57}$Fe ions become magnetic ions with high spins and can be used as nanoscaled probes at atomic levels [5,6]. The enriched $^{57}$Fe ions are necessary for Mössbauer spectrometry as the natural abundance of $^{57}$Fe atoms is only 2%.

On the other hand, a chemical preparation method is preferred to a physical vapor deposition in order to use the enriched $^{57}$Fe ions effectively. The features of a sol-gel method are summarized as follows: (i) The oxides with a certain composition can be...
prepared at relatively low temperatures, compared with the sintering of ceramics at high temperatures of more than 1000 °C; (ii) It is possible to mix some ions easily on a molecule (atomic) level, and it is easy to control a minor constituent; (iii) It is easy to adjust the various compositions and concentrations of magnetic ions doped into samples for material research; (iv) The uniform powder is available for a relatively short time; (v) The samples are producible in large quantities since the manufacturing efficiency is high; (vi) Mössbauer nucleus of $^{57}\text{Fe}$ can be effectively used as magnetic nanoprobes.

The Sb$^{5+}$ ions substituted at the Sn$^{4+}$ site in SnO$_2$ can induce an n-type electrical conductivity of SnO$_2$ as donor impurities [7]. Sb ions can also enhance the solubility of Fe ions in SnO$_2$. Impurity phases have not been clearly detected in X-ray diffraction (XRD) patterns of (Fe,Sb)-doped SnO$_2$, however, all XRD peaks of the rutile structure of SnO$_2$ are broadened symmetrically and reduced in the intensity by Sn doping in SnO$_2$. The lattice parameters showed a tendency to decrease with increasing the amounts of doped Sb and Fe [8].

In the case of only Fe-doped SnO$_2$, the ferromagnetism appears with the increase of Fe ions doped, whereas in the case of only Co doping, the ferromagnetism is weaken with the increase of Co ions doped [9]. We studied what magnetic behavior is obtained by co-doping with Fe and Co. It is found that the addition of both dilute (Fe,Co) ions enhances the behavior of magnetization [10], compared with single-ions-doped SnO$_2$.

In this paper, we have prepared SnO$_2$ samples co-doped with three elements, i.e., Fe, Co, and Sb. We report on the addition effect of Sb on dilute (Fe,Co)-doped SnO$_2$ and on Fe-doping effect observed for (Sb,Co)-doped SnO$_2$. It is confirmed that Mössbauer spectrometry is a good tool to characterize nanoscaled magneto-semiconductors.

**EXPERIMENTAL DETAILS**

Samples of SnO$_{2-\delta}$ co-doped with $^{57}\text{Fe}$, Co, and Sb were obtained by a sol-gel method. 0.01 M solutions of Sn, Sb, Co, and $^{57}\text{Fe}$ were prepared, respectively, and mixed at the appropriate amounts of each ion. Sn and Sb solutions were obtained by adding ethylene glycol, citric acid monohydrate, and SnCl$_2$·2H$_2$O or Sb(III) acetate, respectively, whereas $^{57}\text{Fe}$ solutions were prepared by mixing citric acid solutions of metal $^{57}\text{Fe}$. Some solutions were prepared using HCl solutions of SnCl$_4$, CoCl$_2$, and FeCl$_3$. The proper amount of enriched $^{57}\text{Fe}$ was added into natural abundant Fe solution in advance when the initial compositions were adjusted. The solutions were prepared by addition of ethylene glycol and citric acid solution to the mixed chloride solutions, and condensed by heating at around 90 °C. The xerogel obtained was fired at a temperature of about 250 °C, annealed at 550 °C for one hour, mixed, and annealed further for 3.5 hours. Doping percentage of impurities for Sn oxides shows atomic percentage of initial compositions. The products were characterized by X-ray diffraction (XRD), vibrating sample magnetometer (VSM), and Mössbauer spectrometry.

We have prepared powders with nanoparticles with 20–50 nm in a diameter using a sol-gel method. XRD showed only the rutile structure of SnO$_2$ without peaks belonging to any impurities.
RESULTS

Sb doping effect on (Fe,Co)-doped SnO$_2$

The doping effect of Sb ions were investigated by doping with 1, 3, 5, and 10% of Sb into (1% Fe, 1% Co)-doped SnO$_2$ and (2% Fe, 1% Co)-doped SnO$_2$ as shown in Fig. 1. The color of samples changed from brown to grey brown with an increase in the Sb doping rates. XRD showed only rutile structure of SnO$_2$, and the crystalline diameters were obtained by the Scherrer formula. The coercivity of all samples was ~1000 Oe. Sb$^{5+}$ was effectively incorporated into SnO$_2$ matrix in such a way that the Sb doping enhanced the magnetization of (Fe,Co)-doped SnO$_2$ except for doping with 10% of Sb.

![Graphs showing relationship between crystalline sizes and Sb concentrations, saturation magnetization, and crystalline size of SnO$_2$ doped with Sb, Fe, and Co.](image)

FIGURE 1. (a) Relationship between crystalline sizes and Sb concentrations of (Fe,Co)-doped SnO$_2$, (b) relationship between saturation magnetization and Sb concentrations, and (c) relationship between saturation magnetization and crystalline size of SnO$_2$ doped with Sb, Fe, and Co. No impurity peaks in XRD were observed in addition to the rutile structure peaks of SnO$_2$. Crystalline sizes of the SnO$_2$ powders were 42–76 nm.
As shown in Fig. 1, the saturation magnetization has a tendency to become bigger as the crystalline sizes increase, especially for (1% Fe,1% Co)-doped SnO$_2$. Saturation magnetizations were not much changed for crystalline sizes between 50 and 70 nm; the maximum in saturation magnetization was observed for the doping level from 3 to 5% of Sb for (2% Fe,1% Co)-doped SnO$_2$ and (1% Fe,1% Co)-doped SnO$_2$.

Mössbauer spectra were first decomposed into two paramagnetic doublets and one magnetic sextet. The isomer shifts ($IS$) and quadruple splitting ($QS$) values of two doublets are plotted in Fig. 2. $IS$ and $QS$ values of doublet 1 (D1) were found between 0.35 and 0.37 mm/s, and 0.7 and 0.9 mm/s, respectively. D1 is assigned to paramagnetic Fe$^{3+}$, located at the site of Sn$^{4+}$ in the rutile structure. The other doublet 2 (D2) is assigned to paramagnetic Fe$^{3+}$ species, coordinated with less than 6 oxygen ions as the $IS$ values of D2 are relatively small (0.27 to 0.29 mm/s), and the $QS$ values are large (1.5 to 1.9 mm/s). The large $QS$ values of D2 are due to the distorted structure induced by the oxygen deficiency around Fe$^{3+}$ species.

**FIGURE 2.** (a) Mössbauer spectra of (1% Fe,1% Co)-SnO$_2$ doped with various % of Sb ions, (b) relationship between $IS$ and $QS$ values of doublets, and (c) dependence of the area intensity of D2 on Sb concentration.
With the increase of Sb, the area intensity of D2 decreased from 17.5 to 13% for (1% Fe,1% Co)-doped SnO$_2$ and from 18 to 14% for (2% Fe,1% Co)-doped SnO$_2$. This suggests that Sb$^{5+}$ with a small ionic radius reduced the number of oxygen deficiency by incorporation in the lattice of SnO$_2$. For doping with 10% of Sb, paramagnetic Fe$^{2+}$ species were detected as a doublet (D3). This suggests that a large amount of Sb$^{5+}$ is easily oxidized from Sb$^{3+}$ by annealing, however, a part of Fe$^{3+}$ is inversely reduced into Fe$^{2+}$.

**Fe doping effect on (Co,Sb)-SnO$_2$**

Next, the Fe doping effects have been investigated using (1% Co,3% Sb)-doped SnO$_2$. The magnetization curves and the relationship between the saturation magnetization and Fe concentration are shown in Fig. 3. The saturation magnetization reached the maximum value of 0.20 $\mu_B$/Fe or Co. The coercivity was $\sim$2000 Oe, which was larger than for the low Fe doping. The saturation magnetization increased with Fe doping, however, it was not constantly related with the Fe concentration.

![Graph showing magnetic hysteresis curves and saturation magnetization values](image.png)

**FIGURE 3.** (a) Magnetic hysteresis curves and (b) saturation magnetization values of (1% Co,3% Sb)-SnO$_2$ doped with various Fe contents.

The Mössbauer spectra of SnO$_2$, including 1% of Co and 3% of Sb, doped with various Fe contents are shown in Fig. 4a. The Mössbauer spectra were decomposed into two doublets and two sextets as the magnetic sextet peaks were asymmetric. For the sextet (M2), hyperfine magnetic field $B_{hf} = 51.4$ T, $\mathcal{I}S = 0.38$ mm/s, $QS = -0.20$ mm/s, and linewidth $\Gamma = 0.31$ mm/s were derived. The other sextet (M1) consists of broad peaks with $B_{hf} = 49.4$ T, $\mathcal{I}S = 0.35$ mm/s, $QS = -0.09$ mm/s, and $\Gamma = 0.60$ mm/s. The former magnetic component is due to presence of hematite ($\alpha$-Fe$_2$O$_3$) and the latter can be assigned to maghemite ($\gamma$-Fe$_2$O$_3$)-like clusters or to configured spins in dilute magnetic oxides.

As shown in Fig. 4b, the area intensity of M1 against Fe concentrations showed a change similar to that of magnetization as shown in Fig. 3. The broad sextet may reflect a dilute ferromagnetic behavior present at the Fe doping rate below 2%. Above
3% Fe doping, the ferromagnetic clusters might be formed together with a formation of hematite clusters although the impurity such as hematite was not clearly detected by XRD.

**FIGURE 4.** (a) Mössbauer spectra and (b) relationship between Fe concentration and area intensity of subspectra components (D1, D2, M1) of (1% Co, 3% Sb)-doped SnO₂ with various Fe contents.

**DISCUSSION**

⁵⁷Fe Mössbauer spectra of (Fe,Co)-doped SnO₂ consisted of two paramagnetic doublets and two sextets of high-spin Fe³⁺ species. The broad magnetic sextet was drastically modulated by doping with 0.5–2% of Co and 1% of Fe. With further increase of Co ions, magnetic components for 1% Fe-doped SnO₂ decreased and the saturation magnetization also decreased [10]. With an increase in Fe contents for 1% Co-doped SnO₂, the magnetization increased and a sharp sextet of α-Fe₂O₃ appeared additionally when the concentration of Fe exceeded 4% Fe [11]. In the case of 3% Sb-, 1% Co-, and various % Fe-doped SnO₂, identical results were obtained. The sharp sextet observed is similar to that of α-Fe₂O₃.

We have experienced that the magnetic hysteresis of some doped SnO₂ was enhanced after annealing in vacuum (10⁻⁴ torr). It is found that the magnetic defects produced by annealing in vacuum are one of important factors for induced dilute ferromagnetism. On the other hand, we tried to prepare SnO₂ doped with 1 % of Fe³⁺ and 1% of V⁵⁺ in a place of Sb⁵⁺. The compound showed a very weak magnetic hysteresis. The Mössbauer spectrum did show a sharp sextet of hematite in addition to two doublets of Fe³⁺. Addition of V⁵⁺ did induce solely a precipitation of Fe₂O₃ and prevent from a growth of SnO₂ grains. The magnetization decreased with an increase.
of V doping. V\(^{5+}\) is so small in ionic radius (0.054 nm) to incorporate into the SnO\(_2\) lattice. The ionic radii for O\(^{2-}\), Sn\(^{4+}\), Sb\(^{5+}\), and Fe\(^{3+}\) are 0.140, 0.069, 0.060, and 0.064 nm, respectively.

If Fe ions are overdoped in the (Sb,Co)-doped SnO\(_2\), there is a high possibility that hematite and maghemite clusters are precipitated. At the nanograin boundary of hematite precipitated from SnO\(_2\), magnetic defects might be induced at great extent. It is considered that ferromagnetism is enhanced together with the formation of the ferromagnetic clusters by dilute Fe ions or Co ions through electron spin trapped at grain boundary defects of SnO\(_2\). \(^{119}\)Sn can be sensitive to magnetic defects and seen by in-field Mössbauer spectrometry [12]. This is similar to a magnetic behavior of Ni-doped SnO\(_2\), annealed repeatedly at a temperature of 200 °C [13].

**CONCLUSIONS**

Sb doping effect on (Fe,Co)-doped SnO\(_2\) and Fe doping effect on (Sb,Co)-doped SnO\(_2\) were investigated. The crystalline grains of SnO\(_2\) were grown and the magnetic properties were improved at the doping range of 3–5% of Sb. In the case of non Co-doped SnO\(_2\), a high amount of Fe and Sb up to ~20% can be incorporated into SnO\(_2\) [8]. However, when even 1% of Co ions were doped, for concentration of Fe higher than 3%, hematite clusters were produced in addition to maghemite-like clusters or defects induced ferromagnetism below 3% of Fe doping. It is found that the intensity of magnetic broad sextet in the Mössbauer spectra correlates with the saturation magnetization, which increases with an increase in Fe concentration when it exceed a value of 3% for (3% Sb,1% Co)-doped SnO\(_2\). Even if magnetic nanoparticles were precipitated, quantum dots might be formed in the SnO\(_2\) semiconductor.

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