

Magnetic property and Mössbauer analysis of $\text{SrSn}_{1-x}\text{Fe}_x\text{O}_3$ prepared by a sol-gel method

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Abstract The dilute magnetic properties of $\text{SrSn}_{1-x}\text{Fe}_x\text{O}_3$ ($x = 0.01 - 0.15$) prepared by sol-gel and thermal decomposition methods were investigated by ^{57}Fe Mössbauer spectrometry, magnetometry, and X-ray diffractometry. It was found that SrSnO_3 doped with 2–8 % Fe show weak ferromagnetism although only paramagnetic doublets are observed in ^{57}Fe Mössbauer spectra at room temperature (RT), whereas SrSnO_3 doped with 10–15 % Fe show relatively strong ferromagnetism, and the sextets are additionally observed in the ^{57}Fe Mössbauer spectra at RT. The weak ferromagnetism by doping 2–8 % Fe is considered to be caused by the induced magnetic defects, and the ferromagnetism by doping 10–15 % Fe are considered mainly due to the magnetic coupling between dilute Fe^{3+} partially substituted at Sn^{4+} sites in the orthorhombic structure of $\text{SrSnO}_{3-\delta}$ accompanying the oxygen deficiencies. It is further remarkable that poor crystalline 8 % Fe doped $\text{SrSnO}_{3-\delta}$ obtained by annealing at 600 °C shows relatively high saturation magnetization and low coercivity.

Keywords Fe doped SrSnO_3 · Dilute magnetism of perovskite oxides · Mössbauer spectrometry · XRD

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1 Introduction

Wide-bandgap oxide semiconductors and insulators such as ZnO, SnO₂, TiO₂, IZO (indium zinc oxides), SiO₂, Al₂O₃ etc. doped with dilute ⁵⁷Fe ions have been reviewed to clarify dilute magnetism and/or to develop room temperature (RT) spintronics materials [1]. It is generally known that perovskite oxides with ABO₃ (A = mono-, di-, or trivalent metal ions; B = penta-, tetra-, trivalent metal ions) composition have interesting properties such as superconductivity, ferroelectricity, half metallicity, magnetism, and so on. Concerning perovskite SrSn_{1-x}Fe_xO_{3-δ} (x = 0 – 0.2), the electrical conductivity and oxygen sensing behavior have already been reported as follows [2]. The electric conductivity increases with doping rate of Fe as the activation energy decreases, and the perovskite oxide is sensitive to oxygen gas at working temperature of 500 °C. The crystal was a cubic structure in the doping ranges of less than 20 % Fe. ⁵⁷Fe Mössbauer spectra of Fe doped SrSnO₃ were decomposed into three singlets with tetra-, tri-, and divalent states. However, the quality of ⁵⁷Fe Mössbauer spectra measured was not statistically good because the enriched ⁵⁷Fe was not used for doping Fe. There remains the possibility of another deconvolution analysis for the ⁵⁷Fe Mössbauer spectra. According to a phase transition in perovskite SrSnO₃-SrFeO₃ solid solutions [3], SrSn_{1-x}Fe_xO_y doped with Fe (x = 0 – 0.3) show orthorhombic structure, the samples doped with Fe (x = 0.4 – 0.9) show cubic structure, and the end member of SrFeO_{2.74} tetragonal structure. ⁵⁷Fe Mössbauer spectra of all these perovskite oxides did not show any magnetic sextet, but only paramagnetic doublets of Fe⁴⁺, Fe³⁺ and Fe²⁺.

On the other hand, there are a few paper concerning dilute magnetic properties of perovskite oxides. The magnetic and magneto-optical properties of Fe-doped BaTiO₃ films [4] and Fe-doped SrTiO₃ films [5] were reported. G. Prathiba et al. [6] studied magnetic properties of SrSn_{1-x}Fe_xO₃ (x = 0.03, 0.04, 0.05) films, and showed that the Curie temperatures of SrSn_{1-x}Fe_xO₃ with x = 0.04 and 0.05 are 618 and 638 K, respectively. These compounds are orthorhombic perovskite oxides, which are different from the cubic structure studied in reference [2]. The magnetic properties of SrSn_{0.9}Sb_{0.05}Fe_{0.05}O₃ film co-doped with Fe and Sb was also investigated by the same group [7]. Another interesting paper on perovskite oxides analyzed by using a full-potential linearized augmented plane-wave (FP-LAPW) method reported that the spin polarization is induced by substitution of oxygen atoms with nonmagnetic 2p impurities (C, N) in nonmagnetic cubic perovskite SrMO₃, where M = Ti, Ir, Sn [8]. According to this report, perovskite SrSnO₃ is a diamagnetic compound with the bandgap of 4.04 eV.

In order to resolve the above discrepancy and confirm the dilute magnetism of perovskite oxides, we have studied the magnetic properties, crystal structures and ⁵⁷Fe Mössbauer analyses of SrSn_{1-x}Fe_xO₃ (x = 0.01 – 0.15) prepared systematically by sol-gel and thermal decomposition methods.

2 Experimental

Perovskite oxides, SrSn_{1-x}Fe_xO₃ (x = 0.01–0.15), including 1 % ⁵⁷Fe were prepared by using sol-gel and thermal decomposition methods [9]. Metal ions mixed solutions with nominal concentrations were prepared using 0.1 M SrCO₃, 0.1 M SnCl₄, 0.01 M FeCl₃ and

Fig. 1 XRD patterns by Cu $K\alpha$ X-rays of 8 % Fe doped $SrSnO_3$, heated at 600 °C, 700 °C, 800 °C, 900 °C, and 1000 °C for 2 hours

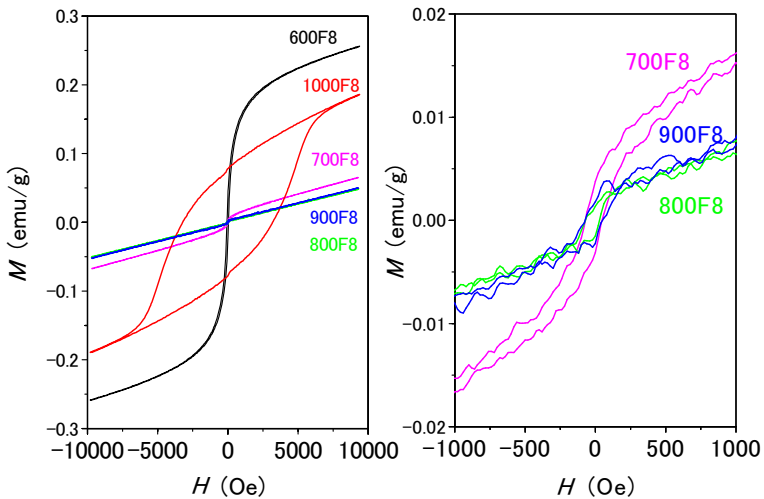
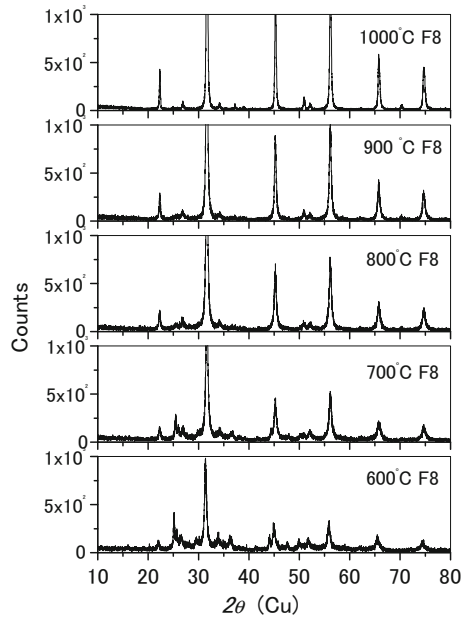
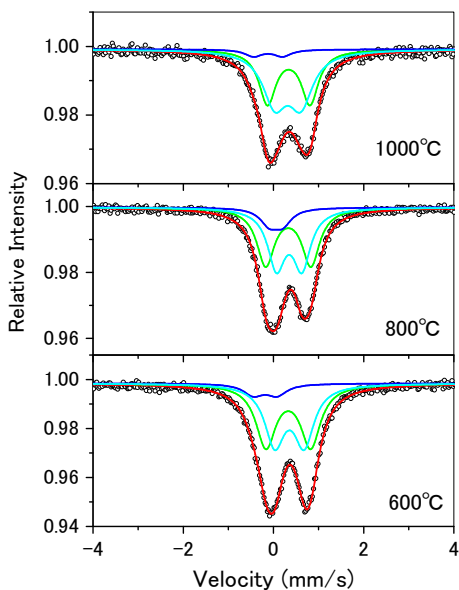


Fig. 2 Magnetization curves of $SrSn_{0.92}Fe_{0.08}O_3$ obtained by heating at 600 °C, 700 °C, 800 °C, 900 °C and 1000 °C for 2 hours. *Right* figure shows the expanded magnetization curves of samples heated at 700 °C, 800 °C and 900 °C. External magnetic field : H , Magnetization : M

Fig. 3 ^{57}Fe Mössbauer spectra of 8 % Fe doped SrSnO_3 , prepared by heating at different temperatures of 600 °C, 800 °C and 1000 °C



0.01 M $^{57}\text{FeCl}_3$ solutions. After adding citric acid and ethylene glycol, each solution was condensed and baked. The xerogel precursors obtained by heating at 400 °C for 2 hours were further heated at temperatures of 600 °C, 700 °C, 800 °C, 900 °C and 1000 °C. These oxides were characterized by X-ray diffraction (XRD), vibration magnetometer (VSM) and ^{57}Fe Mössbauer spectrometer using ^{57}Co (Rh) source. Doppler velocity of ^{57}Fe Mössbauer spectra was calibrated by relative to the Mössbauer spectrum of an $\alpha\text{-Fe}$ foil.

3 Results and discussion

3.1 Perovskite oxides treated at various temperatures

We checked first a heating temperature suitable to form a perovskite structure of Fe-doped SrSnO_3 . Figure 1 shows the XRD patterns of $\text{SrSn}_{0.92}\text{Fe}_{0.08}\text{O}_3$, heated at 600 °C, 700 °C, 800 °C, 900 °C, and 1000 °C for 2 hours. The crystallinity of the samples increased with heating temperatures. The monophasic crystal of perovskite oxide was obtained at 1000 °C. Under the heating temperatures of 900 °C, the oxides showed poor crystallinity and mixed intermediate phases. Therefore, SrSnO_3 doped with various Fe contents were finally treated at 1000 °C for 2 hours or 4 hours.

We performed magnetization measurements for 8 % Fe doped SrSnO_3 , treated at various heating temperatures in order to investigate the relationship between magnetic property and crystallinity of perovskite oxides. All SrSnO_3 doped with 8 % Fe obtained by heating at various temperatures showed magnetic behavior mixed with ferromagnetic and paramagnetic properties since the magnetization increases linearly with applied magnetic fields and over the maximum applied magnetic field of 10 kOe as shown in Fig. 2. The saturation magnetization of ferromagnetic components was obtained by subtracting the paramagnetic linear components.

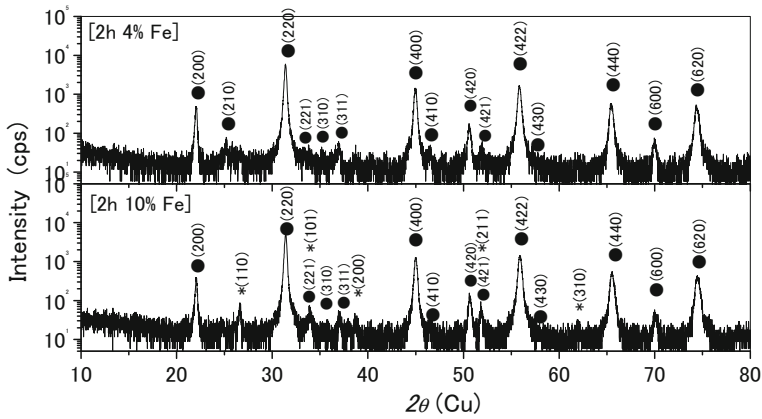


Fig. 4 XRD patterns of 4 % Fe and 10 % Fe doped SrSnO₃ heated at 1000 °C for 2 hours. ●: Orthorhombic phase of SrSn(Fe)O₃, *: SnO₂

Fig. 5 Dependence of cell volume for SrSn_{1-x}Fe_xO_{3-δ} on Fe doping ratio, after heating the samples at 1000 °C for 2 hours and 4 hours

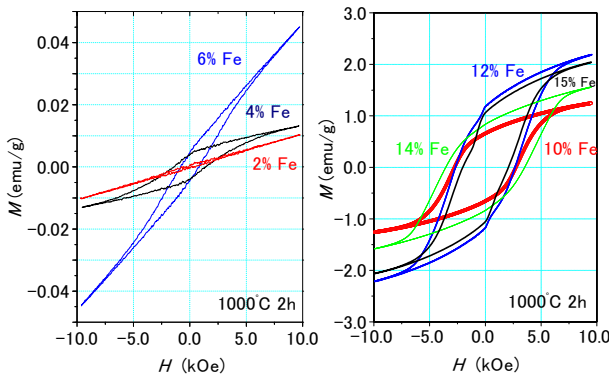
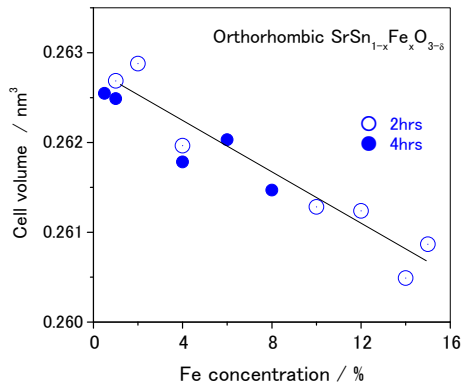
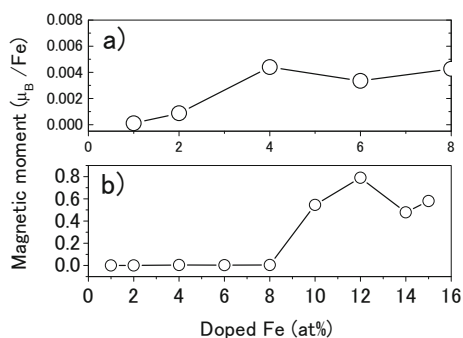


Fig. 6 Magnetic hysteresis of 2 %, 4 %, and 6 % Fe doped SrSn_{1-x}Fe_xO₃ annealed at 1000 °C for 2 hours. External magnetic field: *H*, Magnetization: *M*

Fig. 7 Magnetic moment of Fe in $\text{SrSn}_{1-x}\text{Fe}_x\text{O}_3$ ($x = 0.01 - 0.15$) annealed at 1000°C for 2 hours. Fe concentration: **a** ($x = 0.01 - 0.08$), **b** ($x = 0.01 - 0.15$)



The following interesting results were obtained by heating at various temperatures. XRD pattern of the poor-crystalline oxide heated at 600°C is almost similar to those of samples heated at 700°C and 800°C although the crystallite size and the content ratio of the perovskite oxide to the intermediate compound were different. However, a huge saturation magnetization was obtained for the sample heated at 600°C . The magnetization of samples heated at temperatures higher than 600°C decreased abruptly, but the crystalline sample heated at 1000°C showed a relatively high saturation magnetization (1.8 emu/g) and a large coercivity (3.2 kOe). The small saturation magnetization of samples heated at the temperature ranges between 700°C and 900°C may be explained by imperfect substitution or disordering of diluted Fe incorporated into the crystallized perovskite oxides. However, we cannot explain the reason why the sample heated at 600°C showed the high saturation magnetization, but it is very remarkable phenomenon as compared with those of samples heated at the higher temperatures.

^{57}Fe Mössbauer spectra of all samples are composed of two doublets of Fe^{3+} and one doublet of Fe^{4+} with the small intensity as shown in Fig. 3. Two doublets of Fe^{3+} are similar also to those of crystalline perovskite oxides doped with Fe as described next paragraphs. As one cause of the large saturation magnetization of the sample obtained at 600°C , carbon included is considered to play an important role of magnetic interaction because the carbon produced after firing may remain in the sample as well as oxygen defects produced, and further the full potential calculation [8] suggested that nonmagnetic 2p impurity carbon induces the spin polarization for SrSnO_3 .

3.2 Doping effect of Fe in crystalline perovskite oxides

Figure 4 shows typical XRD patterns of 4 % Fe and 10 % Fe doped SrSnO_3 heated at 1000°C for 2 hours. The main peaks of both XRD patterns indicate the orthorhombic structure of SrSnO_3 (Fe) as shown in reflection index of SrSnO_3 [10]. It is estimated from XRD peak widths that the crystallite sizes of these oxides are around 30–50 nm in diameter. The trace peaks of impurity correspond to those of SnO_2 [11]. 6 % and 8 % Fe doped samples heated for 2 hours showed a cubic phase. The crystal structure changed from the cubic phase to an orthorhombic phase by annealing for 4 hours. The crystal structure changes easily by the preparation conditions. It is understandable that SrSnO_3 (Fe) with the same composition showed different structures in the previously reported papers [2, 3]. In log scale XRD pattern of 10 % Fe doped SrSnO_3 , the trace peaks of impurity SnO_2 were also recognized

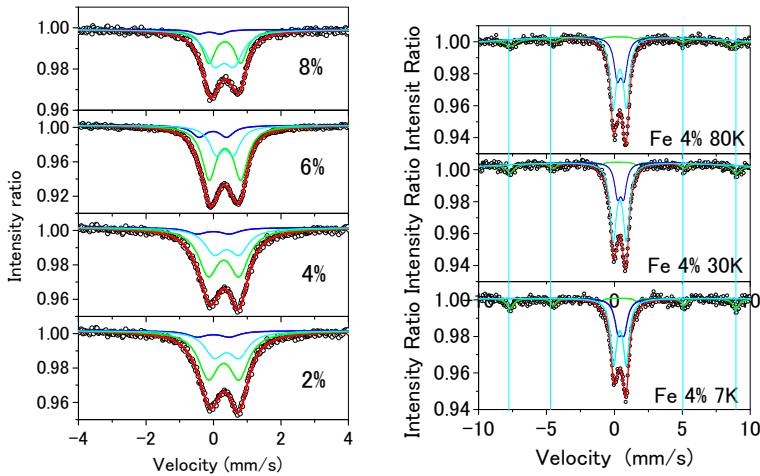


Fig. 8 *Left side:* ^{57}Fe Mössbauer spectra at RT for 2 %, 4 %, 6 % and 8 % Fe doped $\text{SrSnO}_{3-\delta}$ annealed at 1000 °C for 2 hours. *Right side:* ^{57}Fe Mössbauer spectra at 7 K, 30 K, and 80 K for 4 % Fe doped $\text{SrSnO}_{3-\delta}$ annealed for 4 hours

in addition to the main peaks of orthorhombic SrSnO_3 although the peaks of SnO_2 were hardly observed in liner scale XRD pattern.

The crystal cell volume of the orthorhombic structure decreased linearly with Fe doping rates although the deviation was large as shown in Fig. 5. The cell volume of 6 % and 8 % Fe doped perovskite oxides heated for 2 hours was not plotted because of their cubic structure. The crystal cell volume of samples heated for 4 hours are also added in Fig. 5. The crystallite size of 4 % Fe doped SrSnO_3 increased from 32 nm to 45 nm in diameter, and the lattice cell volume decreased by annealing for 4 hours. The decrease of the lattice cell volume means the more Fe incorporation in SrSnO_3 crystal structure since the ionic radius of Fe^{3+} (0.064 nm) is smaller than that of Sn^{4+} (0.074 nm). The oxygen deficiency is also produced around Fe^{3+} incorporated into the lattice because of the charge neutral condition. If one oxygen atom linked at two octahedrons is removed, two pentahedrons may be produced, but they may change immediately into the distorted tetrahedron and octahedron by sharing another oxygen atom of the pentahedrons produced. It is considered that the local structure around Fe doped is like the brownmillerite ($\text{ABO}_{2.5}$) structure.

The magnetization hysteresis of the perovskite oxides are shown in Fig. 6, and the Fe magnetic moments in these oxides are shown in Fig. 7. It is found that the magnetic behavior is obviously different between less than and over 8 % Fe doping. For less than 8 % Fe doped samples, the coercivity and saturated magnetization (or iron magnetic moments) were very small, whereas the saturation magnetization increased abruptly above 8 % Fe doping. 12 % Fe doped perovskite oxide showed the maximum saturation magnetization (ca. 3.2 emu/g) and Fe magnetic moment ($0.8 \mu_B/\text{Fe}$) among all the samples, whereas $\text{SrSnO}_{3-\delta}$ doped with 2 – 8 % Fe showed weak ferromagnetism (at highest $0.0045 \mu_B/\text{Fe}$). In XRD patterns of $\text{SrSnO}_{3-\delta}$ doped with 10 % or more Fe, trace peaks of SnO_2 were recognized.

In the magnetic hysteresis curves of 12 % and 15 % Fe doped $\text{SrSnO}_{3-\delta}$, a zigzag behavior was observed. It suggests the presence of two magnetic phases or defects.

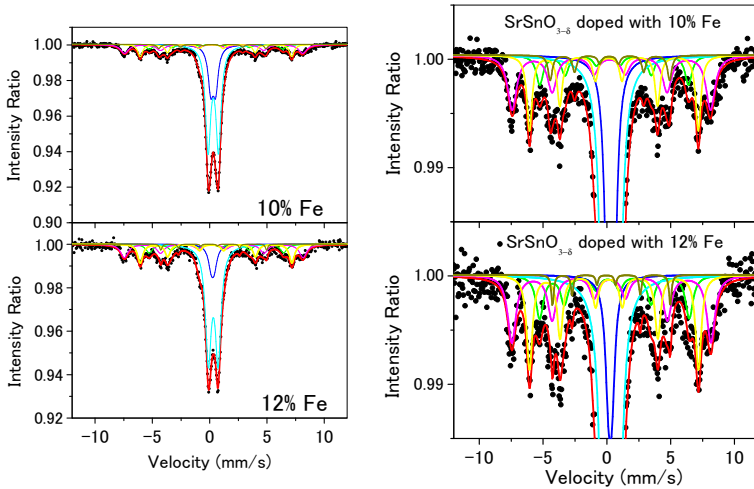


Fig. 9 ^{57}Fe Mössbauer spectra at RT for 10 % and 12 % Fe doped SrSnO_3 . Right side figures are expanded from the left figures

Table 1 Typical ^{57}Fe Mössbauer parameters of Fe doped SrSnO_3 prepared at 1000 °C. Measuring temperature: RT

Sample,	Species	B_{hf} (T)	δ (mm/s)	Δ (mm/s)	Γ (mm/s)	Int. Ratio(%)
4 % Fe doped, 2h	Fe^{4+}	-	0.03	0.96	0.56	14.2
	Fe^{3+}	-	0.36	0.52	0.56	27.0
	Fe^{3+}	-	0.35	0.93	0.56	58.8
4 % Fe doped, 4 h	Fe^{4+}	-	0.09	1.00	0.45	17.1
	Fe^{3+}	-	0.40	0.37	0.45	19.9
	Fe^{3+}	-	0.39	0.90	0.45	63.0
10 % Fe doped, 2h	Fe^{3+}	-	0.30	0.42	0.54	20.0
	Fe^{3+}	-	0.32	0.90	0.54	48.3
	Fe^{3+} in octa	48.4	0.29	0.11	0.80	13.3
	Fe^{3+} in tetra	41.1	0.36	0.40	0.49	10.6
	Fe^{3+}	36.9	0.36	0.52	0.59	4.1
	Fe^{3+}	32.5	0.43	0.60	0.58	3.6
12 % Fe doped, 2h	Fe^{3+}	-	0.27	0.23	0.60	8.1
	Fe^{3+}	-	0.32	0.85	0.60	50.3
	Fe^{3+} in octa	48.6	0.33	0.08	0.74	15.3
	Fe^{3+} in tetra	41.1	0.37	0.40	0.57	16.6
	Fe^{3+}	36.9	0.36	0.49	0.30	2.8
	Fe^{3+}	33.5	0.44	0.89	0.75	6.9

^{57}Fe Mössbauer spectra of these perovskite oxides are shown in Figs. 8 and 9. Typical ^{57}Fe Mössbauer parameters are listed in Table 1.

In ^{57}Fe Mössbauer spectra of SrSnO_3 doped with 2–8 % Fe (Fig. 8), three paramagnetic doublets were observed at room temperature. Two doublets with $IS = 0.3$ mm/s are assigned to paramagnetic Fe^{3+} occupying tetrahedral and octahedral sites, although the tetrahedron and octahedron are distorted or each spin is disordering. When ^{57}Fe Mössbauer spectra of 4 % Fe doped $\text{SrSnO}_{3-\delta}$ were measured at 80, 30, and 7 K, a magnetic sextet appeared. The hyperfine field did not depend so much on the measuring temperatures. Mössbauer parameters of the magnetic sextet observed at 30 K were $B_{hf} = 51.8$ T, $IS = 0.49$ mm/s, $QS = 0.35$ mm/s, $FWHM = 0.66$ mm/s and the area intensity = 15 %. These results suggest that the spins of Fe^{3+} located in distorted lattice are easily arrayed at low temperatures and that the large polaron is formed in the partial area of $\text{SrSnO}_{3-\delta}$ grains.

The Mössbauer parameters of 4 % Fe doped $\text{SrSnO}_{3-\delta}$ annealed for 2 and 4 hours are listed in Table 1. The intensity of the doublet due to Fe^{4+} increased, and the intensity of the doublet due to Fe^{3+} with large QS increased by annealing for 4 hours. Annealing for long hours induces changes in the distorted lattice as well as the incorporation of Fe ions into the lattice. The saturation magnetization showed 0.32 emu/g (the magnetic moment = $0.36 \mu_B/\text{Fe}$) after annealing for 4 hours.

As shown in Fig. 9, at least two magnetic sextets were observed in addition to two paramagnetic doublets in ^{57}Fe Mössbauer spectra at RT of SrSnO_3 doped with more than 10 % Fe although cubic $\text{SrSn}_{1-x}\text{Fe}_x\text{O}_3$ ($x > 0.2$) shows only paramagnetic doublets by Fe doping, with mixed valence states [3]. The main two sextets may be due to the ordering of condensed Fe^{3+} occupied at the octahedral and tetrahedral sites of $\text{Sr}(\text{Sn}, \text{Fe})\text{O}_{3-\delta}$. Another minor two sextets may be due to more diluted Fe^{3+} doped SrSnO_3 . That is, in addition to uniformly dispersed paramagnetic behavior area of doped Fe in the crystal structure, there are two ferromagnetic regions of the polycrystalline: little condensed Fe and diluted Fe areas by doping relatively high Fe doped $\text{SrSnO}_{3-\delta}$.

4 Conclusion

Perovskite oxides of ^{57}Fe doped SrSnO_3 were prepared by sol-gel and thermal decomposition methods. It was confirmed that $\text{SrSn}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ ($x = 0.1 - 0.15$) with 30–50 nm in the crystallite diameter show magnetic behavior mixed with ferromagnetic and paramagnetic properties. SrSnO_3 doped with less than 8 % Fe showed a weak ferromagnetism although the ^{57}Fe Mössbauer spectra at RT gave only paramagnetic peaks, whereas SrSnO_3 doped with higher than 10 % Fe showed a relatively strong magnetization and the ^{57}Fe Mössbauer spectra at RT gave magnetic sextets in addition to the paramagnetic doublets. Two pair of sextets in the ^{57}Fe Mössbauer spectra at RT is considered due to spin orientation between dilute Fe^{3+} partially substituted at Sn^{4+} sites in octahedral and tetrahedral sites of $\text{SrSnO}_{3-\delta}$.

In addition, it is also remarkable that poor crystalline perovskite oxides heated at 600 °C showed a large saturation magnetization and a low coercivity. In this case, there is the possibility that impurity carbons, which would come from decomposition of organic reagents used for preparation of samples, affect the magnetic properties.

The models based on arrangement of Fe^{3+} and oxygen vacancies should be further studied to explain the magnetic ordering present in these samples.

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