Mössbauer studies of SnO_2 powders doped with dilute ^{57}Fe, prepared by a sol-gel method

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1. **TiO_2 films doped with Fe (ICAME05)**
2. **SnO_2 powders doped with ^{57}Fe (MSMS06)**

Both material candidates for spintronics applications

Background

Diluted magnetic semiconductor (DMS), which shows ferromagnetism at room temperature, is prospected as new materials with both semiconductor and magnetic properties. The development is currently attracting interest due to their potential use in spintronics applications, such as a new transistor and spin FET.

A lot of study of GaAs, GaN and InP semiconductors doped with Mn have been reported. Unfortunately, these materials showed ferromagnetism only below room temperature.

It was found recently by Y. Masumoto et al that DMS transparent films of TiO_2 doped with Co show the ferromagnetic properties at room temperature [1]. (Y.Masumoto,et al,APL 78(2001)

Hi Min Lee et al reported that the ferromagnetic behavior of $Ti_{1-x}{}^{57}Fe_xO_2$ increases with the decrease of doped ^{57}Fe [2].

(Hi Min Lee et al,TRANSACTION ON MAGNETICS,39(2003)2788)

ICAME05

CEMS study on diluted magneto-transparent titanium oxide films deposited by pulsed laser ablation

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Acknowledgement

Prof.* Z. Homonnay, *Eotvos Lorand University,

Preparation method of thin films;

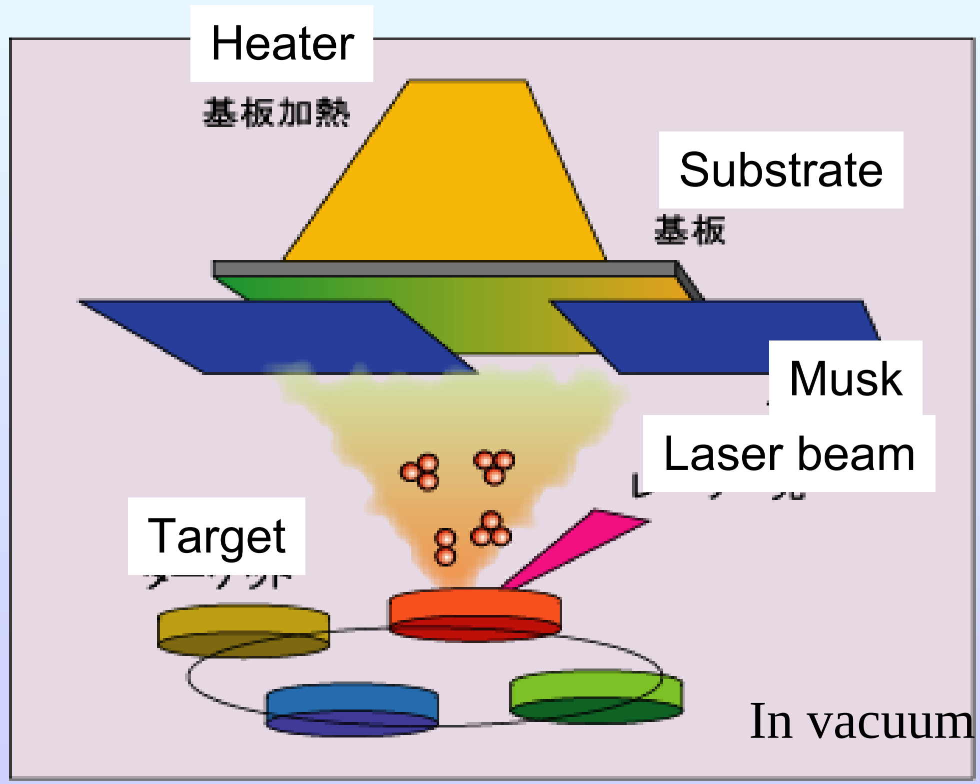
Pulsed laser ablation PLA

Pulse Laser : KrF excimer laser (Wave length ; 248 nm)

Pulse rate ; 2 Hz,

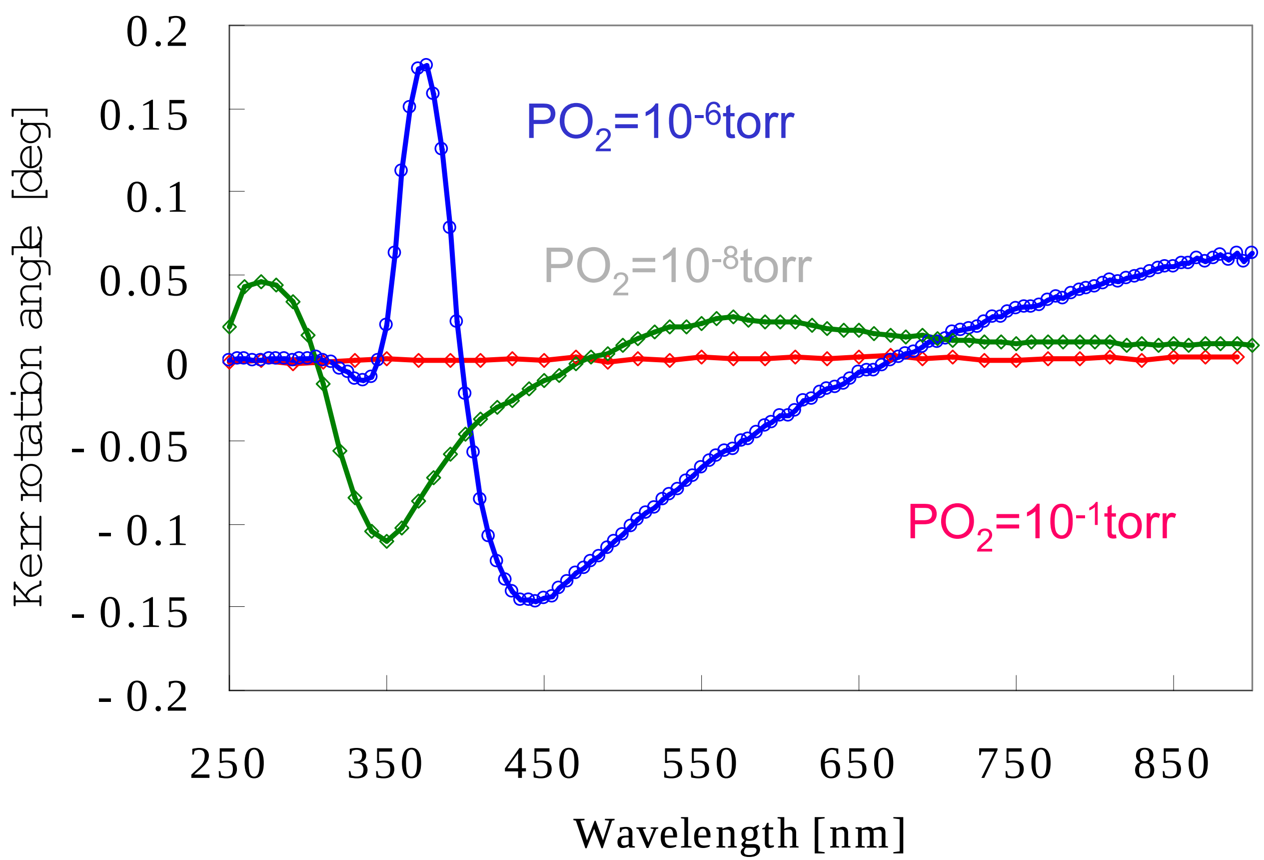
Energy density ; 5 J/cm^2.shot

Target; Mixed pellet of TiO_2 (99.9 %) and enriched $^{57}Fe_2O_3$ (Fe:99.99 %,enrich ^{57}Fe:>95%), annealed at 1200 ^{o}C for 12 hrs.



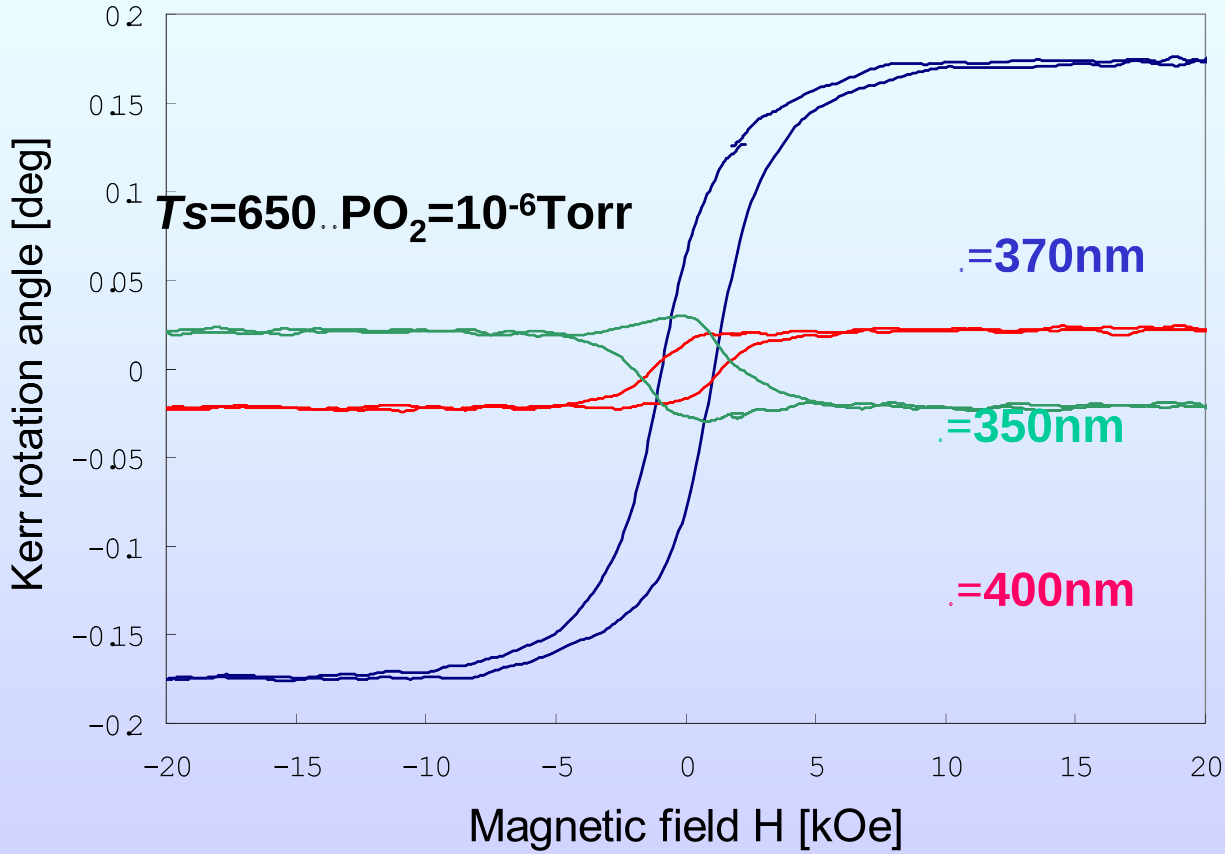
Schematic diagram of film preparation by PLA

Dependence of oxygen pressure on Kerr rotation angle



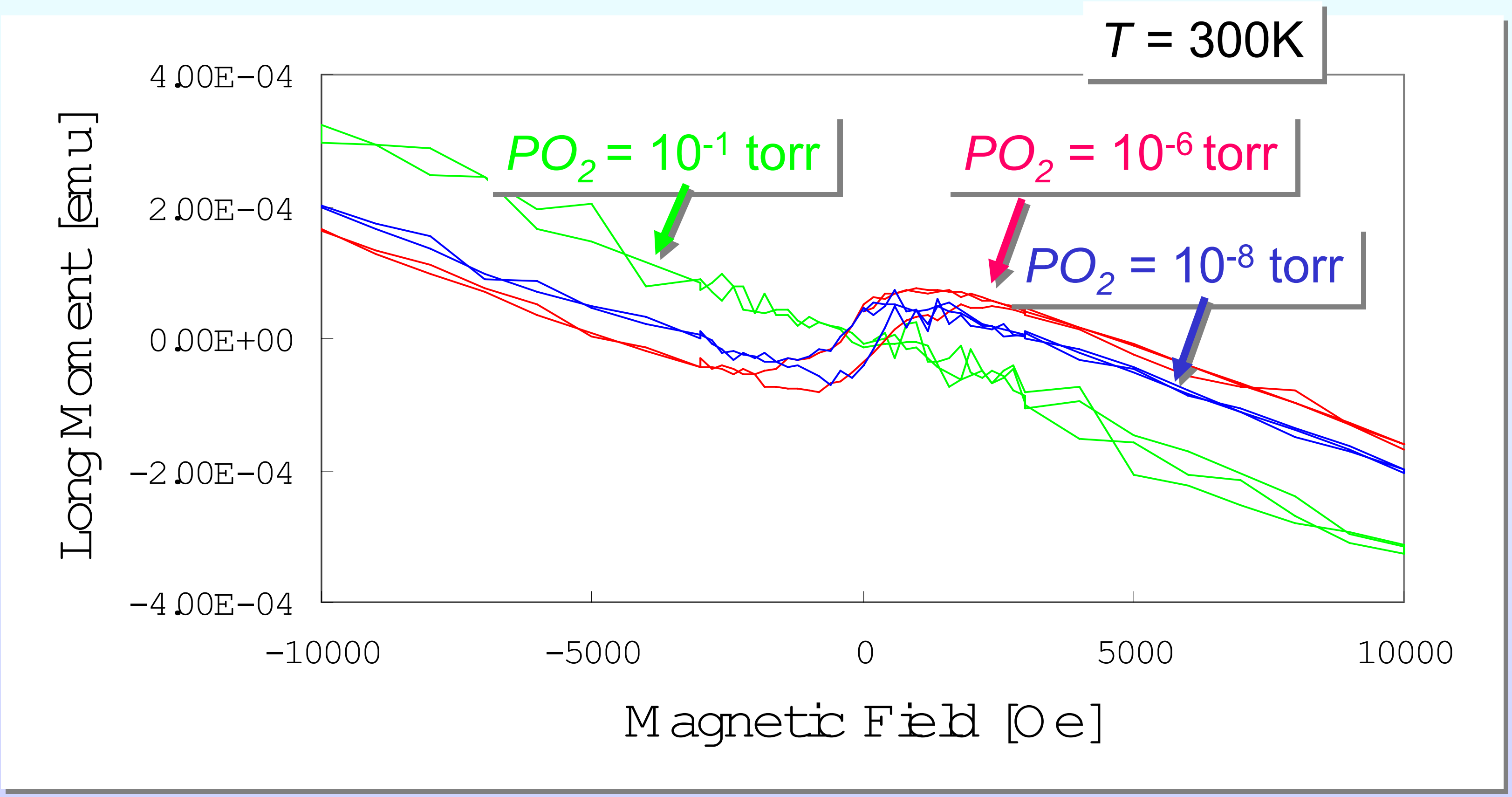
The films prepared by Ts : 650. and PO_2:10^{-6}torr show strong Kerr effect.

Kerr rotation angles as function of magnetic fields



Hysteresis of Kerr rotation angles was observed at any wavelength of light, and maximum rotation angle was shown at wavelength of 370nm

M-H curve by SQUID

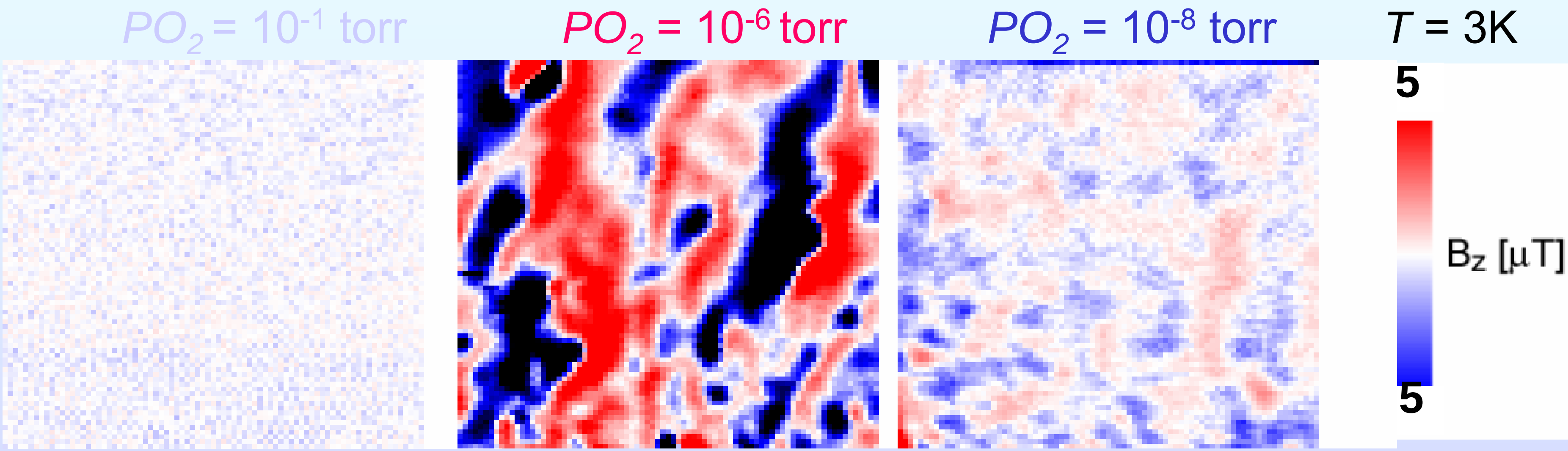


Hysteresis of magnetization was clearly observed at 300K.
These show that these films are ferromagnetic else a film prepared at 10^{-1} torr.

Magnetic moment μ_B

Characterization of films

Scanning SQUID microscope images taken at 3K for 6%Fe doped TiO_2 films



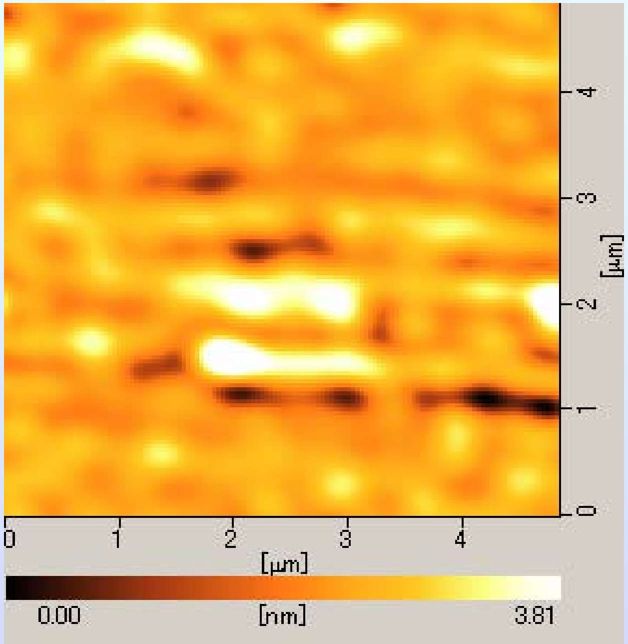
Red parts; Flux from surface to over
Blue part ; Flux from surface to inner.

Under Zero field
Scanning ranges; 200μm x 200μm

Magnetic domain structures were observed in ^{57}Fe doped TiO_2 films prepared in 10^{-6} torr, suggesting the presence of long range ordering of magnetic moment induced by Fe doping in these thin films

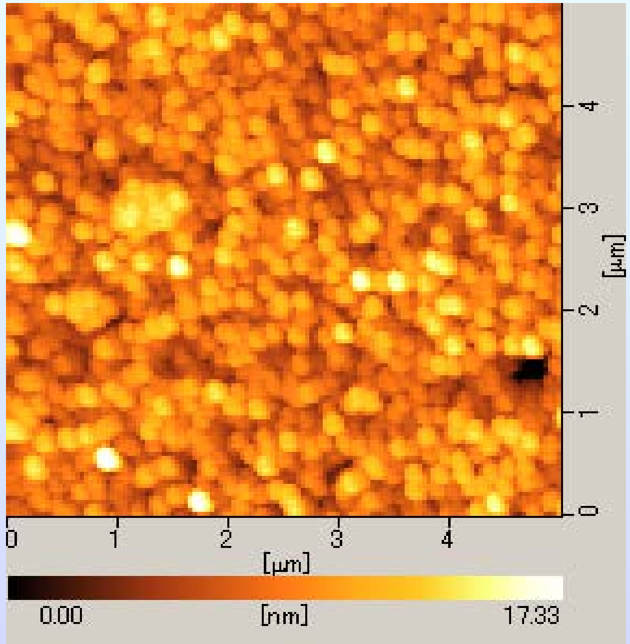
Characterization of Films by AFM

$PO_2 = 10^{-1}$ Torr



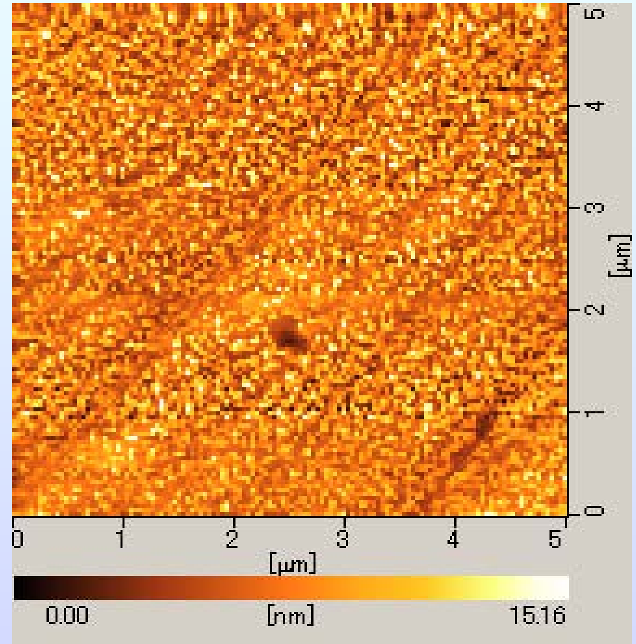
Grain size: 0.5um

$PO_2 = 10^{-6}$ Torr



Grain size: 0.2um

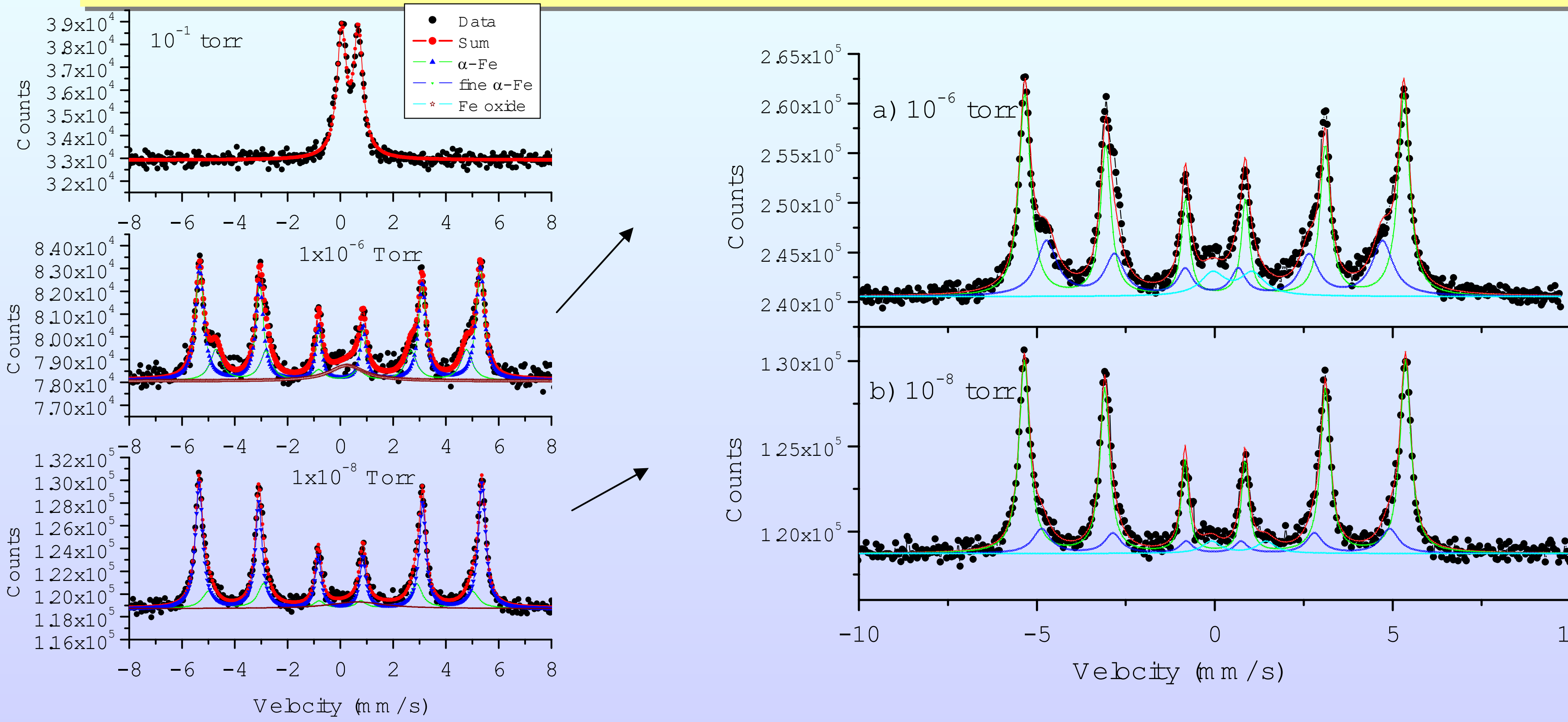
$PO_2 = 10^{-8}$ Torr



Grain size:<0.1um

From these micro images, it was found that the grain sizes are about 0.5 µm, 0.2 µm and less than 0.1 µm for the samples prepared at 10^{-1} torr, 10^{-6} torr, and 10^{-8} torr, respectively. This shows that the increase of the degree of vacuum reduces the grain size in the film.

CEMS spectra of TiO_2 film doped with 6% $^{57}Fe_2O_3$ by Pulsed Laser ablation under different atmospheres



A paramagnetic doublet of Fe^{3+} was observed for TiO_2 films under the low vacuum condition of 10^{-1} Torr. Two magnetic sextets were observed in CEMS spectra of the films prepared under 10^{-6} Torr and 10^{-8} Torr.

Mysterious subspectra obtained in CEMS spectra

Tentative results of TiO2 films doped with Fe

- Fe doped TiO_2 epitaxial film deposited by PLA in 10^{-6} torr was a rutile type with particle size of 0.2 μm, and Fe doped TiO_2 film deposited in 10^{-8} torr was an different type film with particle size of 0.. μm in diameter.
- The films prepared under $P_{O_2}=10^{-6}$ Torr and at $T_s=650$ showed the strong Kerr effect. SQUID magnetometer and Scanning SQUID microscope confirm that their films are ferromagnetic.
- Three kinds of Fe species were observed in CEMS spectra ;a sextet with B_{hf} =33T due to metallic Fe, another sextet with B_{hf} =29.T due to high spin Fe(IV) (now metallic clusters in TiO2 films), and a doublet due to Fe(III) doped in TiO_2.
- Which species play a important role of DMS properties?

K. Nomura et al., *ICAME05 proceeding*, in press.

Mössbauer studies of SnO_2 powders doped with dilute ^{57}Fe, prepared by a sol-gel method

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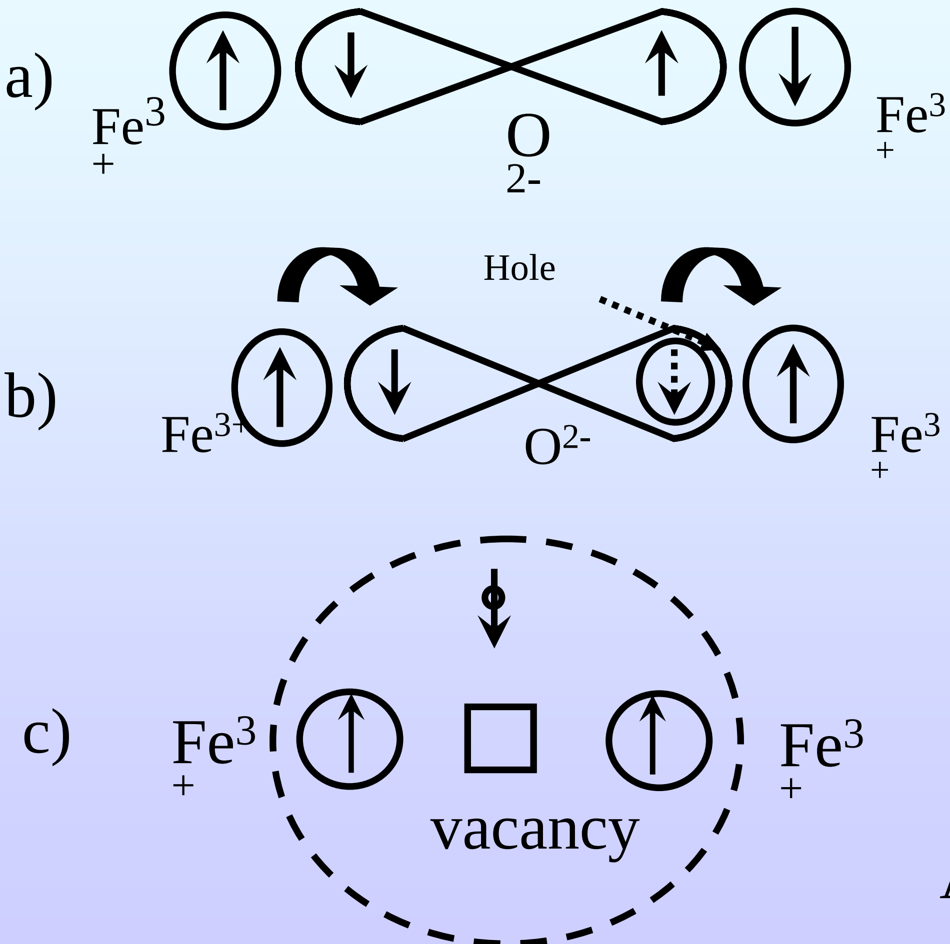
1. Purpose
2. Experimental details a sol gel method
3. Results XRD, VSM, Mössbauer Spectra
4. Summary SnO_2 powders

The deposited films of SnO_2 doped with Fe also showed the ferromagnetic behavior [4]. ← J.M.D.Coey et al., *Appl. Phys. Lett.*, 84(2004)1332

Schematic diagrams showing a comparison of super-exchange and F-center exchange



super-exchange

anti-ferromagnetic

F-center exchange

Hole-mediated exchange as a stronger interaction than electron-mediated exchange

Almost all n-type semiconductors have been reported

High temperature magnetism in SnO_2 was prepared from the chemical synthesis of $FeCl_3$, $SnCl_2$ and NH_4OH solutions. (A. Punnoose et al . Phys. Rev. B72, 054402 (2005)). → Ferromagnetically ordered Fe^{3+} spins are converted to a paramagnetic spin system. The paramagnetic behavior is due to the incorporation of Fe ions into host lattices.

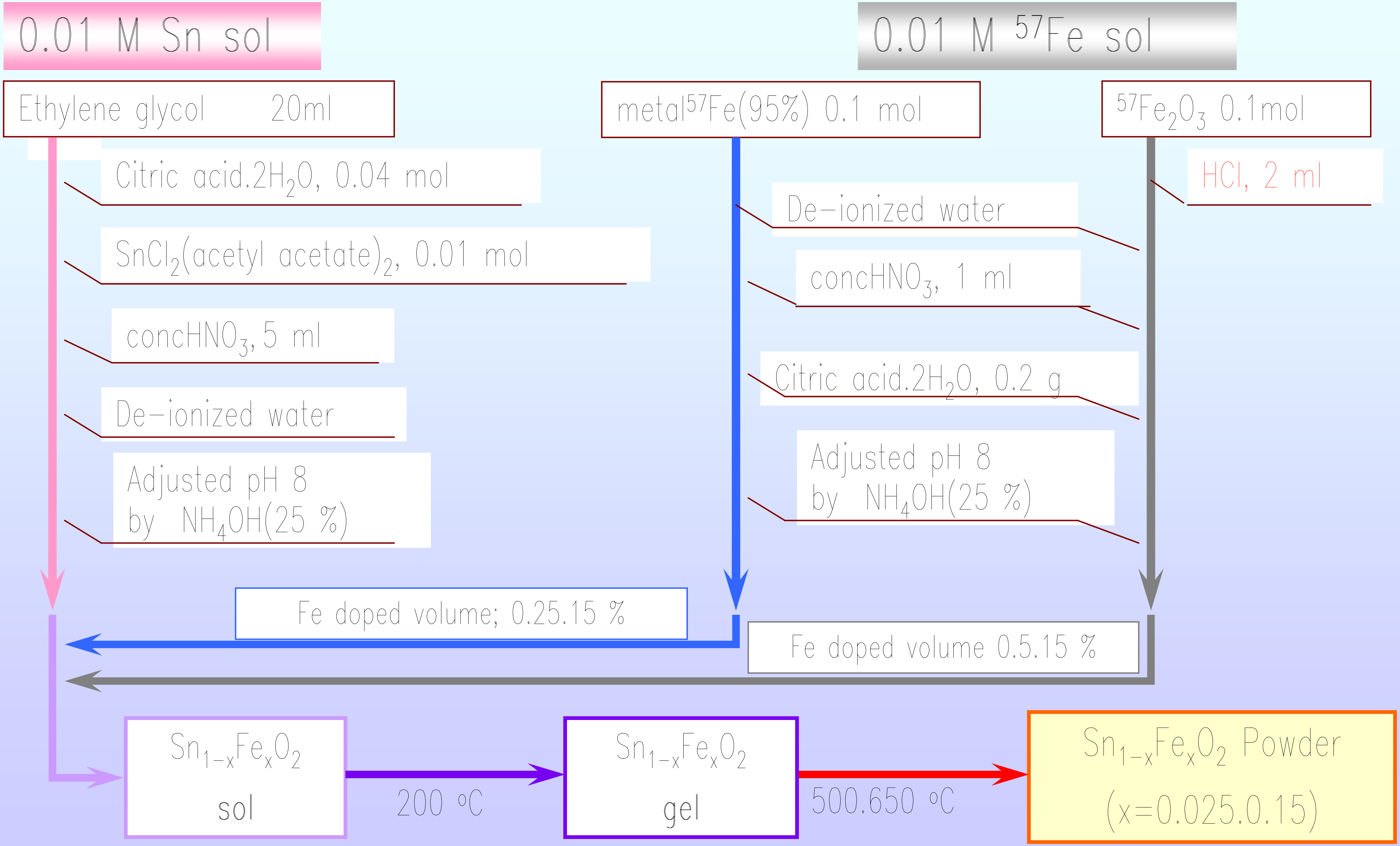
Purpose

SnO_2 structure is similar to TiO_2 structure. The films prepared with these oxides are transparent. Magneto-optical properties are expected by doping Fe into the transparent materials with large wide gap.

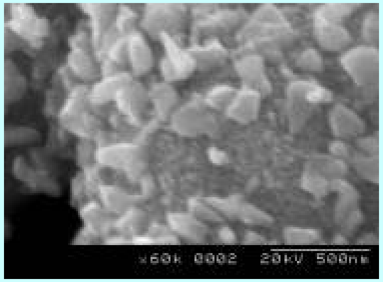
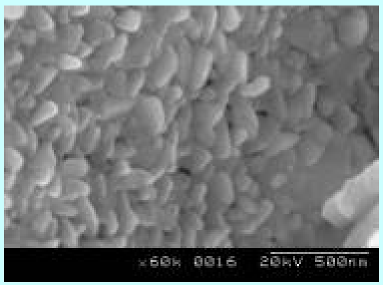
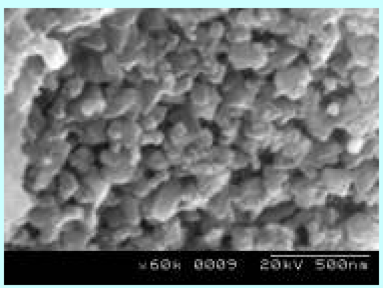
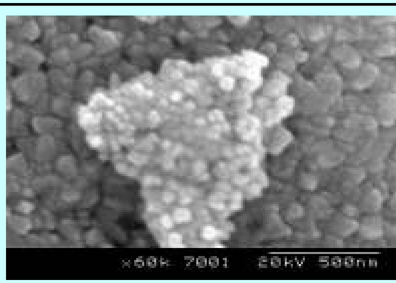
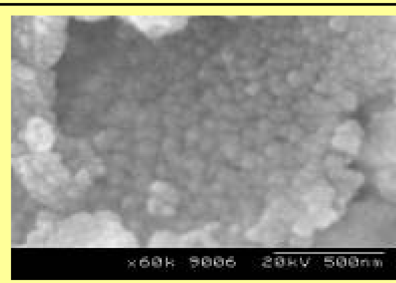
We have prepared uniform powders of SnO_2 (Fe) by a sol-gel method.

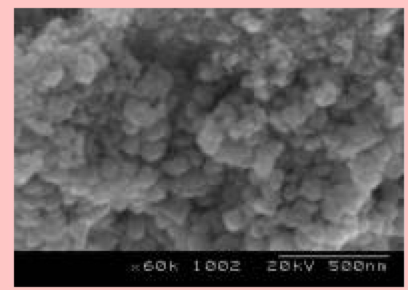
In order to confirm the ferromagnetism in detail, we have studied on nano-size powders of Fe doped SnO_2 mainly by Mössbauer spectroscopy.

$Sn_{1-x}Fe_xO_2$ preparation by a sol-gel method.



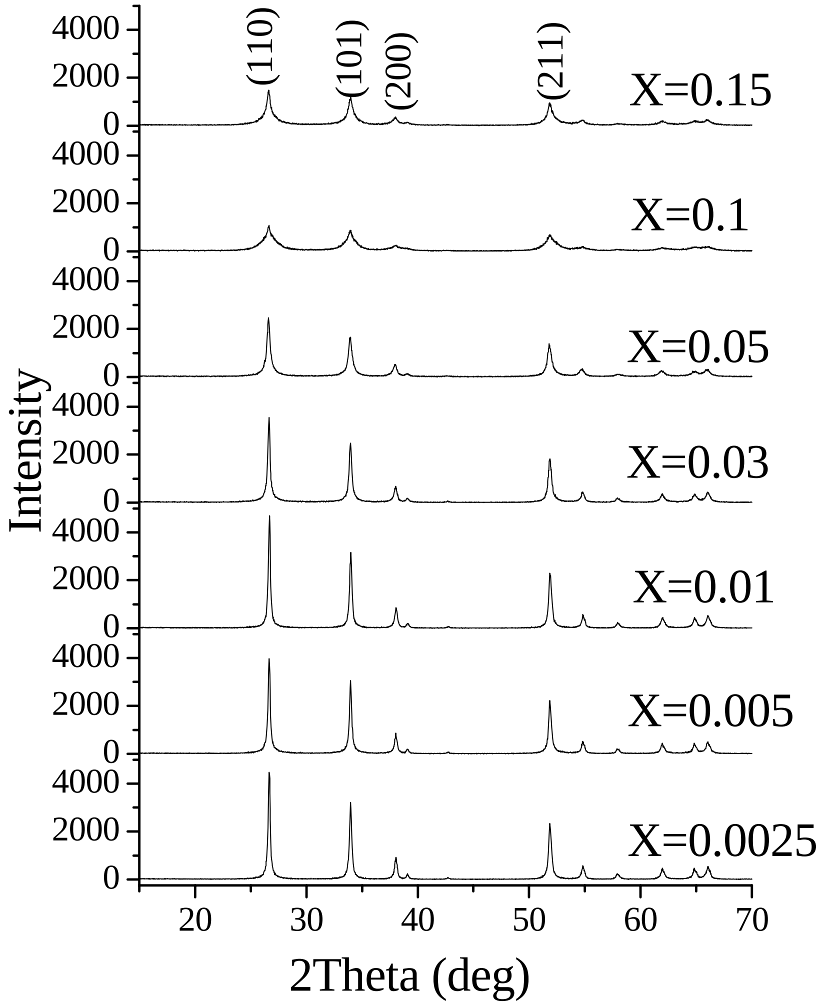
SEM images and grain size of $Sn_{1-x}{}^{57}Fe_xO_2$

x	500°C for 2 hrs	650°C for 2 hrs
0.005	 225 nm	 289 nm
0.01	 167 nm	 258 nm
0.03	 144 nm	 94 nm
0.05	 90 nm	 93 nm

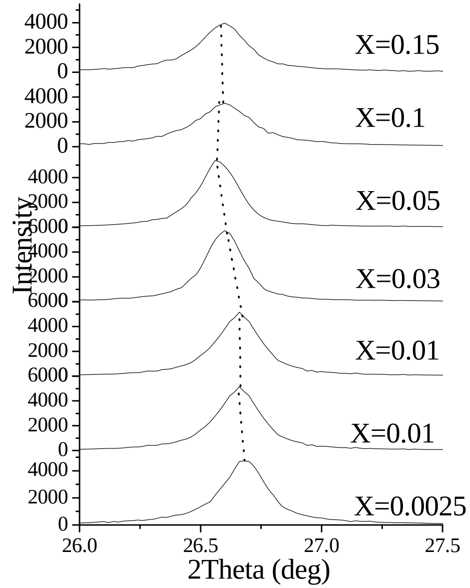
x	600°C for 6 hrs
0.01	 160 nm
0.02	 95 nm
0.06	 96 nm
0.1	 63 nm

XRD patterns of $Sn_{1-x}{}^{57}Fe_xO_2$ annealed at 500°C for 2 hrs

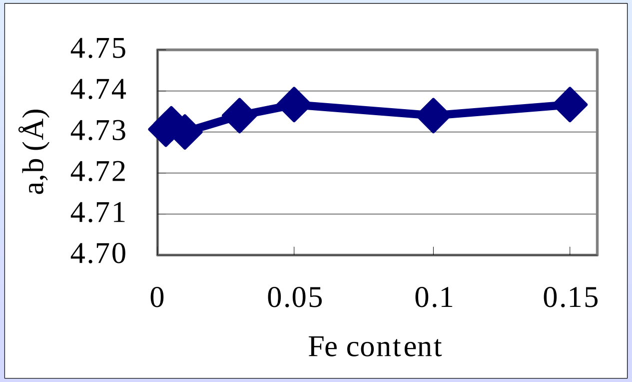
x	a,b (Å)	c (Å)	V (Å3)	(110)2Teata (deg)	(110) Intensity
0.0025	4.7307	3.1822	71.22	26.6400	3167
0.005	4.7322	3.1809	71.23	26.6600	2821
0.01	4.7300	3.1798	71.14	26.6400	3209
0.03	4.7339	3.1793	71.25	26.6200	2464
0.05	4.7370	3.1834	71.43	26.5800	1666
0.1	4.7340	3.1810	71.29	26.6600	712
0.15	4.7367	3.1805	71.36	26.5800	973

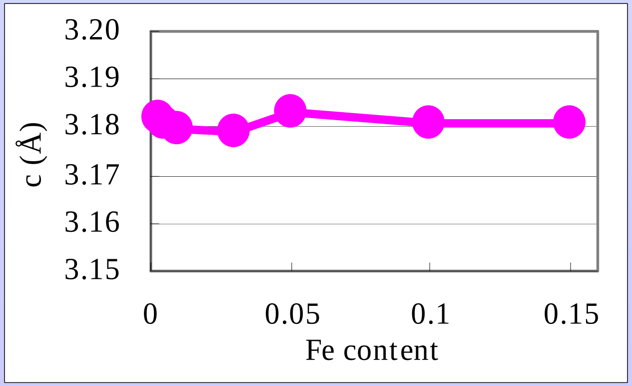


XRD of $Sn_{1-x}Fe_xO_2$ annealed at 500 °C

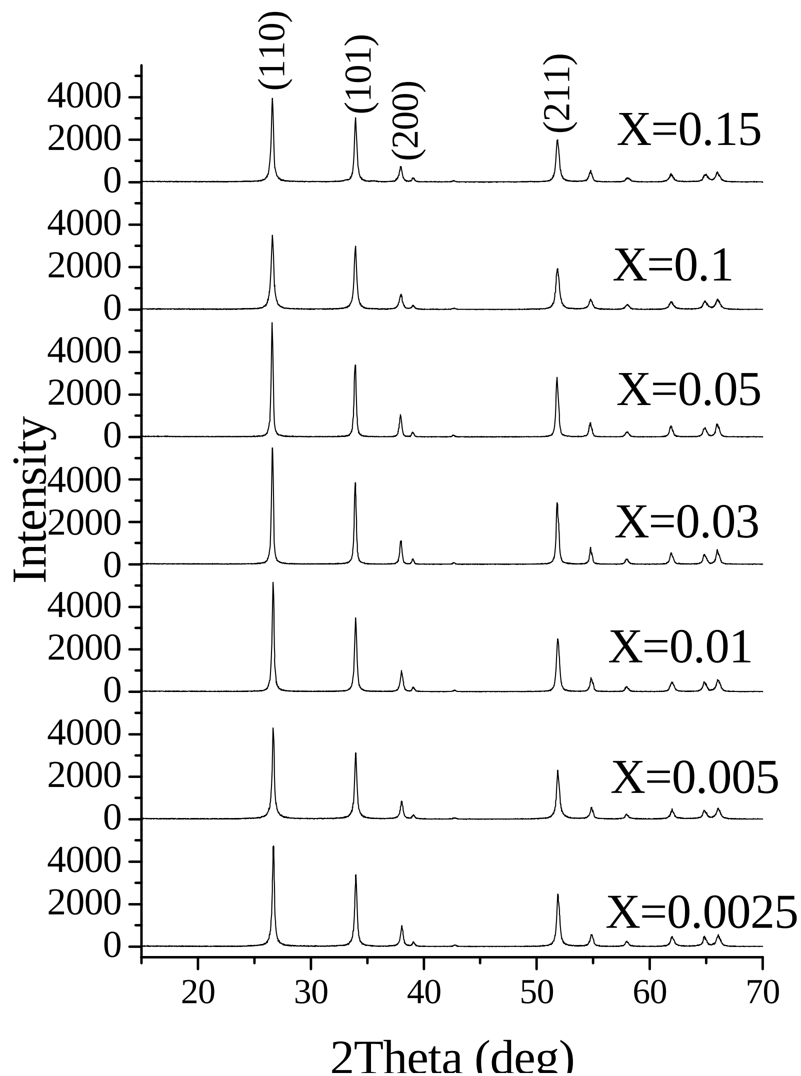


XRD (110) peaks



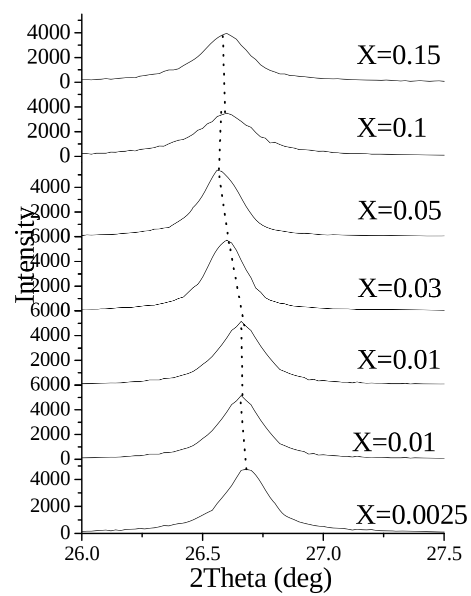


XRD patterns of $Sn_{1-x}{}^{57}Fe_xO_2$ annealed at 650ºC for 2 hours

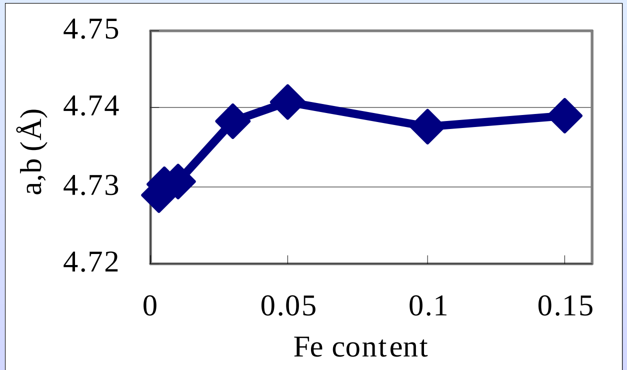


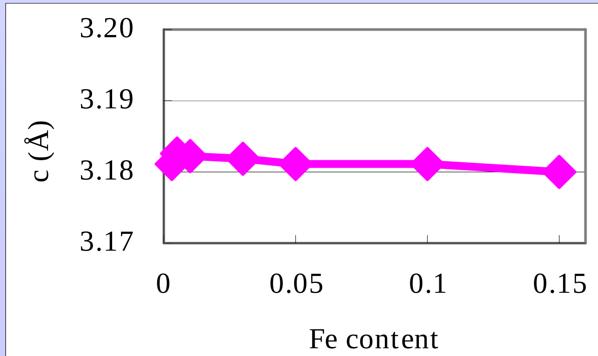
XRD of $Sn_{1-x}Fe_xO_2$ annealed at 650 ºC

x	a,b (Å)	c (Å)	V (Å3)	(110)2Teata (deg)	(110) Intensity
0.0025	4.7287	3.1809	71.13	26.6600	3347
0.005	4.7302	3.1827	71.21	26.6600	2975
0.01	4.7307	3.1822	71.22	26.6400	3515
0.03	4.7383	3.1818	71.44	26.5800	4045
0.05	4.7409	3.1812	71.50	26.5600	3750
0.1	4.7376	3.1811	71.40	26.5800	2385
0.15	4.7390	3.1798	71.41	26.5800	2723

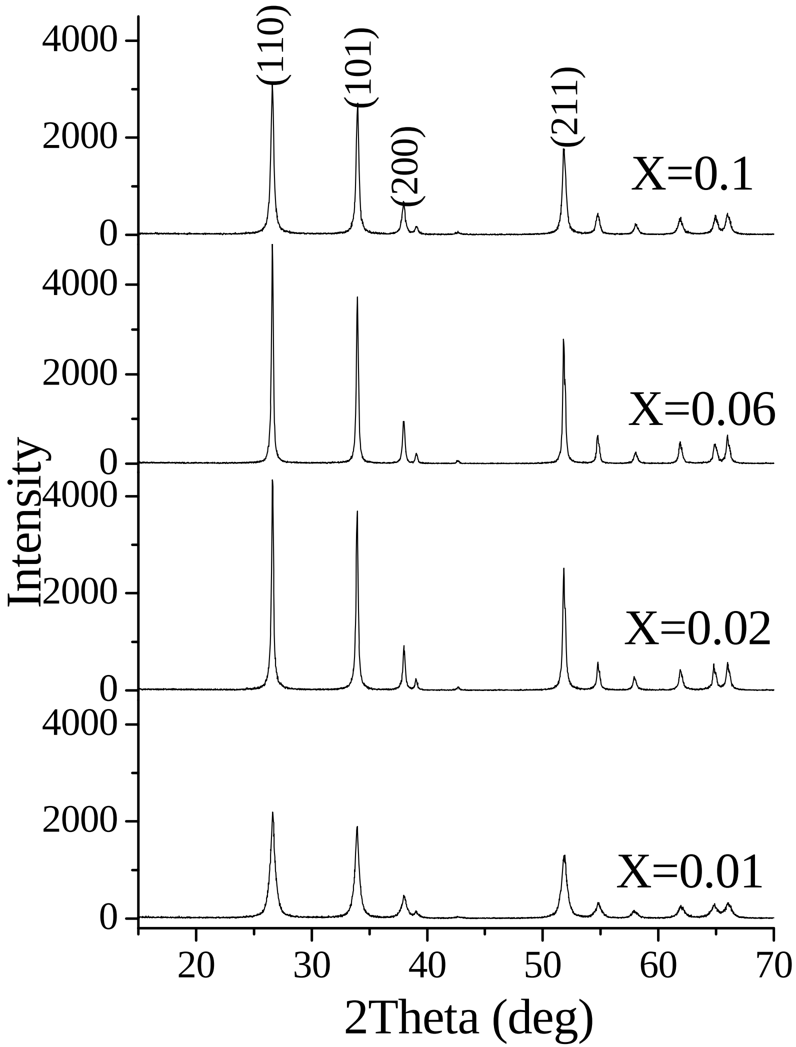


XRD(111) peaks



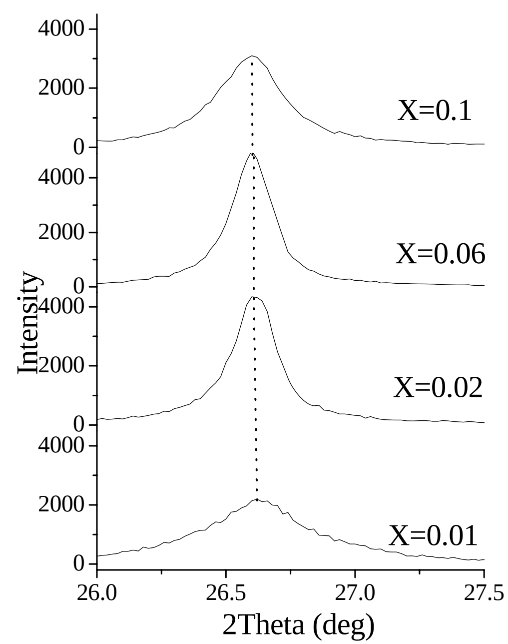


XRD of $Sn_{1-x}{}^{57}Fe_xO_2$ annealed at 600°C for 6 hours

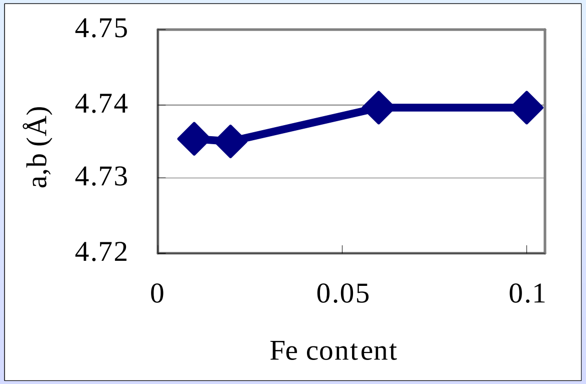


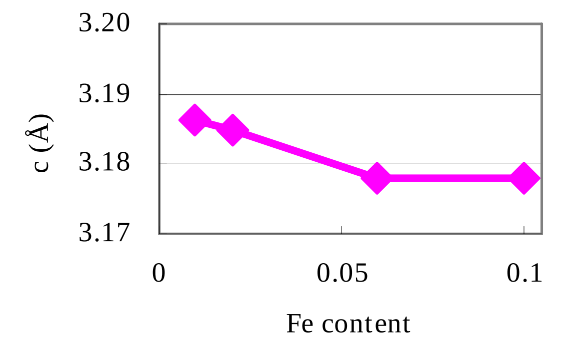
XRD of $Sn_{1-x}Fe_xO_2$ annealed at 600 °C

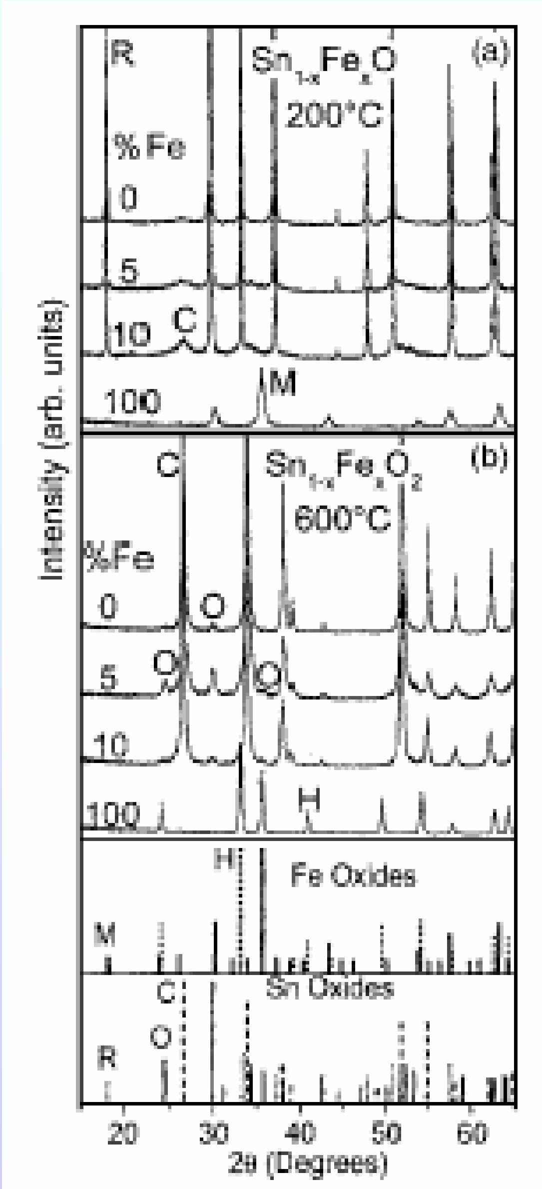
x	a,b (Å)	c (Å)	V (Å3)	(110)2Teata (deg)	(110) Intensity
0.01	4.7353	3.1864	71.45	26.6200	1466
0.02	4.7350	3.1849	71.40	26.6000	3133
0.06	4.7396	3.1780	71.39	26.5800	3448
0.1	4.7396	3.1780	71.39	26.5800	2116

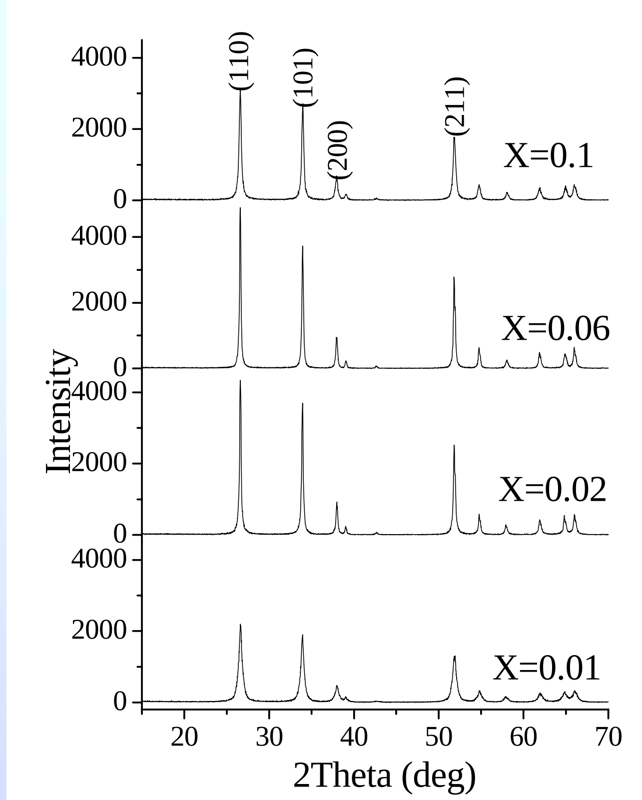


XRD(111) peaks







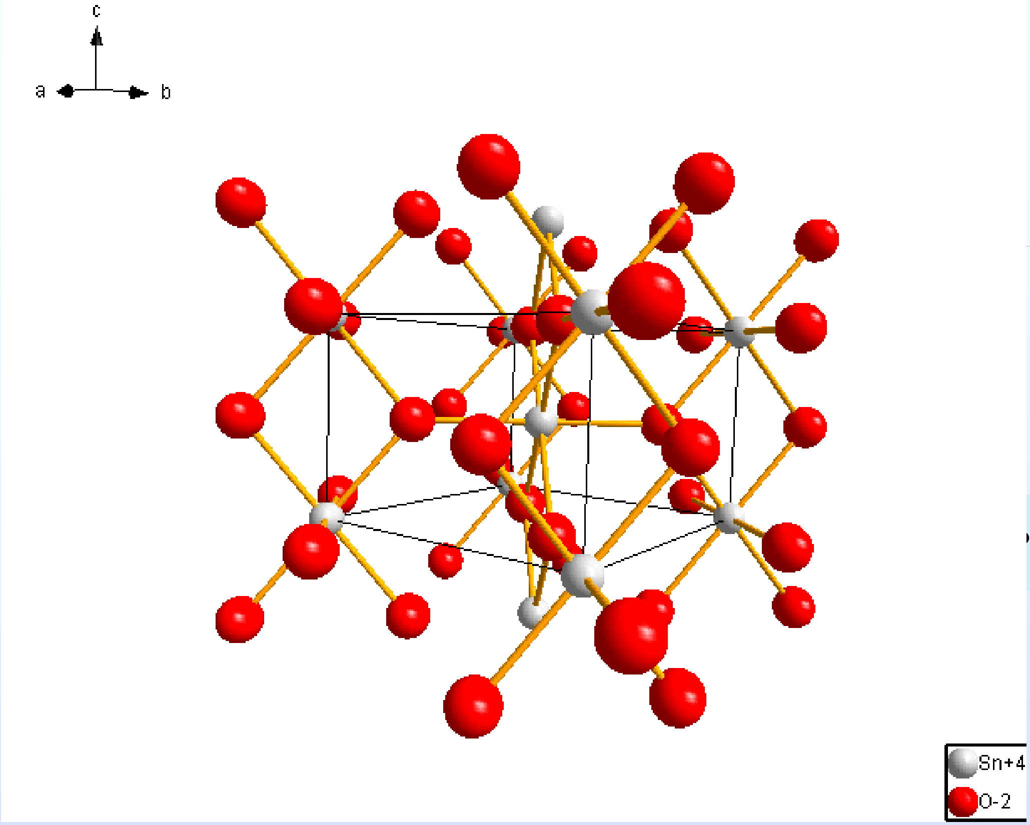


XRD of $Sn_{1-x}Fe_xO_2$ annealed at 600 °C

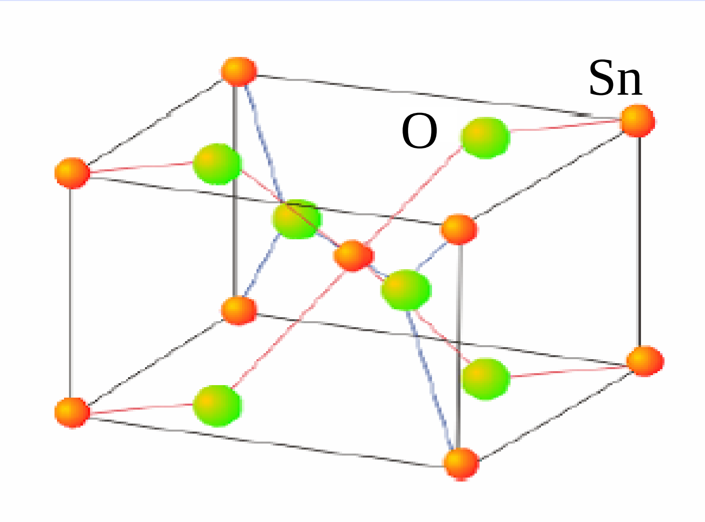
Our XRD patterns of the samples prepared by a sol-gel methods. Only Cassiterite SnO_2 was observed.

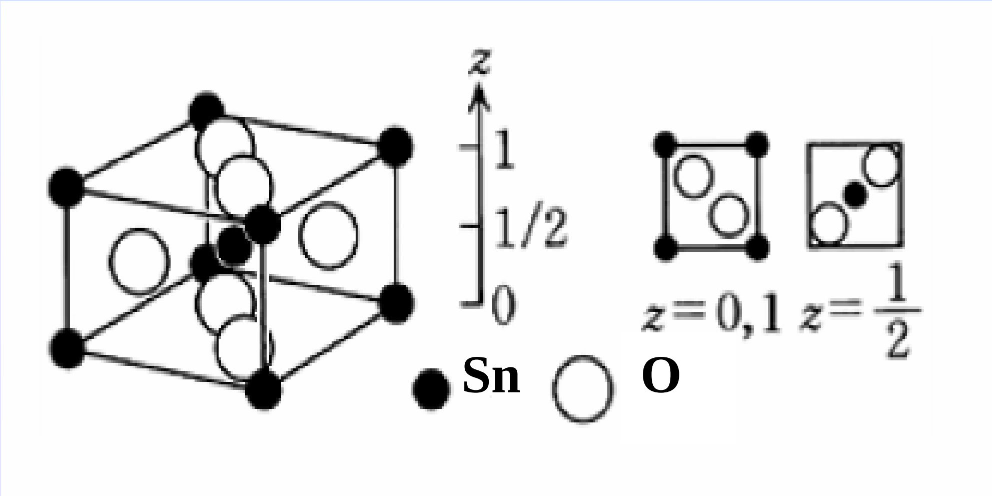
← Punnoose studied on chemically synthesized powders of SnO_2 doped with Fe.(Phy. Rev. B72 054402(2205)

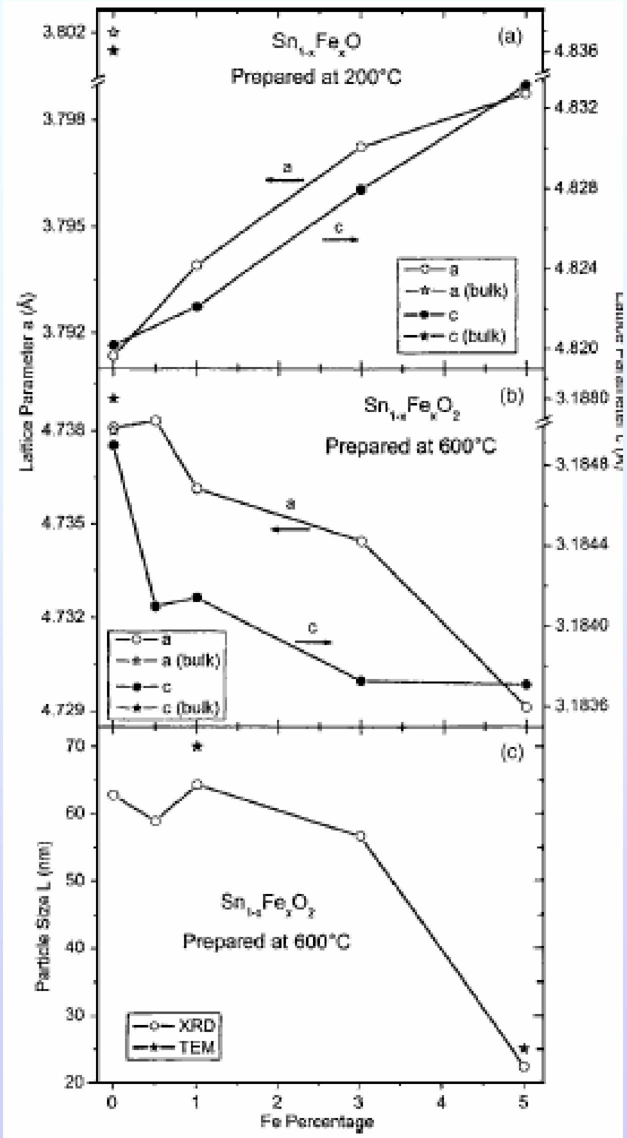
FIG. 2. Panels (a) and (b) show XRD patterns of $Sn_{1-x}Fe_xO$ (prepared at 200 °C) and $Sn_{1-x}Fe_xO_2$ (prepared at 600 °C), respectively, along with reference lines of orthorhombic SnO_2 (solid lines, marked "O"), romarchite SnO (dotted lines, marked "R") cassiterite SnO_2 (dashed lines, marked "C") phases, hematite (marked "H"), and maghemite (marked "M") phases of Fe_2O_3.



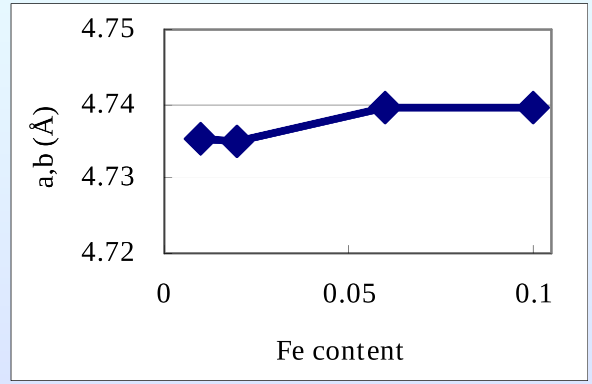
Rutile structure of SnO_2

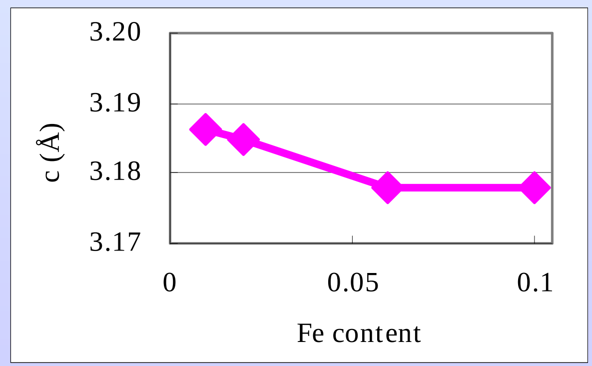






Comparison of our data with Punnoose data





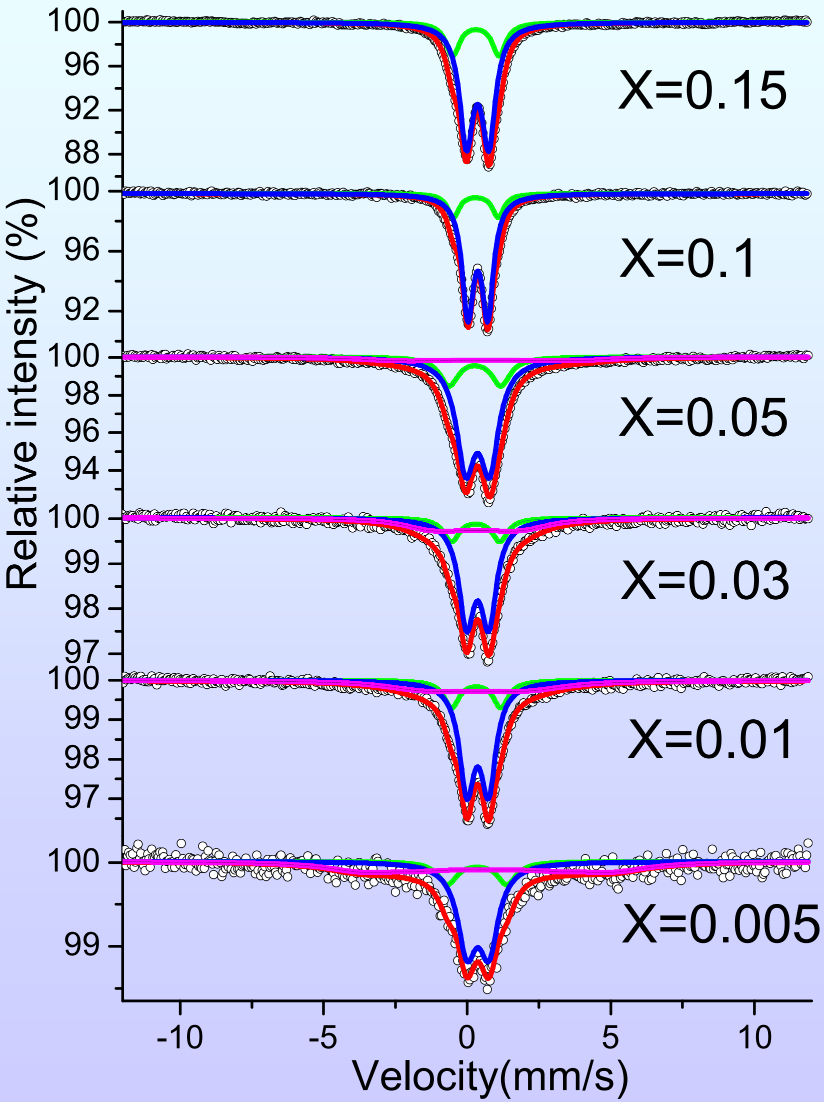
XRD of $Sn_{1-x}{}^{57}Fe_xO_2$ annealed at 600°C

Summary of the results by XRD

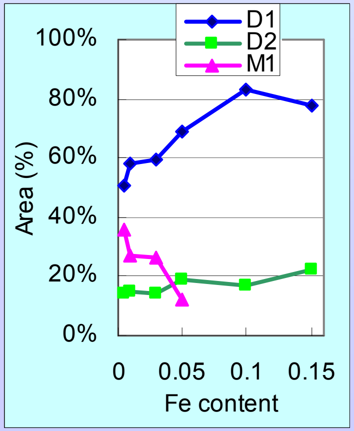
1. XRD of the samples prepared by a sol-gel method showed only the single phase of Rutile structure of SnO_2.

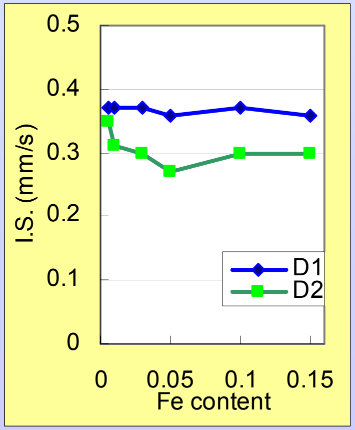
2. The XRD peaks shifted to low angles with the increase of doped Fe□the lattice constants of *a*, and *b* axes are longer and the lattice constant of *c* axis are shorter with doping Fe.
   →Fe doping bring up the lattice distortion.
3. When annealed at 500 ^{o}C, the peak intensity weakened with doping Fe. →Fe disturbed the growth of crystalline.
   Supported by Wang J. et al, □ Non-Cryst. Solids 351,(2005)228)

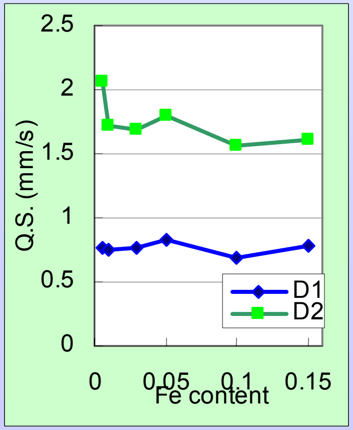
R.T. Mössbauer spectra of $Sn_{1-x}{}^{57}Fe_xO_2$ annealed at 500°C for 2 hrs



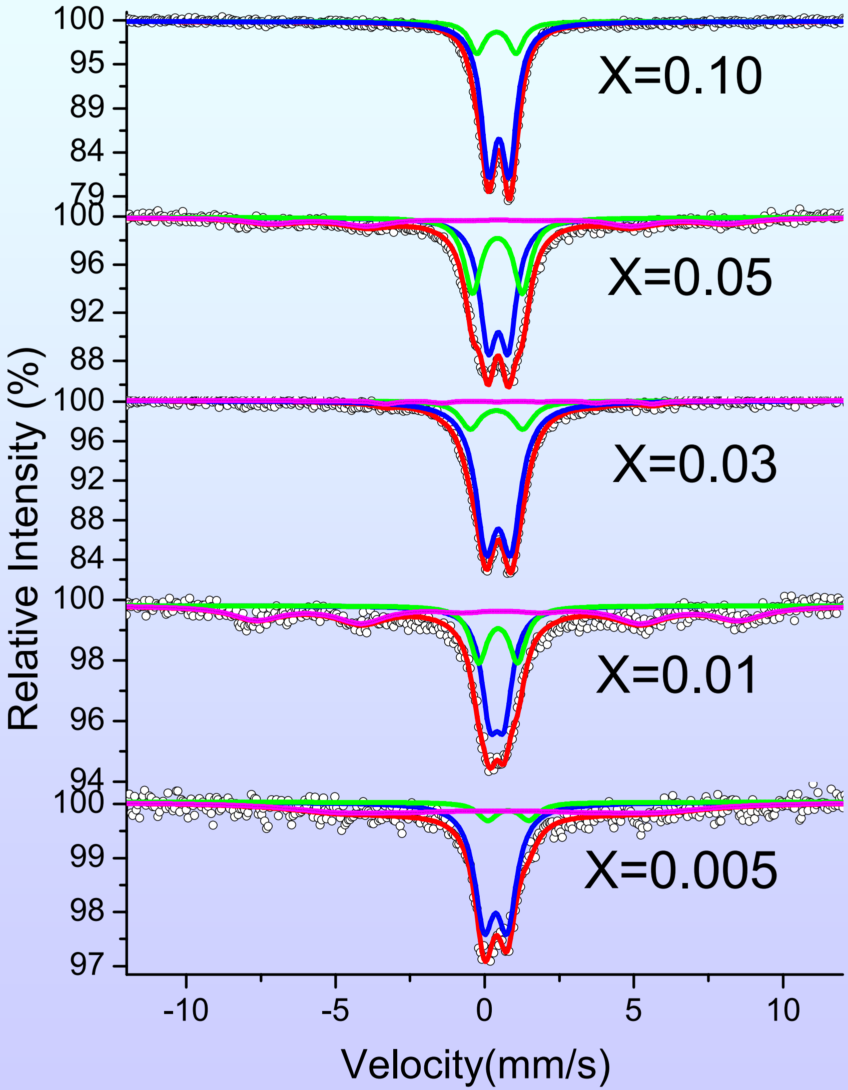
	parameter	0.005	0.01	0.03	0.05	0.1	0.15
DOUBLET (1)	Area (%)	50.50%	57.90%	59.70%	68.90%	83.10%	77.80%
	δ (mm/s)	0.37	0.37	0.37	0.36	0.37	0.36
	Δ (mm/s)	0.76	0.75	0.77	0.83	0.69	0.78
	Γ (mm/s)	0.8	0.64	0.66	0.79	0.49	0.58
DOUBLET (2)	Area (%)	13.90%	15.10%	14.00%	19.00%	16.90%	22.20%
	δ (mm/s)	0.35	0.31	0.3	0.27	0.3	0.3
	Δ (mm/s)	2.07	1.72	1.68	1.8	1.56	1.61
	Γ (mm/s)	0.8	0.64	0.66	0.79	0.49	0.58
MIXED M+Q (1)	Area (%)	35.60%	27.00%	26.30%	12.10%		
	δ (mm/s)	0.69	0.31	0.31	0.64		
	B_{HF} (T)	27.35	13.05	10.9	20.62		
	Δ (mm/s)	0.01	0.01	0.01	0.01		
	Γ (mm/s)	2.95	2.95	2.1	2.95		



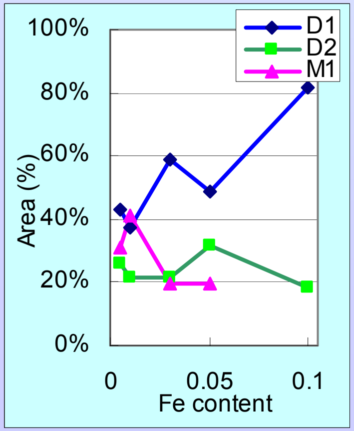


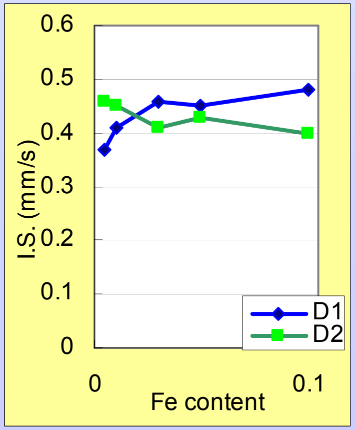


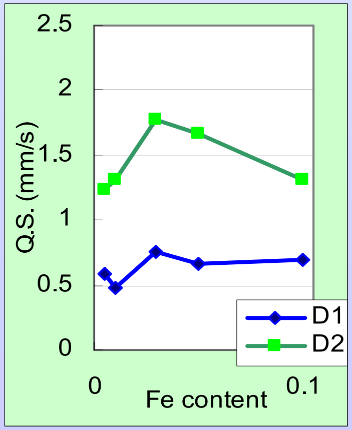
10 K Mössbauer spectra of $Sn_{1-x}{}^{57}Fe_xO_2$ annealed at 500°C for 2 hrs



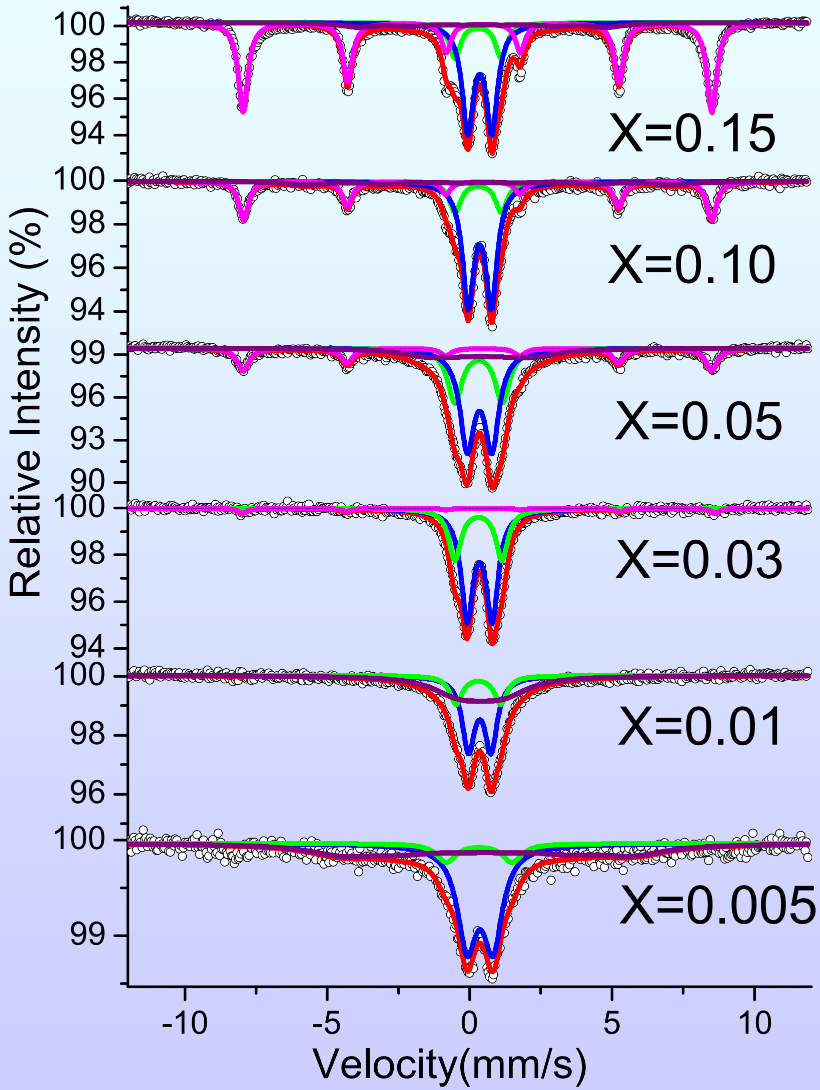
	parameter	0.005	0.01	0.03	0.05	0.1
DOUBLET (1)	Area (%)	42.90%	37.50%	58.70%	48.90%	81.37%
	δ (mm/s)	0.37	0.41	0.46	0.45	0.48
	Δ (mm/s)	0.58	0.48	0.76	0.67	0.69
	Γ (mm/s)	0.68	0.68	0.68	0.68	0.61
DOUBLET (2)	Area (%)	25.90%	21.60%	21.50%	31.40%	18.63%
	δ (mm/s)	0.46	0.45	0.41	0.43	0.4
	Δ (mm/s)	1.23	1.31	1.78	1.67	1.31
	Γ (mm/s)	0.68	0.68	0.68	0.68	0.61
MIXED M+Q (1)	Area (%)	31.20%	40.90%	19.80%	19.70%	
	δ (mm/s)	0.27	0.49	0.45	0.47	
	B_{HF} (T)	30.87	50.16	50.46	47.45	
	Δ (mm/s)	0	-0.1	-0.11	0	
	Γ (mm/s)	2.05	2.06	2.05	2.05	



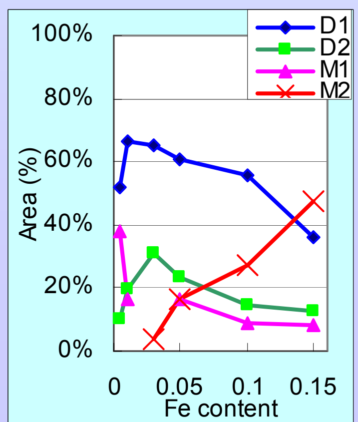


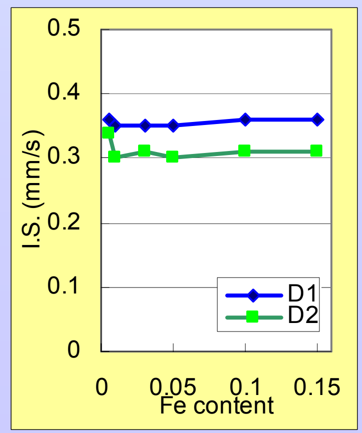


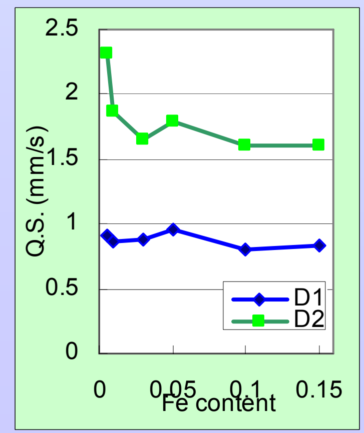
R.T. Mössbauer spectra of $Sn_{1-x}{}^{57}Fe_xO_2$ annealed at 650^{o}C for 2 hrs



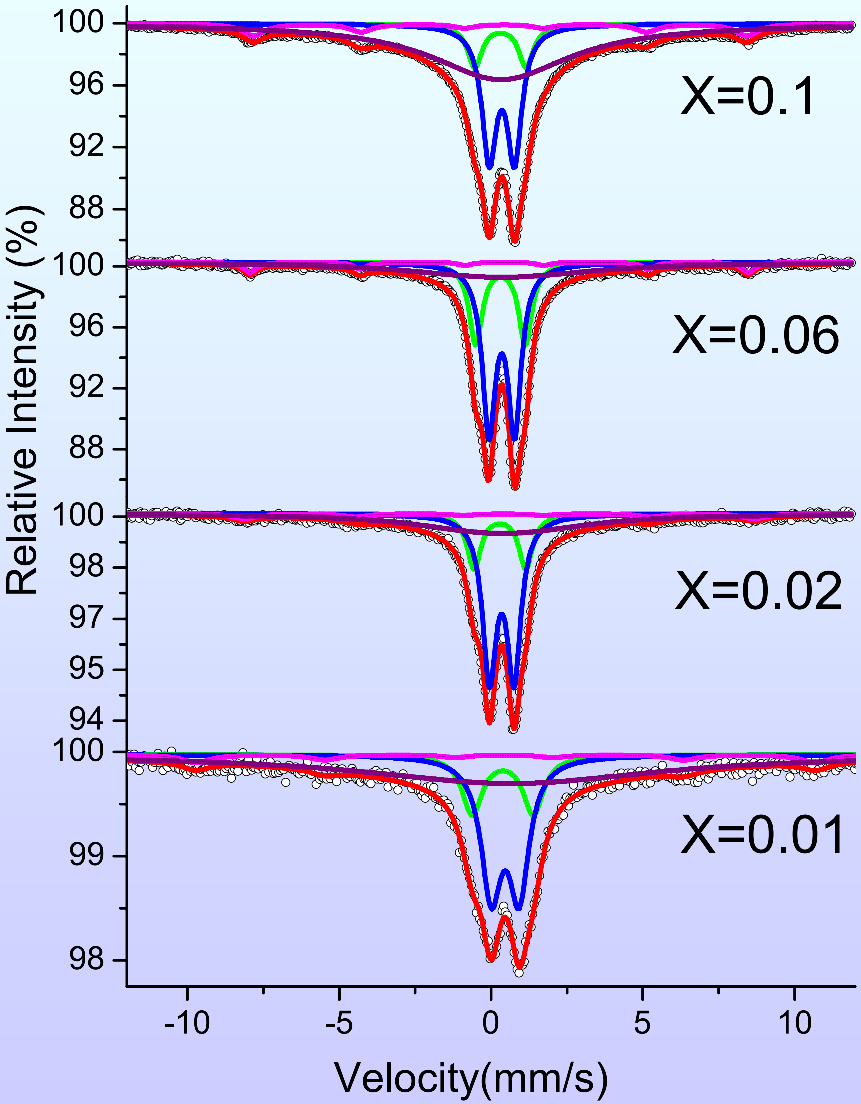
	parameter	0.005	0.01	0.03	0.05	0.1	0.15
DOUBLET (1)	Area (%)	51.90%	66.20%	65.00%	60.50%	55.40%	35.90%
	δ (mm/s)	0.36	0.35	0.35	0.35	0.36	0.36
	Δ (mm/s)	0.91	0.87	0.88	0.96	0.81	0.84
	Γ (mm/s)	0.82	0.71	0.52	0.75	0.49	0.49
DOUBLET (2)	Area (%)	10.00%	19.40%	31.10%	23.30%	14.80%	12.40%
	δ (mm/s)	0.34	0.3	0.31	0.3	0.31	0.31
	Δ (mm/s)	2.31	1.86	1.65	1.79	1.6	1.6
	Γ (mm/s)	0.82	0.71	0.52	0.75	0.49	0.49
MIXED M+Q (1)	Area (%)	38.10%	16.40%		16.20%	9.00%	8.10%
	δ (mm/s)	0.57	0.39		0.39	0.67	0.45
	B_{HF} (T)	31.52	6.03		12.42	39.86	27.01
	Δ (mm/s)	0.13	0		0.02	0.03	0.02
	Γ (mm/s)	2.93	2.01		2.06	1.51	1.51
MIXED M+Q (2)	Area (%)			4.00%	16.40%	27.00%	47.50%
	δ (mm/s)			0.4	0.37	0.38	0.38
	B_{HF} (T)			51.43	51.03	50.98	51.04
	Δ (mm/s)			-0.16	-0.19	-0.18	-0.2
	Γ (mm/s)			0.36	0.5	0.4	0.41



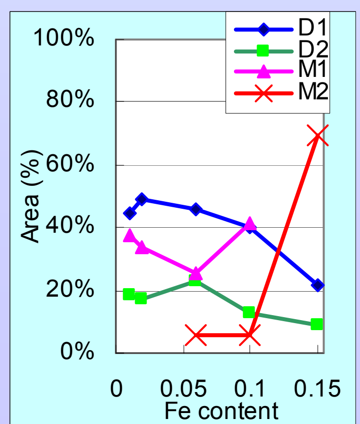


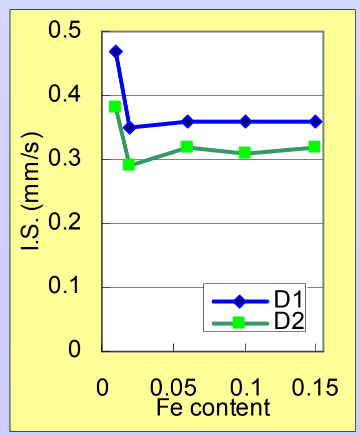


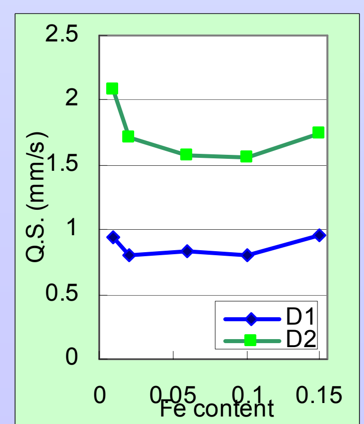
RT Mössbauer of $Sn_{1-x}{}^{57}Fe_xO_2$ annealed at 600ºC for 6 hrs



	parameter	0.01	0.02	0.06	0.1
DOUBLET (1)	Area (%)	44.30%	49.30%	45.80%	40.30%
	δ (mm/s)	0.47	0.35	0.36	0.36
	Δ (mm/s)	0.94	0.81	0.83	0.81
	Γ (mm/s)	0.86	0.56	0.53	0.7
DOUBLET (2)	Area (%)	18.30%	16.90%	22.80%	12.60%
	δ (mm/s)	0.38	0.29	0.32	0.31
	Δ (mm/s)	2.09	1.72	1.57	1.56
	Γ (mm/s)	0.86	0.56	0.53	0.7
MIXED M+Q (1)	Area (%)	37.40%	33.80%	25.60%	41.50%
	δ (mm/s)	0.37	0.42	0.37	0.39
	B_{HF} (T)	24.78	11.78	25.14	25.67
	Δ (mm/s)	0	0	0.03	0.04
	Γ (mm/s)	7.11	5.53	0.15	0.26
MIXED M+Q (2)	Area (%)			5.90%	5.50%
	δ (mm/s)			0.35	0.37
	B_{HF} (T)			50.91	51.08
	Δ (mm/s)			-0.2	-0.2
	Γ (mm/s)			0.54	0.7







Mössbauer spectra results and considerations

1. The large intensity of magnetic relaxation subspectra were obtained for $Sn_{1-x}Fe_xO_2$ (x=0.1), which were prepared by a sol-gel method, and annealed at 600 ^oC for 6 hours.

2. The magnetic components increased with the decrease of doped Fe.

3. When SnO_2 powders doped with more than 5% Fe were annealed at 650^oC for 2 hours and 600 ^oC for 6 hours, antiferromagnetic α-Fe_2O_3 is grown with high doping and high temperature annealing. ← phase decomposition.

4. Assignment of components

Doublet1 : Fe^{3+} substituted at Sn site in SnO_2 lattice.

Doublet2 : Fe^{3+} occupied at interstitial site among SnO_2 lattice

A broad magnetic component : Fe^{3+} in SnO_2 lattice

A sharp magnetic sextet : α-Fe_2O_3 separated out of SnO_2 lattice

.SEM observation .

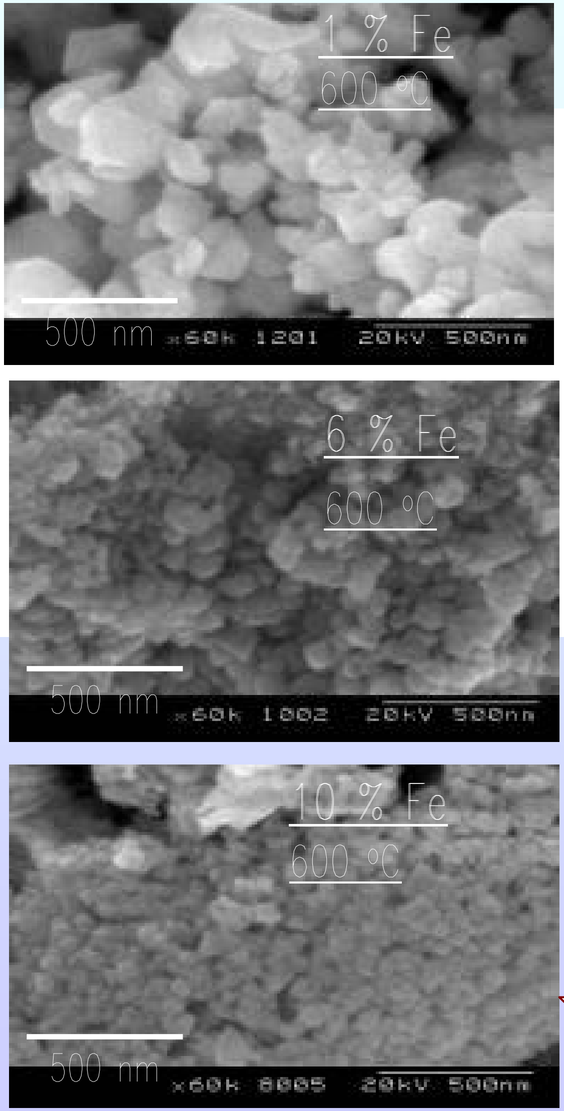
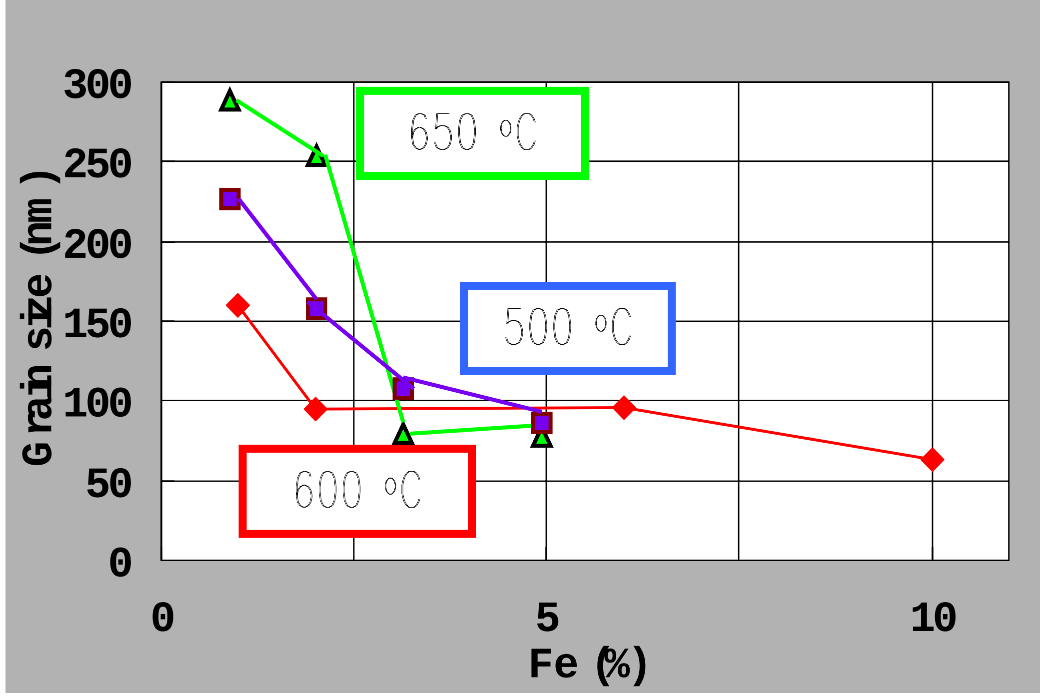


Fig.1 SEM images of $Sn_{1-x}Fe_xO_2$ annealed at 600 ºC

Fig.2 Relation of grain size and Fe% about $Sn_{1-x}Fe_xO_2$



The grain size decreased with doping Fe. The grains size became less than 100nm when more than 3% Fe was doped.

The uniformed particles are obtained by a sol-gel method.

.XRD results .

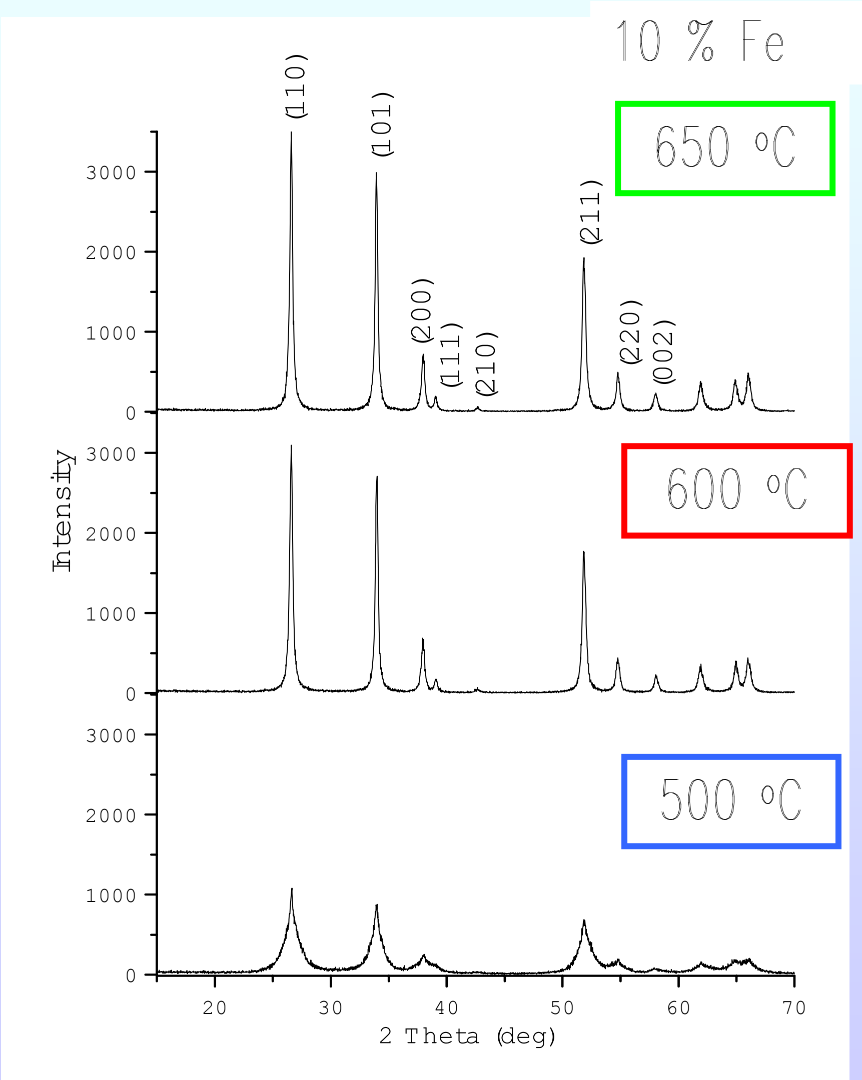


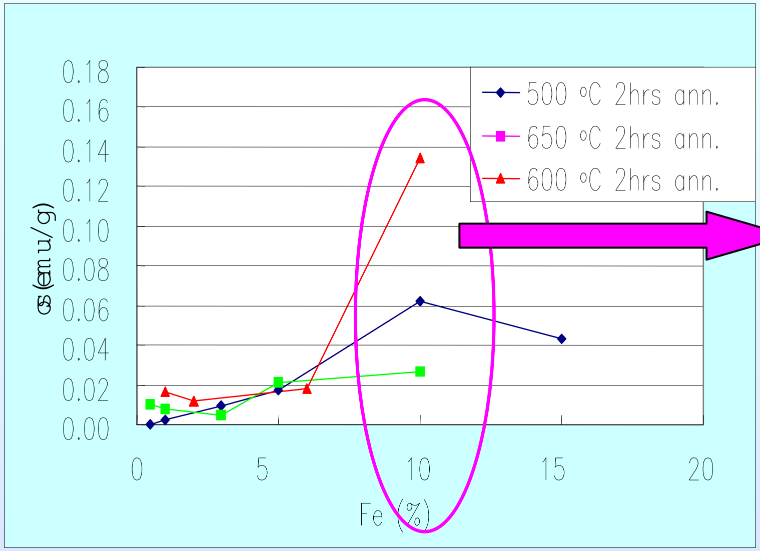
Fig.3

The XRD peaks of Iron oxides and impurity were not observed for the samples with more than 5% doped iron.

All samples showed the rutile type crystalline although the crystalline were so poor for the sample annealed at low temperature.

VSM

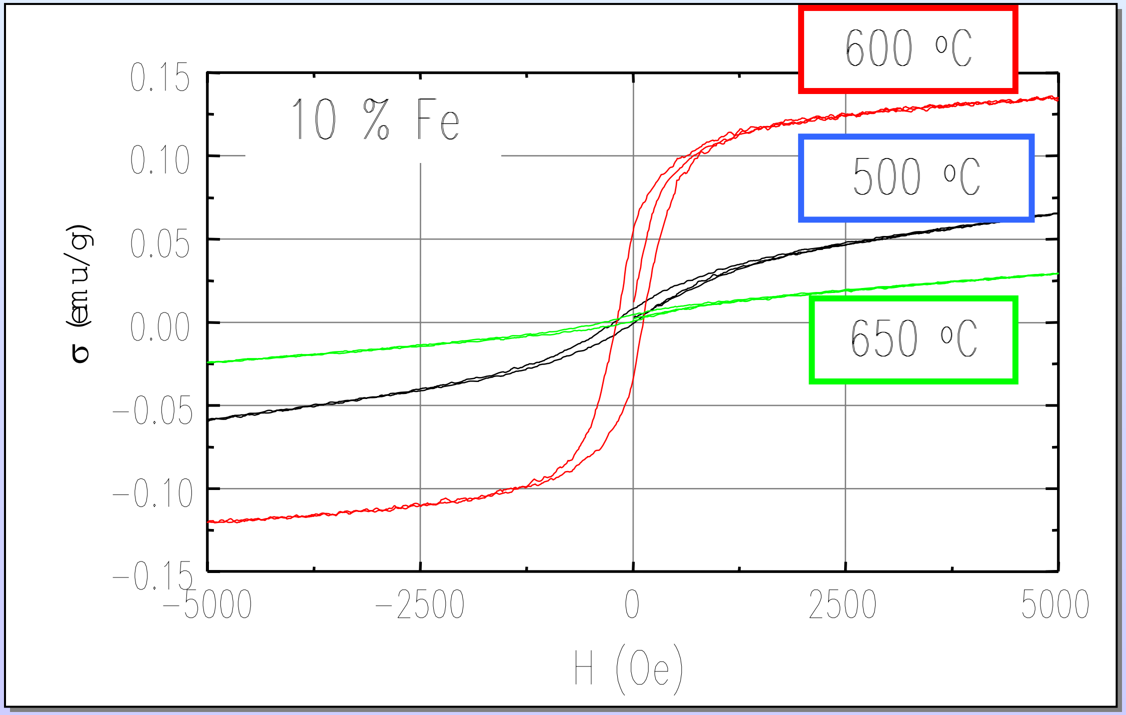
Fig.4 R.T. VSM saturated magnetization of $Sn_{1-x}Fe_xO_2$



The ferromagnetism appeared due to the long range ordering at Room temperature .

The saturation magnetization showed the maximum for 10% Fe doped SnO_2.

Fig.5 R.T. magnetizations curve of $Sn_{0.9}Fe_{0.1}O_2$



600 ºC → large hysteresis

500 ºC → meddle

650 ºC →small hysteresis

Why the different hysteresis was obtained should be confirmed by Mössbauer spectra analysis.

.RT ^{57}Fe Mössbauer spectra of $Sn_{0.9}Fe_{0.1}O_2$.

Fig.6 Mössbaure spectra at R.T. of $Sn_{0.9}Fe_{0.1}O_2$

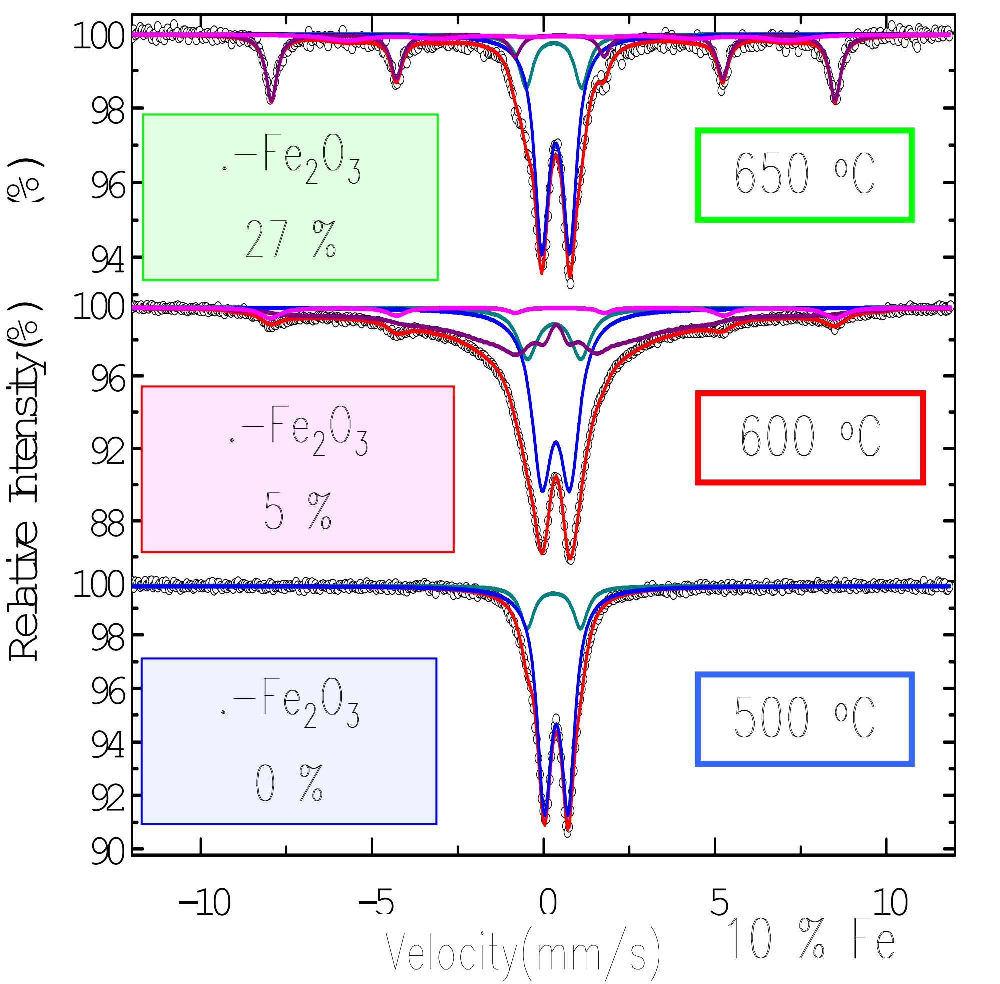
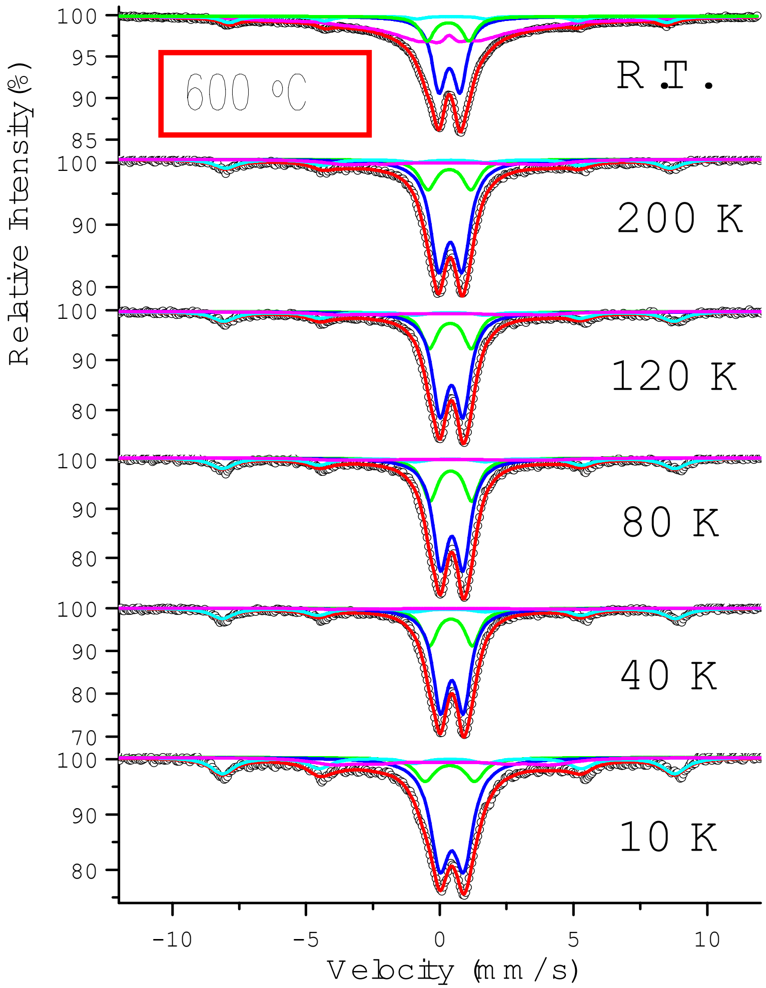


Table.1 Mössbaure spectra parameters of $Sn_{0.9}Fe_{0.1}O_2$

	parameter	500 °C	600 °C	650 °C
DOUBLET (1)	Area (%)	83.10%	40.30%	55.40%
Fe(.) O_h	δ (mm/s)	0.37	0.36	0.36
	Δ (mm/s)	0.69	0.81	0.81
	Γ (mm/s)	0.49	0.70	0.49
DOUBLET (2)	Area (%)	16.90%	12.60%	14.80%
Fe (.) T_d	δ (mm/s)	0.3	0.31	0.31
	Δ (mm/s)	1.56	1.56	1.6
	Γ (mm/s)	0.49	0.70	0.49
MIXED M+Q (1)	Area (%)	–	41.50%	9.00%
Magnetic Relaxation	δ (mm/s)	–	0.39	0.67
	BHF (T)	–	25.67	39.86
	Δ (mm/s)	–	0.04	0.03
	Γ (mm/s)	–	0.26	1.51
MIXED M+Q (2)	Area (%)	–	5.50%	27.00%
.–Fe_2O_3	δ (mm/s)	–	0.37	0.38
	BHF (T)	–	51.08	50.98
	Δ (mm/s)	–	−0.20	−0.18
	Γ (mm/s)	–	0.70	0.40

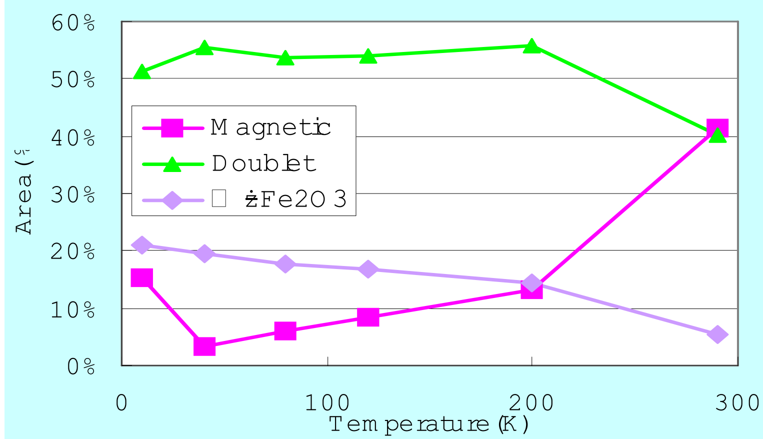
With the increase of annealing temperatures, the intensity ratio of anti-ferromagnetic .–Fe_2O_3 increased. It results in the decrease of saturated magnetization.

Low temperature Mössbauer spectra of $Sn_{0.9}Fe_{0.1}O_2$



Various temperatures Mossvaure spectra of $Sn_{1-x}Fe_xO_2$ (X=0.10) annealed at 600 °C for 6h

Fig.8 Temperature dependence of three components in $Sn_{1-x}Fe_xO_2$ (x=0.10)



With lowering temperature,

Mag. relaxation decreased, and

Magnetic sextet increased.

parameters	$Sn_{0.9}Fe_{0.1}O_2$ Magnetic comp.	.–Fe_2O_3	
Temp.	10 K	4.2 K	
δ (mm/s)	0.36	0.49	0.49
Δ (mm/s)	−0.06	0.41	−0.20
B_{HF} (T)	52.45	51.75	54.17

The Mössbauer parameters of $Sn_{0.9}Fe_{0.1}O_2$ were different from that of .–Fe_2O_3. The magnetic relaxation is similar to Ferromagnetic γ–Fe_2O_3.

Summary

From the results of XRD, it is found that lattice parameters, a and b, increased, and c decreased with the increase of Fe concentration. The lattice be distorted with doping of Fe

Large magnetic hysteresis was observed for 10% Fe doped $Sn_{0.9}Fe_{0.1}O_2$. The magnetization showed the maximum for Sn0.9Fe0.1O2 annealed at 600^{o}C.

When the annealing temperature was high, the magnetization decreased due to the phase separation of anti-ferromagnetic a-Fe_2O_3.

It is considered from Low temperature Mössbauer spectra that the magnetic relaxation components are due to superparamagnetism of ferric -Fe_2O_3.

Coey et al. reported that $Sn_{0.86}Fe_{0.14}O_2$ film show the magnetixation 2.2 Am^2kg^{-1} at room temperature, and explained the mechanism due to Superexchange and F-centor exchange(FCE) model (Coey et al., Appl. Phys. Lett.,84(2004)1332)

a) General speaking, oxides show antiferromagnetic behavior due to minus exchange interactions for Fe^{3+}-$O^{2-}$$Fe^{3+}$ covalent bond

b) If hole defect of O^{2-} orbital, 1 electron is covalent with 2 Fe orbital to make ferromagnetic behavior of Fe^{4+}-O^{2-}-Fe^{3+} due to plus super exchange interactions.

c) Ferromagnetic coupling of ferric ions via an electron trapped in a bridging oxygen vacancy (F centor) is proposed to explain the high Curie temperature.

d) Long range interactions through Sn $^{3+}$ are possible?