

## SnO<sub>2</sub> doped with Mn, Fe or Co: Room temperature dilute magnetic semiconductors

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Room temperature ferromagnetism is found in (Sn<sub>1-x</sub>M<sub>x</sub>)O<sub>2</sub> ( $M = \text{Mn, Fe, Co, } x = 0.05$ ) ceramics where x-ray diffraction confirms the formation of a rutile-structure phase. Room temperature saturation magnetization of 0.2 and 1.8 Am<sup>2</sup>kg<sup>-1</sup> for (Sn<sub>0.95</sub>Mn<sub>0.05</sub>)O<sub>2</sub> and (Sn<sub>0.95</sub>Fe<sub>0.05</sub>)O<sub>2</sub>, respectively, corresponds to a moment of 0.11 or 0.95 μ<sub>B</sub> per Mn or Fe atom. The Curie temperatures are 340 and 360 K, respectively. The magnetization cannot be attributed to any identified impurity phase. <sup>57</sup>Fe Mössbauer spectra of the Fe-doped SnO<sub>2</sub> samples, recorded at room temperature and 16 K, show that about 85% of the iron is in a magnetically ordered high spin Fe<sup>3+</sup> state, the remainder being paramagnetic. © 2004 American Institute of Physics.

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Dilute magnetic semiconductors (DMS) produced by doping transition metal ions into nonmagnetic semiconductors are of interest for potential applications in spin electronics.<sup>1</sup> Wide gap DMSs combine their electrical conductivity with ferromagnetism and optical transparency, thereby opening up the possibility of other device concepts. High temperature ferromagnetism has been reported in several oxide and nitride materials such as ZnO with Co or Mn doping,<sup>2-4</sup> TiO<sub>2</sub> (anatase) with Co,<sup>5</sup> GaN with Mn,<sup>6</sup> or AlN with Cr,<sup>7</sup> although it is questionable whether all of these are uniform, single phase materials. Recent reports of a giant magnetic moment in Co-doped SnO<sub>2</sub> thin films<sup>8</sup> led us to investigate Mn, Fe,<sup>9</sup> and Co doped SnO<sub>2</sub>.

Here we focus on bulk ceramic material. The oxides Sn<sub>1-x</sub>M<sub>x</sub>O<sub>2</sub>, with  $x = 0.05$ , were synthesized from stoichiometric amounts of high purity SnO<sub>2</sub> and MO ( $M = \text{Mn, Fe, Co}$ ) powders. A second Sn<sub>0.95</sub>Fe<sub>0.05</sub>O<sub>2</sub> sample was prepared using <sup>57</sup>Fe-rich α-Fe<sub>2</sub>O<sub>3</sub>. In addition, a series of Sn<sub>1-x</sub>Co<sub>x</sub>O<sub>2</sub> ( $x = 0.005 - 0.05$ ) ceramics was prepared, to determine the solubility limit of cobalt in these ceramics. The oxide powders were ground under isopropanol for one hour, then pressed into pellets and sintered for 24 h at 1150 °C. Phase analysis was carried out using x-ray Diffraction (XRD) and scanning electron microscopy, with energy dispersive x-ray analysis (EDAX) for elemental analysis and mapping. Magnetization measurements were made in a superconducting quantum interference device magnetometer both at 300 and 5 K, and Curie temperatures ( $T_C$ ) were measured using an alternating gradient force magnetometer. <sup>57</sup>Fe Mössbauer spectra (MS) were collected at room temperature (RT) and at 16 K in transmission geometry with a

<sup>57</sup>Co(Rh) source. <sup>119</sup>Sn MS of SnO<sub>2</sub> and Sn<sub>0.95</sub>M<sub>0.05</sub>O<sub>2</sub> ( $M = \text{Mn, Fe, or Co}$ ) were collected at RT and 85 K in transmission geometry, with a Ba<sup>119</sup>SnO<sub>3</sub> source.

Energy dispersive x-ray analysis (EDAX) indicates that all samples show the nominal transition metal concentration. However, elemental mapping of the  $x = 0.05$  samples revealed the presence of small oxide clusters ( $\sim 2 \mu\text{m}$ ), rich in 3d transition metal. X-ray diffraction confirms the formation of a rutile SnO<sub>2</sub> structure (P4<sub>2</sub>/mnm) in all samples (Fig. 1). Rietveld analysis of the x-ray diffraction patterns of the FeO doped SnO<sub>2</sub> showed traces of α-Fe<sub>2</sub>O<sub>3</sub>. The transition metal rich secondary phase in the Co doped material was identified as SnCo<sub>2</sub>O<sub>4</sub>, but no impurity phases were identified by XRD in the Mn doped sample. Figure 2 illustrates the variation of lattice parameters “a” and “c” in Sn<sub>1-x</sub>Co<sub>x</sub>O<sub>2</sub> with  $x$ . Both saturate at  $x \approx 0.02$ , indicating the solubility limit for cobalt in SnO<sub>2</sub>. Substitution of transition metal ions dilates the lattice and the unit cell volume expansion is about 0.4% for all samples with  $x = 0.05$  (Table I).

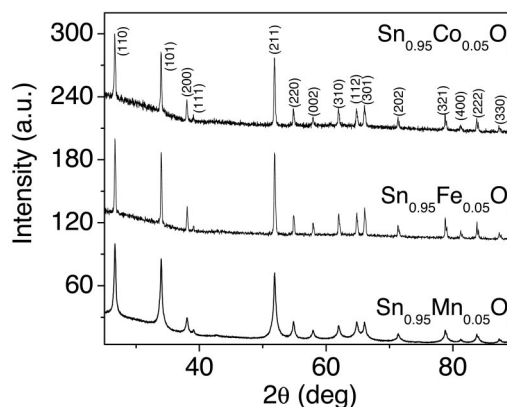


FIG. 1. X-ray diffraction pattern of (Sn<sub>0.95</sub>Mn<sub>0.05</sub>)O<sub>2</sub>, (Sn<sub>0.95</sub>Fe<sub>0.05</sub>)O<sub>2</sub>, and (Sn<sub>0.95</sub>Co<sub>0.05</sub>)O<sub>2</sub>.

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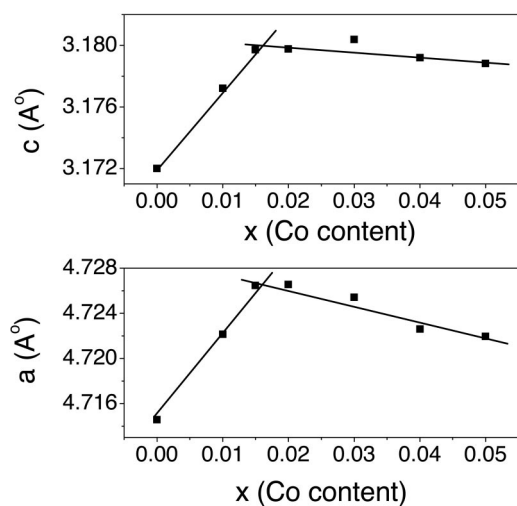


FIG. 2. Variation of lattice parameters in  $\text{Sn}_{1-x}\text{Co}_x\text{O}_2$  with  $x$ .

Figure 3 compares magnetization data for the 5% doped samples, at 300 and 5 K. Room temperature saturation magnetization is 0.2 and  $1.8 \text{ Am}^2 \text{ kg}^{-1}$  for  $(\text{Sn}_{0.95}\text{Mn}_{0.05})\text{O}_2$  and  $(\text{Sn}_{0.95}\text{Fe}_{0.05})\text{O}_2$ , respectively. The Co-doped samples are paramagnetic at room temperature. The corresponding ferromagnetic moments are 0.11, 0.95, and  $0.0 \mu_B$  per Mn, Fe, and Co atom. Hysteresis is not observed in any bulk samples. The room temperature ferromagnetism of the Mn and Fe material cannot be attributed to the impurity phases. Possible impurity phases in the Mn doped samples are  $\text{SnMn}_2\text{O}_4$  or  $\text{Mn}_3\text{O}_4$  with Curie temperatures in the range of 40–50 K; they may be responsible for the increased ferromagnetism at 5 K seen in Fig. 3. The Sn-doped hematite is only very weakly magnetic.<sup>10</sup> The Curie temperatures were found to be 340 and 360 K for the Mn and Fe samples, respectively. In all cases, Curie temperatures and magnetic moments are enhanced significantly ( $\geq 1 \mu_B/3d$  metal ion) in thin films deposited by pulsed laser deposition from the ceramic targets.

<sup>57</sup>Fe MS of the  $(\text{Sn}_{0.95}\text{Fe}_{0.05})\text{O}_2$  samples prepared using FeO and <sup>57</sup>Fe enriched  $\alpha\text{-Fe}_2\text{O}_3$  recorded at room temperature and 16 K, show the presence of a magnetically split and weak paramagnetic contribution (Fig. 4). A set of one magnetic sextet and one paramagnetic doublet was used to fit the experimental data for both samples at both temperatures, and the resultant values of the Mössbauer parameters from these fits appear in Table II. As can be seen from these values, all components correspond to high spin ( $S=5/2$ )  $\text{Fe}^{3+}$  ions in octahedral oxygen environment. The magnetic hyperfine spectra do not allow us to distinguish the Sn-doped  $\alpha\text{-Fe}_2\text{O}_3$

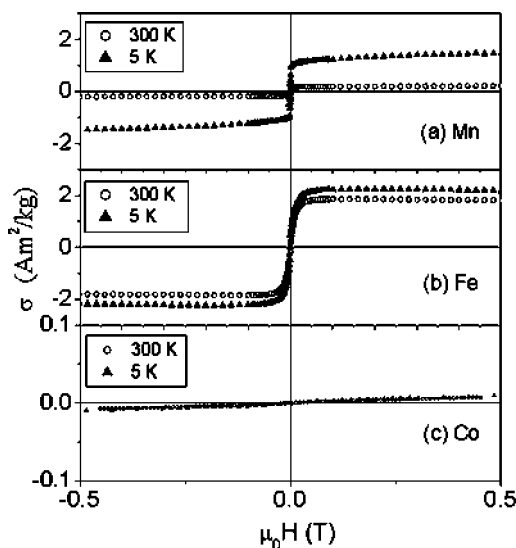


FIG. 3. Magnetization of polycrystalline (a)  $(\text{Sn}_{0.95}\text{Mn}_{0.05})\text{O}_2$ , (b)  $(\text{Sn}_{0.95}\text{Fe}_{0.05})\text{O}_2$ , and (c)  $(\text{Sn}_{0.95}\text{Co}_{0.05})\text{O}_2$ .

(which does not undergo the Morin transition) from the ferromagnetically ordered  $\text{Fe}^{3+}$  ions substituting the  $\text{Sn}^{4+}$  ions on the  $\text{SnO}_2$  rutile structure, because the hyperfine parameters of the magnetic sextet are close to those of Sn doped  $\alpha\text{-Fe}_2\text{O}_3$ .<sup>10</sup> However the presence of  $\alpha\text{-Fe}_2\text{O}_3$  can only account for a fraction of the magnetically split absorption area. Rietveld refinement of x-ray diffraction data yields approximately 1.7 (2) wt % of  $\alpha\text{-Fe}_2\text{O}_3$  phase. If the magnetic components were to be associated entirely to the  $\alpha\text{-Fe}_2\text{O}_3$  contribution, we would expect a 2.7 wt %. Some of the iron ions have indeed substituted the tin ions in the rutile structure and they are responsible for the observed ferromagnetism with a Curie temperature of 360 K. The saturation magnetization at room temperature far exceeds the value of  $0.02 \text{ Am}^2 \text{ kg}^{-1}$ , which is expected if the only magnetic component was the Sn doped  $\alpha\text{-Fe}_2\text{O}_3$  phase. Similarly for the Mn-doped  $\text{SnO}_2$ , the impurity phases, which order at  $\sim 50$  K, cannot account for the room temperature ferromagnetism. Thus both manga-

TABLE I. Lattice parameters and magnetic properties of  $\text{Sn}_{1-x}\text{M}_x\text{O}_2$  ( $M = \text{Mn, Fe or Co}$ ).

Sample	$a$ (Å)	$c$ (Å)	$V$ (Å <sup>3</sup> )	$\mu_B/M$ atom	$T_C$ (K)
$\text{SnO}_2$	4.71	3.172	70.5	...	...
$(\text{Sn}_{0.95}\text{Mn}_{0.05})\text{O}_2$	4.72	3.181	71.1	0.11	340
$(\text{Sn}_{0.95}\text{Fe}_{0.05})\text{O}_2$	4.73	3.181	71.2	0.95	360
$(\text{Sn}_{0.95}\text{Co}_{0.05})\text{O}_2$	4.72	3.179	70.9	0.0	...

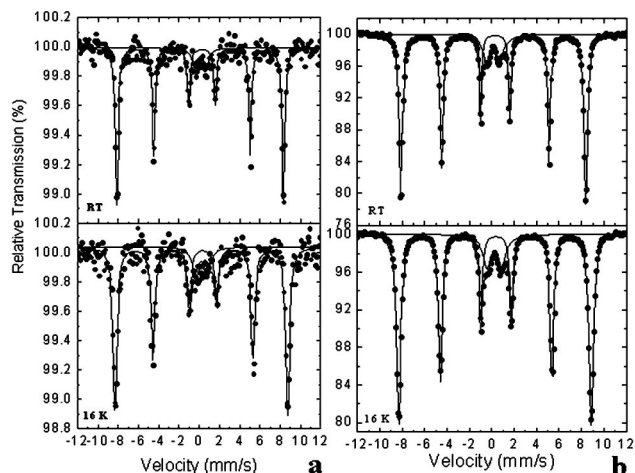


FIG. 4. <sup>57</sup>Fe Mössbauer spectra of the 5% Fe doped  $\text{SnO}_2$  samples prepared using (a) natural FeO and (b) <sup>57</sup>Fe enriched  $\alpha\text{-Fe}_2\text{O}_3$ , recorded at RT and 16 K.

TABLE II. Hyperfine parameters of  $\text{Sn}_{0.95}\text{Fe}_{0.05}\text{O}_2$  prepared using  $^{57}\text{Fe}$ -enriched  $\alpha\text{-Fe}_2\text{O}_3$ . ( $\delta$ : isomer shift quoted related to metallic Fe at 300 K,  $\Gamma/2$ : line width,  $\Delta$  or  $2\epsilon$ : quadrupole shift,  $B_{\text{hf}}$ : hyperfine field,  $A$ : Area).

Temperature	IS $\text{mm s}^{-1}$ $\pm 0.01$	$\Gamma/2$ $\text{mm s}^{-1}$ $\pm 0.01$	$\Delta$ or $2\epsilon$ $\text{mm s}^{-1}$ $\pm 0.01$	$B_{\text{hf}}$ T $\pm 0.5$ T	$A$ % $\pm 3\%$
RT	0.38	0.13	-0.19	51.6	86
	0.30	0.40	1.20	...	14
16 K	0.50	0.17	-0.13	53.6	87
	0.40	0.45	1.30	...	13

nese and iron ions in the rutile structure must experience strong ferromagnetic coupling. We suggest the exchange mechanism in  $\text{SnO}_2$  involves an electron trapped at an oxygen vacancy adjacent to the transition metal ions (F-center exchange).<sup>9</sup>

$^{119}\text{Sn}$  spectra at room temperature and 85 K showed no discernible transferred hyperfine field ( $<0.5$  T), which might have been expected when Sn ions are surrounded by magnetic Mn or Fe neighbors. The transferred magnetic hyperfine field on the  $^{119}\text{Sn}$  nucleus of the Sn doped  $\alpha\text{-Fe}_2\text{O}_3$  phase is 12.0–13.0 T,<sup>11</sup> but there was insufficient tin present in this phase ( $<1\%$  of total tin) for it to be visible in the  $^{119}\text{Sn}$  spectrum.

In conclusion, room temperature ferromagnetism is observed in  $(\text{Sn}_{1-x}\text{M}_x)\text{O}_2$  ( $M = \text{Mn, Fe}$ ) polycrystalline samples with magnetic moments of 0.11 and  $0.95 \mu_{\text{B}}$  per Mn and Fe ion, respectively. Curie temperatures are 340 and 360 K for 5% Mn and Fe doped  $\text{SnO}_2$  samples. The ferromag-

netism cannot be associated with the minor impurity phase; it is a feature of the doped  $\text{SnO}_2$  which may be explained by F-center exchange.<sup>9</sup> The ferromagnetic moments and Curie temperature are enhanced significantly in epitaxial thin films with Mn, Fe,<sup>9</sup> or Co (Ref. 8) where no secondary phases are detected.

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