EPR investigations of Sn$_{1-x}$Fe$_x$O$_2$ nanopowders

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Abstract. An X-band electron paramagnetic resonance (EPR) investigation of Fe$^{3+}$ ions in Sn$_{1-x}$Fe$_x$O$_2$ nanopowders with $x = 0.005$-$0.07$ is reported. These samples are interesting to investigate as Fe doping produce ferromagnetism in SnO$_2$, making it a promising ferromagnetic semiconductor at room temperature.

1. Introduction
SnO$_2$ is an attractive system for quite a wide variety of practical applications, being a chemically stable oxide semiconductor. It has been shown that Fe doping produces ferromagnetic semiconductor at room temperature [1]. This material, therefore, has the potential for use in spintronic devices such as spin transistors, spin light emitting diodes, very high density nonvolatile semiconductor memory and optical emitters. It is believed that oxygen vacancies and substitutional incorporation are important to produce ferromagnetism in semiconductor oxide doped with transition metal ions.

The present paper reports our electron paramagnetic resonance (EPR) studies on Sn$_{1-x}$Fe$_x$O$_2$ ($x = 0.005$-$0.07$) nanopowders in order to determine the oxidation state and site occupancy of the dopant ions in the host SnO$_2$ lattice, and also to detect a possible ferromagnetic ordering of these ions.

2. Experimental
A series of nanopowders of Fe$^{3+}$ ions-doped SnO$_2$ having the general formula Sn$_{1-x}$Fe$_x$O$_2$ ($x = 0.005$, $0.01$, $0.03$, $0.05$ and $0.07$) were obtained and investigated by EPR.

The samples were prepared using stannous chloride dihydrate (SnCl$_2$·2H$_2$O 95%) and oxalic acid dihydrate (H$_2$C$_2$O$_4$·2H$_2$O 99.4%) in stoichiometric amounts doped with iron by using FeCl$_3$ monocristalline needles [2]. Appropriate quantities were dissolved in distilled water using a magnetic stirrer, and finally a homogenous solution was obtained. The homogeneous solution was then decomposed at 523 K in air until dry. The temperature is raised gradually over 2-3 days. After heat treatment this mass precursor was ground to give fine powder. Fractions of the obtained powders have been calcinated at 873 K for 2 h in air.

The EPR measurements on the samples were performed with a Bruker ELEXSYS 500 spectrometer at X-band.

3. Results and discussion
Figure 1 shows X-band EPR spectra recorded at room temperature for Sn$_{1-x}$Fe$_x$O$_2$ nanopowders with different Fe concentration $x$. 

From the experimental spectra (figure 1), one can distinguish that there exists an overlap of three types of Fe-related EPR spectra: (i) a sharp line (LS) arising from interstitially incorporated low-spin Fe$^{3+}$ ions, $S = \frac{1}{2}$, (ii) a spectra (HS) due to the substitutionally incorporated high-spins Fe$^{3+}$ ions, $S=\frac{5}{2}$, which are probably situated in the interior of the nanodomains [1] and (iii) a broad signal (FM) which could be attributed to the ferromagnetically coupled Fe$^{3+}$ ions.

The assignment of the above contributions is based on the corresponding simulations which are shown in figure 2.

In the spectra simulations, we have used the X-sophe software where the following spin Hamiltonians were considered:

$$H_S = \mu_B B \cdot g \cdot S, \text{ for the low spin } (S=1/2)$$

$$H = g \mu_B B \cdot S + D \left[ S_x^2 - (1/3)S(S+1) \right] + E[S_y^2 - S_z^2], \text{ for high spin } (S = 5/2)$$
Here, D and E are axial and nonaxial parameters, respectively.

Table 1 summarizes the spin Hamiltonian parameters, the line widths and the spin assignments used to simulate the observed three EPR spectra.

|       | g_x  | g_y  | g_z  | D [G] | E [G] | ΔH [G] | S   |
|-------|------|------|------|-------|-------|--------|-----|
| LS    | 3.612| 3.612| 3.612| 0     | 0     | 20     | 1/2 |
| HS    | 2.004| 2.004| 2.004| 700   | -190  | 100    | 5/2 |
| FM    | 2.412| 2.412| 2.412| 0     | 0     | 2000   | 3/2 |

The values of the g-tensors for HS and LS spectra are very close to the other values reported in the literature [3]. The effective g-factor for the broad signal (FM) is greater than 2 which represents a clear signature of ferromagnetism in Sn$_{1-x}$Fe$_x$O$_2$ nanopowders [4]. Therefore, the FM signal could be attributed to the ferromagnetic resonance arising from the exchange interactions between Fe$^{3+}$ ions.

One can observe in figure 3 that in the low concentrations domain ($0.005 \leq x \leq 0.03$) the line width ($\Delta H_{1/2}$) corresponding to FM signal increases with increasing the concentration. This tendency could be attributed to the dominance of the dipolar interactions. In the high concentration limit ($x > 0.03$) the line width decreases with increasing the concentration. It could mean that in this range of concentrations the ferromagnetic behavior is present and the magnetic exchange interaction is dominant.

![Figure 3](image.png)

**Figure 3.** Concentration dependence of $\Delta H_{1/2}$ linewidth for FM resonance in Sn$_{1-x}$Fe$_x$O$_2$ nanopowders.

### 4. Conclusions

We have investigated by EPR the incorporation of Fe ions into SnO$_2$ nanopowders. EPR measurements reveal that Fe doping results in interstitial and substitutional incorporation of Fe$^{3+}$ ions into the SnO$_2$ lattice as well as in a ferromagnetic coupling of these ions. For higher x concentration of Fe$^{3+}$ ions the FM linewidth decreases with increasing the concentration due to the dominance of magnetic exchange interaction in Sn$_{1-x}$Fe$_x$O$_2$ nanopowders.

### References

[1] Misra S K and Andronenko SI 2007 *J. Appl. Phys.* **101** 09H120

[2] Parra R, Ramajo L A, Goes M S, Varela J A and Castro M S 2008 *Mater. Res. Bull.* **43** 3202

[3] Dusausoy Y, Ruck R and Gaite J M 1988 *Phys. Chem. Miner.* **15** 300

[4] Karmakar D, Mandal S K, Kadam R M, Paulose P L, Rajarajan A K, Nath T K, Das A K, Dasgupta I and Das G P 2007 *Phys. Rev.* B **75** 144404.