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Electron magnetic resonance and Mössbauer studies on iron doped SnO_2 nanoparticles

Maria Nicoleta Grecu · Serban Gr. Constantinescu · Daniela Ghica · Doina Tărăbăşanu-Mihaila · Lucian Diamandescu

Abstract Iron doped (0.25–7.5% molar) hydrothermal nano-SnO_2 was characterized by electron magnetic resonance (EMR) and Mössbauer spectroscopies. Only a small fraction of transition metal ions are in magnetic ordered state, contrary to the similar crystallographic compound TiO_2. Temperature dependences of spectra suggest that by increasing iron concentration, or annealing temperature, iron ions migrate to nanoparticles surfaces forming disordered iron oxides.

Keywords EMR · Mössbauer effect · SnO_2 nanoparticles · Paramagnetic defects

1 Introduction

Tin dioxide (SnO_2) is a semiconductor which combines good electrical conductivity with optical transparency, being very interesting for optoelectronic applications. Also, it has remarkable properties as an oxidation catalyst, or gas sensor. Recent discovery of room temperature ferromagnetism in Co-doped SnO_2 [1] has increased the interest in its study [2]. Numerous investigations have been performed on transition metal doped SnO_2 (V, Mn, Fe, Co, Rh, Ni, Cr) [3, 4]. In spite of this effort the data are often contradictory [4–6], and there is no clear model to explain the behaviour of transition metal ions and the existence or not of the ferromagnetic ordering. All studies have put in evidence the importance of the preparation route and of the thermal treatments. Therefore a study of local magnetic and structural properties of hydrothermal nano-SnO_2 doped with iron was performed with EMR and Mössbauer spectroscopy.

M. N. Grecu (✉) · S. Gr. Constantinescu · D. Ghica · D. Tărăbăşanu-Mihaila · L. Diamandescu
National Institute of Materials Physics, 077125 Magurele-Bucharest, Romania
e-mail: mgrecu@infim.ro

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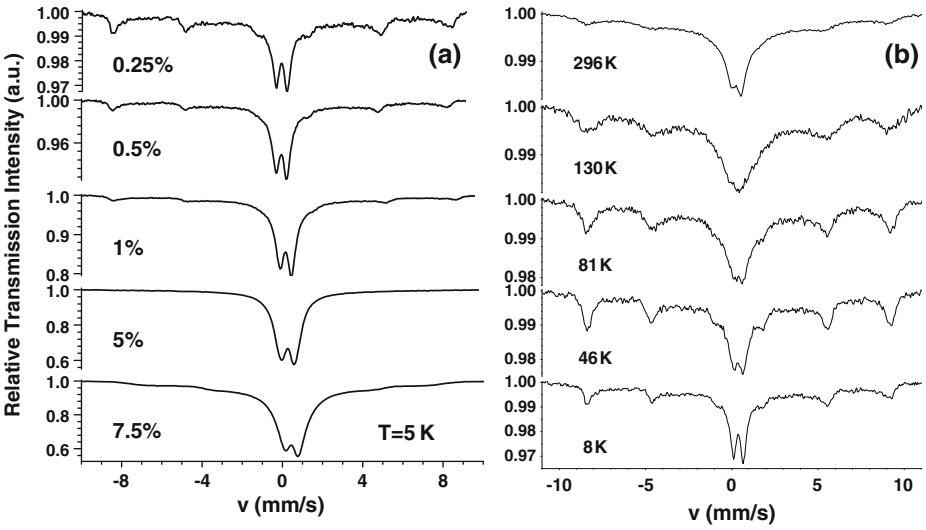

Fig. 1 ^{57}Fe Mössbauer spectra at 5 K vs. iron concentration (a), and the temperature dependence of spectra for the sample with 0.25% iron

2 Experimental

Iron doped SnO_2 nanoparticles, with different concentrations of ^{57}Fe (0.25%–7.5% mol α-Fe_2O_3), were synthesized by a hydrothermal route at 200°C as in [7, 8]. The analysis of X-ray diffraction patterns, performed with a Bruker D8 Advance diffractometer, revealed the formation of the rutile SnO_2 phase without any impurity under the limit of instrument sensitivity. The average crystallite sizes were 3–4 nm for all samples. The EMR spectra for as-prepared and annealed samples, one hour at 550°C in air and/or vacuum, were recorded at different temperatures (100–290 K) on X-band CMS 4800 and Q-band Bruker ELEXSYS-500 spectrometers. ^{57}Fe Mössbauer spectra in transmission geometry were obtained with AM50 Promeda and Wissel-SeeCo spectrometers, in the temperature range 5–298 K, using a ^{57}Co:Rh source. The χ^2 procedure was used for deconvolution of the spectra, with theoretical constrains of intensities, line widths Γ and positions of γ-line-resonances in magnetic and quadrupolar elementary patterns resonances.

3 Results and discussions

Mössbauer data In Fig. 1 the Mössbauer spectra are plotted for as-prepared samples with different ^{57}Fe concentrations (Fig. 1a) and at different temperatures for the sample with 0.25% iron (Fig. 1b). In Fig. 2 spectra for 1% Fe samples (initial and annealed) are shown by comparison.

Standard deconvolution of the spectra evidenced an increasing magnetic contribution with decreasing temperature and iron concentration (see Fig. 3). One remarks the almost symmetric doublet for the sample with 0.25% relative to the asymmetric one for Fe 7.5% at 5 K. It suggests no hidden magnetic patterns under the doublet

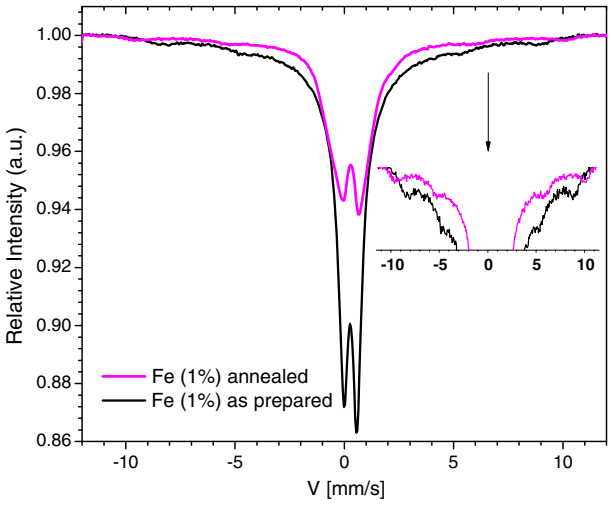

Fig. 2 Mössbauer spectra at RT for 1% ^{57}Fe sample, as prepared and annealed at 550°C

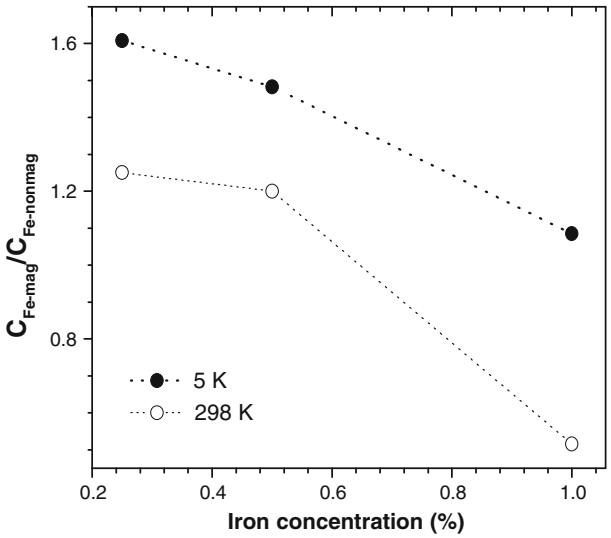

Fig. 3 Ratio of magnetic on nonmagnetic component of MS spectra at 5 and 298 K

for this sample and at this temperature. The doublet could correspond to iron substituting Sn ions. The broadening of doublet component could be explained by iron concentration dependence of grain size [7, 8]. The increasing of the magnetic contribution at low temperatures suggests a superparamagnetic transition; a multimodal distribution of the grain sizes is possible. The spectra of annealed samples at 550°C evidence apparently a smaller magnetic contribution relative to as-prepared sample (see Fig. 2), but under the doublet there is a hidden contribution. We have to note that in the spectrum of annealed sample, ferric ions are about 95–100% and the hyperfine magnetic field is more intense (60 ± 0.3 T) comparative to 53 ± 0.3 T in

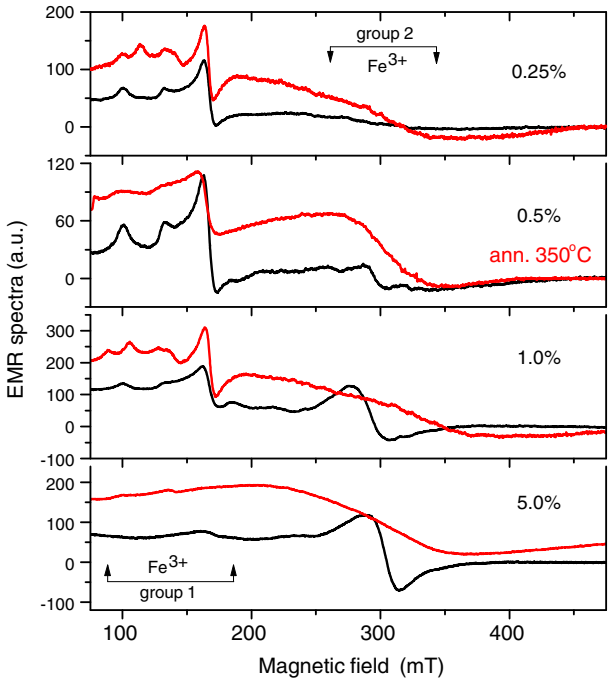

Fig. 4 X-band EMR spectra for as prepared samples (*black*) and annealed at 550°C (*red*)

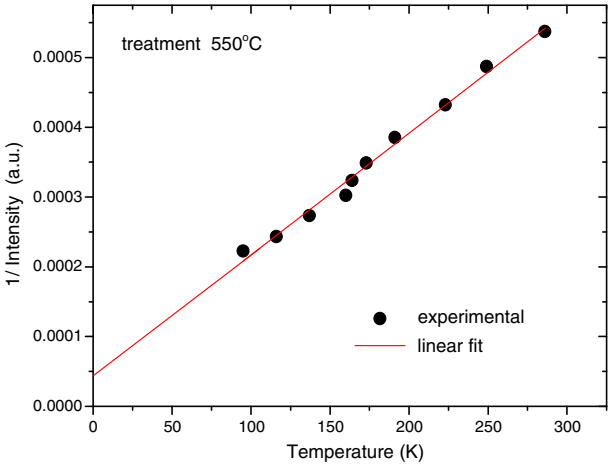

Fig. 5 Temperature dependence of spectral intensity for SnO_2:^{57}Fe (1%) ann. air 550°C

non-treated sample. It suggests a complex magnetic coupling between iron ions and defects [6].

EMR data Typical EMR spectra and their dependence of iron concentrations are given in Fig. 4. Three groups of resonance lines are observed: two important groups of Fe^{3+} ions lines were detected. At low fields ($g_{ef} \sim 4$–8) the lines were attributed to iron ions in low symmetry crystalline fields [5] and can be associated with paramagnetic ions in distorted crystalline positions.

They are responsible for the paramagnetic pattern (quadrupole doublet) observed in Mössbauer spectra. At higher ion concentrations these lines broaden due to dipole-dipole interactions. The other group of lines around $g_{ef} = 2.1$–2.2 presents the characteristics of weakly magnetic coupled ions (small shift towards lower fields and broadening at low temperatures). The air annealing 1h at 550°C (see Fig. 4, red lines) enhances and broadens very much these lines, suggesting that they come from iron distributed in the surface layer. The large broadening is a clear sign of the disorder in the nanoparticle surface. The double integral of spectra, proportional to EMR active iron ions concentration, has an antiferromagnetic temperature dependence (Fig. 5). There is also a third group of EMR lines, better observed in Q-band at higher fields ($g \leq 2.0$), in annealed samples. These lines are associated with the paramagnetic defects—hole ($g = 2.008$, line width 0.4 mT) or trapped electrons ($g = 1.994$; 1.997) in oxygen vacancy sites at the surface of SnO_2 nanoparticles.

4 Conclusions

Both EMR and Mössbauer investigations evidence the disordered distribution of iron ions in the bulk and on the surface of SnO_2 nanoparticles. A part of iron ions are magnetically coupled; they are sensitive to thermal treatment in air supporting the model of their distribution in the nanoparticle surface layer.

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