Structural and hyperfine properties of Cr-doped SnO$_2$ nanoparticles

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Abstract. The structural and hyperfine properties of Cr-doped SnO$_2$ nanoparticles are reported in this work. X-ray diffraction patterns indicate the formation of only the tetragonal phase in samples with Cr content up to 10mol%. The presence of Cr ions drives to the particle size reduction. Mössbauer spectra are well-resolved by a distribution of quadrupole doublets. The solubility limit of the dopant is found to be at ~3mol% Cr base on the quadrupole splitting evolution with the Cr content. The linear increase of the isomer shift as the Cr content is increased is assigned to a linear increase in the concentration of oxygen vacancies.

1. Introduction
Doped wide band-gap semiconducting oxides, such as SnO$_2$, TiO$_2$, ZnO are very interesting materials for the technological and fundamental point of view [1]. The doping of those semiconducting oxides with transition metals (Mn, Fe, Co, Cr, Ni) are reported to provide oxide dilute magnetic semiconductors (ODMS) with ferromagnetic temperature ($T_c$) above the room temperature [2].

Unfortunately, due to the complex solid-state chemistry involved in the preparation, the resulting properties depend on the conditions and preparation technique. Reports indicate that the doping of SnO$_2$ with Co concentrations below 10% is enough to obtain ferromagnetic order at room temperature [3]. Thin films of Cr-doped SnO$_2$ show ferromagnetism well above room temperature, which depends on the kind of substrate they are grown [4]. Despite the intense research in ODMS systems there are controversies mainly related to the origin of the magnetism observed in these materials.

In this work, the structural and hyperfine properties of Cr-doped SnO$_2$ nanoparticles with Cr content up to 10mol% are reported.

2. Experimental details
SnO$_2$ and Cr-doped SnO$_2$ nanoparticles with Cr content up to 10mol% were produced by a polymer precursor method. Details of the preparation are published elsewhere [1]. The phase formation and mean particle size has been determined from X-ray diffraction and corroborated by Transmission Electron Microscopy (TEM) data. Mössbauer spectroscopy measurements were carried out using a
Ca$^{119m}$SnO$_3$ as the radiation source. The analysis of spectra were obtained with a least-square fitting routine assuming a Lorentzian lineshape and considering the hyperfine splitting of I=3/2, 1/2 nuclear levels in a usual way.

3. Results and discussion
Some XRD patterns of the Cr-doped SnO$_2$ nanoparticles are shown in figure 1a. The Rietveld refinement of the XRD pattern of the undoped tin oxide powder indicates the formation of only the tetragonal phase (space group, $P4_2/mnm$) with lattice constants a=4.737nm and c=3.187nm.

![X-ray diffraction patterns of the Cr-doped SnO$_2$ nanoparticles.](image1a)

**Figure 1.** (a) X-ray diffraction patterns of the Cr-doped SnO$_2$ nanoparticles. The numbers between parentheses ($h k l$) represent the corresponding Bragg reflections. (b) Evolution of the mean particle size with the Cr content.

It is found that the Cr doping does not modify the crystal structure since the diffraction patterns of Cr-doped SnO$_2$ particles are also consistent with the tetragonal phase and no signal of a second phase formation is determined even at doping levels up to 10 mol% Cr. The Bragg reflections remain essentially at the same position and the linewidth (full width at the half maximum) increases steadily (see figure 1a). The latter indicates that the particle size decreases as the Cr concentration is increased. The evaluation of the mean particle size using the Scherrer’s relation [5] provides a mean crystalline size of ~13nm for the un-doped sample. This size decreases to ~7nm for the 10 mol% Cr-doped sample. These results are in agreement with TEM data. The particle size evolution with the Cr content is shown in figure 1b.

In figure 2 are shown the Mössbauer spectra for three samples obtained at room temperature. Within the experimental resolution, all spectra seem to show no magnetic components and the preliminary analysis indicates that the whole set is well resolved by fitting with a single doublet. The linewidth ($\Gamma$) of the spectrum of the undoped sample is $\Gamma$\sim1.2 mm/s. That linewidth is larger than that expected for the bulk SnO$_2$ and suggests a distribution of quadrupole splitting (QS) in our samples. The fit considering the histogram distribution of QS is shown in figure 2. For each sample, the QS’s distribution (see right side of figure 2) shows a broad and strong symmetric maximum in the low-QS region. An isomer shift (IS) of $\sim-0.014$ mm/s and a median value of the QS distribution of $\sim0.65$ mm/s are determined for the undoped sample. These values are slightly larger than those reported for bulk SnO$_2$ [6] and the differences could be associated with the size effect (i.e. structural distortions and symmetry breaking on the particle surface) which is expected to affect mainly the surrounding of Sn ions located on the particle surface.
When the Cr content is increased the median distribution value of QS shows a smooth increase reaching the value of +0.68 mm/s for the sample doped with 3mol% Cr content (data not shown here). That increase suggests the occurrence of additional distortions introduced by the substitution of Sn by Cr ions (ions with different size and chemical properties) and remains at around the same value for samples with higher Cr content. However, the width of the QS distribution (σ) shows clear tendency to decrease when the Cr content is above 3mol% (see figure 3a). That tendency of σ suggests the homogenization on the structural distortions which drives to narrow distribution of QS. Based on previous reports [1,7], the ~3mol% Cr is assigned as the region where the regime change from bulk solubility of Cr ions to their segregation onto the particle surface occurs, and the behaviour of σ should reflect that change.

As observed in figure 3b, the IS values shows a linear increase (dIS/dx~0.14 mm/s) when the Cr content is increased. The increase in IS with respect to the Cr-free sample suggests that the s-electronic density [8] reaching the nucleus of Sn ions is larger in Cr-doped sample and that electronic density is enhanced when Cr content increases. It is known that the occurrence of oxygen vacancies provides conduction electrons to the SnO₂ system (n-type doping) [6]. Therefore, if one correlates the linear increasing in the isomer shift with the linear increase in conduction electron density, then it is expected to have a linear increase in the concentration of oxygen vacancies as the Cr content is increased, which is perfectly plausible since the substitution of mainly Cr³⁺ ions by Sn⁴⁺ ions has been determined from magnetic measurements. Those magnetic results will be published elsewhere soon.
Figure 3. (a) Width of the quadrupole splitting (QS) distribution as a function of the Cr content. The line is drawn just for a guide to the eyes. (b) Evolution of the isomer shift (IS) with the Cr content. The solid line represents the fit.

4. Conclusions
The presence of Cr ions drives to the reduction of the particle size. Mössbauer spectra are well-resolved by a distribution of non-magnetic components. The 3mol% Cr is assigned as the concentration where the regime change from the solubility to surface segregation of Cr ions occurs. The linear increase of the isomer shift with the Cr content is assigned to a linear increase in the concentration of oxygen vacancies.

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