

Effects of particle size on the structural and hyperfine properties of tin dioxide nanoparticles

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Abstract In this work, we report on the study of SnO_2 nanoparticles prepared by a polymer precursor method. X-ray diffraction (XRD) data analysis evidenced the formation of only the tetragonal rutile-type phase for the as-grown and thermally annealed samples. A mean grain size of about 11 nm for the as-prepared sample has been determined. This mean size increases after the thermal annealing and with the annealing temperature. The room temperature Mössbauer spectra (MS) were well fitted using a quadrupole splitting (QS) distribution. The isomer shift (IS) tends to increase when the grain size decreases. That increase has been associated to the extra s-electron density generated by the oxygen vacancies.

Keywords X-ray diffraction · Mössbauer spectroscopy · SnO_2 nanoparticle

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1 Introduction

In recent years, physical properties of semiconducting oxides SnO_2 , ZnO , WO_3 and In_2O_3 , have been studied in connection with a search for new materials for solid-state gas sensors [1]. Nowadays, materials with an average grain size of less than 50 nm have attracted considerable scientific interest because of the improvements in a variety of properties related to the grain size. Among those compounds, nanoparticulated SnO_2 is used most extensively since the conductivity of SnO_2 is very sensitive to the surface state in the temperature range of 300–800 K, in which redox reactions can take place. On the other hand, the surface of SnO_2 nanoparticles exhibits good absorption properties and reactivity due to the presence of free electrons in the conduction band and the presence of surface and bulk oxygen vacancies and active chemisorbed oxygens [1]. A main drawback of SnO_2 -based chemical sensors is their low selectivity, which does not allow one to separate the contribution made by a particular type of molecules in the gas phase to the total electric signal. In order to improve that selectivity, SnO_2 nanoparticles are doped with transition metals [2, 3], and that doping introduces a strong effect on the electronic and catalytic properties of the surface. It is known that the generation of oxygen vacancies associated with the particle size reduction or to the charge compensation introduces free electrons to the nanoparticulated system. Therefore, the investigation of properties related with the particle size and their size dependence is important from the technological point of view as well as for scientific interest. In this work, the structural and hyperfine properties of SnO_2 nanoparticles of different sizes (from 10 to 45 nm) are reported and discussed.

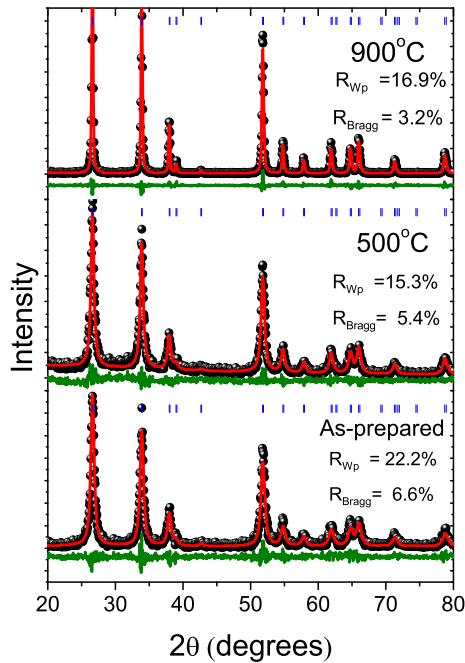
2 Experimental details

SnO_2 nanoparticles were produced by a polymer precursor method (this method was also known as Pechini's method), in which tin dioxide is obtaining from the precursor $SnCl_2 \cdot H_2O$. Details of the sample preparation are published elsewhere [3]. In order to obtain samples with different particle sizes, the samples were submitted to isothermal annealing at different temperatures in air environment (at 500°C, 700°C, 800°C and 900°C) for two hours. The phase formation and mean grain size have been determined by XRD using a Bruker diffractometer, model D8 Advanced with $Cu-K\alpha$ radiation. Mössbauer spectroscopy measurements were carried out with a constant acceleration spectrometer and using a $Ca^{119}SnO_3$ as the radiation source. For calibration, a natural Sn foil was used as absorber and the calibration error was estimated to be less than $\approx 0.5\%$. All spectra was processed at room temperature and the isomer shift (IS) is with respect to the $CaSnO_3$ source. The analysis of the spectra was 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 the usual way.

3 Results and discussion

The XRD patterns of SnO_2 nanoparticles were analysed using the Rietveld refinement method. The analysis of these data indicate the formation of the cassi-

Fig. 1 Room temperature XRD patterns of SnO_2 samples submitted to different annealing temperatures. The observed and calculated data are represented by the *points* and *solid lines*, respectively. The *green solid line* represents the difference between the observed and calculated data. The R values are included in the plots



terite phase, with no evidence of other crystalline or amorphous phase. XRD patterns of samples annealed at different temperatures are shown in Fig. 1, the linewidth (full width at half maximum) of the diffraction peaks tends to decrease as the annealing temperature increases. This effect can be attributed to the increase of the particle size and/or to changes in the residual strain.

In order to obtain additional information, the Rietveld refinement was carried out using the Thompson-Cox-Hastings pseudo-Voigt function (TCH-pV) given by [4]:

$$TCH - pV = \eta L + (1 - \eta)G \quad (1)$$

where, L and G represent the Lorentzian and Gaussian peak functions respectively, and η is a mixing parameter. The line broadening related to the instrumental contribution was corrected by adequately subtracting the linewidth of a standard sample (Si single crystal) from the linewidth of the samples. The deconvolution of the TCH-pV provides the linewidths for the Gaussian and Lorentzian components, which are given by:

$$H_G = (U \tan^2(\theta) + V \tan \theta + W + Z / \cos^2 \theta)^{1/2} \quad (2)$$

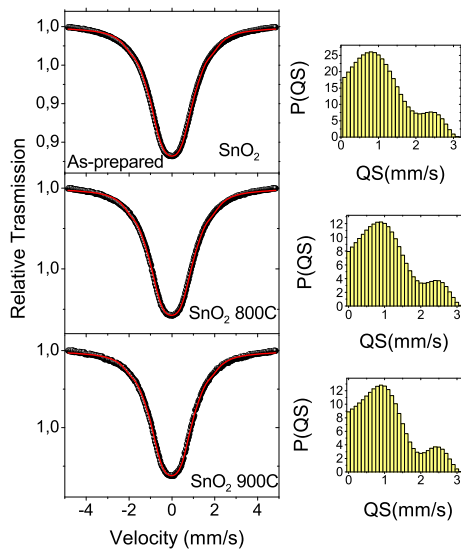
$$H_L = X \tan \theta + Y / \cos \theta \quad (3)$$

where U , V , W , Z and Y are refinable parameters and can be used to determine the mean crystallite size and microstrain [4]. The mean crystallite size, residual strain and some structural parameters are shown in Table 1.

Table 1 Mean particle size, residual strain and some structural parameters obtained from the Rietveld refinement of thermally annealed SnO_2 nanoparticles. The R_{Bragg} , which determines the quality of the refinement, are also included. The number between parentheses are the uncertainties

Annealing temp. ($^{\circ}\text{C}$)	Mean size (nm)	Residual strain (%)	a/c	$x = y$	R_{Bragg} (%)
0	11(3)	0.205	1.487	0.309	6.6
500	12(3)	0.085	1.487	0.302	5.0
700	17(3)	0.119	1.486	0.305	3.0
800	34(3)	0.080	1.487	0.304	5.0
900	45(3)	0.112	1.487	0.305	3.1

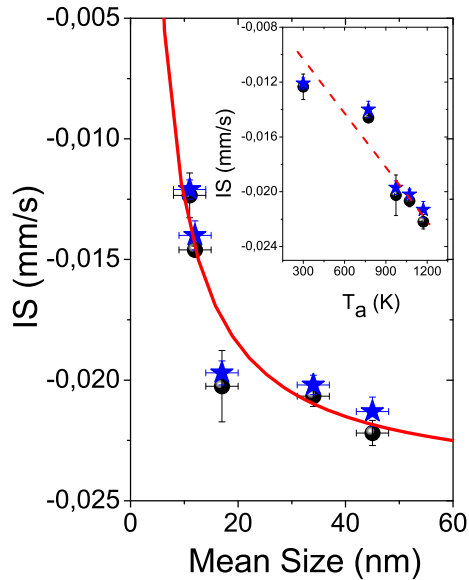
Fig. 2 Room-temperature Mössbauer spectra of SnO_2 nanoparticles. The *points* represent the experimental data and the *lines* represent the fit to a distribution of QS. The QS distributions are shown at the right-hand side



An increase in the annealing temperature drives to an increase in the particle size. More detailed analysis of the particle growth process will be published elsewhere. The value of the residual strain determined for the as-prepared sample is larger than those values obtained for the annealed ones. This result is in agreement with the larger value of the internal parameter (x) that determines the position of oxygen atoms which form the octahedron. Larger values of x means a more distorted octahedron, since an ideal octahedral coordination requires $x = 0.2929$ [5]. The R_{Bragg} values quantify the quality of the refinement (acceptable values are in the range 3–9%).

In Fig. 2 are shown the room-temperature Mössbauer spectra (MS) for the as-prepared sample (no annealed), and thermally treated samples at 800 and 900 $^{\circ}\text{C}$. 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. However, the linewidth of the spectrum of the as-prepared sample is ~ 1.7 mm/s. This linewidth is larger than that expected for bulk SnO_2 and suggests the presence of a distribution of quadrupole splitting (QS) in

Fig. 3 Dependence of the isomer shift (IS) on the mean particle size. The *inset* shows a linear decrease of the IS as a function of the annealing temperature. The *solid spheres* are the IS values determined from the fit of the MS to a QS distribution and the *stars* are the IS values obtained from the fit to only one doublet. The *solid line* represents the fit made using the Eq. 4



our samples [6]. The fit of the Mössbauer spectra with a distribution was carried out using the histogram method of the NORMOS DIST program. The results are shown in Fig. 2. For each sample, the QS's distributions show asymmetrical shapes with a broad peak centered at lower QS values. An isomer shift (IS) of ~ 0.011 mm/s and an average value for the QS distribution of $+0.83$ mm/s are obtained for the as-prepared sample. These values are slightly larger than those reported for bulk SnO_2 [7, 8]. When the annealing temperature is increased the average value of QS shows a statistical fluctuation and no clear tendency has been determined. Moreover, the IS values show a decreasing behavior when the annealing temperature is increased as shown in the inset of Fig. 3. Since higher annealing temperature produces larger particle size, as determined from XRD analysis and corroborated by transmission electron microscopy images, the IS tends to decrease as the particle size grows. This behavior is shown in the main panel of Fig. 3. Since the relative variation of the IS as a function of the particle size is small, the reproducibility has been tested by measuring at least twice each sample. The experimental points plotted in Fig. 3 are the average values of IS.

The size dependence of IS is unexpected since no size dependence of the IS was reported in nanoparticulated systems [9]. However, preliminary studies of Ni-doped SnO_2 nanoparticles [10, 11] suggest the presence of oxygen vacancies, even for the undoped system, which are likely located at the particle surface. It is known that when oxygen vacancies are generated in the SnO_2 system, electrons are transformed from p character to s character by exciting them from the valence band into the conduction band [8, 12]. Therefore, oxygen vacancies provide with extra s-electrons to the nearby Sn nucleus. As the isomer shift is a direct measure of the s-electron density at the nucleus, the increase in the oxygen vacancies induces an increase in the IS. Assuming that the measured IS is composed by two terms: (i) A contribution associated with the s-electron density as in the bulk system and (ii) a contribution

coming from the s-electron density related to oxygen vacancies. The first contribution must be related to the core region of the particle, wherein no defects are assumed to exist, and the second contribution must be related to the grain surface region wherein the oxygen vacancies are located. This core-shell model has been used previously to interpret the Mossbauer data of nanoparticulated SnO_2 [13]. Accordingly, the total IS is given by:

$$IS = IS_{\text{surf}} + IS_{\text{bulk}} \quad (4)$$

As the IS_{surf} contribution is proportional to the density of oxygen vacancies and that density is proportional to the surface-to-volume ratio, we propose that $IS_{\text{surf}} = K/D$, where K is a constant and D is the diameter of the particle. Using the mean particle size determined from XRD analysis, we determined the following values: $IS_{\text{bulk}} = -0.024(1)$ mm/s and $K = 0.120(6)$ mm.nm/s. In Fig. 3 it is shown the data fit. The IS_{bulk} value is in agreement with reported values for bulk SnO_2 system [8]. It is worth mentioning that the density of oxygen vacancies strongly depends on the atmosphere the experiment is carried out. Since our experiments were carried out in air, which is considered as a strongly oxidizing atmosphere, the stoichiometric surface of SnO_2 has 5-coordinated Sn atoms which in air are sites for oxygen absorption. It means that the number of oxygen vacancies is relatively small and concentrated mainly in subsurface sites [10]. This must be the reason for the small relative variation of the IS as a function of the particle size. Moreover, additional Mössbauer measurements, carried out under different oxygen gas flow, are needed in order to elucidate this issue. The effect of oxygen vacancies is to modify the neighborhood of Sn atoms, introduce distortions, and lead to a decrease in the ionic character of the Sn^{4+} state in the $Sn - O$ bond [13]. Since the number of oxygen vacancies is expected to be small, it implies to have a very small population of tin atoms near to an oxygen vacancy. Therefore, Sn^{4+} atoms have about the same nearest surrounding, which implies to have almost the same quadrupole splitting, even when the particle size is changed. However, additional studies are required in order to confirm the effects of the oxygen vacancies on the hyperfine parameters IS and QS. Low temperature Mössbauer measurements should help us to improve our assessment since smaller linewidths are expected. Those measurements are currently underway and the results will be published elsewhere.

4 Conclusion

XRD analysis of thermally annealed SnO_2 powders indicate the formation of the tetragonal rutile-type phase. A higher annealing temperature produces a larger grain size growth. Room-temperature Mössbauer spectra are well-resolved by a distribution of QS's. The IS value for the smaller particle size is larger than that expected for bulk SnO_2 and tends to decrease as the particle size increases. It suggests the presence of an additional contribution to the IS which is associated with the oxygen vacancies, which are generated at the surface of the particle.

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