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Electric quadrupole interactions in nano-structured SnO_2 as measured with PAC spectroscopy

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Abstract Measurements of the electric quadrupole interaction were used to characterize pure and cobalt-doped samples of SnO_2 prepared by the sol-gel method. Perturbed gamma–gamma angular correlation (PAC) spectroscopy using ^{111}In–^{111}Cd probe nuclei was employed for these measurements. A methodology was developed for sample preparation that were prepared by sol-gel method from pure metallic Sn (99.9999%) and Co (99.9998%) as starting materials. Carrier-free ^{111}In was added to the precursor sol-gel solution prior to the formation of gel. PAC measurements were carried out to follow the formation of the SnO_2. PAC measurements were carried out in the temperature range from 10 k to 1123 K and the results show that the electric quadrupole frequency depends on the annealing temperature.

Keywords SnO_2 · PAC spectroscopy · Electric-field gradient

1 Introduction

The search for diluted magnetic semiconductors with ferromagnetic ordering at room temperature has attracted a great deal of interest in recent years. Several wide band-gap semiconductor oxides such as ZnO, TiO_2, and SnO_2 have been doped with transition metals in an attempt to create magnetic properties without significantly affecting the physical properties of the host [1]. Among these materials, SnO_2 is a good candidate to successfully exhibit intrinsic magnetic ordering when doped with transition a metal due to the *n*-type conduction and the presence of native oxygen vacancies in this compound as such vacancies seem to play an important role in the ferromagnetic order of semiconductor oxides [2–4]. In the present work, electric quadrupole interactions in pure and Co doped SnO_2 nanocrystalline samples

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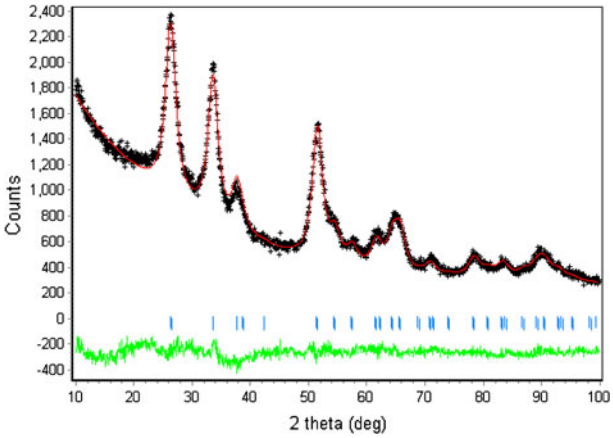
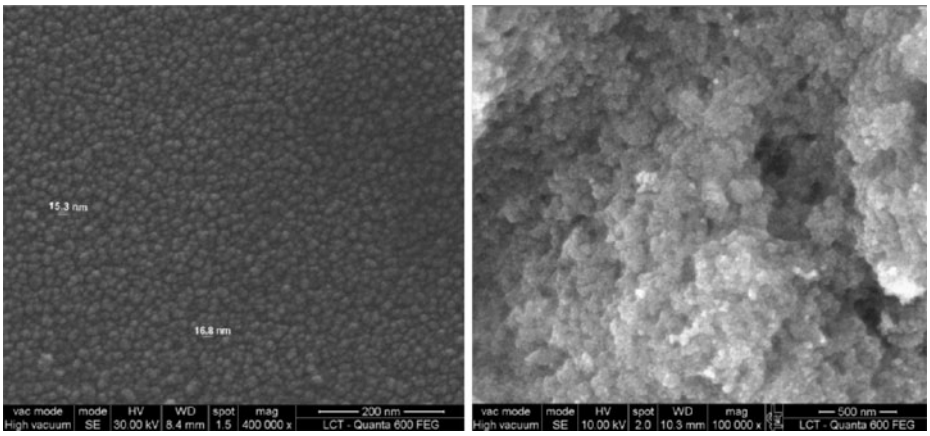


Fig. 1 X-ray diffraction pattern of pure SnO_2 sample prepared by sol-gel method. The *solid line* represents the calculated pattern with the Rietveld method. The residuals are shown in the *lower part of the curve*

have been measured with perturbed gamma–gamma angular correlation (PAC) spectroscopy using ^{111}In–^{111}Cd as probe nuclei, and the results were compared with previous PAC measurements of pure SnO_2 powder samples using ^{111}In–^{111}Cd probe [5]. Also found in the literature are measurements using *Mössbauer* spectroscopy [6]. Single phase nanocrystalline powder samples of SnO_2 produced by the sol-gel method were characterized by Scanning Electron Microscopy (SEM) as well as X-ray Diffraction measurements. The results showed nanometric particles homogeneously distributed, with particle diameter in the range of 15–60 nm.

2 Experimental procedure

The well known sol-gel Pechini method, which is based on metal citrate polymerization with ethylene glycol, and thermal decomposition of polymeric mixed-metal precursor gel was used to prepare pure and cobalt doped SnO_2 powder samples. Details of sample preparation are described in references [7] and [8]. The aqueous solution of metal nitrates was prepared from pure metals by dissolving them in concentrated nitric acid. A hydrocarboxylic acid, such as citric acid, in the ratio of 2:1 to metal ions was added to the aqueous solution to chelate metal ions. A polyalcohol, such as ethylene glycol, was added to this solution to promote the formation of an organic ester. Each step mentioned above was accompanied by constant magnetic stirring to make the solution homogeneous. Polymerization was promoted by heating the mixture at around 343 K on a hot plate. This resulted in a homogeneous gel with metal ions uniformly distributed throughout the organic matrix. The gel was dried at temperatures between 523 K and 653 K for 10 h in a muffle furnace. The xerogel obtained was ground into powders and then annealed at different temperatures from 673–973 K for 10 h in flowing nitrogen. At this stage the organic phase was completely removed which results in the formation of compound with a fine powder. In order to carry out the PAC measurements, approximately 10–20 μCi of $^{111}InCl_3$ solution was added to the metal nitrate solution before the gel formation.



(a) (b)

Fig. 2 SEM Photograph: pure SnO_2 (**a**) and doped with 3% of Co (**b**) after annealing at 653 K

Table 1 Pac measurements at 77 K for the sample doped with Co

Electric quadrupole frequency—ν_Q (MHz)	
3% of Co	
After annealing at 653 K	
Site 1	Site 2
180.6	114.7
After annealing at 873 K	
165.3	115.7 MHz
5% of Co	
After annealed at 653 K	
155.1	117.9
After annealed at 873 K	
140.3	115.5

3 Results and discussion

Phase purity of the powder samples was examined by X-Ray diffraction (XRD) using Cu K_α radiation. XRD results for all samples showed a single phase with $P4_2/mnm$ space group corresponding to the rutile-type structure. Within the resolution of XRD measurements, no secondary phases were observed as shown in Fig. 1 for the pure SnO_2 sample after the first annealing at 653 K in the muffle furnace. From XRD line broadening, the average particle sizes of 7 nm were deduced using Scherrer's equation [9].

The crystal morphology and size of nanoparticles in each sample were determined by scanning electron microscopy (SEM) and the results indicate that the samples are homogeneous. This characterization was made in Laboratory for Technological Characterization at POLI-USP using an ESEM microscope of the FEI Company, version: 3.2.4, 2008. Figure 2 show a SEM image for pure SnO_2 (a) and doped with 3% of Co (b), the samples prepared in our laboratory with the same annealing temperature, 653 K. EDS results indicate SnO_2 and the transition metal used for the doping are present in each sample.

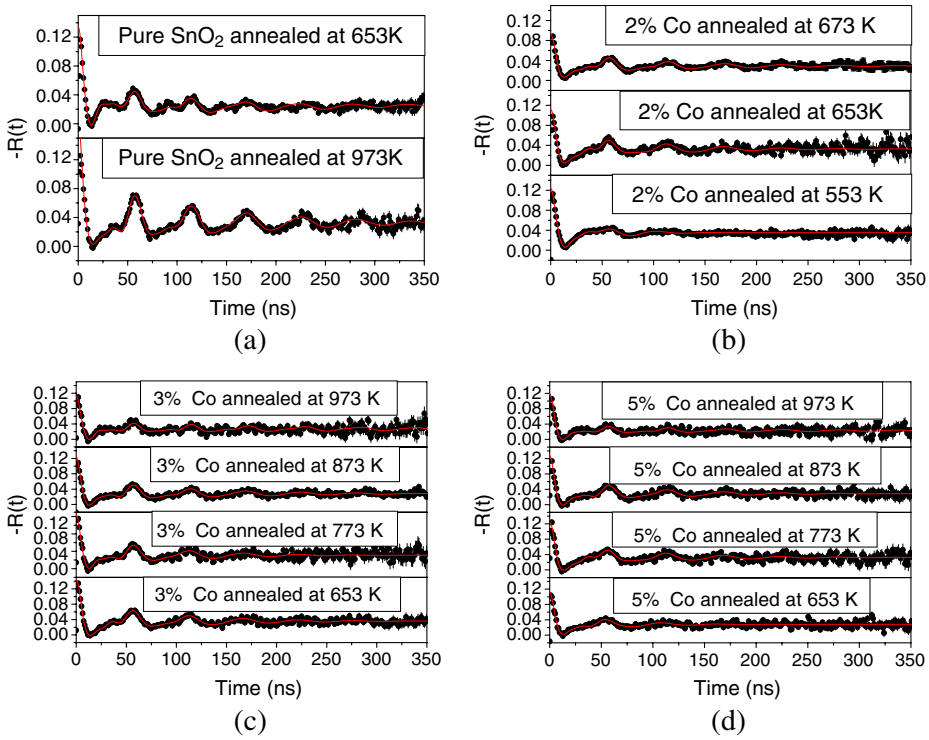


Fig. 3 The perturbation functions for ^{111}Cd probes in (**a**) pure SnO_2 sample measured at 295 K after annealing at 653 K (*top*) and 973 K (*bottom*) and (**b**) doped with 2% of Co measured at 295 K after annealing at 553 K (*bottom*) and 673 K (*top*) and (**c**) doped with 3% of Co measured at 295 K after annealing at 653 K (*bottom*) and 973 K (*top*) and (**d**) doped with 5% of Co measured at 295 K after annealing at 653 K (*bottom*) and 973 K (*top*). *Solid lines* are the least-squares fits of the theoretical function to the experimental data

The Table 1 shows which measurements were made at 77 K, the remainder was measured at 295 K. The least-squares fitted PAC spectra measured at 77 K and 295 K with ^{111}In–^{111}Cd probes for the cobalt-doped SnO_2 nanopowders after annealing at 653 K and 973 K are shown in Fig. 3. These spectra reveal the presence of only pure electric quadrupole interactions. The environment of the ^{111}In probe atoms in the SnO_2 lattice is characterized by two quadrupole frequencies with hyperfine parameters $\nu_{Q1} = 115$ MHz, $\eta \sim 0.1$, $f_1 = 60\%$, $\delta_1 = 12\%$ and $\nu_{Q2} = 146$ MHz, $0,4 \leq \eta \leq 1$, $f_2 = 40\%$, $\delta_2 = 40\%$ [5]. The major fraction was assigned to ^{111}In probe atoms at substitutional Sn sites. The rest of the probe atoms are incorporated in highly disordered, non-unique lattice environments which is quite usual for nano-sized particles when probe atoms are residing on the surface of the nanocrystalline particles where surface to volume ratio is large. The samples doped with Co showed also two quadrupole frequencies with hyperfine parameters in the range of $\nu_{Q1} =$ 115–120 MHz, $\eta \sim$ 0.1–0.2, $f_1 =$ 60–80%, $\delta_1 =$ 5–12% and $\nu_{Q2} =$ 120–180 MHz, $0,4 \leq \eta \leq 1$, $f_2 =$ 20–40%, $\delta_2 = 40\%$ [5].

An increase of probe fraction f_1 has been observed with an increase of annealing temperature which is consistent with the increase of particle size and reveals fewer number of probe atoms on the surface of the nanocrystalline particles. The PAC measurements, which probe the material at an atomic scale, on these SnO_2 powders show no evidence for ferromagnetism. In future work, new measurements will be made using external magnetic field to confirm these results.

4 Conclusion

A methodology to prepare SnO_2 nanoparticle powder samples was successfully established. In all measurements two different electric quadrupole interactions were observed. One of them with $\nu_Q \sim 115$ MHz, $\eta \sim 0.1$, and $\delta \sim 12\%$, which changes very little with temperature has been assigned to ^{111}Cd at Sn sites in SnO_2 structure. The second interaction is characterized by a wider distributed frequency that changes with temperature with values in the range of 120–180 MHz and asymmetry parameter varying from 0.4 to 1. This interaction was associated with ^{111}Cd probes trapped in defects near the surface of the nanoparticles.

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