EXAFS and Raman scattering studies of Y and Zr doped nano-crystalline tin oxide

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Abstract. Nanocrystals of Y and Zr doped SnO₂ have been prepared by sol-gel route and annealed at 200, 400, 600, 800 and 1000 °C. The X-ray diffraction (XRD) results showed the average size of the particles in the freshly prepared samples to be ~ 3 nm. The Extended Absorption Fine Structure (EXAFS) technique was used to study the dopant environments in nanocrystalline tin oxide. In all Y-doped samples, except the one annealed at 1000 °C, there is clear evidence that Y has not entered the SnO₂ lattice. This is clearly supported by the Raman scattering results. In all Zr-doped samples, there is a simple substitution for Sn by Zr.

1. Introduction
The unique physical and chemical properties of nano-crystalline materials in comparison to their bulk counterparts [1-4] have recently aroused a great deal of interest. Reasons for such interest are, for example, that they can adopt different morphologies to bulk crystals leading to extraordinary surface chemistry and can dissolve higher concentrations of impurities and this offers further scope for tailoring new catalytic materials. Furthermore, semiconductors made from nanoparticles have unusual optical, electrical and magnetic properties and nanocrystalline ceramics have greater hardness and plasticity. Tin oxide occurs naturally as cassiterite and has the rutile structure. It is an n-type semiconductor which is widely used in flammable gas sensors. Cation doping is widely used to improve the sensing. In the present study EXAFS, XRD and Raman scattering techniques were used to study the Y³⁺ and Zr⁴⁺ doped nanocrystalline SnO₂. The objective of the studies was to locate the dopant environments in nanocrystalline SnO₂ and in particular to discover whether they were in the crystal matrix or at the surfaces.

2. Experiments
To prepare Y and Zr doped nanocrystalline tin oxide, appropriate amounts of Tin chloride pentahydride and water soluble metal salts (Yttrium chloride hexahydrate and Zirconyl chloride octahydrate, respectively) were dissolved in 40 ml of distilled water to prepare a 0.1M solution. To this solution, 5 ml of aqueous ammonia was added and the resulting white precipitate recovered by evaporation. The byproduct of this reaction is ammonium chloride and was removed by extensive washing with distilled water. The addition of a small quantity of nitric acid also resulted in the
removal of this byproduct. The material was then oven dried at 100 °C overnight and thoroughly ground in an agate pestle and mortar. The absence of ammonium chloride peaks in the XRD patterns confirmed the successful removal of all the ammonium chloride. These samples were prepared with nominal dopant concentrations of 1 and 10 mol% for yttrium and zirconium.

The XRD of all the samples were performed on a Phillips Diffractometer on a Phillips Generator PW1130. The average grain size of the samples, L, was determined by the broadening of peaks on the XRPD pattern, using the Scherrer equation [5]; i.e.

\[ L = \frac{K \lambda}{\beta \cos \theta} \]

where K is the constant dependent on the particle shape (0.89 for spherical particles), \( \lambda \) is the wavelength of the X-ray radiation (Cu K\( \alpha \), \( \lambda = 1.5406 \) Å), \( \theta \) is the diffraction angle and \( \beta \) is the peak width (corrected for instrumental broadening).

All EXAFS measurements were carried out at the CCLRC Daresbury Synchrotron Radiation Source on station 9.3. This station is equipped with a specially designed furnace so that samples can be heated in situ to 1100 °C. Data were collected at room temperature. The synchrotron has an electron energy of 2 GeV and an average current during the measurements was 150 mA. For dilute samples spectra were collected in fluorescence mode. In some cases we were able to use some samples with a higher concentration of dopant (10 atom per cent) and use the more rapid transmission mode. The EXAFS samples were prepared by thoroughly mixing the powders with fumed silica and pressing into pellets in a 13 mm IR press. Data analysis was performed with interactive computer programmes, developed at the Daresbury SRS [6]. For each spectrum a theoretical fit was obtained by adding shells of atoms around the central excited atom and least-squares iterating the Fermi energy, \( E_0 \), the radial distances, \( R_D \), and the Debye-Waller type factors, \( A \) (\( = 2 \sigma^2 \)). This latter factor will contain contributions from both thermal disorder and static variations in \( R_D \). The programme also allowed iteration of the co-ordination number, \( C_N \), but this option was not used in the present work. The data were Fourier filtered to include the region of 1 – 5 Å of the Fourier transform containing the dominant peaks.

The Raman spectra of the samples were collected using a JY – T64000 (Jobin Yvon) Raman spectrometer equipped with a liquid nitrogen cooled CCD detector. An Argon ion laser with the wavelength of 514.5 nm was used as the excitation source. All the spectra were recorded at room temperature.

3. Results and discussion

3.1. Y-doped SnO\(_2\)

K edge EXAFS spectra were collected for 10 atom percent samples. The Fourier transforms (FT’s) of the spectra are shown in figure 1. In all the samples, except the one annealed at 1000°C there is clear evidence for only one shell around 2.3 Å. This is the Y-O correlation and is close to the Y-O distance in Y\(_2\)O\(_3\). From previous studies of doped tin oxide [7,8] the EXAFS are interpreted, i.e. the lack of a second peak, as evidence, that the Y has not entered the SnO\(_2\) lattice. The samples consist of nanocrystals of SnO\(_2\) with Y in the surface layers. The EXAFS of the sample annealed at 1000 °C shows well-defined peaks out to 5 Å. The spectrum shows an excellent fit (table 1) to the crystallographic data for Y\(_2\)Sn\(_3\)O\(_7\) [9], resulting from a high temperature solid-state reaction.
The Raman spectra were also collected for Y doped SnO₂. For SnO₂, three main Raman bands, A₁₈ (630 cm⁻¹), B₂₇ (774 cm⁻¹) and E₆ (472 cm⁻¹) are expected as predicted by group theory [10]. A₁₈ and B₂₇ are related to the expansion and contraction vibration mode of the Sn-O bonds whereas the E₆ is associated with vibration of oxygen in the oxygen plane. The Raman spectra of yttrium doped nanocrystalline SnO₂ are shown in figure 2. The Raman spectrum (not shown) of the as-prepared sample shows a broad Raman band at 572 cm⁻¹ and this is ascribed to the amorphous tin(IV)-hydrous oxide [11]. For the sample heated at 400 °C the band associated with the amorphous phase is still observed but new peaks start to develop at 630 cm⁻¹ and 774 cm⁻¹. At 600 °C the 572 cm⁻¹ peak is no longer visible and at 800 °C the three Raman active modes i.e. A₁₈, B₂₇ and E₆ are observed although only the A₁₈ band is clearly visible due the particle size being small. For the sample heated at 1000 °C, all the three bands are clearly visible with the A₁₈ being the most intense. In addition to those associated with SnO₂, more bands at 508 cm⁻¹, 412 cm⁻¹ and 311 cm⁻¹ are observed. These bands resemble the Raman vibrational modes of yttrium stannate (Y₂Sn₂O₇) [12]. These results show that at 1000 °C, SnO₂ is starting to react with Yttrium (Y) to form Y₂Sn₂O₇ and are consistent with the EXAFS results.
3.2. Zr-doped SnO$_2$

K edge EXAFS spectra were collected for 10 atom percent samples. The FT’s of the spectra are shown in figure 3. In this case there are clearly resolved peaks out to 5 Å. The spectra show an excellent fit to Zr substituting directly for Sn in the lattice. This is expected given that both cations have 4$^+$ charge and are similar in size. The Zr-Sn correlations at ~3.2 and 4 Å clearly grow in size with heating. This is directly related to the growth in the particle size on heating [7,8]. The structural parameters for pure SnO$_2$ are shown in table 2. The results of fitting the Zr K-edge EXAFS for the samples heated at 200 and 1000 °C are shown in table 3 and the similarities with table 2 confirm that Zr is on the Sn site. The differences in the A parameters reflect the particle sizes [7,8].

![Figure 2. Raman spectra of Y doped nano-SnO$_2$.](image)

![Figure 3: FT of the Zr K edge EXAFS for 10% Zr doped SnO$_2$.](image)
4. Conclusions
There is a clear evidence that Y has not entered the SnO$_2$ lattice in all Y-doped samples up to the one annealed at 900 °C. At 1000 °C, SnO$_2$ starts to react with Yttrium (Y) to form Y$_2$SnO$_7$. This is clearly shown by both the EXAFS and Raman scattering results. In all Zr-doped samples, there is a simple substitution for Sn by Zr, even at 10 atom percent doping.

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\begin{table}
\centering
\caption{Structural parameters for bulk SnO$_2$}
\begin{tabular}{|c|c|c|c|c|c|}
\hline
Atom & CN & R/Å & CN & R/Å & A/Å$^2$
\hline
O & 2 & 2.045 & 6 & 2.050 & 0.005
\hline
O & 4 & 2.088 & & & \\
\hline
Sn & 2 & 3.185 & 2 & 3.201 & 0.007
\hline
O & 4 & 3.594 & 4 & 3.571 & 0.001
\hline
Sn & 8 & 3.708 & 8 & 3.730 & 0.007
\hline
\end{tabular}
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\begin{table}
\centering
\caption{Zr K-edge EXAFS for 10 % Zr doped SnO$_2$}
\begin{tabular}{|c|c|c|c|}
\hline
Model & 200 °C & 1000 °C & \\
\hline
Atom & CN & R/Å & A/Å$^2$ & R/Å & A/Å$^2$
\hline
O & 6 & 2.108 & 0.017 & 2.091 & 0.009
\hline
Sn/Zr & 2 & 3.252 & 0.019 & 3.213 & 0.007
\hline
O & 4 & 3.597 & 0.009 & 3.600 & 0.011
\hline
Sn/Zr & 8 & 3.751 & 0.036 & 3.731 & 0.014
\hline
\end{tabular}
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