Defect ferromagnetism in ZnO and SnO2 induced by non-magnetic dopants

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Chapter 6

Raman and optical study of SnO$_2$:Zn$^{2+}$ hierarchical nanostructures*

We noted two main features in the previous chapter that described hierarchical nanostructures in Zn$^{2+}$ doped SnO$_2$, viz. (i) substitution of Sn$^{4+}$ (radius 0.69 Å) ions by the Zn$^{2+}$ (radius 0.74 Å) ions, and (ii) compensation of charge unbalance caused by dopants by the formation of oxygen vacancies (V$_O$). We also noted that the Zn$^{2+}$ ions play an active role in reducing the average crystallite size and act as a structure-directing agent in the growth of Zn-doped SnO$_2$ nanocrystals. Moreover the ferromagnetic and paramagnetic responses were found to be sensitive to the concentration of Zn dopants. In this chapter we report on a Raman scattering spectroscopy investigation of the growth, modified surface states and size effects in the Zn-doped SnO$_2$ hierarchical nanostructures. The observation of the infrared active surface mode “S” at 556 cm$^{-1}$ in Raman spectroscopy and its blue shift with increasing Zn concentration are ascribed to the effects of oxygen deficiency. In addition, we discuss photoluminescence spectroscopy (PL) measurements and show that they give evidence for V$_O$ acting as a radiative defect. In particular the singly ionized oxygen vacancies (V$_{O}^+$) act as recombination centres for the luminescence process. We shall also correlate the presence of these defects with the paramagnetic response of Zn-doped SnO$_2$ and show that optical measurements reveal a decreasing trend of band gap with Zn dopant.

* The results presented in this chapter are summarized in a manuscript ready for submission:
S. Akbar, S. K. Hasanain, O. Ivashenko, W. Gomulya, M. A. Loi, P. Rudolf, “Raman and optical study of SnO$_2$:Zn$^{2+}$ ferromagnetic hierarchical nanostructures”.

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6.1 Introduction

SnO$_2$, a typical n-type semiconductor with a wide band gap (3.6 eV)$^{1, 2}$ has gained attention for applications in solar cells$^3$, flat-panel display$^4$, photocatalysis$^5$, lithium batteries$^6$ and gas sensing$^7$. Its high exciton binding energy (130 meV) makes it a promising UV luminescent material$^{8, 9}$. Ckilic et al.$^{10}$ explained that acceptor-like (negatively-charged) intrinsic defects, namely interstitials O$_i$ and tin vacancies V$_{Sn}$, hardly form as they have high formation energies. Oxygen vacancies (V$_O$) are much easier to create on surfaces than in the bulk because fewer bonds have to be broken. This is why nanoparticles and thin films, where the surface-to-volume ratio is high, can have a higher defect density of oxygen vacancies$^{11, 12}$. To explore the origin of the paramagnetic contribution along with the ferromagnetic one for Zn-doped SnO$_2$ nanoparticles as described in chapter 5, it is important to identify these oxygen defects, since V$_O^+$ has been reported to be paramagnetic in nature$^{13, 14}$.

Raman scattering is an ideal tool to study surface modes and finite-size effects in nanostructured materials$^{15, 16}$ because they give rise to additional bands not present for the bulk material. In our case oxygen deficiencies are enhanced by Zn doping; they can produce large shifts and broadening of some of the spectral bands and thus strongly affect the Raman spectrum of SnO$_2$ nanoparticles.

In this chapter we discuss Raman scattering and photoluminescence (PL) spectroscopy data, collected to understand the origin of the luminescence created by different defects, such as oxygen vacancies or Sn interstitials. UV-visible absorption spectra were measured to see the variation of band gap as a function of Zn concentration. Finally the observed Raman and optical features are correlated with the observed ferromagnetism.

6.2 Experimental details

The Sn$_{1-x}$Zn$_x$O$_2$ nanoparticles with varying Zn concentration (nominal composition x=0.00, 0.02, 0.04, 0.06, 0.10) used in this study were the same as those reported in chapter 5. Raman and photoluminescence spectra were collected as detailed in chapter 2. Absorption spectra were recorded with a Shimadzu 3600 UV-vis-NIR spectrometer.
6.3 Results and Discussion

6.3.1 Raman Spectroscopy

A unit cell of the rutile structure of SnO$_2$ contains two tin ions and four oxygen ions and belongs to the space group P4n/mmm. According to the group theory, the mechanical representation of the normal lattice vibration modes at the centre of the Brillouin zone is given by$^{17}$

$$\Gamma=A_{1g} + A_{2g} + B_{1g} + B_{2g} + E_g + 2A_{2u} + 2B_{1u} + 4E_u$$

![Figure 6.1 Schematic representation of the atomic displacements for (a) the Raman and (b) IR-active modes of SnO$_2$]$^{18}$

As illustrated in Figure 6.1, the modes $A_{1g}$, $B_{1g}$, $B_{2g}$ and $E_g$ are Raman active while $A_{2u}$ and $S$ are infrared active and correspond to transverse optical (TO) phonons and longitudinal optical (LO) phonons, respectively. Among the four first-order active Raman modes of rutile SnO$_2$, the $A_{1g}$ mode is much stronger than the other modes. Figure 6.2 shows the room temperature Raman spectra of the Zn-doped SnO$_2$ samples. The peak at 632 cm$^{-1}$ is attributed to $A_{1g}$ classic vibration mode of SnO$_2$ with tetragonal rutile structure. The spectra for $x=0.02$ and 0.04 are very similar; the 622 cm$^{-1}$ and 684 cm$^{-1}$ peaks are strong and relatively narrow for both compositions. For $x=0.06$ and 0.10 the peak at 622 cm$^{-1}$ merges into the fundamental $A_{1g}$ peak at 632 cm$^{-1}$. It is evident that the intensity of the characteristic $A_{1g}$ mode is weakened and broadens as the Zn concentration increases. The $A_{1g}$ mode is known to be sensitive to particle size$^{19}$; here this peak shows broadening which most likely originates$^{20}$ from the observed reduction in particle sizes with increasing $x$. Next to the fundamental Raman peak of bulk SnO$_2$, additional peaks at 684 cm$^{-1}$ and 556 cm$^{-1}$, which do not appear in bulk SnO$_2$, are clearly visible in the spectra,
Figure 6.2 Room temperature Raman spectra of Sn_{1-x}Zn_{x}O_2 (x= 0.02, 0.04, 0.06, and 0.10) nanoparticles.

suggesting that they are induced by the size effect. These peaks are forbidden in the bulk by the \( \Delta k=0 \) selection rule. It has been reported that relaxation of the \( \Delta k=0 \) selection rule will be progressive if the size decreases or the rate of disorder increases\(^{21-23}\). Infrared (IR) modes become weakly active as a result of the structural changes, \( i.e. \) disorder and size effects. As the crystallite size is reduced to the nanoscale, phonon scattering will not be limited to the centre of the Brillouin zone and the phonon dispersion near the centre of the Brillouin zone (\( \Delta k \sim 0 \)) must also be considered. As a result, the symmetry-forbidden modes will be observed, in addition to the shift and broadening of the first-order optical phonon. Therefore, the weak Raman peak at 684 cm\(^{-1}\) could be induced by the IR-active \( A_{2u} \) LO modes due to the size effect; it can be seen that the 684 cm\(^{-1}\) peak intensity gets enhanced with the addition of Zn. The reduction of particle sizes with increasing Zn concentration was already confirmed by XRD studies as described in chapter 5. The peak at 470 cm\(^{-1}\), attributed the \( E_g \) modes of SnO\(_2\), prominently appears for \( x=0.02 \) and 0.04. The mode at 556 cm\(^{-1}\) is inactive in bulk rutile SnO\(_2\) for both Raman and IR, and thus can be ascribed to a “surface mode”. A similar peak has also been reported in the literature\(^{20,24}\) and could be due to the aggregation of SnO\(_2\) nanostructures or related with defects appearing during growth. One possible location for these defects could be the needle like structures on the surfaces that we have discussed in chapter 5. These needles contribute to
surface disorder and could also add defect-induced phonon modes. The 556 cm\(^{-1}\) surface mode shifts toward 568 cm\(^{-1}\) (blueshift) when the Zn concentration increases to x=0.10. According to Shek \textit{et al.}, this blue shift is attributed to the effects of oxygen deficiency \(^{25}\). As discussed, in the Sn\(_{1-x}\)Zn\(_x\)O\(_2\) hierarchical nanostructures oxygen vacancies (V\(_O\)) are produced to maintain a charge balance; therefore the increase of Zn concentration promotes the increase of V\(_O\) defects. According to our XPS results discussed in chapter 5, the x=0.10 composition contains the highest number of V\(_O\) defects. We therefore conclude that the surface mode originates from oxygen vacancies occurring in nanoscale structures. Interestingly the intensity of this mode also goes up over the same concentration range (x=0.06 to 0.10) where the ferromagnetic moment decreases. Later on we shall argue that in view of results of the PL and magnetic measurements, this feature of the Raman spectra is associated with singly ionized oxygen vacancies.

\subsection*{6.3.2 Optical Properties}

Figure 6.3 shows the UV-visible absorption spectra of the undoped SnO\(_2\) and Zn-doped SnO\(_2\) hierarchical nanostructures. For a semiconductor, the optical absorption near the band edge is determined by the equation \(^{26,27}\)

\begin{equation}
(\alpha hv)^2 = A(hv - E_g)^{n/2}
\end{equation}

where \(\alpha\) is the adsorption coefficient, \(h\) Planck’s constant, \(v\) the frequency of the light, \(E_g\) the band gap, and \(A\) a constant. The exponent \(n\) decides the characteristics of the transition. In our experiment, the value of \(n\) for Zn-doped SnO\(_2\) is 1\(^{28}\). Figure 6.4 shows the Tauc plots of \((\alpha hv)^2\) versus \(hv\) of the undoped and Zn-doped SnO\(_2\) nanoparticles where \(E_g\) can be estimated from the intercept of the linear portion of the plot. For undoped SnO\(_2\) nanoparticles, the optical band gap was found to be 3.71±0.05 eV, which is larger than the bulk value\(^{1}\) of 3.6 eV. With Zn doping the band gap decreases to 3.67 eV for Sn\(_{1-x}\)Zn\(_x\)O\(_2\) with x=0.02, and then reaches the minimum value of 3.51±0.08 eV for x=0.04 but then slightly increases for higher Zn concentration. In general Figure 6.5 shows the decreasing trend of band gap values as a function of nominal Zn doping. The observed behaviour of the optical band gap may be due to structural defects introduced in the SnO\(_2\) nanoparticles by Zn\(^{2+}\), such as tin interstitials and oxygen vacancies, which give rise to the electronic states in the gap close to the conduction band. When a Zn\(^{2+}\) ion
is located at a surface site or in the bulk lattice which is not occupied in the perfect crystal, a rearrangement of the nearest neighbors takes place which gives rise to a lattice deformation\(^{29}\). Therefore lattice strain is expected and should affect the electronic structure and the band-gap shift\(^{30}\).

\(\text{Zn}^{2+}\) doping at the lattice sites of SnO\(_2\) introduces oxygen vacancies due to the charge compensation effect and the decrease in the grain size observed (as described in chapter 5). These oxygen vacancies can exist in various charge configurations and the associated electronic states are located within the original band gap (Figure 6.8). These oxygen vacancies might be singly occupied to form \(\text{V}_\text{O}^+\) (also known as \(\text{F}^+\) centre\(^{31}\)) as discussed later in the context of the PL measurements.

\(\text{Zn}^{2+}\) and \(\text{V}_\text{O}^+\) could combine to form defect pairs in the SnO\(_2\) lattice, which may act as a doubly occupied vacancies. The energy of this excited state should lie somewhere in the band-gap, which becomes the reason for the band-gap shift. The increase in \(\text{Zn}^{2+}\) dopant increases the number of oxygen vacancies and hence the location may differ, which opens the possibility for a variation in band-gap due to a modification of the lattice relaxation\(^{32}\). In summary, the band-gap energies changes due to surface effects, doping-induced vacancies and lattice strain.

![Absorption spectrum for Sn\(_{1-x}\)Zn\(_x\)O\(_2\) (\(x=0.00, 0.02, 0.04, 0.06, \text{ and } 0.10\)) nanoparticles.](image)

**Figure 6.3** Absorption spectrum for Sn\(_{1-x}\)Zn\(_x\)O\(_2\) (\(x=0.00, 0.02, 0.04, 0.06, \text{ and } 0.10\)) nanoparticles.
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Figure 6.4 Tauc plot for the determination of the band gap of Sn$_{1-x}$Zn$_x$O$_2$ ($x = 0.00$, 0.02, 0.04, 0.06, and 0.10) nanoparticles.

Figure 6.5 Energy band gap variation as a function of Zn concentration ($x$) for Sn$_{1-x}$Zn$_x$O$_2$ nanoparticles.
6.3.3 Photoluminescence analysis

The optical properties of undoped and Zn-doped SnO$_2$ hierarchical structures were investigated by photoluminescence spectroscopy. Figure 6.6 (a) shows visible broadband emission spectrum (400 nm-700 nm) centred at 468 nm (2.65 eV) and 462 nm (2.68 eV) for undoped SnO$_2$ and Sn$_{0.96}$Zn$_4$O$_2$ respectively. The emission peaks of the PL are much lower than the band gap of undoped SnO$_2$ nanoparticles (3.71 eV) as determined from the UV-visible absorption spectrum; they do not originate from the direct interband transitions and cannot be ascribed to the direct recombination of a conduction electron in the Sn 4$d$ band with a hole in the O 2$p$ valence band$^{33,34}$. Moreover for Sn$_{0.96}$Zn$_4$O$_2$ the emission becomes much more prominent, three times higher as compared to the case of undoped SnO$_2$, and can therefore be attributed to electron transition mediated by defect states in the band gap$^{35}$. When Zn is added, the enhancement in the PL emission can be correlated with the decrease in the grain size observed and the formation of trapped states due to the introduction of dangling bonds$^{36}$ by the Zn dopant.

To better understand these broadband defect emissions in the visible, the PL spectra were deconvoluted with a Gaussian fitting. Figure 6.7 (b) shows the results for x=0.00 where three contributions to the emission peak can be distinguished, two blue emissions at 460 nm (2.69 eV), 495 nm (2.50 eV) and a green emission at 558 nm (2.22 eV). For x=0.04 shown Figure 6.7 (c), the fitting gives an additional new blue emission at 442 nm (2.8 eV).

The luminescence peaks observed for SnO$_2$ in the visible region are related to defect energy levels originating from tin and oxygen vacancies formed during the growth process$^{37,38}$. The interaction between oxygen vacancies and interfacial tin vacancies leads to formation of a significant number of trapped states, which are responsible for various PL signals in the visible region$^{39}$. These defect-related energy levels within the band gap can trap electrons from the valence band and thereby make a contribution to the luminescence. Generally, the oxygen vacancies are the most common defects in the nanocrystalline oxide materials and act as radiative centres in luminescence processes. Three types of oxygen vacancies$^{34}$ are present in any type of oxide: V$_O^0$, V$_O^+$ and V$_O^{++}$. However at room temperature, all neutral V$_O^0$ centres (oxygen vacancies without any positive charge) are dissociated into singly ionized oxygen vacancies, V$_O^+$ (oxygen vacancies with a positive charge) and conduction band electrons.
Figure 6.7 Room temperature PL spectra of (a) Sn$_{1-x}$Zn$_x$O$_2$ nanoparticles with $x=0.00$ and 0.04 Zn-SnO$_2$. Gaussian fit for Sn$_{1-x}$Zn$_x$O$_2$ with (b) $x=0.00$ and (c) $x=0.04$. 
Figure 6.8 Schematic representation of the relaxation processes in the photoexcited SnO$_2$ lattice.

The V$_{O}^{++}$ defect is formed when an active hole recombines with an electron in a V$_{O}^{+}$ centre, and this defect can give rise to visible emission $^{40}$.

If we translate our findings into an energy level scheme as shown in Figure 6.8, we can reason as follows: photons with an energy of 2.8 eV (442 nm) will not be emitted through a transition of an electron from the conduction band to a V$_{O}^{+}$ level, as such a transition effectively occurs between the conduction band edge and the V$_{O}^{0}$ level. However, recombination of a conduction band electron with a V$_{O}^{++}$ centre (an oxygen vacancy containing no electrons, having an effective divalent positive charge with respect to the normal O$^{2-}$ site) can yield such a blue emission band. Such V$_{O}^{++}$ centres can be formed when a hole is trapped at a V$_{O}^{+}$ centre.

The green emission is related to the crystallinity and the existence of structural defects, such as tin interstitials $^{41}$, vacancy clusters, dislocations, and/or dangling bonds, surface states $^{42}$.

### 6.4 Conclusions

We prepared SnO$_2$ nanoparticles with and without Zn$^{2+}$ doping using a solvothermal method, and systematically studied the impacts of the Zn$^{2+}$ doping on the surface mode, band gap energy and photoluminescence. In Sn$_{1-x}$Zn$_x$O$_2$ nanoparticles the Raman fundamental $A_{1g}$ classical mode broadens with addition of Zn, and this broadening most likely originates from the reduction in particle size$^{20}$. The weak Raman peaks at 684 cm$^{-1}$ was ascribed as induced by the IR-active $A_{2u}$
LO modes due to the size effect of the Zn-doped SnO₂ nanocrystals. Raman studies also reveal a band originating from oxygen vacancies with the intensity of the surface mode (545 cm⁻¹) increasing over the same concentration range (Sn₁₋ₓZnₓO₂ with x=0.06 to 0.10) where the ferromagnetic moment decreases, as discussed in Chapter 5.

For undoped SnO₂ and Sn₁₋ₓZnₓO₂ nanoparticles the photoluminescence results testify to the presence of singly ionized oxygen vacancies. V₀⁺ appear as the recombination centres for the luminescence process, and the PL intensity associated with this defect increases in the zinc doped system.

The magnetic behaviour of the oxygen vacancies in pure and transition metal-doped SnO₂ has been object of different studies: EPR measurements of Armelao et al. have shown that the V₀⁺ defect is paramagnetic¹⁴, while according to Pushpa et al.⁴³ singly ionized oxygen vacancies are magnetic on the (001) surface and nonmagnetic on the (110) surface. For pristine SnO₂ thin films Ghosh et al.¹³ reported the presence of large amounts of singly ionized oxygen vacancies (V₀⁺), which they related to the observed ferromagnetism.

Taking the magnetic characterisation and PL results together, we suggest that Zn doping enhances the V₀⁺ defect density and these defects not only contribute to the paramagnetic background that is prevalent in all the compositions but also to the ferromagnetism when such defects are created at (001) surfaces. Based on the Raman band centred at 545 cm⁻¹ and the photoluminescence of the samples, we suggest that the weak blue emission 442 nm and the broad green emission 558 nm primarily originate from singly ionized oxygen vacancies and tin interstitials, respectively. Moreover the band gap narrowing was ascribed to the oxygen vacancies with different charge states caused by incorporation of Zn.

References


