Defect ferromagnetism in ZnO and SnO2 induced by non-magnetic dopants
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Chapter 7

Defect ferromagnetism in Li-doped SnO₂ nanoparticles

Figure 7.1 Schematic representation of the structural relaxation of a Li dopant in SnO₂. Green, yellow, and red balls represent Sn, O, and Li atoms, respectively. The Sn vacancy ($V_{\text{Sn}}$) is represented by a green dashed circle. The arrow represents the movement of the Li atom towards $V_{\text{Sn}}$ during the structural relaxation.

7.1 Introduction

In Chapter 5 we discussed the role of Zn dopants in SnO₂ as a source of inducing ferromagnetism (FM) in SnO₂. The difference between the valence of divalent Zinc and tetravalent Sn was shown to play an important role in the generation of various defects and thereby in inducing FM. In this chapter we move on to the case of a cation dopant of group 1A, i.e. monovalent Li, in SnO₂ and study how it affects the magnetic properties. A theoretical study by Peng et al.\(^1\) has shown that lower valance cation doping introduces holes or weaker anion electronegativity, which in turn play a vital role in mediating ferromagnetism in \(d^0\) semiconductors. From the experimental point of view, magnetism induced by non-magnetic doping has been observed in N-, Mg- and K-doped SnO₂.\(^2\)\(^-\)\(^5\) Rahman et al.\(^6\) theoretically predicted that Li-doped SnO₂ is a good candidate in the field of spintronics since Li behaves as a spin polarizer. Figure 1 shows its schematic representation of the structural relaxation of a Li doped SnO₂. These authors also found that Li can act as vacancy stabilizer by reducing the defect formation energies of the native defects and that Li induces magnetism in SnO₂ when substituting at the Sn site but becomes nonmagnetic when occupying O and interstitial sites. In a perfect SnO₂ crystal the nominal valence of Sn is Sn\(^{4+}\) and when Li\(^{1+}\) is introduced at the Sn site, it donates one electron to compensate one hole among the four holes generated by the absence of Sn. The three uncompensated holes, localized at the O sites, give a magnetic moment of 3.00 \(\mu_B\) per supercell\(^6\). There have been a few experimental studies of this system; recently Srivastava et al.\(^7\) reported that in Sn\(_{1-x}\)Li\(_x\)O\(_2\) for a small window of concentrations (0.03 \(\leq x \leq 0.09\)) Li induces magnetism at low temperature (3 K). Within this concentration range the compounds exhibit weak paramagnetism but the long-range ferromagnetic coupling in this system needs to be discussed further. Other experimental reports on Li-doped SnO₂ thin films\(^8\) and nanoparticles\(^9\) have shown room temperature ferromagnetism (RTFM), however the part played by Li as cation substitutional or interstitial defect in SnO₂ remains unclear. In this chapter we report on a systematic study of the structural, electronic, optical and magnetic properties of Li-doped SnO₂ compounds in different size regimes, from nanoparticles to bulk crystal, carried out to explore the role of Li in establishing room temperature ferromagnetism in SnO₂.
Direct ferromagnetism in Li-doped SnO$_2$ nanoparticles

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7.2 Experimental

7.2.1 Synthesis

Sn$_{1-x}$Li$_x$O$_2$ nanoparticles with varying Li concentration (x = 0.0, 0.02, 0.04, 0.1) were synthesized by a simple solvothermal method at room temperature. All chemicals were of analytical grade and were used without further purification. 0.1 Molar of SnCl$_4$·5H$_2$O and Li(NO$_3$)$_2$ were separately dissolved in 100 mL of a water/ethanol mixture (1:1, v/v) and then mixed together to form a single solution. Then under constant stirring, a solution of ethanol and deionized water containing 2.8 g NaOH was slowly dropped into the above solution. The solution of the resultant mixture was maintained at pH value ~11 and transferred into a 100 mL Teflon-lined stainless steel autoclave, where it was kept at 453 K for 22 h. The resulting precipitates were centrifugally separated and washed with ethanol and deionized water for several times. Finally the products were dried in air at 353 K for several hours.

In order to favour the formation of smaller crystallites, we also processed two Sn$_{1-x}$Li$_x$O$_2$ samples with nominal composition x=0.04 where the autoclave temperature was set at 433 K and 443 K (< 453 K) respectively, while the rest of the protocol was kept the same. A bulk powder sample was also prepared by annealing one of the dried Sn$_{1-x}$Li$_x$O$_2$ samples with nominal composition x=0.04 in the furnace at 873 K for 8 h.

7.3 Result and discussions

All characterization measurements were performed as detailed in chapter 2.

7.3.1 X-ray diffraction analysis

Crystal structure and phase analysis were performed using X-ray diffraction (XRD). Figure 7.2 (a) depicts the polycrystalline XRD patterns for a series of Sn$_{1-x}$Li$_x$O$_2$ (x = 0.0, 0.02, 0.04 and 0.10) samples. A step size of 0.02 and time-per-step of 1.50 s were used for each scan. All the diffraction peaks can be indexed to the rutile structure of SnO$_2$ with tetragonal lattice parameters $a = 4.728$ Å and $c = 3.187$ Å (JCPDS No. 45-1445).
Figure 7.2 (a). XRD patterns of Sn_{1-x}Li_xO_2 samples with x=0.00, 0.02, 0.04, 0.10. Inset: (101) peak shift with Li addition (b) variation of lattice parameter “a” deduced from the (200) peak and (c) average particle size as a function of Li concentration (d) XRD patterns of Sn_{0.96}Li_{0.04}O_2 samples prepared under different synthesis conditions (see text for details) to obtain a size variation of the particles from the nanometer to the bulk regime.

There is no indication of any secondary phases within the resolution of the diffractometer even up to highest doping, Sn_{0.90}Li_{0.10}O_2. The broad peaks are characteristic of nanometer size crystallites. To further confirm the complete absence of lithium segregation, high resolution scans near the expected positions of Li_2O peaks were performed and no such phase was
observed. The results in Figure 7.2 (a) clearly demonstrate that the intensity of the diffraction peaks decreases and the full width at half-maximum (FWHM) increases with increasing Li concentration. The changes in intensity and FWHM show that the incorporation of Li dopants results in the deterioration of crystallinity and the decrease of the crystallite size in Sn\textsubscript{1-x}Li\textsubscript{x}O\textsubscript{2} samples. Furthermore, the average crystallite size can be obtained using Debye Scherrer’s formula\textsuperscript{10} \( D = K \lambda / \beta \cos \theta \), where \( D \) is the average crystallite size, \( \beta \) the FWHM in radians, \( \lambda \) the X-ray wavelength (Cu-K\( \alpha \) = 0.154 nm), \( \theta \) the Bragg diffraction angle, and \( K \) a correction factor which is taken as 0.9. As shown in Figure 7.2 (b), the calculated grain size decreased from 51.0 nm to 16.0 nm with increasing Li concentration.

The inset in Figure 7.2 (a) shows the non-monotonic shift of the SnO\textsubscript{2} (101) diffraction peak with varying Li concentration. In general, a slight decrease in the lattice parameter is expected when Sn\textsuperscript{4+} ions are replaced by Li\textsuperscript{+} ions because of the difference in ionic radius, 0.68 Å for Li\textsuperscript{+} and 0.71 Å for Sn\textsuperscript{4+},\textsuperscript{11} while the incorporation of Li ions at interstitial sites (Li\textsubscript{i}) expands the lattice\textsuperscript{9}. Figure 7.2 (c) shows a general trend of expansion of the lattice for all concentrations as compared to pure SnO\textsubscript{2}. There is a dip at \( x=0.04 \) which may indicate that along with interstitial Li, preferred at low concentrations due to its low formation energy\textsuperscript{6}, there may be also substitutional Li defects, Li\textsubscript{Sn}. As the Li concentration increases, the interstitial sites get saturated and Li starts to occupy the substitutional sites (Li\textsubscript{Sn}). This hypothesis will be further elaborated in the discussion of the X-ray photoelectron spectroscopy (XPS) results.

For a fixed concentration of Li different size particles were prepared to study the effect of size on the magnetization. Figure 7.2 (d) shows XRD patterns of these Sn\textsubscript{1-x}Li\textsubscript{x}O\textsubscript{2} samples, all with \( x=0.04 \). These XRD patterns were refined by the Rietveld refinement technique\textsuperscript{12} with the help of the fullprof programme, as shown in Figure 7.3 (a-d). Changes in the diffraction pattern were noticeable when the autoclave temperature (453 K, 443 K and 433 K) was decreased or when the sample was additionally annealed at 873 K, but the analysis of the data by the Rietveld refinement technique showed no impurity phases. The absence of impurity peaks in Li substituted samples implies that Li substitution did not trigger the formation of the impurity phase, thereby confirming the high control of the synthesis procedures. The Rietveld refinement of the peaks gives an accurate description of the changes in crystallite sizes, lattice parameters and cell volume; the values extracted via Rietveld fitting for all compositions are summarized in Table 7.1.
Figure 7.3 (a-d) Rietveld refinement fitting results of the X-ray powder diffraction patterns of Sn$_{0.96}$Li$_{0.04}$O$_2$ (presented in Figure 7.2 (d)) showing the observed pattern (diamonds in red colour), the best fit Rietveld profiles (black solid line), reflection positions (vertical bars), and difference plot (grey solid line at the bottom).

One deduces indeed that the autoclave treatment at 453 K (as the other samples with different Li dopant contents) yielded an average particle size of 11.69(16) nm, while the autoclave treatments at 443 K and 433 K produced samples with an average particle size of 4.772(95) nm and 2.978(71) nm respectively. The additional annealing at 873 K instead produced a bulk sample with a crystallite size of 133.1(91) nm.
Table 7.1: Structural parameters for Sn$_{0.96}$Li$_{0.04}$O$_2$ samples as obtained from Rietveld refinement.

<table>
<thead>
<tr>
<th>Sn$<em>{0.96}$Li$</em>{0.04}$O$_2$</th>
<th>Cassiterite Phase (P4$_2$/mnm)</th>
<th>Vol.$(\text{Å}^3)$</th>
<th>Crystallite size(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Autoclave at 433 K</td>
<td>a(Å)</td>
<td>c(Å)</td>
<td></td>
</tr>
<tr>
<td>Autoclave at 443 K</td>
<td>4.7410(26)</td>
<td>3.1982(29)</td>
<td>71.89(10)</td>
</tr>
<tr>
<td>Autoclave at 453 K</td>
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<td>3.1606(17)</td>
<td>70.244(61)</td>
</tr>
<tr>
<td>Additional annealing at 873 K</td>
<td>4.73540(12)</td>
<td>3.18455(14)</td>
<td>71.4105(47)</td>
</tr>
</tbody>
</table>

### 7.3.2 Microstructural and morphology analysis

Figure 7.4 (a and b) presents the scanning electron microscopy (SEM) micrographs of the synthesized Sn$_{1-x}$Li$_x$O$_2$ samples with x=0.02 and x=0.10. Both samples consist of agglomerated nanoparticles. The incorporation of Li does not modify the morphology creating differently shaped nanocrystals as was seen in the case for Zn-doped SnO$_2$ (previous chapter of this dissertation). We also verified the absence of magnetic contaminants in the nanoparticles by energy-dispersive X-ray spectroscopy (EDX); the results are shown Figure 7.4 (c and d) (right panels). Only signals of Sn, Na, Si and O were found, and this confirms that within the instrumental limit no magnetic impurity is present in the samples. Na and Si are residues from chemical precursors; Li could not be detected by EDX, which has only limited sensitivity for elements lighter than Na. Transmission electron microscopy (TEM) micrographs were acquired for Sn$_{0.96}$Li$_{0.04}$O$_2$ nanoparticles and are shown in Figure 7.4 (e). Particles exhibited a size distribution, ranging between 10 and 19 nm. Figure 7.4 (f) shows the high resolution transmission electron microscopy (HRTEM) micrographs for Sn$_{0.96}$Li$_{0.04}$O$_2$; the two groups of crystallographic planes marked in the images have interplanar distances of ~0.34 nm and ~0.26 nm respectively. These separations match well with the (110) and (101) planes of rutile SnO$_2$. 
Figure 7.4 Characterisation of Sn$_{1-x}$Li$_x$O$_2$ nanoparticles: (a and b) SEM micrographs, (c and d) EDX scan of the samples with $x=0.02$ and $x=0.10$, (e) TEM and (d) HRTEM images of the sample with $x=0.04$.

7.3.3 X-ray photoelectron spectroscopy analysis

The representative XPS spectra of the Sn 3$d$, O 1$s$ and Li 1$s$ core-level regions of Sn$_{0.96}$Li$_{0.04}$O$_2$ nanoparticles are shown in Figure 7.5 (a–c). Figure 7.5 (d) presents the Li 1$s$ XPS spectrum for nanoparticles with a higher Li content, Sn$_{0.90}$Li$_{0.10}$O$_2$. 
Figure 7.5. XPS spectra of the Sn 3d (a), Li 1s (b) and O 1s (c) core level regions of Sn_{0.96}Li_{0.04}O_2 nanoparticles. XPS spectrum of the Li 1s core level region (d) of Sn_{0.90}Li_{0.10}O_2 nanoparticles.

The two components of the Sn 3d doublet are located at binding energies of 488.1 eV (Sn 3d_{5/2}) and 496.6 eV (Sn 3d_{3/2}), in agreement with the literature values for Sn^{4+} bound to oxygen in the SnO_2 matrix^{13}.

The most informative part of the XPS spectra concerns the Li atoms. For Sn_{1-x}Li_xO_2 nanoparticles with composition x=0.04, the Li 1s peak was asymmetric, indicating the presence of more than one component. When deconvoluting with two Lorentzian-Gaussian curves, the best fit is obtained with components situated at 53.0 eV and 55.4 eV respectively, as shown in
Figure 7.5(c). The lower binding energy component (LBEC) can be assigned to interstitial lithium\textsuperscript{8}, Li\textsubscript{i}, while the higher binding energy component (HBEC) peak is related to substitutional lithium, Li\textsubscript{Sn}, involved in Li\textsubscript{Sn}-O bonds\textsuperscript{14}. This confirms that doping results in the coexistence of Li\textsubscript{i} and Li\textsubscript{Sn} in SnO\textsubscript{2} matrix. The relative intensity of the two components indicates that Li predominantly substitutes at Sn sites, and fully agrees with the lattice parameter decrease for this compositions (x=0.04) determined by XRD, which suggests that Li\textsuperscript{+} with smaller ionic radius substitutes for the larger Sn\textsuperscript{4+}. However at higher concentration (x=0.10) Li prevalently occupies interstitial sites, as deduced from the symmetric single Li 1s peak with binding energy 54.5 eV shown in Figure 7.5 (d). This peak while not being exactly at the expected position of LBEC (L\textsubscript{i}) has definitely shifted to a lower binding energy as compared to the major peak (55.4 eV) for the x=0.04 composition. We suggest that this shifting of the peak to lower binding energy is consistent with an increasing number of Li ions entering the interstitial positions for this higher Li concentration. This again agrees with the XRD results discussed above, where for higher doping (x=0.10) an expansion of the lattice was found and interpreted as due to additional Li atoms going into interstitial sites (Li\textsubscript{i}), due to the limited solubility\textsuperscript{9}.

The role of Li defects, both substitutional and interstitial in forming a stable defect complex that includes a Sn vacancy has been discussed by Yi \textit{et al.}\textsuperscript{15}, The significance of such a defect is that it is magnetic. Hence our observation of the presence of both interstitial and substitutional defects could be an indicator of such a complex defect.

The XPS O 1\textsubscript{s} core level spectra were also measured; Figure 7.5(c) shows the result for Sn_{0.96}Li_{0.04}O_{2} composition. The asymmetric O 1\textsubscript{s} can be fitted with three components, O1 at 530.3 eV in binding energy is attributed with oxygen bound to Sn\textsuperscript{3+}, O2 at 531.6 eV is associated with the presence of Sn with a nearest neighbour oxygen vacancy (V\textsubscript{O}), and O3 at 533.0 eV is due to the presence of chemisorbed surface hydroxyl, -CO\textsubscript{3}, absorbed H\textsubscript{2}O or absorbed O\textsubscript{2}\textsuperscript{16}.

Various defects (Li\textsubscript{Sn}, Li\textsubscript{i}, and V\textsubscript{Sn}) formed by Li at different concentration can play a significant role in determining the defect mediated ferromagnetism in Li-doped SnO\textsubscript{2}; in the following we shall emphasize how.

\textbf{7.3.4 Magnetic Analysis}
Direct ferromagnetism in Li-doped SnO\textsubscript{2} nanoparticles

All samples were handled with particular care to avoid any possibility of magnetic contamination. Ferromagnetic (FM) hysteresis loops were measured at room temperature (300 K) and low temperature (5 K) for all samples. Pure SnO\textsubscript{2} was synthesized and treated under the same condition as the doped SnO\textsubscript{2} samples. The diamagnetic response of the sample holder alone is shown in the inset of Figure 7.6 (a). The background of the sample holder was subtracted from the raw data of all compositions measured at 300 K and 5 K and the resultant magnetization is shown in Figure 7.6 (a and b).

As seen in Figure 7.6(a) while undoped SnO\textsubscript{2} is diamagnetic at room temperature, clear hysteresis loops for Sn\textsubscript{1-x}Li\textsubscript{x}O\textsubscript{2} with x=0.02 and 0.04 confirm the ferromagnetic behaviour of these compositions. For the sample with x=0.04 the higher field moment appears to be saturated except for a slight decrease presumably from the subtraction of the diamagnetic background. The high field (saturation) magnetization for this composition has a value of 0.0054±0.00031 emu/gm and magnetic moment per Li atom amounts to 0.035 \(\mu_B\)/Li atom, whereas for x=0.02 the magnetization at high field is 0.0012±0.00022 emu/gm (0.0016 \(\mu_B\)/Li atom). At the highest Li concentration (x=0.10) a paramagnetic component can be seen alongside a small ferromagnetic one. The marked difference between the x=0.04 composition and the other compositions is a significant feature of this data.

The data measured at 5 K and presented in Figure. 7.6(b) show a paramagnetic response for undoped SnO\textsubscript{2}, while for the Li-doped samples the clear hysteresis loop points to ferromagnetic behaviour along with some linear part indicative of the coexistence of a paramagnetic contribution (as also observed in chapter 5 for Zn-doped SnO\textsubscript{2}). The saturation magnetization (0.0044±0.00037 emu/gm for x=0.02) is enhanced as compared to magnetization value at 300 K. We noticed that for highest concentration (x=0.10) the hysteresis contains a ferromagnetic plus a paramagnetic response, although the moment present is very low. The inset in Figure. 7.6(b) shows enlarged view in order to highlight the coercivity 255.2±2.5 Oe, 176.5±2.9 Oe and 329.1±3.1 Oe for x=0.02, 0.04, 0.10 respectively.

Comparing the variation in magnetic moment with Li concentration, we note that the moment is largest for x=0.04 where both XRD and XPS indicate the presence of substitutional Li. Conversely where the sample contains mainly interstitial Li (x=0.10), the FM moment is lowest. To further explore the observed ferromagnetism, the temperature dependent zero-field-cooling (ZFC) and field cooling (FC) magnetizations of the Sn\textsubscript{1-x}Li\textsubscript{x}O\textsubscript{2} with x=0.04 and x=0.10 were
measured and the results are shown in Figure 7.7. In the case of ZFC measurements, the sample was cooled under zero field down to 5 K, and the net magnetization was measured when heating the sample under an applied field of 300 Oe. For FC magnetization measurements the field of 300 Oe was applied both during cooling and heating of the sample.

For both compositions the FC moment increases monotonically with decreasing temperature but shows a slight upturn at lowest temperatures. For the x=0.04 sample this upturn is at about 30 K. The ZFC data for the same composition exhibits a broad maximum at about 120 K suggesting the blocking of the moment below this temperature. However the ZFC and FC curves remain separated up to the room temperature indicating the presence of progressive blocking of moments presumably against a magnetic anisotropy. For x=0.10 the FC data increases very gradually when the temperature is lowered and then increases significantly below ≈ 60 K. The FC and ZFC moments converge at ≈ 315 K but thereafter for the ZFC moment, there is a consistent decrease with decreasing temperature. The ZFC also shows a clear change of slope at ≈ 60 K, where the FC moment shows an upturn. The field cooled data shows the moment continuing to increase all the way down to 5 K with a change in curvature ≈ 60 K, which becomes a pronounced upturn below 15 K. Taken together the two sets of data (ZFC and FC) clearly indicate the presence of blocking of some magnetic entities or clusters even at room temperature; this blocking becomes dominant at 120 K.

Figure 7.6 Magnetization (M) versus magnetic field (H) at (a) 300 K and (b) 5 K of Sn\textsubscript{1-x}Li\textsubscript{x}O\textsubscript{2} nanoparticles with x=0.00, 0.02, 0.04 and 0.10. The inset in (a) shows the response of the sample holder alone, the inset in (b) shows an enlarged view to highlight the coercivity.
Figure 7.7 FC and ZFC magnetization versus temperature for Sn$_{1-x}$Li$_x$O$_2$ nanoparticles with x=0.04 and x=0.10, measured at 300 Oe.

These results suggest both the presence of a local anisotropy that blocks the moments as well as a spread in the sizes of the magnetically correlated entities. This latter conclusion is drawn from the gradual freezing of the moments, presumably due to the larger magnetic entities being blocked earlier and the smaller ones being blocked at lower temperatures. Below 120 K a large number of smaller clusters block leading to the peak. From the magnitude of the peak temperature (120 K) for x=0.04 it is clear that the anisotropy energy is moderate (k_B T=12 mV ~ E_a) \textit{i.e.} E_a is activation energy and indicates that defect-induced moments on various sites are coupled to form a cluster that blocks along a locally preferred direction. In contrast the blocking even at 315 K for x=0.10 indicates the presence of large size magnetic entities albeit with a net smaller moment. In conclusion the presence of irreversibility may be attributed, as is usual, to the presence of a magnetically glassy phase. The system, we note, has inherent disorder where Li ions that induce the magnetic behaviour are randomly distributed in SnO$_2$ host material. The interactions between these randomly distributed magnetic complexes can also result in a phase with glassy-like magnetic properties$^{17}$.
Effect of size on magnetic behavior:

**Figure 7.8** M-H curves at 300 K, showing diamagnetic behaviour for different average nanoparticle sizes for Sn$_{0.90}$Li$_{0.10}$O$_2$.

Figure 7.8 shows diamagnetic behaviour of Sn$_{1-x}$Li$_x$O$_2$ nanoparticles with $x=0.04$ and different particle sizes (4.8 nm, 2.98 nm and 133.1 nm respectively). In contrast the particles discussed above that exhibited ferromagnetic behaviour had sizes in the range of 16 to 51 nm. It thus appears that in addition to the amount of Li dopant also the particle size has an important influence on the magnetic behaviour. This may be due to the prevalence of different defects (interstitial or substitutional) in particles of different size. Combining the results of XRD and XPS we can draw the following conclusions on the origin of ferromagnetism in Li doped SnO$_2$ nanoparticles: as predicted by Rahman *et al.*$^6$ the substitution of Sn atoms by Li introduces three holes in the O 2p state which give a total magnetic moment 3.00 $\mu_B$. Li behaves as a spin polarizer and the oxygen atoms surrounding the Li$_{Sn}$, which are polarized, are the main contributors to magnetism$^6$. In this picture the $M_S$ value is large when Li is present in substitutional sites. The presence of Li$_{Sn}$ is key for enhancing ferromagnetism in Li-doped SnO$_2$ nanoparticles. The spin ordering occurs through $p$–$p$ interaction between holes trapped in oxygen 2p orbital adjacent to Li$_{Sn}$ site.
7.4 Conclusions

In summary, Sn$_{1-x}$Li$_x$O$_2$ nanoparticles with varying Li concentration (x=0.00, 0.02, 0.04, 0.10) were synthesized and their structural, morphology, electronic and magnetic properties were systematically investigated. The polycrystalline structure of the nanoparticles was confirmed by XRD and no diffraction from other phases such as Li$_2$O was detected. The incorporation of Li in SnO$_2$ lattice was indicated by XRD and confirmed by XPS. Li-doped nanoparticles showed ferromagnetic ordering (plus a paramagnetic contribution) for particle sizes in the range 16-51 nm. However, other Li-doped compounds, including undoped SnO$_2$, are diamagnetic below and above this particular range of sizes. This is unlike the case of Srivastava et al.\textsuperscript{7} who reported that magnetization increases sharply with average nanoparticle radius. We determined the variation of the moment with increasing Li content and correlated the changes with the presence of Li at substitutional or interstitial sites. XPS data shows the presence of Li$_{Sn}$ and Li$_i$ defects. Li prefers to occupy the interstitial positions at low concentration, and substitutes Sn at moderate concentrations. Comparing the variation in magnetic moment with Li concentration, we note that the moment for compositions where the Li substitutes for Sn is larger than that of compositions where Li prevalently occupies interstitial sites.

The ferromagnetism of this system is verified to be intrinsic and it is concluded that the observed ferromagnetic ordering in Li-doped SnO$_2$ nanoparticles is mainly due to the holes created by Li$_{Sn}$. Li$_i$ acts as electron donor and may combine with the holes induced by Li$_{Sn}$ to decrease the ferromagnetism. The $M_S$ value of the Sn$_{1-x}$Li$_x$O$_2$ nanoparticles is dependent on the Li concentration. Sn$_{1-x}$Li$_x$O$_2$ nanoparticles with x=0.04 have the highest magnetic moment because at that concentration Li occupies more substitutional sites as compared to interstitial sites. The role of Li defects, both substitutional and interstitial in forming a stable defect complex that includes a Sn vacancy has also been discussed in the literature\textsuperscript{15}. The significance of such a complex defect is that it is also magnetic. Hence our observation of the presence of both interstitial and substitutional defects could also be an indicator of such a complex defect. However beyond a certain concentration of the Li dopant, when the Li$_i$ prevail, the ferromagnetism decreases. To stabilize such defects also at higher dopant concentrations where the magnetic moments and critical temperatures are larger, remains as one of the main challenge for the development of materials with defect mediated ferromagnetism.
Direct ferromagnetism in Li-doped SnO$_2$ nanoparticles

Chapter 7

References


