Chapter 5

Optical and magnetic studies of Mn doped ZnO (ZnO:Mn) nanorods synthesized by hydrothermal method

5.1 Introduction

Manganese doped ZnO (ZnO:Mn) nanostructures in the form of nanowires and nanorods are of great interest owing to their unique and fascinating properties, which made it a potential candidate for nano-devices and spintronic applications [255, 256]. ZnO exhibit strong UV emission at room temperature whereas, nanostructured ZnO:Mn exhibit ferromagnetism at room temperature [257, 244, 258]. A single material that exhibits UV emission property as well as ferromagnetism at room temperature is of particular interest for fabricating spintronic devices. Solution-based hydrothermal synthesis is an efficient way to prepare ZnO:Mn nanorods and nanowires [259, 260, 261]. The
research reports on transition metal alloyed ZnO nanostructures, especially ZnO:Mn nanorods are comparatively less. Among them, most of the works are related to the magnetic properties of Mn doped ZnO; nevertheless, there are few papers dealing with the optical properties of this material. It has been previously reported that the concentration of Mn has a significant influence on the optical properties of ZnO [262, 263]. Bhat et al. observed an initial red shift in the band gap of ZnO:Mn for Mn concentration less than 3% mol followed by increase with Mn concentration [262]. Investigations on UV and blue light emission properties of Mn doped ZnO nanocrystals reveals that the optical properties of ZnO can be tuned by using manganese as a dopant [264]. There is a decrease of optical transmittance, optical band gap and the particle size of ZnO:Mn nanopowder on increasing the Mn concentration [265]. The optical band gap of ZnO:Mn decreased to values 3.06, 2.90 and 2.78 eV with Mn concentration 1, 2 and 3 mol%, respectively, as compared to that of ZnO (3.37 eV) [265]. Bhat et al. also reported a non-monotonic variation of band gap in Mn doped ZnO nanocrystals [262].

Further, Diluted magnetic semiconductors (DMS), which combine ferromagnetism with semiconductivity, are identified to be potential building blocks for spintronic devices [52, 266, 267]. Nonmagnetic materials like TiO\textsubscript{2}, SnO\textsubscript{2}, HfO\textsubscript{2} showed room-temperature ferromagnetism while doping it with a suitable quantity of transition metal elements [268, 269, 270, 271]. Prellier et al. [272] reported ferromagnetism in transition metals (TM) doped DMSs with a Curie point above room temperature and are useful for advanced spintronic applications. In semiconductor materials, ferromagnetism occurs at doping levels far below the percolation threshold and the average magnetic moment per dopant cation progressively increases with decreasing dopant concentration [273]. Room-temperature ferromagnetism is theoretically predicted in Mn doped ZnO (ZnO:Mn) [121]. Following to the theoretical prediction, ZnO
would become ferromagnetic at room temperature by doping with 3d transition elements, intensive experimental work has been carried out to understand the DMS behavior [274, 275, 276]. Manganese is a good transition metal candidate to be used as dopant because of its better thermal solubility (10 mol%) [275]. High-temperature and vapor phase methods are mostly employed for the fabrication of 1D nanostructures of ZnO:Mn [277]. Mn doped ZnO nanowires are also obtained by doping Mn into ZnO by using various techniques, such as ion implantation, thermal evaporation, and wet chemical method [58]. Solution based synthesis like solvothermal and hydrothermal methods are the efficient strategies to synthesize Mn-doped ZnO 1D semiconductor nanostructures [278, 244, 260, 261, 279, 280]. As stated previously, there are several reports on the magnetic characteristics of ZnO:Mn and inconsistencies exist in these reports [281, 282, 283, 284, 285]. A recent first-principles based study could open new ways to the understanding of the ferromagnetic interactions in this material [286].

In this context, it requires more experimental and theoretical support to understand the origin of luminescence and ferromagnetism in ZnO:Mn with different nanostructures. In the present chapter, the structure, morphology, and optical behavior of ZnO:Mn (3 wt%), ZnO:Mn (4 wt%) and ZnO:Mn (5 wt%) nanorods have been studied. Magnetic properties of ZnO:Mn (3 wt%) and ZnO:Mn (5 wt%) were investigated.

5.2 Experimental

For the synthesis of ZnO and ZnO:Mn nanorods, an aqueous solution made of Zn(CH$_3$COO)$_2$ 2H$_2$O (0.1 M), Mn(CH$_3$COO)$_2$ 2H$_2$O (0.1 M) and NaOH (1 M) were placed in a sealed teflon reaction vessel. The sealed reaction vessel is subjected to hydrothermal reaction under autogenous pressure at a growth
temperature of 200 °C for a time of 3 hours. The detailed synthesis procedure is given in chapter 3. The samples were examined by using a Hitachi S-4800 scanning electron microscope (SEM). The transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) images of the samples were obtained with a JEOL JEM-2100 transmission electron microscope. The X-ray diffraction (XRD) pattern of the synthesized samples were recorded by employing a Rigaku (D.Max.C) X-ray diffractometer with CuKα radiation (\(\lambda = 1.5414 \text{ Å}\)). The X-ray diffraction data of as synthesized samples were processed with the Rietveld refinement analysis in order to extract unit cell parameters of the hydrothermally grown ZnO and ZnO:Mn using FullProf program [258, 214]. Fourier transform infrared (FTIR) spectroscopy measurements of the samples were performed in the wave number range 400 - 4000 cm\(^{-1}\) using the Shimadzu Prestige spectrometer by KBr pellet method. The experimental conditions for recording the Raman spectra, UV-Vis spectra and room temperature photoluminescence spectra of the samples are presented in chapter 3. X-ray photoelectron spectroscopy (XPS) measurement was carried out by using a Kratos AXIS Ultra spectrometer. Magnetic properties of the samples were studied with a SQUID magnetometer (QUANTUM DESIGN).

5.3 Results and discussion

SEM images of hydrothermally grown ZnO:Mn nanorods (Mn - 0, 3, 4, and 5 wt%) are shown in figure 5.1. The ZnO sample exhibits flower like morphology as described in chapter 3 whereas, ZnO:Mn (Mn - 3 - 5 wt%) samples have nanorod morphology. The observed change in morphology, from nanoflower-like to nanorod shape on Mn doping may be due to the change in growth dynamics of ZnO:Mn attributed to the presence of Mn\(^{2+}\) ions. Interestingly,
a decrease in the size (length and diameter) of the nanorods were observed on increasing Mn doping concentration from 3 to 5 wt%, which is an indication of low growth rate of ZnO:Mn (Figure 5.1). The TEM, HRTEM and SAED of the as synthesized ZnO and ZnO:Mn(5 wt%) are shown in figure 5.2 for comparison. The size of the nanorods decreased on increasing the Mn doping concentration which is similar to that of previously mentioned observation with SEM. The diameter of the nanorods varies in the range ~ 90 - 280 nm for ZnO (Chapter 3) and ~ 80 - 120 nm for ZnO:Mn (5 wt%). Its aspect ratios are determined as ~ 5 - 13 for ZnO and ~ 3 - 12 for ZnO:Mn (5 wt%). HRTEM and SAED data of both ZnO and ZnO:Mn (5 wt%) indicate the crystalline nature of the samples. HRTEM images also shows that the interplanar distance corresponds to ‘d’ value are 0.25 nm for ZnO and 0.26 nm for ZnO:Mn (5 wt%) respectively.

The elemental composition of as synthesized samples are confirmed with EDX and XPS analysis. The EDX spectra of the hydrothermally grown ZnO:Mn (3, 4 and 5 wt%) are shown in figure 5.3 and the corresponding atomic and weight percentage of each elements are presented in table 5.1 which indicates the incorporation of Mn into the ZnO crystalline system. Further, we carried out the XPS measurements on ZnO:Mn (3 wt%) and ZnO:Mn (5 wt%) for comparison purpose. Figure 5.4 shows the high resolution XPS Mn-2p spectra of ZnO:Mn nanorods (Mn - 3 and 5 wt% doped samples). The Mn-2p peak of ZnO:Mn nanorods is observed at 642.29 eV. This result is in agreement with previously reported binding energy values of the Mn$^{2+}$ ionic state (Mn 2P$_{3/2}$) [287]. This indicates the presence of the Mn$^{2+}$ ions in the samples as well as incorporation of Mn$^{2+}$ ions into the ZnO lattice. This observation also confirms the XRD of the present sample, in which there is no additional phase or Mn clusters or crystalline Mn oxides detected.
Figure 5.1: SEM images of hydrothermally grown (a) ZnO, (b) ZnO:Mn (3 wt%), (c) ZnO:Mn (4 wt%) and (d) ZnO:Mn (5 wt%) (inset is the magnified image of ZnO:Mn (5 wt%))

Figure 5.2: TEM image of hydrothermally grown (a) ZnO, (b) HRTEM and SAED (inset) of ZnO, (c) ZnO:Mn (5 wt%), (d) HRTEM and SAED (inset) of ZnO:Mn (5 wt%)
The XRD pattern shows that ZnO:Mn nanorods are preferentially oriented along (1 0 1) plane and having good crystallinity (Figure 5.5). All the X-ray diffraction peaks of ZnO:Mn (Mn - 0, 3, 4 and 5 wt%) nanorods can be indexed according to the hexagonal wurtzite structure of ZnO (JCPDS: 36-1451). Further, we carried out Rietveld refinement analysis on XRD data of hydrothermally grown ZnO:Mn in order to extract the lattice parameters (figure 5.6). The lattice parameters of the as synthesized ZnO:Mn samples enhanced on increasing the doping percentage of Mn$^{2+}$ ions (Figure 5.7). Further, the observed increase of the lattice parameters of Mn-doped ZnO indicates the Mn incorporation into the ZnO lattice/replacement of Mn$^{2+}$ ions in the sites of Zn$^{2+}$ ions. The lattice parameters ‘a’ and ‘c’ of the as synthesized samples were found to be slightly increased with respect to the doping percentage of Mn$^{2+}$ ions (Table 5.2). The slight variation in calculated lattice constants can be understood if we consider the larger radius of Mn$^{2+}$ ions (0.66 Å) with respect to that of the Zn$^{2+}$ ions (0.60 Å) [288]. This incorporation of Mn into the ZnO lattice alters the lattice parameters, and induces lattice strain that generates a stress on the host lattice. Nevertheless, the wurtzite structure remains unchanged by the substitution of Mn$^{2+}$ ions instead of Zn$^{2+}$ ions into the ZnO crystal system.

The replacement of Zn$^{2+}$ with less ionic radius (0.60 Å) by Mn$^{2+}$ ions of larger ionic radius (0.66 Å) is likely to generate a lattice stress on the ZnO host lattice that in turn modify the lattice parameters which is consistent with present observation [288]. The wurtzite structure is retained by the ZnO:Mn samples, even though Zn$^{2+}$ ions are substituted by Mn$^{2+}$ ions as observed in XRD (Figure 5.5) [265]. It is interesting to note that on increasing the Mn concentration, all the diffraction peaks were shifted towards lower 2θ values and intensity of the XRD peaks also decreases. The shifting of the peak position to lower 2θ values with increase in Mn doping concentration shows the expansion
of the lattice parameters of ZnO:Mn [289]. The decrease in intensity of X-ray diffraction peaks of ZnO:Mn on increasing Mn concentration is probably associated to the lattice disorder and strain induced in the crystalline lattice due to the substitution of Zn$^{2+}$ by Mn$^{2+}$ having comparatively higher ionic radius [288].

**Figure 5.3:** EDX spectra of hydrothermally grown (a) ZnO:Mn (3 wt%), (b) ZnO:Mn (4 wt%), and (c) ZnO:Mn (5 wt%) nanorods
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Figure 5.4: XPS spectra of hydrothermally grown ZnO:Mn (3 wt%) and ZnO:Mn (5 wt%) nanorods

Table 5.1: EDX data of hydrothermally grown ZnO:Mn (3, 4, 5 wt%) nanostructures

<table>
<thead>
<tr>
<th>Elements</th>
<th>ZnO:Mn (3 wt%)</th>
<th>ZnO:Mn (4 wt%)</th>
<th>ZnO:Mn (5 wt%)</th>
</tr>
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<tr>
<td>Zn</td>
<td>72.33</td>
<td>67.03</td>
<td>67.58</td>
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<tr>
<td>O</td>
<td>21.20</td>
<td>23.15</td>
<td>21.07</td>
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<tr>
<td>Mn</td>
<td>2.12</td>
<td>3.13</td>
<td>3.46</td>
</tr>
<tr>
<td>wt%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>at%</td>
<td>39.31</td>
<td>34.55</td>
<td>35.00</td>
</tr>
<tr>
<td></td>
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<td>1.37</td>
<td>1.92</td>
<td>2.13</td>
</tr>
</tbody>
</table>

The absence of vibrational bands above 1000 cm\(^{-1}\) in hydrothermally grown ZnO nanorods in the FTIR spectra suggest that there is no organic impurities are present in the sample (Figure 5.8). A weak FTIR band at 1430 cm\(^{-1}\) in ZnO:Mn indicate the presence of organic impurity like acetate (COO\(^-\))
probably contributed to acetate salts used for the synthesis of present materials [290]. The FTIR band at 545 cm$^{-1}$ is assigned to the stretching mode of ZnO [291] which is present in all the samples indicates that the incorporation of Mn is not affected the crystalline structure of ZnO:Mn nanorods consistent with X-ray observation. This band is shifted to lower frequency side while increasing the Mn concentration and appeared at 541, 538 and 534 cm$^{-1}$ in 3, 4 and 5 wt% Mn doped ZnO. This shift in the band position of the ZnO absorption bands by Mn incorporation shows that the Zn-O-Zn network is perturbed by the presence of Mn [142].

Figure 5.5: X-ray diffraction pattern of hydrothermally grown ZnO, ZnO:Mn (3 wt%), ZnO:Mn (4 wt%) and ZnO:Mn (5 wt%)
Figure 5.6: Rietveld refined XRD pattern of hydrothermally grown (a) ZnO:Mn (5 wt%), (b) ZnO:Mn (4 wt%), and (c) ZnO:Mn (3 wt%) nanorods.
Table 5.2: Lattice parameters of hydrothermally grown ZnO and ZnO:Mn with the doping concentration of Mn.

<table>
<thead>
<tr>
<th>Lattice constants</th>
<th>standard JCPDS values [36-1451] in Å</th>
<th>Unit cell parameters obtained with Rietveld refinement analysis (Å)</th>
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</thead>
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<tr>
<td></td>
<td>ZnO</td>
<td>ZnO:Mn (3 wt%)</td>
</tr>
<tr>
<td>a</td>
<td>3.2498</td>
<td>3.2455</td>
</tr>
<tr>
<td>c</td>
<td>5.2066</td>
<td>5.1982</td>
</tr>
</tbody>
</table>

Raman spectra recorded from ZnO:Mn (Mn 0, 3, 4 and 5 wt%) nanorods are shown in figure 5.9. The intense Raman band observed at 437 cm\(^{-1}\) corresponds to \(E_2\) (high) mode [244, 292]. The weak bands are also seen in the Raman spectra of hydrothermally grown ZnO nanorods at 330, 382, 541, 583 cm\(^{-1}\) which are assigned in detail (Table 5.3) [244, 218]. The Raman bands at 583 and 660 cm\(^{-1}\) are associated with structural disorders, such as oxygen vacancy, Zn interstitial, impurity atoms like Mn and their combination [244, 293, 220, 294]. The broad, intense peak at 1150 cm\(^{-1}\) contains contributions of \(2A_1\) (LO) and \(2E_1\) (LO) modes at the point of the Brillouin zone [218].

The slight shift of Raman bands at 437 cm\(^{-1}\) toward lower frequencies with Mn incorporation shows that the Mn\(^{2+}\) is substituted at Zn\(^{2+}\) sites in the ZnO lattice. Raman band at 330 cm\(^{-1}\) of ZnO:Mn shifted toward lower frequency region of the order of 3, 4 and 7 cm\(^{-1}\) on increasing Mn concentration to 3, 4, and 5 wt% respectively. The defect related Raman band at 583 are shifted toward lower wave number side with increasing Mn concentration (Table 5.3). Previous studies showed that Mn incorporation leads to the shifting of Raman...
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Figure 5.7: Variation of lattice parameters ‘a’ and ‘c’ of ZnO:Mn nanorods with nominal Mn doping concentration)

bands toward lower frequencies [295]. In the present study, Raman band at 660 cm\(^{-1}\) become stronger with respect to Mn doping concentration which is similar to that observed by Wang et al. [296]. The shift of Raman band at 660 cm\(^{-1}\) toward higher frequency side (3 cm\(^{-1}\) in 3 wt%, 5 cm\(^{-1}\) in 4 wt%, 8 cm\(^{-1}\) in 5 wt%) is observed in Mn doped ZnO nanorods. The presence of E\(_2\) (high) mode in the Raman spectra with slight reduction in intensity even with 5 wt% Mn doping indicated that the Mn doped ZnO nanorods retained the wurtzite structure in agreement with XRD data FTIR spectral information discussed previously.

The intensity of Raman band at 437 cm\(^{-1}\) decreased with Mn doping concentration into ZnO that may be attributed to the degradation of crystalline
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Figure 5.8: FTIR spectra of hydrothermally grown ZnO, ZnO:Mn (3 wt%), ZnO:Mn (4 wt%) and ZnO:Mn (5 wt%) nanostructures

quality similar to that of reported in Mn doped hierarchical microspheres [142]. This could arise due the substitution of Mn into the Zn site that introduced defects and lattice distortions, due to larger ionic radius of Mn$^{2+}$ ions. The Raman profile of ZnO:Mn sample shows intensity enhancement with respect to increase in concentration of Mn in the region 585 - 665 cm$^{-1}$ which is in agreement with previous report by Phan et al. [297, 298]. The Raman modes associated with the defect states at 541 and 583 cm$^{-1}$ are very weak in both ZnO:Mn and ZnO samples indicating comparatively low population of defects.

The diffuse reflection spectra (DRS) of hydrothermally grown ZnO and ZnO:Mn nanorods measured at room temperature is shown in figure 5.10. The optical absorption edge of hydrothermally grown ZnO:Mn was red shifted by 10, 9, 8 and 4 nm for 0, 3, 4 and 5 wt% of Mn respectively as compared...
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Figure 5.9: Raman spectra of hydrothermally grown ZnO, ZnO:Mn (3 wt%), ZnO:Mn(4 wt%) and ZnO:Mn (5 wt%)

to the bulk ZnO exciton absorption (372 nm) [225]. The observed red shift in absorption edge/optical energy gap can be due to the oriented attachment of the nanorods [244, 198]. The band gap of ZnO and ZnO:Mn are estimated from $[(k/s)h\nu]^2$ versus $h\nu$ plot in which ‘k’ and ‘s’ denotes the absorption and scattering coefficients respectively and ‘$h\nu$’ is the photon energy [226]. The ratio of $(k/s)$ is calculated from the reflectance via the Kubelka-Munk equation [226] as mentioned in chapter 3. The band gap of ZnO:Mn is slightly increased from 3.23 to 3.28 eV on increasing the Mn concentration from 0 to 5 wt% (Figure 5.11). The Burstein-Moss effect in which the Fermi level merges into the conduction band with increasing carrier concentration resulting in lower energy transitions, will also contribute to increase in band gap [299].
Table 5.3: Raman spectral data (cm\(^{-1}\)) (Note: w, weak; vw, very weak; vs, very strong; s, strong. \(\Delta S\), change in wave number position with respect to ZnO nanoflowers (cm\(^{-1}\))

<table>
<thead>
<tr>
<th>Single crystal ZnO</th>
<th>Raman bands of ZnO and ZnO:Mn</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ZnO (3 wt%)</td>
<td>ZnO:Mn (4 wt%)</td>
</tr>
<tr>
<td>Raman</td>
<td>Raman</td>
<td>(\Delta S)</td>
</tr>
<tr>
<td>99</td>
<td>99 s</td>
<td>98 w</td>
</tr>
<tr>
<td>203</td>
<td>205 v</td>
<td>202 vw</td>
</tr>
<tr>
<td>333</td>
<td>330 w</td>
<td>327 w</td>
</tr>
<tr>
<td>378</td>
<td>382 w</td>
<td>379 w</td>
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<tr>
<td>438</td>
<td>437 vs</td>
<td>436 s</td>
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<tr>
<td>536</td>
<td>541 w</td>
<td>535 vw</td>
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<tr>
<td>590</td>
<td>583 w</td>
<td>580 vw</td>
</tr>
<tr>
<td>657</td>
<td>660 w</td>
<td>663 s</td>
</tr>
<tr>
<td>1158</td>
<td>1150 s</td>
<td>1127 w</td>
</tr>
</tbody>
</table>

Figure 5.12 shows the photoluminescence (PL) spectra recorded from ZnO:Mn (Mn - 0, 3, 4 and 5 wt%) at room temperature. ZnO sample shows UV emission centered at 392 nm, which could pertain to the recombination of free exciton between the conduction and valance bands through an exciton-exciton collision process as described in chapter 3.
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Figure 5.10: Diffuse reflectance spectra of hydrothermally grown ZnO, ZnO:Mn (3 wt%), ZnO:Mn(4 wt%) and ZnO:Mn (5 wt%).

Figure 5.11: $(k/s)hv^2$ versus $hv$ plot of hydrothermally grown ZnO, ZnO:Mn (3 wt%), ZnO:Mn(4 wt%) and ZnO:Mn (5 wt%) (Inset: Variation of band gap with doping concentration of Mn).
One could observe that with increase in concentration of Mn on ZnO:Mn, the PL emission intensity decreases (Figure 5.12). This observation indicates that Mn incorporation into ZnO lattice quenches PL emission of ZnO [300] and is similar to that of reported in Mn doped ZnO nanorods grown by thermal diffusion and ZnO:Mn nanowires by CVD [297, 298]. Quenching of photoluminescence emission in the present samples may be attributed to the loss of photogenerated carries through non-radiative transitions to the defect states that are generated due to Mn incorporation into ZnO crystalline lattice. The reduction in intensity of NBE PL band as well as Raman band at 438 cm$^{-1}$ ($E_2$ (high)) suggest an intrinsic relation between the $E_2$ (high) mode of Raman and NBE emission of PL. In addition, Mn incorporation into the ZnO host lattice resulted in shifting of UV emission towards shorter wavelength region and the ZnO:Mn nanorods grown by thermal diffusion also exhibit similar phenomena [297]. The blue shift of the order of $\sim$57meV is observed in the case of ZnO:Mn (5 wt%) with respect to ZnO.

The HRTEM and SAED results confirms that the hydrothermally grown ZnO and ZnO:Mn (5 wt%) having crystalline nature. The observed quenching of PL emission intensity in ZnO:Mn (5 wt%) is probably due to the increase of non-radiative recombination processes with increasing Mn concentration. It is worthwhile to note that ZnO:Mn even at 5 wt% doping shows only NBE emission and this indicate that the nominal doping of Mn in the ZnO crystal grown by hydrothermal method have less number of defects. This asserts the fact that ZnO:Mn grown using hydrothermal method under optimized growth condition favour the formation of ZnO:Mn nanorods with low density of radiative defects, which is of interest when we consider these nanorods for device application. SEM images of the sample indicate that the diameter of the ZnO nanorods decreases with increase in Mn concentration. This size reduction in ZnO:Mn nanorods may be one of the reasons for the reduction of
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Figure 5.12: PL spectra of hydrothermally grown ZnO, ZnO:Mn (3 wt%), ZnO:Mn(4 wt%) and ZnO:Mn (5 wt%) (Inset: Variation of PL intensity with doping concentration of Mn)

Note that the luminescence of manganese in the ZnO host lattice is not observed in the PL spectrum, which indicates Zn$^{2+}$ ions are substituted by Mn$^{2+}$ ions in the ZnO host lattice [301]. This is further confirmed with the red shift of Raman band at 660 cm$^{-1}$ with respect to increase in Mn concentration. The substitution of Mn$^{2+}$ into the Zn$^{2+}$ site introduces more defects and lattice distortions, because the ionic radius of Mn$^{2+}$ is larger than that of Zn$^{2+}$. The strong UV emission located at 392 nm in the PL spectrum of ZnO nanorods indicate that it have good crystal quality with few oxygen vacancies.
which corresponds to the self-activated luminescence [244]. The improvement in the crystal quality such as low structural defects, oxygen vacancies, zinc interstitials and decrease in the impurities may cause the appearance of sharper and stronger UV emission and a suppressed and weakened green - red emission from the as prepared samples [302]. Previous studies on Mn doped ZnO shows that the defect related emission in the range 400-650 nm. But, the absence of defect related emission in our sample clearly indicates that Mn$^{2+}$ ions are incorporated in Zn$^{2+}$ site in the wurtzite ZnO [303, 304].

M-H characteristics of hydrothermally grown ZnO nanorods at 10 and 300 K are shown in figure 5.13. These samples exhibit diamagnetic nature at both temperatures (10 and 300 K), which is the expected result from the ZnO nanorods. On the other hand, the M-H curve at 300 K is almost a straight line without any hysteresis loop for ZnO:Mn (3 wt%) sample (Figure 5.14). In the ZnO:Mn (3 wt%) sample, the magnetization reaches a maximum value at an applied field strength of about 69.56 kOe, and showing a magnetic moment of 0.067 emu/g, and being not saturated.

The magnetic susceptibility shows a positive value that indicates the paramagnetic behavior of the material. Interestingly, the ZnO:Mn (5 wt%) sample shows an increase in its magnetic moment as compared to ZnO:Mn (3 wt%) samples at 300 K. The M-H curve at 300 K of ZnO:Mn (5 wt%) shows a hysteresis loop with coercivity ($H_c$) of the order of 0.017 kOe, remanence ($M_r$) $\sim$ 1.611 x 10$^{-4}$ emu/g (Figure 5.15). This result indicates that the ZnO:Mn (5 wt%) nanorods exhibit room temperature weak ferromagnetic behavior.
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Figure 5.13: M-H curve of hydrothermally grown ZnO nanorods at 10 and 300 K

Figure 5.14: M-H curve of hydrothermally grown ZnO:Mn (3 wt%) nanorods at 300 K
On the other hand, at low temperature (10 K) (Figure 5.16), hysteresis loops with relatively low coercivity were observed from all the samples under investigation. ZnO:Mn (3 wt%) samples show coercivity ($H_c$) $\sim$ 0.3129 kOe and a remanence value of ($M_r$) $\sim$ 0.0123 emu/g. In the ZnO:Mn (5 wt%) sample, coercivity ($H_c$) $\sim$ 0.4256 kOe and remanence ($M_r$) $\sim$ 0.0205 emu/g, respectively. Even at this temperature, magnetization is not saturated for all the samples. The hysteresis loop has a nonlinear behavior which shows that the crystalline system is a mixture of paramagnetic and ferromagnetic states.
Figure 5.16: M-H curve of hydrothermally grown ZnO:Mn (3 wt%) and ZnO:Mn (5 wt%) nanorods at 10 K.

The temperature dependence of magnetization, under field cooling (FC) with an applied magnetic field of 50 Oe and zero field cooling (ZFC) of ZnO:Mn (3 wt%) nanorods is shown in figure 5.17. The FC and ZFC curves overlap above 47 K and separate from each other below this temperature. Under FC conditions, the magnetization increases slowly with decreasing temperature from 300 to 95 K, and then followed by a rapid increase up to 10 K. ZFC is also gradually increased with respect to the decrease of the sample temperature.

The FC and ZFC curves overlap in the measuring range of temperatures from 15 to 300 K. The magnitude of the ZFC and FC condition continues to increase without saturation while lowering the temperature, which indicates the presence of diamagnetic ordering in the sample. The magnetization increases slowly with decreasing temperature from 300 to 100 K, followed by a
Figure 5.17: M-T plot (FC and ZFC) of hydrothermally grown ZnO:Mn (3 wt%) nanorods at an applied field of 50 Oe. The inset shows the enlarged portion in the low temperature region steep increase up to 10 K in the plot of ZnO:Mn (5 wt%) sample (Figure 5.18). The figure shows the bifurcation of FC and ZFC at 34 K.

There are different possibilities for the occurrence of ferromagnetism in transition-metal-doped ZnO. Dietl et al. [121] theoretically explained that the room-temperature ferromagnetism in transition-metal-doped ZnO is on the basis of hole doping contributed to the substitution of transition metal in Zn$^{2+}$ sites. The above theoretical explanation is not vivid, because the substitution of the equal valence ions (Mn$^{2+}$ instead of Zn$^{2+}$) will not create holes. Another model suggests the formation of nanosized Mn$_3$O$_4$ with a Curie temperature of 44 K could be a reason for the origin of ferromagnetism in ZnO:Mn [277].

As described previously, there is no MnO, Mn$_3$O$_4$, etc. detected in the
ZnO:Mn nanorods synthesized by the hydrothermal process. The observed increase in lattice constants suggest that the substitution of Mn$^{2+}$ ions instead of Zn$^{2+}$ sites rather than the formation of oxide phase of Mn. There will be the possibility to have different types of defects in hydrothermally grown ZnO:Mn nanorods. The native crystal defects like vacancies of O$_2$ and Zn interstitials on the ZnO host lattice may also generate ferromagnetism in the ZnO nanorods. However, our studies on photoluminescence spectra of ZnO nanorods even with Mn doping reveal the absence of defect level emission. So there is no possibility for defect-level-activated ferromagnetism to occur in hydrothermally grown ZnO:Mn nanorods (Figure 5.15). ZnO and transition-metal-doped ZnO samples exhibit ferromagnetic behavior only when the specific area of grain boundaries exceeds a certain threshold value [305]. Straumal et al. [305] re-
ported that a threshold value of specific area of grain boundaries in ZnO is $5.3 \times 10^7$ and that for ZnO:Mn is $2.4 \times 10^5$ m$^2$/m$^3$. In the case of the present sample, these values are found to be $6.7 \times 10^6$, $1.7 \times 10^6$, and $10 \times 10^6$ m$^2$/m$^3$ in ZnO and ZnO:Mn 3 and 5 wt%, respectively. The Mn dopant promotes formation of grain boundaries and the ferromagnetic transition [306]. Further, the solubility of Mn increases with the size of grains and ferromagnetic properties of doped structures are nonmonotonic [305]. The observance of room-temperature ferromagnetism in ZnO:Mn (5 wt%) is attributed to the presence of the increased specific area of grain boundaries and higher solubility of Mn ions in its grains as evidenced by the reduction in diameter of ZnO:Mn (5 wt%) (Figure 5.1). From these results, it is inferred that the paramagnetic behavior observed from ZnO:Mn (3 wt%) at 300 K probably due to the reduction of the specific area of grain boundaries as compared to that of ZnO:Mn (5 wt%). Also, an increase in band gap is observed with the increase in content of Mn into ZnO, the origin of ferromagnetism is also due to Mn doping in the ZnO lattice, which is closely related to the change in band gap energy of nanorods by the substitution of Mn$^{2+}$ in Zn$^{2+}$ sites [307].

A nonzero difference between the FC and ZFC curves of ZnO:Mn (3 wt%) and ZnO:Mn (5 wt%) indicates the short-range ferromagnetic ordering while decreasing the temperature of the sample, as usually observed in spin glass systems [308]. This ferromagnetic ordering is further confirmed by the presence of the hysteresis loop at 10 K. The FC and ZFC curves bifurcate each other from a temperature below $T_c$, indicating the influence of the aging on the spin-glass state, as was previously reported in La$_{0.95}$Sr$_{0.05}$CoO$_3$ and Ag(Mn) spin-glass systems [309, 310].

In the FC - ZFC curve of the ZnO:Mn (5 wt%) sample, the magnetization increases with the decrease in temperature in the range of 300 - 100 K and a rapid increase occurs below 100 K. This behavior is similar to the paramagnetic
one. However, this sample shows remanent magnetization and coercivity at room temperature as well. The rapid increase of magnetization at low temperature in ZnO:Mn (5 wt%) can be related to the ferromagnetic properties. Our ZnO sample (Figure 5.13) exhibits only diamagnetic behavior at room temperature as well as at 10 K. So, the magnetic properties detected in ZnO:Mn nanorods are due to the interaction between the manganese ions in the ZnO host lattice. The detected magnetism point to a superexchange interaction between Mn$^{2+}$ ions and Zn$^{2+}$ ions as well as an increase in specific area of the grain boundaries [311, 305].

One can clearly observe that the ZFC magnetization of both samples does not saturate in the entire measurement range. This is due to the glassy state; the magnetic moments are randomly frozen such that it will take a longer time for the field to turn those spins along the field direction [312]. In addition, the FC magnetization is not saturating at low temperature, which indicates the short-range spin ordering in the material [313]. In order to understand the spin-glass ordering, the magnetization irreversibility ($M_{irr}$) vs. T, the temperature is plotted. The irreversible magnetization, $M_{irr} = M_{FC} - M_{ZFC}$ as a function of temperature for ZnO:Mn (3 wt%) and ZnO:Mn (5 wt%) nanorods is shown in figure 5.19.

From the graph, one can see that $M_{irr}$ become non-zero at a temperature of 150 K ($T_g$-1) for Mn (3 wt%) doped ZnO and that of Mn (5 wt%) doped ZnO is at 140 K ($T_g$-2). This temperature is termed as the spin-glass transition temperature ($T_g$). The spin-glass transition temperature $T_g$-1 and $T_g$-2 corresponds to Mn 3 and 5 wt% doped ZnO, respectively. The $M_{irr}$ is found to rapidly increase and shows a linear behavior from a temperature of about 88 K ($T_{cro}$-1) in Mn (3 wt%) doped ZnO and 82 K ($T_{cro}$-2) in Mn (5 wt%) doped ZnO. This temperature is termed as the crossover temperature, as reported by Svedberg et al. [314]. The temperature dependence of $M_{irr}$ in Mn
3 and 5 wt% doped ZnO is an indication of spin-glass ordering attributed to the competing interaction of frozen disorders and magnetic frustrations [315]. However, there are two regimes that can be observed in the graph representing the temperature-dependent irreversibility of magnetization for the spin-glass ordering of the present sample (Figure 5.19). The first one is between the $T_g$ and $T_{cro}$ of each sample for which the rate of variation remains small. But below $T_{cro}$, a rapid, roughly linear increase is determined in both the samples. The linear upward curve seen in the low temperature region suggests that the spin-glass transition observed in the present sample is similar to that of the Ising model predicted by De Almeida-Thouless [316, 317].


5.4 Conclusions

We successfully demonstrated the capability of hydrothermal method to grow ZnO:Mn (Mn - 3, 4 and 5 wt%) nanorods having reduced optical radiative defects. Hydrothermally grown ZnO retains the rod-like morphology with low percentage of Mn doping. The presence of E\textsubscript{2} (high) mode at 437 cm\textsuperscript{-1} in the Raman spectra with slight reduction in intensity in Mn doped ZnO nanorods reveals that wurtzite structure is retained in ZnO:Mn. The intensity enhancement of Raman bands at 660 cm\textsuperscript{-1} in ZnO:Mn confirms the increase in structural defects with respect to the Mn concentration in ZnO:Mn as compared to ZnO nanoflower. The Raman and PL analysis confirms the good crystalline quality of ZnO which slightly reduces as the Mn concentration increases in ZnO:Mn systems. The quenching of PL emission intensity in the UV region around 392 nm as a result of nominal doping of Mn (Mn - 3 - 5 wt%) in ZnO is attributed to the increase of non-radiative recombination process, reduced size of ZnO:Mn nanorods as well as comparatively lower quality of crystallites caused by Mn\textsuperscript{2+} incorporation into ZnO lattice. The absence of radiative defect bands around 450 - 550 nm range in PL spectra of hydrothermally grown ZnO:Mn (Mn - 3 - 5 wt%) indicates that there exist less number of defects. The blue shift of PL emission from ZnO:Mn is attributed to the band gap broadening due to the nominal incorporation of Mn. Hydrothermally grown ZnO nanorods exhibit a diamagnetic nature at 10 and 300 K. At room temperature (300 K), weak ferromagnetism is observed in ZnO:Mn (5 wt%) nanorods, while ZnO:Mn (3 wt%) nanorods show paramagnetism. The ZnO:Mn (3 wt%) and ZnO:Mn (5 wt%) nanorods exhibit spin-glass behavior below 150 and 140 K, respectively. The variation of magnetic behavior with respect to the level of Mn doping can be attributed to the population of Mn\textsuperscript{2+} ions in the ZnO crystalline lattice. The exchange interaction between doped Mn\textsuperscript{2+} ions, the substitution of Mn\textsuperscript{2+} ions into Zn\textsuperscript{2+} sites and the increase in
specific area of the grain boundaries are the contributing factors in the origin of magnetic behaviour.