CHAPTER 5

Synthesis, Characterization and Magnetic properties of ZnO:Co and ZnO:Mn Nanoparticles
5.1. Introduction

Semiconductor spintronics is one of the most perspective directions for the modern technology development. The crucial point to ensure creation of semiconductor spintronics devices is the development of appropriate materials, having a ferromagnetic ordering at room temperature and high values of magnetization. Diluted magnetic semiconductors (DMSs) are the potential candidates to be used in semiconductor spintronics. Since Dietl et al. [1] proposed the idea of ferromagnetism introduced in the semiconductors by the presence of magnetic cations like Mn doped in semiconductor matrix, there has been a number of reports of these doped semiconductors [1-8]. Diluted magnetic semiconductors (DMSs) formed by substituting the cations of III–V or II–VI nonmagnetic semiconductors by ferromagnetic Mn, Fe, Co and Ni exhibit a number of unique, magneto-optical and magneto-transport properties, pertinent for magneto-electronic and spintronic devices [2,6]. Room temperature [RT] ferromagnetism (FM) in transition metal (TM) doped ZnO has been continually envisaged by numerous groups using variety of theoretical and experimental studies [1, 3]. ZnO-based diluted magnetic semiconductors have been predicted to have ferromagnetic properties with Curie temperature (T_C) above room temperature [1, 4, and 5]. Rath et al. [6] also studied the magnetic property of ZnO:Co nanoparticles and reported that the material exhibits paramagnetic behaviour. Rao et al. [7] investigated the structural, optical and electrical properties of ZnO thin films prepared by spray pyrolysis technique. ZnO, which is a direct band gap semiconductor with a band gap of 3.37 eV having an excitonic binding energy of 60 meV [7], because of its potential applications, makes one of the most encouraging materials for probable applications in spintronics and as diluted magnetic semiconductor (DMSs) material. Although much experimental research has been focussed in this area, the origin of ferromagnetism in DMS materials is still under debate [9].

There have been reports of exceedingly high magnetic moments per impurity atoms in diluted magnetic semiconductors. A “Giant magnetic moment” of 22.9 Bohr magneton (\(\mu_B\)) per impurity atom has been reported for TiO\(_2\) doped with Co [10]. A high value of magnetic moment equal to 18.9 \(\mu_B\) per impurity atom was reported for Co doped ZnO films [11]. The magnetic moment values of 2.6-3.87 \(\mu_B\) [6, 10], 7.5 \(\mu_B\) [12] and 8.2 \(\mu_B\) [13] were found correspondingly, for semiconducting materials ZnO, SnO\(_2\) and CeO\(_2\) doped with Co.
Chapter 5: Synthesis, characterization and magnetic properties of ZnO:Co and ZnO:Mn nanoparticles

In the present work, a simple technique is used to synthesize ZnO nanoparticles undoped as well as doped with transition metal ions. Transition metal, Cobalt (Co) and Manganese (Mn) ions, are used as dopant in this work and doping of these ions are done at different concentrations to obtain ZnO:Co and ZnO:Mn nanoparticles. The structural, magnetic and optical properties of ZnO:Co and ZnO:Mn nanoparticles are then investigated. Many possible mechanisms such as Ruderman-Kittle-Kasuya-Yosida (RKKY) [14, 15], double-exchange mechanism [16, 17], and percolation of bound magnetic polarons (BMPs) have been reviewed [18]. The PL spectra show the presence of defects. These defects, magnetic cations and carriers made up BMPs. Thus ferromagnetism can be understood within the framework of percolation of bound magnetic polarons.

5.2 Experimental

5.2.1. Synthesis of ZnO:Co Nanoparticles

2 gms of Zinc chloride (Sigma-Aldrich 99.99% purity) and appropriate amount of Cobalt acetate (Sigma-Aldrich 99.999% purity) to make the desire doping percentage is dissolved in 50 ml distilled water. 150 ml of Ethylene glycol is added to the above solution. 6 gm of Urea is then added to the above solution. The solution is heated in a round bottom flask fitted with condenser and the temperature is maintained at 140°C for 2 hours. The precipitates formed are collected by centrifugation after washing with Methanol and finally with distilled water. The precipitates are dried at around 80°C to 100°C for 24 hours. In our experiment six samples has been prepared at different doping percentages of Cobalt. The Cobalt atomic percentages taken were 0% (undoped), 0.5%, 1%, 4%, 9% and 15%. The dried precipitates of all the samples of Zn$_{1-x}$Co$_x$O nanoparticles (x = 0, 0.005, 0.01, 0.04, 0.09 and 0.15 to make the corresponding atomic percentages of Co doping) so prepared are finally annealed at 500°C for 2 hours.

5.2.2. Synthesis of ZnO:Mn Nanoparticles

ZnO nanoparticles has been synthesized at low temperature by chemical precipitation method using zinc acetate in Isopropanol and distilled water medium with Diethanolamine (DEA) as capping agent at 60°C. The pH value of the solution containing the reactants are adjusted between 9 and 10 by adding ammonia solution and reaction is carried out for 2 hours. The precipitates formed in the reaction are collected by centrifugation and wash with excess methanol and dry at 100°C. The nanoparticles
thus collected are finally annealed at 350°C for 2 hours. Similar procedures are then employed to synthesized Mn doped ZnO nanoparticles and thus undoped and Mn doped ZnO nanoparticles, at different Mn doping concentrations namely 0.5, 1, 3 and 7 at. %), are synthesized.

5.3. Characterization

The samples are characterized for crystal phase identification by powder X-ray diffraction (XRD) using Bruker-Nonius FR-590, MACH-3, Single Crystal X-Ray Diffractometer. The XRD lines are identified with the Joint Committee for Powder Diffraction Standards (JCPDS) standard data files. Compositions of the synthesized nanoparticles are analyzed by energy-dispersive X-ray (EDS) spectrometer attached to scanning electron microscope (SEM). The morphology and particle size of the samples are examined with transmission electron microscope (TEM) by using JEOL JEM-2100. For TEM measurements, a few droplets of powder, ultrasonically dispersed in alcohol, are put on standard carbon coated copper grids. Magnetic properties measurements has been carried out using Vibrating Sample Magnetometer (VSM), Lakeshore Model no. 7407, for M-H curves at temperatures 80K, 150K and 300 K and up to 1.5 Tesla field. Photoluminescence measurements are taken on a LS 55 PerkinElmer fluorescence spectrophotometer with a Xenon lamp as excitation source at room temperature.

5.4. Results and Discussions of ZnO:Co Nanoparticles

5.4.1. Powder XRD analysis of ZnO:Co Nanoparticles

Figure 5.1 shows the XRD spectra of the Zn$_{1-x}$Co$_x$O nanoparticles synthesize in the present work. XRD spectra show peaks at positions which are in agreement with the standard JCPDS file for ZnO (JCPDS 36 – 1451, $a = b = 3.249\text{Å}$, $c = 5.206\text{Å}$) and can be indexed as the hexagonal wurtzite structure of ZnO having space group $P6_3mc$ [19]. With increasing concentration of cobalt dopants in the samples, the spectra remain the same with decrease in XRD intensity, indicating that Co ions substituting the Zn sites in the wurtzite structure. Only for the sample with $x = 0.15$, there are some small peaks corresponding to Co$_3$O$_4$ [20]. The crystallite size, $D$, of Zn$_{1-x}$Co$_x$O nanoparticles were estimated by Scherrer’s equation [19, 21]. The crystallite sizes were estimated from the first three most prominent X-ray diffractions; corresponding
to (101), (002) and (100) peaks and then mean values was calculated from those three values.

Figure 5.1: XRD spectra of Zn$_{1-x}$Co$_x$O nanoparticles at different x values.

The sizes of the nanoparticles were found to be in 34 - 45 nm range for different samples. The almost same crystallite size, stable wurtzite structure and absence of impurity phases with increasing concentration of Co$^{2+}$ doping for all samples could be attributed to the similarity of size of Zn$^{2+}$ and Co$^{2+}$ ions [19].

5.4.2. EDS studies of ZnO:Co Nanoparticles

EDS measurements have been performed, in order to confirm the presence of Co$^{2+}$ in the synthesized Zn$_{1-x}$Co$_x$O nanoparticles and to determine their compositions. EDS analysis demonstrates the precise composition of the elements in the prepared doped samples. The EDS spectra in figure 5.2 (a), (b), (c), (d), (e) and (f) show peaks corresponding to elements Zn, O and Co for samples with x values corresponding to 0, 0.5, 1, 4, 9 and 15 atomic percentage of Co$^{2+}$ doping concentrations respectively.
5.4.3. TEM studies of ZnO:Co Nanoparticles

Figure 5.3 (a) shows the representative TEM image of the x = 0.09 sample. The histogram is being given in figure 5.3 (b). The mean particle size is found to be 45 nm in agreement with that obtained from XRD.
5.4.4. Magnetic Properties of ZnO:Co Nanoparticles

The magnetic properties of a material are a consequence of the interactions between an external magnetic field and magnetic dipole moments of the constituent atoms. The total magnetization of the material is just the appropriately weighted vector sum of the magnetizations of all its constituents. As an external magnetic field is applied, domains having magnetization vectors oriented in the direction of the field grow at the expense of domains that have unfavourable magnetizations orientations. Thus magnetization/magnetic moment (M) versus the applied field (H) behaviour can be utilised to study the magnetic property of the materials.

![M-H plots for Zn$_{1-x}$Co$_x$O at 80 K, 150 K and 300 K for (a) x = 0.005, (b) x = 0.01, (c) x = 0.04, (d) x = 0.09 and (e) x = 0.15](image)

Figure 5.4: M-H plots for Zn$_{1-x}$Co$_x$O at 80 K, 150 K and 300 K for (a) x = 0.005, (b) x = 0.01, (c) x = 0.04, (d) x = 0.09 and (e) x = 0.15
The magnetic properties of the Zn$_{1-x}$Co$_x$O ($x = 0.005, 0.01, 0.04, 0.09, 0.15$) at three temperature values of 80 K, 150 K and 300 K are shown in the figure 5.4 by the M-H measurements using VSM. In all the samples the magnetization does not approach saturation even at 1.5 Tesla. The M-H curves are linear in case of $x = 0.005$ and 0.01 samples, figure 5.4 (a) and (b), showing paramagnetic behaviours. Samples corresponding to $x = 0.04, 0.09$ and 0.15, figures 5.4 (c), (d) and (e), show clear hysteresis loops showing these samples are ferromagnetic.

Figure 5.5: Hysteresis loop at low field range at 80 K for (a) $x = 0.04$, (b) $x = 0.09$ and $x = 0.15$
Figure 5.5 shows the hysteresis loops of sample corresponding to $x = 0.04$, $x = 0.09$ and $x = 0.15$ sample at 80 K at low field range and the corresponding values of Coercivity field ($H_C$) and Remanence magnetization ($R_m$) are given in the table 5.1 (a). At 80 K the $x = 0.4$ sample has value of $R_m$ equal to 0.32 $\mu_B$/cations and the $x = 0.15$ sample has this value equal to 0.04 $\mu_B$/cations. This decrease in $R_m$ shows decreasing tendency of ferromagnetism as the $Co^{2+}$ doping concentration increases from $x = 0.04$.

Table 5.1(a): Remanence magnetization ($R_m$) and Coercivity field ($H_C$) for $x = 0.04$, 0.09 and 0.15 samples of $Zn_{1-x}Co_xO$.

<table>
<thead>
<tr>
<th>Temp.</th>
<th>$x = 0.04$</th>
<th>$x = 0.09$</th>
<th>$x = 0.15$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R_m$ ($\mu_B$/cations)</td>
<td>$H_C$ (Tesla)</td>
<td>$R_m$ ($\mu_B$/cations)</td>
</tr>
<tr>
<td>80 K</td>
<td>0.32</td>
<td>0.007</td>
<td>0.09</td>
</tr>
<tr>
<td>150 K</td>
<td>0.26</td>
<td>0.006</td>
<td>0.08</td>
</tr>
<tr>
<td>300 K</td>
<td>0.20</td>
<td>0.006</td>
<td>0.06</td>
</tr>
</tbody>
</table>

Table 5.1 (b): Magnetization moment of $Zn_{1-x}Co_xO$ in ($\mu_B$/cations) at 1.5 Tesla for different $x$ values and at three temperature (Temp.) values.

<table>
<thead>
<tr>
<th>Temp.</th>
<th>$x = 0.005$</th>
<th>$x = 0.01$</th>
<th>$x = 0.04$</th>
<th>$x = 0.09$</th>
<th>$x = 0.15$</th>
</tr>
</thead>
<tbody>
<tr>
<td>80 K</td>
<td>0.31</td>
<td>0.58</td>
<td>8.54</td>
<td>3.25</td>
<td>1.43</td>
</tr>
<tr>
<td>150 K</td>
<td>0.16</td>
<td>0.09</td>
<td>7.94</td>
<td>2.72</td>
<td>1.23</td>
</tr>
<tr>
<td>300 K</td>
<td>0.02</td>
<td>0.03</td>
<td>7.09</td>
<td>2.14</td>
<td>1.06</td>
</tr>
</tbody>
</table>

Table 5.1 (b) shows the value of Magnetization moment in $\mu_B$/cations units. The values of magnetization moment increases from $x = 0.005$ sample to $x = 0.04$ sample then shows decreasing trend for higher values of $x$. The $x=0.04$ sample shows highest value of magnetization moment per cation, a value equal to 8.54 $\mu_B$/cations. Thus the VSM measurements show an evolution from paramagnetic to ferromagnetism and then to antiferromagnetism depending on the $Co^{2+}$ doping concentrations.
To explain this phenomenon, we have to understand the origin of this magnetism. There are several mechanisms for the origin of ferromagnetism in DMSs. The RKKY interaction is based on free electrons, but ZnO cannot transform into a metal at low doping. Direct interactions such as double-exchange cannot be responsible for the ferromagnetism at low doping of magnetic cations [9]. One origin which is due to the small secondary phases of Co can also be ruled out except in case of $x = 0.15$ sample as the XRD of other samples show no secondary phases. Scharwatz and Gamelin [22] reported that the room-temperature ferromagnetic ordering in Co$^{2+}$ doped ZnO could be switched between ‘on’ and ‘off’ when introducing or removing defects of ZnO. The increasing dependence of ferromagnetic ordering on Co$^{2+}$ content was observed [23].

According to literature [9, 18], magnetic cations, carriers and defects can make up bound magnetic polarons (BMPs). For semiconductors with low carrier densities such as oxides, the magnetic polaron mechanism is applicable [24, 25]. In this model, the spins of magnetic dopants incorporated into the semiconductor lattice interact through a donor-impurity band, formed by lattice defects such as oxygen vacancies ($V_o$) [21]. Coey et al. [18] explain the spin-alignment of the 3d transition-metal cations by coupling of their spins, which are antiparallel to the spin of donor electrons residing in hydrogenic orbits. Due to this coupling, all spins within this expanded orbit are aligned. Because of the overlap of different orbits, an impurity band is formed, aligning a huge number of 3d magnetic spins parallel, resulting in ferromagnetism. In the framework of this theory, not only the dopant concentration but also the number of donor electrons must be quite large in order to obtain ferromagnetism. Nanoparticles possess a lot of such defect sites because of their comparatively large surface, which, naturally, has many defects in the form of unsaturated bonds [24]. Rubi et al. demonstrate that magnetism of Co-doped ZnO powders can be switched reversibly from ferro- to paramagnetic behaviour by annealing in either oxygen-poor or oxygen-rich atmosphere, resulting in the generation or cancellation of $V_o$, respectively [26].

Contrary to small particles, bulk single crystals of ZnO:Co, grown at near-equilibrium, exhibits a very low defect concentration and show no ferromagnetism but behave paramagnetically [27]. These observations strengthen the concept of an impurity-band exchange by magnetic polarons evoked by $V_o$ in the ZnO:Co nanoparticles. The magnetic phase diagram evolves from para at lower polaron concent-
tration to ferromagnetic ordering at concentration below percolation threshold and then to antiferromagnetic ordering beyond the percolation threshold [18]. In low doping samples, the BMPs are isolated so that paramagnetic interaction is observed. More doping produces more BMPs, leading to the overlap of BMPs at which point the ferromagnetic interaction becomes long-range [9]. There is distinct dependency on the maximum attainable magnetization of Zn$_{1-x}$Co$_x$O samples on the Co$^{2+}$ doping percentage [24]. From these theoretical and experimental results, it becomes evident that not only the dopant concentration but also the amount of defect sites has to be substantial enough to get a ferromagnetic coupling of the magnetic spins.

In present work magnetism evolves from paramagnetic at x = 0.005 and x = 0.01 to ferromagnetic at x = 0.04 as the BMPs are about to percolate and then to antiferromagnetic interaction as the doping concentration goes up beyond x = 0.04. Above x = 0.04 the magnetic moment decreases with dopant concentration. Theoretical calculations [28] by Risbud et al. suggested that this system is characterized by antiferromagnetic coupling between nearest neighbour ions [29]. This behaviour can be explained by the fact that for high concentrations it is more probable for dopant atoms to occupy next-nearest lattice sites. Such Co$^{2+}$ pairs couple by super-exchange over the intermediate oxygen atom in an antiferromagnetic way. Antiferromagnetic coupling of Co$^{2+}$ is responsible for decreasing the net moment [29]. The enhanced antiferromagnetic interaction between neighbouring Co$^{2+}$- Co$^{2+}$ ions suppressed the ferromagnetism at higher doping concentration of Co$^{2+}$ [30].

### 5.4.5. Photoluminescence studies of ZnO:Co Nanoparticles

The room temperature photoluminescence spectra of Zn$_{1-x}$Co$_x$O nanoparticle samples are shown in figure 5.6. The spectra were recorded with excitation at 325 nm radiation for detecting PL peaks in the range 350 - 600 nm. The sample with x = 0.005 exhibits three peaks centred around 390 nm, 420 nm and 438 nm and two other weaker peaks at 480 nm and 508 nm. The fluorescence at 390nm corresponds to the characteristic band edge emission [8]. The peak at 420nm corresponds to the transitions from Co$^{2+}$ ions substituting Zn$^{2+}$ ions [31]. The violet luminescence at 438nm has been assigned to transitions from Zn$_i$ level to valence band [8]. The weak emissions at 480 nm and 508 nm correspond to Zn-vacancy ($V_{Zn}$) and O-vacancy ($V_O$) respectively [32]. Emissions in the range 381- 389 nm are originated from excitonic recombination corresponding to near band edge (NBE) exciton emission of wide band
gap ZnO [33]. As the doping concentration increase the intensity of the UV emission peaks decreases successively and this peak position shifts to lower wavelength. The weak defect emissions become prominent at higher Co$^{2+}$ doping if we consider the relative decrease in intensities. More defect states below the conduction band occurred by Co$^{2+}$ doping, so that some of the excited electrons in the conduction band relax to the defect states, leading to decrease in UV emission intensity [31, 34, 35]. So it can be concluded that PL confirms the presence of defects which are the constituents of the bound magnetic polarons BMPs.

![PL spectra for Zn$_{1-x}$Co$_x$O at different x values with excitation wavelength of 325 nm and emission range 350-600 nm.](image)

**Figure 5.6:** PL spectra for Zn$_{1-x}$Co$_x$O at different x values with excitation wavelength of 325 nm and emission range 350-600 nm.

5.5. **Results and Discussion of ZnO:Mn Nanoparticles**

5.5.1. **Powder XRD analysis of ZnO:Mn Nanoparticles**

Figure 5.7 shows the XRD patterns of the prepared undoped ZnO and Mn doped ZnO nanoparticle samples with different dopant concentrations of Mn$^{2+}$. It clearly shows the characteristic diffraction peaks of ZnO (JCPDS file for ZnO (Card no. 36-1451, $a = b = 3.249$ Å and $c = 5.206$ Å) and can be indexed as the hexagonal wurtzite structure [19]. The crystallite sizes of the nanoparticles were found to be 42.4 nm for the undoped ZnO and 31.5 nm, 33.6 nm, 31 nm, and 35 nm for ZnO:Mn$^{2+}$ nanoparticles with Mn$^{2+}$ doping concentrations of 0.5, 1, 3 and 7 at. % respectively.
Figure 5.7: XRD spectra of undoped and Mn doped ZnO at different doping concentrations.

5.5.2. EDS studies of ZnO:Mn Nanoparticles

Figure 5.8: EDS spectra of ZnO:Mn$^{2+}$ for (a) 0.5, (b) 1, (c) 3 and (d) 7 at. % of Mn$^{2+}$ doping concentrations.
EDS measurements has been performed, in order to confirm the presence of Mn$^{2+}$ in the synthesized ZnO:Mn$^{2+}$ nanoparticles and to determine their compositions. The EDS analysis provides precise composition of the elements. The EDS spectra in figure 5.8 (a), (b), (c) and (d) show peaks corresponding to elements Zn, O and Mn for the 0.5, 1, 3 and 7 at. % doped samples respectively.

5.5.3. TEM studies of ZnO:Mn Nanoparticles

The transmission electron microscope (TEM) and high-resolution transmission electron microscope (HRTEM) observations of the samples are carried out. Figure 5.9 (a) gives the TEM image of the 3 atomic % Mn doped ZnO showing well-distributed rod-shaped particles having average diameters in the range from 40 nm to 50 nm and length varying from 90 nm to 120 nm.

![TEM image](image1)

**Figure 5.9:** (a) TEM micrograph of 3 atomic % Mn doped ZnO (b) HRTEM image and (inset) SAED pattern.

This size will be consistent with the estimated values (31 nm) from XRD peak broadening because the TEM image confirms the presence of smaller as well as bigger particles. Very small and finer particles in the size range below 5 nm are found to be sticking to the bigger rod-shaped particles. Figure 5.9 (b) shows the HRTEM image of the sample and lattice spacing of values 0.26 nm and 0.28 nm are obtained corresponding to the (202) and (100) lattice planes respectively. The selected area electron diffraction (SAED) (inset of figure 5.9 (b)), indicates high crystallinity. Diffraction spots corresponding to the (100), (002), (110), (103), (112) and (202)
lattice planes are identified with respective inter-planer lattice spacing of 0.28 nm, 0.26 nm, 0.16 nm, 0.15 nm, 0.14 nm and 0.13 nm corresponding to JCPDS Ref. Card No. 36-1451 for wurtzite ZnO.

5.5.4. Magnetic Properties of ZnO:Mn Nanoparticles

The magnetic properties of the undoped and Mn doped ZnO nanoparticles at temperature 300 K are shown in the figure 5.10. The M-H curve shows diamagnetic behaviour for the undoped ZnO samples as indicated in the inset (a) of figure 5.10. In all the samples the magnetization does not approach saturation even at 1.5 Tesla.

![M-H curve for ZnO nanoparticles](image)

**Figure 5.10:** Moment verses Field (MH) plots of Mn doped ZnO taken at 300K for different doping concentration of Mn. Inset (a) M-H plot for undoped ZnO and (b) Hysteresis loop at low field range for the 0.5 % Mn.

The M-H curves are linear for the doped samples showing paramagnetic behaviours except for the 0.5 at. % Mn\(^{2+}\) doped samples. For 0.5 at. % Mn\(^{2+}\) doped sample a weak ferromagnetic nature is observed as indicated by the hysteresis loop in the low field region as shown in the inset (b) of figure 5.10. The Remanence magnetisation \(R_m = 0.022 \mu_B/\text{cations}\) and coercivity field \(H_C = 0.007 \text{ Tesla}\) are evaluated from
the hysteresis loop of 0.5 at. % sample. This value of $R_m$ is lesser than that of Co doped ZnO. For 1, 3 and 7 at. % Mn doped samples, the linear M versus H curves indicate that the samples appear to show paramagnetism. This reveals that on doping ZnO with Mn, the magnetic hysteresis gets quenched as a function of Mn concentration. Here again the moment at 1.5 Tesla field are 1.33, 0.77, 0.83 and 0.71 $\mu_B$ for the 0.5, 1, 3 and 7 at. % Mn doped ZnO nanoparticles samples respectively.

If comparison is made between these values and with that of the Co doped ZnO system at 300 K, the 0.5 at. % Mn doped sample has a value of moment near to that of the 15 at. % Co doped ZnO which has the lowest value of moment among the ferromagnetically interacting samples, viz, 4, 9 and 15 at. % Co doped. The value of 0.5 atomic % Mn doped sample is higher than the values of moment for the paramagnetically interacting Co doped samples, viz, 0.5 and 1 at. % doped sample whose moment values are 0.2 and 0.3 respectively. The values of moment for 1, 3 and 7 at. % Mn doped ZnO samples, which are interacting paramagnetically, are higher than the paramagnetically interacting Co doped sample and smaller than the ferromagnetically interacting Co doped samples. In this Mn doped system the singly charged oxygen vacancy site electron can couple antiferromagnetically with near neighbour Mn ions. This entity could be like a bound magnetic polaron. These magnetic polarons interact antiferromagnetically among themselves. As indicated by the moment values, the Mn doped system has lower values of moment than the Co doped system. When the antiferromagnetic interaction become dominating, the M versus H curves shows linearity depicting paramagnetism in case of Mn doped system at a lower value of Mn doping concentration in comparison to the doping concentration of Co doped system. In the case of Mn doping ferromagnetism quenches completely at 0.5 at. % of Mn concentration. But in case of Co doping ferromagnetism could be observed even upto 15 at. % of Co concentration. So ferromagnetism is optimum at 0.5 at. % Mn doping concentration for the Mn doped system while it is optimum at 4 at. % Co doping concentration for the Co doped system. The VSM measurements show an evolution from diamagnetic for the undoped ZnO to ferromagnetic for the 0.5 at. % Mn$^{2+}$ doped ZnO sample and then to paramagnetism for higher Mn$^{2+}$ doping concentrations.
5.5.5. Photoluminescence studies of ZnO:Mn Nanoparticles

Photoluminescence excitation and emission spectra of the nanoparticles were recorded at room temperature. Figure 5.11 (a) shows excitation spectra of the undoped ZnO nanoparticle, taken in the excitation range from 200 nm to 400 nm by monitoring emission at 383 nm. This has been reported earlier in chapter 3 for the undoped ZnO and is being reproduced here for further reference. Three peaks are observed at 238 nm, 256 nm, and 280 nm.

Figure 5.11: (a) PL excitation spectra and (b) (Colour online) emission spectra of undoped ZnO with decomposed Gaussian components.

Figure 5.11 (b) shows the emission spectra of the undoped ZnO nanoparticles taken in the emission range from 350 nm to 600 nm when excited by 280 nm wavelength. The PL emission is very well fitted with four Gaussian peaks. It is seen from the figure that the PL spectrum can be decomposed into four Gaussian components whose peaks are located at 381 nm, 407 nm, a broadband centred at 472 nm and another smaller peak at 480 nm. The fluorescence at 381 nm corresponds to the characteristic band edge emission [36]. The violet luminescence (407 nm) has been assigned to electronic transition to energy levels for oxygen interstitial (O$_i$), which are 0.4 eV above the top of valence band [37]. Energy levels for neutral oxygen vacancy V$_O$ is 2.57 eV from the valence band and thus responsible for the emission at 480 nm [19, 39, 37]. The broadband emission centred at 472 nm arises from the recombination of electron-hole pairs trapped at shallow and deep surface states formed by vacancy of oxygen (V$_O$) and other defects [40].
Figure 5.12: PL excitation spectra of Mn$^{2+}$ doped ZnO.

Figure 5.12 shows the excitation spectra of the ZnO:Mn$^{2+}$ samples at different percentages of Mn doping concentrations, taken in the excitation range from 200 nm to 400 nm by monitoring emission at 485 nm. Four peaks are observed at 238 nm, 255 nm, 290 nm and 342 nm. The wavelengths of these peak positions were used as excitation wavelength for further study of emission spectra.

Now Figure 5.13 (a) shows the emission spectra of ZnO:Mn$^{2+}$ nanoparticles, at different percentages of Mn doping concentrations, taken in the wavelength range of 350 nm to 700 nm at 238 nm excitation wavelength. Figures 5.13 (b), (c) and (d) show emission spectra when wavelengths of excitation used are 255 nm, 290 nm and 342 nm respectively. The doped samples show emission peaks centred at (387 nm and 398 nm), 404 nm, 422 nm, 448 nm, 466 nm, 486 nm 532 nm and 575 nm for all the Mn concentrations. The peak intensity for the doped samples is highest for 0.5 at % of Mn$^{2+}$, beyond that it decreases as the concentration of doping increases. This may be due to the concentration quenching of the Mn$^{2+}$ ions. It is also observed that the intensity of emissions at the violet end of the spectrum decreases as the excitation wavelength increases.

The peaks at 404, 422 and 448 nm originate from defect state such as Zn and oxygen interstitials and oxygen vacancies [27, 41, 42]. The blue-green emission at 466 nm probably ascribed to oxygen vacancies and to the presence of dopant Mn [43]. The energy level for the antisite oxygen O$_{Zn}$ defect is 2.38 eV below the conduction band and energy level for singly ionized oxygen vacancy V$_{O}^{+}$ is 2.36 eV from the valence
band [43]. These two energy levels are responsible for green emission at 532 nm. So we conclude that PL confirms the presence of defects which are the constituents of the BMPs.

Figure 5.13: PL Emission spectra at different doping concentrations of ZnO:Mn taken in the emission range from 350 nm to 700 nm with excitation wavelength (a) 238 nm, (b) 255 nm, (c) 290 nm and (d) 342 nm.

5.6. Conclusions

We have successfully synthesized undoped ZnO nanoparticles as well as diluted magnetic semiconductor ZnO:Co and ZnO:Mn nanoparticles by chemical precipitation method. The average size ZnO:Co nanoparticles, which are spherical, are in the range of 34 – 45 nm and ZnO:Mn nanoparticles having rod shape structure have an average diameter in the range of 40-50 nm. Photoluminescence shows the presence of doped impurities and various defects which are the constituents of the BMPs. There is quenching of PL emission intensity as the doping concentration increases.

The undoped ZnO nanoparticles are diamagnetic. Initially ZnO:Co nanoparticles at low Co²⁺ concentrations show paramagnetic behaviour. At x = 0.04 the ferromag-
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Magnetic behaviour is most prominent. However at higher doping percentage of Co\(^{2+}\) the ferromagnetic behaviour is suppressed and antiferromagnetic nature is enhanced. This evolution from paramagnetic behaviour to ferromagnetic behaviour depending on the doping concentration and then to antiferromagnetic behaviour in Zn\(_{1-x}\)Co\(_x\)O nanoparticles systems can be understood within the framework of percolation of bound magnetic polarons.

The ZnO:Mn nanoparticles does not show any saturation in moment up to 1.5 Tesla magnetic fields. The M-H plots of the samples show paramagnetic behaviour. But a weak ferromagnetism is observed in 0.5 at. % Mn doped samples. So it can be concluded that ZnO nanoparticles when doped with Mn, ferromagnetism is observed at low doping concentrations (up to 0.5 at. %). At higher concentrations the paramagnetic behaviour is predominant.

As indicated by the moment values, the Mn doped system has lower values of moment than the Co doped system. When the antiferromagnetic interaction become dominating, the M versus H curves shows linearity depicting paramagnetism in case of Mn doped system at a lower value of Mn doping concentration in comparison to the doping concentration of Co doped system. In the case of Mn doping ferromagnetism quenches completely at Mn concentration beyond 0.5 at. %. But in case of Co doping ferromagnetism could be observed even upto 15 at. % of Co concentration. So ferromagnetism is optimum at 0.5 at. % Mn doping concentration for the Mn doped system while it is optimum at 4 at. % Co doping concentration for the Co doped system. The VSM measurements show an evolution from diamagnetic for the undoped ZnO to ferromagnetic for the 0.5 at. % Mn\(^{2+}\) doped ZnO sample and then to paramagnetism for higher Mn\(^{2+}\) doping concentrations. In ZnO:Co system, magnetism evolves from paramagnetic, at 0.5 and 1 at. % of Co doping concentration, to ferromagnetic at 4 at. % of Co and then ferromagnetism decreases as antiferromagnetic interaction become dominant as the doping concentration increases beyond 4 at. % of Co ions.
References


Chapter 5: Synthesis, characterization and magnetic properties of ZnO:Co and ZnO:Mn nanoparticles


