Chapter-4

4. ZnO based DMS nanostructures

The study of nanostructures with controlled morphology, shapes and size is essential for developing materials with novel properties and tailorable functions. Different types of semiconducting nanomaterials have attracted a large group of scientific community because of their exceptional properties, which are different from bulk materials [211, 212]. Zinc oxide (ZnO), one of the very important and versatile semiconductors with direct band gap of gap of $\sim 3.37$ eV and a large exciton binding energy of $\sim 60$ meV at room temperature (RT) is a promising candidate for functional components of devices. Selective doping with transition metal ions into ZnO lattice host is capable of tailoring its physical properties. In this chapter, the structural as well as optical properties of bare ZnO and transition metal (TM: Mn, Co, Ni, Cu) doped ZnO is highlighted. We have fabricated TM doped ZnO and bare ZnO by adopting solid state chemical reaction route which has been described in chapter-2. The concentration of TM were varied from 1% to 5%, accordingly they were indexed as TM-1, TM-3 and TM-5 (TM: Mn, Co, Ni, Cu). At the end of synthesis, all samples were obtained in the form of powder. Structural and optical investigations of the as fabricated samples were carried out by utilizing XRD, EDS, HRTEM, FTIR, PL and UV-Vis spectroscopy. The change of structural and optical properties due to different TM-doping is one of the major directions of our investigation
4.1 Mn doped ZnO

We have fabricated undoped ZnO and Mn:ZnO nanostructures for 1-3% Mn-doping cases, accordingly the samples were indexed as ZnO, Mn-1, Mn-3 and Mn-5. TEM analysis confirmed the formation of bare ZnO and Mn:ZnO nanorods having average aspect ratio ~3.7 and ~3.3 respectively.

(i) X-ray diffraction study

Figure 4.1: XRD pattern of undoped ZnO nanorods showing prominent diffraction peaks which can be perfectly indexed to the hexagonal wurtzite structure of ZnO (JCPDS card no. 36-145).

The phase and purity of the as prepared samples were determined by X-ray powder diffraction pattern. For identification of structural phase and crystallographic orientation we have utilized Rigaku Miniflex diffractometer employing Cu-Kα radiation at 1.54 Å with a scanning rate of 0.02 deg/s. XRD measurements have showed that the undoped and Mn doped ZnO crystallize into hexagonal wurtzite structures. The XRD pattern for undoped ZnO as
presented in figure: 4.1. Shows prominent diffraction peaks which can be perfectly indexed to the hexagonal wurtzite structure of ZnO according to JCPDS data card no.36-145. The XRD data of the Mn:ZnO samples have ensured wurtzite structure of ZnO with a high degree of crystallinity. The comparative X-ray diffraction pattern for bare ZnO and Mn:ZnO system is shown in figure: 4.2. No extra phases e.g. MnO$_2$ etc. were observed for Mn-doped ZnO systems. Thus Mn is expected to occupy Zn-sites of the host ZnO lattice. Owing to lattice mismatch introduced by Mn-doping, there is a slight shifting of XRD peaks [figure: 4.3] for different Mn concentrations. The most intense (101) peak for bare ZnO sample was observed at a Bragg angle ($2\theta$) of ~36.6°.

Figure 4.2: XRD patterns of Bare ZnO and Mn doped nanorods: Mn-1, Mn-2 and Mn-3.
A close observation to detect the shifting of XRD peaks for the plane (101) was recorded from Lorentzian fit of the curves in between 35° and 38° is presented in figure: 4.3, which indicates clear shifting for Mn-1, Mn-3 and Mn-5 samples from bare ZnO. The shifting of peaks for (101) plane are measured as 0.32° and 0.11° towards lower angle for Mn-3 and Mn-5 samples respectively, while for Mn-1 sample, it was shifted towards higher angle by 0.05°. The ionic radius of Zn²⁺ is 0.60 Å, and that of Mn²⁺ is 0.66 Å, for four-fold coordination [213]. Hence, Mn incorporation into the ZnO lattice through Zn replacement will lead to an expansion of the ZnO lattice. Previously, several research groups have observed linear increase of a and c with Mn concentration [214-216].

Lattice parameter for hexagonal ZnO nanostructures were estimated by utilizing the equation:

\[
\frac{1}{d_{hkl}^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \quad \text{ .................} 4.1
\]

Being a and c the lattice parameters and h,k and l the Millar indices and \(d_{hkl}\) the interplanar spacing for the plane (hkl).
This interplanar spacing can be calculated from the equation (3.1)

\[ 2d \sin \theta = n \lambda \]

Where \( \lambda \) is the wavelength of X-ray used, \( \theta \) is the diffraction angle and \( n \) is the order of diffraction (\( n=1 \)). The experimental results of ‘a’ and ‘c’ estimated for our samples were compared with their theoretical values for wurtzite phase of bulk ZnO (\( a = 3.250 \text{ A}^0 \), \( c = 5.265 \text{ A}^0 \)). In our study, though lattice parameters get enhanced in Mn-doping cases compared to undoped specimen, the amount of increment is not substantial between Mn-doped samples (table: 4.1). For Mn-3 sample highest values of enhancement were observed.

Table: 4.2 shows ‘d’ spacing values for the planes (001) and (002) as estimated for all samples. We observed that compared to other samples, Mn-3 sample exhibited maximum value for ‘d’ spacing.

**Table 4.1 :** Values of lattice parameters for the samples ZnO, Mn-1, Mn-3 and Mn-5

<table>
<thead>
<tr>
<th>Lattice parameter</th>
<th>ZnO</th>
<th>Mn-1</th>
<th>Mn-3</th>
<th>Mn-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a \text{ (A}^0 )</td>
<td>3.2173</td>
<td>3.2232</td>
<td>3.2474</td>
<td>3.2265</td>
</tr>
<tr>
<td>( c\text{ (A}^0 )</td>
<td>5.1520</td>
<td>5.1747</td>
<td>5.1995</td>
<td>5.1701</td>
</tr>
</tbody>
</table>

**Table 4.2 :** Values of lattice lattice spacing ‘d’ for the planes (100) and (002) for the samples ZnO, Mn-1, Mn-3 and Mn-5

<table>
<thead>
<tr>
<th>(h k l)</th>
<th>ZnO ( \text{ (A}^0 )</th>
<th>Mn-1 ( \text{ (A}^0 )</th>
<th>Mn-3 ( \text{ (A}^0 )</th>
<th>Mn-5 ( \text{ (A}^0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1 0 0)</td>
<td>2.786</td>
<td>2.791</td>
<td>2.812</td>
<td>2.794</td>
</tr>
<tr>
<td>(0 0 2)</td>
<td>2.576</td>
<td>2.587</td>
<td>2.599</td>
<td>2.585</td>
</tr>
</tbody>
</table>
(a) Size determination

Size determination of the nanostructures so formed was performed by utilizing three methods (i) Scherrer formula, (ii) Williamson-Hall Plot and (iii) TEM analysis. The Scherrer formula is described in chapter 3. It is the simplest approach to calculate size from XRD line broadening. The Scherrer equation (3.2) is given by:

\[ d = 2R = \frac{0.98 \lambda}{\beta \cos \theta} \]

Where \( d \) is the crystallite size, \( \lambda \) the wavelength of X-ray diffraction, \( \beta \) the full width at half maximum (FWHM) of the diffraction peak (in radians), \( \theta \) is the maximum scatter angle.

![Figure 4.4: Individual Gaussian fit for the peak broadening reflected by the plane (101) for the samples (A) ZnO, (B) Mn-1, (C) Mn-3 and (D) Mn-5](image-url)
For size determination of the nanocrystals, usually, the most intense peak has been selected from the XRD spectra. In our case the most intense peak is obtained from the reflection of (101) plane for all the samples. The individual Gaussian fit for the peak broadening reflected by the plane (101) for the samples (A) ZnO, (B) Mn-1, (C) Mn-3 and (D) Mn-5 is presented in figure:4.4.

The sample Mn-3 showed maximum broadening of ~0.57° (figure: 4.4C). The lowest peak broadening was obtained for ZnO sample (figure: 4.4A). The variation of Full width half maxima (FWHM) corresponding to different peak positions with crystallite sizes is given in the table : 4.3. The average crystallite size as obtained from individual XRD line broadening and using Scherrer formula [217] for the ZnO, Mn-1, Mn-3 and Mn-5 were 17.15, 16.47, 14.61 and 15.37 nm; respectively. A decrease in the average particle size with increasing Mn content has been reported earlier [218, 219]. Similar result was observed in our analysis.

**Table 4.3 : Variation of FWHM, peak position of (101) plane and crystallite size for all samples.**

<table>
<thead>
<tr>
<th></th>
<th>FWHM (In degree)</th>
<th>θ value (In degree)</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>0.482</td>
<td>36.59</td>
<td>17.15</td>
</tr>
<tr>
<td>Mn-1</td>
<td>0.502</td>
<td>36.64</td>
<td>16.47</td>
</tr>
<tr>
<td>Mn-3</td>
<td>0.566</td>
<td>36.27</td>
<td>14.61</td>
</tr>
<tr>
<td>Mn-5</td>
<td>0.538</td>
<td>36.48</td>
<td>15.37</td>
</tr>
</tbody>
</table>

(b) **Williamson Hall plot**

Calculation of size and strain were also performed by plotting Williamson-Hall plots for the samples. The Williamson-Hall plot gives information regarding the size and strain of the nanostructures.
The Williamson-Hall equation is given by

$$\beta \cos \theta = C_{e} \ 4 \sin \theta + \frac{K \lambda}{L} \quad \text{...............................................4.1}$$

By plotting $\beta \cos \theta$ versus $4 \sin \theta$ we obtained the strain component from the slope ($C_{e}$) and the size component from the intercept ($K \lambda / L$). The Williamson-Hall plot for pure ZnO sample is shown in figure: 4.5. The values for $\beta$ and $\theta$ were taken from four different peaks of the respective XRD pattern of the sample. From the slope of the graph, the strain was obtained as $14.46 \times 10^{-2}$ and from the intercept of the straight line the particle size ($L$) was estimated as $12.82$ nm by considering $K = 0.9$ and $\lambda = 1.54$ Å. The strain and particle size of other nanostructures so fabricated were calculated from the analysis of Williamson-Hall plot and presented in the table. The respective values for particle strain and size are presented in the table 4.4. There is a linear increase in strain with increasing particle size. An anomaly regarding the particle size was observed in this case. This may be due to the fact that, Scherrer approach is based upon the assumption where strains and faulting are ignored for a small cubic crystal and the peak broadening is only due to the small size.

![Figure 4.5: Williamson-Hall plot for bare ZnO sample.](image)
However the Williamson-Hall method has many assumptions: its absolute values should not be taken too seriously but it can be a useful method if used in the relative sense; for example a study of many powder patterns of the same chemical compound, but synthesised under different conditions, might reveal trends in the crystallite size/strain which in turn can be related to the properties of the product.

Table 4.4: Strain and size of the nanostructures ZnO, Mn-1, Mn-3 and Mn-5 as obtained from their respective Williamson-Hall plots.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Strain</th>
<th>Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>$14.46 \times 10^{-2}$</td>
<td>12.82</td>
</tr>
<tr>
<td>Mn-1</td>
<td>$36.96 \times 10^{-2}$</td>
<td>24.2</td>
</tr>
<tr>
<td>Mn-3</td>
<td>$27.72 \times 10^{-2}$</td>
<td>18</td>
</tr>
<tr>
<td>Mn-5</td>
<td>$8.69 \times 10^{-2}$</td>
<td>9.5</td>
</tr>
</tbody>
</table>

(ii) Electron microscopy study

(a) ZnO nanostructures

One-dimensional (1D) ZnO nanostructures have been studied intensively and extensively over the last decade not only for their remarkable chemical and physical properties, but also for their current and future diverse technological applications. ZnO is an amphoteric oxide (an oxide that can act as either an acid or as base in a reaction) with an isoelectric point value of about 9.5 [220]. ZnO, in general, is expected to crystallize by the hydrolysis of Zn salts.
in a basic solution that can be formed using strong or weak alkalis. Zn$^{2+}$ is known to coordinate in tetrahedral complexes. Due to the 3d$^{10}$ electron configuration, it is colourless and has zero crystal field stabilization energy. Depending on the given pH and temperature [221], Zn$^{2+}$ is able to exist in a series of intermediates, and ZnO can be formed by the dehydration of these intermediates. Chemical reactions in aqueous systems are usually considered to be in a reversible equilibrium, and the driving force is the minimization of the free energy of the entire reaction system, which is the intrinsic nature of wet chemical methods [222]. Wurtzite structured ZnO grown along the c axis has high energy polar surfaces such as ± (0001) surfaces with alternating Zn$^{2+}$-terminated and O$^{2-}$-terminated surfaces [223]. So when a ZnO nucleus is newly formed, owing to the high energy of the polar surfaces, the incoming precursor molecules tend to favourably adsorb on the polar surfaces. However, after adsorption of one layer of precursor molecules, the polar surface transforms into another polar surface with inverted polarity. For instance, a Zn$^{2+}$-terminated surface changes into an O$^{2-}$-terminated surface, or vice versa. Such a process is repeated over time, leading to a fast growth along the ± [0001] directions, exposing the non-polar {1100} and {2110} surfaces to the solution. This is essentially how a 1D nanostructure is formed [224]. In our study, we have observed the formation of one dimensional nanostructures of as synthesised bare ZnO and transition metal (Mn,Co,Cu) doped ZnO samples synthesised via solid state chemical reaction route. The elongated nanostructure was confirmed through transmission electron microscope (TEM) study. For TEM study we have utilised JEM-2100 model with resolution 1.9Å to 1.4Å, accelerating voltage 60-200 KV in 50 steps having magnification 50 to 1500000 times.

During our TEM observations, focussing the electron beam on the ZnO cluster, the presence of one dimensional ZnO nanostructures was confirmed.
Figure 4.6: TEM image of the ZnO sample, with increasing resolution from figure: A to C. With high resolution TEM micrograph three isolated elongated nanostructures having different lengths and diameters, (a)47 nm, 20 nm; (b) 500 nm, 200 nm; and (c) 93 nm, 28 nm; respectively. (d) Selected area electron diffraction pattern (SAED) focussed on the isolated nanorod (c).

Various TEM images for the bare ZnO sample are presented in figure: 4.6. Changing the resolution from low to high with increasing magnification (from figure: 4.6A to 4.6C) we confirmed the formation of ZnO nanorods. During TEM investigation few ZnO nanorods were found to be isolated, three of them are presented in figure: 4.6(a) - 4.6(c). Interestingly, a knife like elongated structure with maximum length and diameter ~500 nm and ~200 nm respectively was observed in the TEM micrograph (figure: 4.6b). Estimated
lengths and diameters of other two isolated rods as presented in figure: 4.6(a) and figure: 4.6(c) were 47 nm, 20 nm and 93 nm, 28 nm respectively. Uniformly distributed ZnO lattice points are observed in the selected area electron diffraction (SAED) pattern [figure: 4.6(d)]. All points correspond to the hexagonal wurtzite structure of ZnO. Four points within two inner rings are ascribed for the planes (101) and (002) corresponding to their lattice spacing 2.4Å and 2.6 Å.

![HRTEM image of ZnO nanorod](image)

**Figure 4.7:** HRTEM image of ZnO nanorod, inset isolated nanorod on which the beam is focussed to get the HRTEM image (a) at low magnification with 20 nm scale, (b) at high magnification with 5 nm scale.

The HRTEM study was performed on the isolated nanorod as presented in figure: 4.7(a), the resolution was increased to get the pattern shown in the inset (b) of figure: 4.7. On further increasing the resolution, lattice planes with few defect states were observed. The lattice spacing was estimated to be ~2.1Å at a position where lattice fringes are clear enough, this lattice spacing ‘d’ corresponds to the plane (102) as calculated from the XRD pattern of the ZnO
sample. Thus, the growth direction of small crystallite is identified to be along (102) plane. It has been noticed that the surface of the small crystallite exposed to the beam consists of several lattice distortion. This structural property may play important role to change the optical, magnetic and other properties of the sample.

(b) ZnO and Mn doped ZnO

The transmission electron micrographs (TEM) of the ZnO, Mn-1, Mn-3 and Mn-5 samples give clear visual evidence on the formation of nanorods as presented in Figure: 4.8. Nanorods of different lengths and diameters with a random orientation can be seen from the micrographs. For systematic measurement of the lengths and diameters of the nanorods we have utilized Sun Microsystems, Inc. software “Java SE runtime environment (JRE) version 6” and “Java FX runtime version 1”. For ZnO sample we have selected 10 nanorods which are almost straight and isolated. The average length of the rods was found to be ~70 nm. The average diameter of the nanorods is measured as ~19 nm which is comparable with the average size predicted from XRD data. The average aspect ratio of the ZnO nanorods obtained as 3.7. We speculate that the most of the rods are composed of monocrystallites over a definite length. The average length, diameter, and aspect ratio for the samples as calculated from TEM image were shown in table: 4.5. Compared to bare ZnO sample a slight decrease in aspect ratio was observed for Mn doped samples but it was not substantial. Mn-3 sample yields nanorods with average length as 91 nm which is higher than any other sample.

Table 4.5: Lengths and diameters of ZnO nanorods (10 nos) as measured from TEM images (figure: 4.8A) by using standard software.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length</td>
<td>64</td>
<td>54</td>
<td>71</td>
<td>75</td>
<td>73</td>
<td>76</td>
<td>46</td>
<td>101</td>
<td>75</td>
<td>72</td>
</tr>
<tr>
<td>(nm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diameter</td>
<td>11</td>
<td>15</td>
<td>18</td>
<td>25</td>
<td>20</td>
<td>18</td>
<td>24</td>
<td>21</td>
<td>15</td>
<td>24</td>
</tr>
<tr>
<td>(nm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**Table 4.6**: Average length, diameter, aspect ratio for the samples ZnO, Mn-1, Mn-3 and Mn-5 as obtained from TEM analysis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Av. length L (nm)</th>
<th>Av. Diameter D (nm)</th>
<th>Aspect ratio (L/D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>70.6</td>
<td>19</td>
<td>3.7</td>
</tr>
<tr>
<td>Mn-1</td>
<td>63.28</td>
<td>18.38</td>
<td>3.4</td>
</tr>
<tr>
<td>Mn-3</td>
<td>91</td>
<td>28</td>
<td>3.2</td>
</tr>
<tr>
<td>Mn-5</td>
<td>62</td>
<td>17.5</td>
<td>3.5</td>
</tr>
</tbody>
</table>

**Figure 4.8**: TEM image of the samples (A) ZnO, (B) Mn-1, (C) Mn-3, (D) Mn-5
Figure 4.9: (A) HRTEM image collected for the sample Mn-3, (B) SAED pattern for the sample Mn-3.

High resolution transmission electron microscopy (HRTEM) image for the Mn-3 sample as presented in figure: 4.9(A) yields formation of high crystalline nature of the nanocrystals as prepared. The lattice spacing as measured from the image is 2.5 Å corresponding to the plane (101), it indicates the growth direction of the nanocrystal is along (101). Clear fringe pattern also reveals nonexistence of lattice distortion of the as fabricated Mn-3 sample. The selective area electron diffraction (SAED) pattern for the sample Mn-3 is presented in Figure: 4.9(B). It reveals diffused rings which correspond to the hexagonal wurtzite structure of ZnO without any impurity phase. As observed from the pattern, we ascribe two inner rings as (100) and (002) planes for which the $d$-spacings is calculated to be 2.86 nm and 2.47 nm. The values correspond to the $d$-spacing parameters as calculated from XRD data (Table 4.2).

(iii) Fourier Transform Infrared spectroscopy study

An infrared spectrum is considered to be the fingerprint of a given specimen with absorption peaks corresponding to the frequencies of inter-atomic vibrations in the molecular system. Infrared spectrum can be
considered as an important asset in the qualitative analysis of a given system, because no two different compounds can ever exhibit identical infrared spectra. In the FTIR spectrum, as presented in the figure: 4.10, for the bare ZnO and Mn doped samples shows similar feature for all samples. Pure ZnO and Mn-doped ZnO have wurtzite structure and are further supported by FTIR. Undoped ZnO, Mn doped ZnO (Mn-1, Mn-3, Mn-5) exhibit similar FTIR spectra and the corresponding broadening peaks due to stretching and vibration of different elements present are presented in the table: 4.7.

The identical IR peak for metal-oxide band stretching is observed near 500 cm$^{-1}$. It has been noted that all samples exhibited IR peak near 500 cm$^{-1}$, but from the comparative FTIR plot (figure: 4.10) it was clear that compared to other samples, Mn-3 sample exhibited minimum %transmittance at ~500 cm$^{-1}$ due to Zn-O and Mn-O stretching and bending. Observing the intense nature of the IR peak broadening for the sample Mn-3, it can be speculated that Mn concentration plays an important role in shifting IR peak position.

**Table 4.7**: FTIR peak broadening positions corresponding to different molecular bands for the samples (A) ZnO, (B) Mn-1, (C) Mn-3, (D) Mn-5.

<table>
<thead>
<tr>
<th>Elements</th>
<th>ZnO (cm$^{-1}$)</th>
<th>Mn-1 (cm$^{-1}$)</th>
<th>Mn-3 (cm$^{-1}$)</th>
<th>Mn-5 (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-H</td>
<td>832</td>
<td>839</td>
<td>834</td>
<td>763</td>
</tr>
<tr>
<td>ZnO</td>
<td>1403</td>
<td>1415</td>
<td>1383</td>
<td>1408</td>
</tr>
<tr>
<td>C=O</td>
<td>1554</td>
<td>1473</td>
<td>1494</td>
<td>1630</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>2372</td>
<td>2378</td>
<td>2367</td>
<td>2378</td>
</tr>
<tr>
<td>H</td>
<td>2844</td>
<td>2853</td>
<td>2849</td>
<td>2849</td>
</tr>
<tr>
<td>C</td>
<td>2914</td>
<td>2919</td>
<td>2919</td>
<td>2929</td>
</tr>
<tr>
<td>OH</td>
<td>3413</td>
<td>3418</td>
<td>3385</td>
<td>3429</td>
</tr>
</tbody>
</table>
IR peak for O-H stretching is obtained within the range 3385 cm\(^{-1}\) - 3429 cm\(^{-1}\), this ‘O-H’ band arises due to water absorbed from the atmosphere.

Zinc acetate and Manganese acetate stretching were utilized as reacting components during synthesis, for this symmetric ‘COO’ stretching IR peaks have been observed within 1473 cm\(^{-1}\) - 1630 cm\(^{-1}\); The IR peaks due to atmospheric Co\(_2\) are counted within the range 2367 cm\(^{-1}\) – 2378 cm\(^{-1}\); for oxide from ZnO related IR peaks are observed within 1383 cm\(^{-1}\) – 1415 cm\(^{-1}\); corresponding IR peaks for C-H stretching are seen within 763 cm\(^{-1}\) - 839 cm\(^{-1}\). From the table: 4.7, it is evident that there is a considerable IR peak shift for all the samples. Shifting of IR peak may contribute some important information regarding the samples. There are two basic thoughts in interpreting the so-called positional fluctuation of peaks of IR spectra under the influence of environmental factors, i.e., temperature and concentration. The peak position change may be caused by the actual frequency shift of a single absorption band.
or alternatively by the relative intensity changes of overlapped bands. The classical view that has been widely accepted for many decades in the field of vibrational spectroscopy is that gradual changes occur in the vibrational frequency associated with a specific chemical bond. Many previous works concerning the peak position shift of IR spectra are based on the notion that the extent of frequency shift can be directly correlated with the level of specific molecular interactions, such as hydrogen bonding and dipole–dipole interactions [225-231]. The apparent frequency shift of OH stretching or C=O stretching band under temperature or concentration change was attributed to the gradual weakening of such interactions. An alternative view is that the apparent peak position shift is caused by the change in the population of different chemical species. In this case, the position of peak maximum tends to shift due to the variation in the relative intensity contributions of closely overlapped bands with their individual frequencies essentially unchanged.

(iv) Photoluminescence (PL) spectroscopy

‘ZnO’ have achieved stimulated interests in the last two decades in the field of optoelectronics. Out of many reasons, few of them are:

i) Possible quantum confinement as observed in nanosized ZnO system may lead to the enhancement in radiative recombination.

ii) Nanostructures of certain morphology with increased surface area and therefore reduced reflection at the air-semiconductor interface, better light extraction may be expected.

iii) From ‘ZnO nanostructures’ photonic crystal effect may be expected in carefully arranged periodic arrays of nanostructures [232].

The attractiveness of ZnO for optoelectronics lies in its ability to emit light in the ultraviolet (UV) spectral range, which might enable the design of UV light emitting diodes (UV LED’s). The recombination processes in ZnO occur via radiative and non-radiative channels. The different types of defects in ZnO may serve as non-radiative recombination centres: point defects, dislocations,
surface/interface states etc. Efficient light emission may be obtained via a decrease in the non-radiative contribution. This can be achieved by improved crystal quality of the material. However, even in the case of dominating radiative recombination, the light emission may occur in the UV range (~ 380 nm) as well as in the visible range of spectra (~ 450 – 650 nm). The latter is so-called defect emission and is commonly observed in ZnO independently of growth technique or substrate temperature [233]. The possible origin of visible emission is deep level defects: oxygen vacancies, zinc interstitials or their combination [234-236]. Despite concerted efforts, the origin of defect emission in ZnO is still under debate.

Photoluminescence (PL) is a powerful technique to explore many properties including light emission properties of semiconductors. In our study the light emission properties of doped and undoped ZnO systems have been studied. The luminescence response as exhibited by doped ZnO is somewhat complicated. This may be due to the presence of various kinds of defects which exist as non radiative centres. The room temperature photoluminescence spectra were studied by using a Perkin Elmer LS-55 spectrometer at excitation wavelength $\lambda_{ex} = 325$ nm (Xe-source), the data were collected by a computer controlled standard monochromator based photo detector. In some cases we have collected data at different excitation wavelength to compare the result and also to identify Raman peaks which may appear near the $\lambda_{ex}$ in the spectrum. PL spectra for undoped ZnO nanords are presented in figure: 4.12. After Gaussian fit for multiple peaks (figure 4.13), in the PL spectra of undoped ZnO specimen, mainly two asymmetrically broadened PL responses were observed: the first, in the UV region at 392 nm and the other in the green region at 425 nm. The UV-band is attributed to the near band edge emission, while the green band is attributed to the emission which has originated due to the intrinsic defect states of ZnO, such as oxygen vacancy, zinc interstitial and oxygen antisite [237,238].
Various assignments of visible emission involve vacancies and interstitial atoms, including cationic and anionic sites in ZnO [239], while some of them reported completely different theoretical and experimental results. At this point, the origin of the defect responsible for the green emission cannot yet be definitely determined only with the experimental results, because visible spectra were greatly affected by preparation methods, environmental conditions, and roles of the coordinating ligands [240, 241]. In general, most defects are considered as a result of the surface states located in the band gap of the nanocrystals, which act as trapping states for the photo generated carriers, while the surface states of the nanoparticles might be investigated by x-ray photoelectron spectroscopy. ZnO has a characteristic green emission peak along with the typical band edge emission peak near UV ($E_g = 3.37$ eV, $\lambda = 386$ nm). On the basis of theoretical and experimental studies P.S. Xu et al. and B.D. Aleksandra et al. [242, 243] have showed different types of defect states related with ZnO nanostructures are:

- $V_{Zn} = \text{neutral, singly or doubly charged Zn vacancies}$;
- $V_o = \text{neutral or singly charged Oxygen vacancies}$;
- $Zn_i = \text{neutral or singly charged interstitial Zn}$;
- $O_i = \text{interstitial O}$;
- $V_oZn_i = \text{a compex of } V_o \text{ and } Zn_i$;
- $V_{Zn}Zn_i = \text{a complex of } V_{Zn} \text{ and } Zn_i$;
- $O_{Zn} = \text{substitution of O at Zn position}$;

The singly charged oxygen vacancy ($V_o^+$) is located at 1.62 eV [24], below the conduction band in the ZnO band gap and results in an emission at ~500 nm. The electron-hole recombination on singly ionized oxygen vacancies is the most widely but not universally accepted mechanism for green luminescence from ZnO. The schematic feature of the energy levels for different defect states in ZnO nanostructure is shown in figure: 4.11. The oxygen vacancies appear to be intrinsic in solution-based synthesis and may result from the abrupt heterogeneous nucleation and growth, mediated by the uneven surface energies. Synthetic protocol and passivation processes are very
often responsible for the concentration of surface states. For charge carriers and excitons, these surface states act as surface traps, which generally degrade the optical and electronic properties of the nanocrysystems. For radiative transitions, the surface states can be suitably used. Spanhel, Lubomir and Anderson, Mark A., reported that if the radiative centre is associated in part with surface, their concentration would be expected to decrease with the aggregation of nanostructures [244]. From the PL spectra analysis of our ZnO nanorod systems as presented in figure: 4.12, we speculate that among all the defect states quoted above, neutral or singly charged interstitial Zn (Zn\textsubscript{i}) is considered to be the most prominent one which suppress the other defects.

![Diagram of energy levels in ZnO nanostructure](image)

Figure 4.11: The schematic feature of the energy levels for different defect states in ZnO nanostructure.

It is generally accepted that there are two emission bands in the PL spectrum of ZnO. One is in the UV range, which is associated with exciton emission, and another is in the visible range, which originates from the electron–hole recombination at a deep level, caused by oxygen vacancy or zinc interstitial defects [245]. The Gaussian fit for multiple peaks for the PL spectra of bare ZnO is shown in figure: 4.13. The UV peak position and green peak position are recorded at 392 nm and 425 nm respectively. It has been reported that the high-crystallinity and more perfection in surface states may enhance the UV emission in the PL spectrum [246].
Figure 4.12: Room temperature Photoluminescence (RTPL) spectra of ZnO nanorods with excitation wavelength 325 nm, inset: TEM image of ZnO nanorods.

Figure 4.13: RTPL spectra of ZnO nanorods with Gaussian fit for multiple peaks (UV and green) at excitation wavelength 325 nm.
In our case the UV emission is more intense compared to green emission. HRTEM image study also inferred high-crystallinity nature of the as fabricated Mn-3 sample. The intensity of UV emission is also dependent on the nanostructure size. Below a certain size, the luminescence properties of ZnO nanostructures should be dominated by the properties of the surface [247]. An enhanced UV emission for thinner nanostructures like nanochips has been reported [248], which was attributed to their larger surface area and fewer defects. Thus, fewer defects in the surface and high crystalline nature of the samples respond to the intense UV emission in case of pure ZnO nanostructures.

The optical quality and the possible effects of Mn-doping were investigated using room temperature photoluminescence (PL). A comparison of the PL spectra of the pure ZnO nanorods and that of Mn-doped ZnO nanostructures is illustrated in Figure: 4.14. It has been observed that due to Mn doping the UV peak gets lowered and additional defect related peaks are generated.

In the PL spectra of Mn doped ZnO sample (Mn-3), we have observed three characteristic peaks after Gaussian fit for multiple peaks, which is presented in figure: 4.15. As observed from the plot, the peak positions are recorded as 393 nm, 438 nm and 544 nm. Compared to the PL spectra of bare ZnO, the UV peak position in case of Mn-3 sample remains almost same but the PL intensity is lowered by about three times. The other two peaks are considered to be defect related peaks in the visible region. The peak position at 438 nm may be attributed due to Zn interstitial while at 544 nm due to oxygen vacancy. As noticed from the spectra the peak at 438 nm is more intense while the peak at 544 nm is suppressed. Khalid Mahmood et al.[248] observed a strong UV emission peak around 377 nm for In-doped ZnO nanostructures along with very weak visible emission centred at 530 nm, which indicated the high crystalline quality and low concentration of defects for In-doped ZnO nanostructures.
Figure 4.14: RT PL spectra for pure ZnO and Mn:ZnO system at excitation wavelength 325 nm.

Figure 4.15: Multiple peaks Gaussian fit for RT PL spectra of Mn-3 sample at excitation wavelength 325 nm.
Green emission peak is commonly referred to as a deep level or trap-state emission. The green band is generally explained by the radial recombination of a photo-generated hole with the electron in a singly ionized oxygen vacancy [249]. It has been reported that due to the excess exciton impurity and crystalline defect scattering, there exists a deep-level emission around 2.4 eV in ZnO Nanowires [250,251].

On the other hand, surface states have also been identified as a possible cause of the visible emission in ZnO nanomaterials [252], Zhang et al. [253] have reported that surface states may play a more important role in the green emission. Hence, it might be reasonably inferred that oxygen vacancy, zinc interstitial along with surface state may respond to the green emission of Mn doped ZnO nanostructures.

(v) UV-Visible Spectroscopy

Figure 4.16: UV-Visible spectroscopy of Bare ZnO, Mn-1, Mn-3 and Mn-5 samples.
The optical properties of the Mn-doped and pure ZnO nanostructures have been further investigated with the help of the UV-Visible spectrum as shown in figure: 4.16. The band gap values for undoped nano ZnO and Mn-1, Mn-3 and Mn-5 (1%, 3%, and 5%) doped ZnO were calculated from the onset of absorption. The respective values are found to be 3.52, 3.44, 3.49 and 3.45 eV. Earlier, the blue shift of the band edge and increased hexagonal lattice parameters were shown as the evidence of Mn\(^{2+}\) incorporation in the ZnO lattice host [219]. We had not witnessed such effects though a minimal variation in band gap is observed due to Mn-related substitutional doping.

For wide band gap semiconductors, doping in them often induces dramatic changes in their electrical and optical properties [254, 255] and markedly alters the band gap. According to the theory of semiconductor–metal transition, the band gap energy (\(E_g\)) decreases when the impurity is more than the Mott critical density [256]. Hence, heavy doping leads to an obvious narrowing of \(E_g\). It was examined in Figure 4.11 that, with Mn-doping, the UV-visible band shifts to a longer wavelength, which could be possibly due to the narrowing of \(E_g\), which was similar to the results reported by other researchers [257].

### 4.2 Co doped ZnO

For experimental investigations three different Co doped ZnO samples were prepared by adopting the same solid state chemical reaction route. The Co concentrations in the samples were varied as 1%, 3% and 5% and indexed as Co-1, Co-3 and Co-5.

(i) **X-Ray diffraction studies**

The as-synthesized powder samples thus obtained were characterized by powder x-ray diffraction (XRD) by using Philips 1730, Cu-K\(\alpha\) radiation, \(\lambda =1.54 \text{ Å}\). The X-ray diffraction pattern of undoped ZnO and Co-1, Co-3 and Co-5
samples is presented in figure: 4.17. All the diffraction peaks can be indexed to a hexagonal wurtzite structured ZnO (space group P63mc), without any additional impurity phases, thereby indicating that the wurtzite structure might have not affected due to the substitution of Cobalt. Further, as no excess peaks were detected, it has been concluded that all the starting organic precursors might have been completely decomposed and the Co ions successfully occupy the lattice site rather than interstitial ones. Previous report revealed that XRD study of Co powder alone shows one intense peak at around 44° [258]. In our XRD study with Co doped samples no such peak around 44° has been detected, it indicated that Co was doped well in the ZnO sublattice. However we can’t deny the existence of Co, CoO clusters or other impurity phases in the samples since the sensitivity of the X-ray diffractometer may not go beyond to measure their existence. Further, the existence of Co phases had been detected by J. Cui et al.[259] in their Co:ZnO samples annealed above 700°C, but in our case, fabrication of all samples were done below 100°C.

In a recent work on Co doped ZnO, B. Pal et al. reported that compared to undoped ZnO, the XRD intensities of Co doped samples showed lowering of intensity and increase in full width at half maxima (FWHM) of the XRD pattern. In our case, we have observed slight decrease in the intensity of doped samples but no clear evidence of increase in FWHM for all Co doped samples has been detected. As noted from the table 4.3, considering the reflection from the plane (101), only Co-1 sample shows maximum FWHM. Further, as observed from the XRD pattern, the sharpness of the peaks reflected from the crystallographic planes (004) and (202) are considerably lowered for Co doped samples.

It has been noticed from a slow scan comparison of the (101) peak of Co-doped and the undoped ZnO NSs that the centres of diffraction peaks of doped ZnOs shift towards high angle compared to undoped ZnO (figure: 4.18). The diffraction peaks along with their relative intensities are found to be in agreement with those from the other reports [260,261]. The shift of peak position is attributed due to the change of size and strain of the NS
for incorporation of Co in the ZnO lattice host induced by mechanical stressing during synthesis. Since the ionic radius of Co and Zn are 0.72 Å and 0.74 Å respectively, which are very close, Co doping induced strain is expected to be less significant. However, as a result of ball milling, a compressive strain is introduced in the ZnO NPs [262]. We estimated a reduction in interplanar spacing of ∼0.29% from the measured shift in 2θ for (101) plane. This strain in the NPs is expected to influence the electronic, optical, magnetic and other properties including band-structure of ZnCoO.

**Table 4.8**: Relative data showing FWHM and 2θ corresponding to the plane (101) for determination of crystallite size and interplanner spacing of ZnO, Co-1, Co-3 and Co-5 samples.

<table>
<thead>
<tr>
<th></th>
<th>FWHM (in degree)</th>
<th>2θ theta (in degree)</th>
<th>Crystallite size (nm)</th>
<th>d(101) Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>0.4985</td>
<td>36.1464</td>
<td>16.5701</td>
<td>2.4823</td>
</tr>
<tr>
<td>Co-1</td>
<td>0.5347</td>
<td>36.2499</td>
<td>15.4537</td>
<td>2.4751</td>
</tr>
<tr>
<td>Co-3</td>
<td>0.4903</td>
<td>36.3543</td>
<td>16.8575</td>
<td>2.4683</td>
</tr>
<tr>
<td>Co-5</td>
<td>0.4923</td>
<td>36.3459</td>
<td>16.7879</td>
<td>2.4689</td>
</tr>
</tbody>
</table>

Further, the average crystallite size of all the samples was estimated using the most intense diffracted peak (101) broadening technique and are found to be in the range of 15.45 nm to 16.86 nm. Table: 4.8 shows the FWHM and corresponding 2θ values corresponding to the plane (101) for calculation of crystallite size of as synthesized nanostructures (NS). The sizes estimated from the XRD data for bare ZnO, Co-1, Co-3 and Co-5 samples are 16.57 nm, 15.45 nm, 16.86 nm and 16.79 nm respectively.
Figure 4.17: XRD pattern of Co-1, Co-3, Co-5 and bare ZnO samples.

Figure 4.18: XRD pattern showing shifting of the centres of (101) diffraction peaks.
(ii) Electron Microscopy study

(a) Co-1

Structural study of the bare ZnO and Co doped ZnO was further extended by performing Transmission electron microscopy (TEM) study. A clear visual evidence of the formation nonords with the bare ZnO and Co doped ZnO is being depicted by electron microscopy study. The TEM images of the as fabricated Co-1 sample are presented in figure: 4.19. At some lower magnification formation of rod like nanostructures were found [figure: 4.19(A)], while at higher magnification on a selected section, few irregularly shaped rods were confirmed (figure: 4.19B). Using standard software the length and diameters of few rods were measured from which we found that the average length and diameter of the nanorods so formed lie within range 80-100 nm and 10-30 nm respectively. By adopting Ball milling method other researchers found different shaped nanoparticles for Co doped ZnO cases, particularly for bare ZnO they found mostly spherical nanoparticles [258,261]. Since, we have adopted mechanical milling (manual) and interest was paid in unidirectional motion of milling during synthesis of Co:ZnO system. Probably this may be the reason why we are getting elongated nanostructures of our samples. The corresponding HRTEM image as shown in figure: 4.19C indicates the lattice space 2.4 Å, matching the space of the lattice plane (101) for the wurtzite ZnO. It confirms that the preferable crystal growth direction is (101). The HRTEM image reveals existence of defect states in the surface of nanords as fabricated. Further, no lattice distortion was observed in the SAED pattern.
Figure 4.19: (A) TEM image of Co-1 sample (A) rod like nanostructures at lower magnification (B) Few Co-ZnO (1at% Co) Nanorods at higher magnification (C) High resolution TEM image of a small crystallite showing surface defect without lattice distortion with lattice spacing ~2.4 Å corresponding to (101) plane (B) Electron diffraction pattern (SAED) obtained from the same section of the Co-1 sample.

The selected area electron diffraction pattern (SAED) for Co-1 is presented in Figure: 4.18(D). All values for d-spacing calculated from SAED pattern are close to ZnO structure, indicating wurtzite phase of the sample. It clearly indicates non-existence of Co, CoO clusters or other impurity phases in selected area of the nanorod. As the SAED pattern was obtained by focussing the beam on a few nanostructures of the sample and also due to law concentration of Co doping, there was no Co clusters observed in the as prepared nanostructures.
Figure 4.20: (A) TEM micrograph of Co-3 sample, (B) An isolated nanorod obtained from Co-3 sample with length ~44 nm and diameter ~16 nm, (C) HRTEM image of Co-3: Beam focussed on the small crystallite showing clear lattice fringes without any lattice distortion with lattice spacing ~2.4 Å corresponding to (101) plane, (D) Electron diffraction pattern obtained from the same section of the Co-3 sample.

The high resolution TEM images of Co-3 sample are presented in figure: 4.20. It could be seen from the micrograph of figure: 4.20A that the nanoclusters are generally elongated with average length 71 nm and diameter 19 nm. During the study many isolated rods for Co-3 sample were detected. As indicated in figure: 4.20B, high resolution of TEM image focussed on a single rod with length 44 nm and diameter 16 nm has been observed. It has been noticed that compared to Co-1 sample, elongated shapes are more regular in
case of Co-3 sample. The high resolution TEM image of the small crystallite is presented in figure 4.20C, it indicates uniform lattice structure with clear lattice spacing $\sim 2.4 \, \text{Å}$ corresponding to the plane (101). Thus, we can infer that the growth direction of small crystallite is along (101). Further, from the formation of clear lattice fringes, we can conclude that there is no lattice defect and the nanoclusters are single crystallite state. The estimated lattice spacing ‘d’s are a little bit higher than those of bulk ZnO, suggesting that the Co atoms are substitutes. Several separated rings in the electron diffraction pattern from the inset are identified as being consistent with wurtzite ZnO structure, implying the unchanged structure of Co-doped ZnO clusters to that of wurtzite ZnO structure [263].

(c) Co-5

Structural investigation of Co:ZnO system was further extended higher concentration of Co. The TEM micrographs and HRTEM image and SAED pattern for 5 at% Co doped (Co-5) is presented in figure: 4.21. For this sample, though nanostructures are irregularly shaped and agglomerated, most of the nanostructures are identified to be elongated in shape (figure: 4.21A). Few isolated well shaped nanorods were found during TEM investigation. One such isolated rod with length $\sim 70$ nm and diameter $\sim 16$ nm is presented in figure: 4.21B. The corresponding HRTEM image as shown in figure: 4.21C indicates the lattice space 0.24 nm, matching the space of the lattice (101) for the wurtzite ZnO at diffraction angle, $2\theta = 36.68^\circ$ in the XRD pattern. Single crystalline nature of the as prepared sample (Co-5) is indicated from its HRTEM image.

Fine structure and clear fringe pattern as observed in this image depicts that the surface of the nanocrystal is free from any defect. Few diffracting points as noticed from the SAED pattern (figure4.21D) of the sample are indexed for (101) and (100) planes.
Figure 4.21: (A) TEM micrograph of Co-5 sample, (B) An isolated nanorod with length ~70 nm and diameter ~16 nm. (C) High resolution TEM image: Beam focussed on the small crystallite showing no lattice defect with lattice spacing ~2.4 Å corresponding to (101) plane (D) Electron diffraction pattern obtained from the same section of the Co-5 sample.

(iii) **Energy dispersive X-ray study (EDX)**

Energy dispersive X-ray study (EDX) gives the signature of atoms of different materials contained in the sample along with their relative content. The EDX analyser produces a spectrum of the elements present in targeted areas of the samples allowing detectable elements to be quantified or mapped. We have performed EDX study for the samples ZnO, Co-1, Co-3 and Co-5 and is presented in figure: 4.22. During the spectrum processing, no extra peaks were omitted and all elements were analyzed.

In general EDX is studied as an additional option with SEM study. For EDX investigation, our materials were coated with carbon, for which carbon ‘C’ related peaks were observed in each spectrum.
Figure 4.22: Energy dispersive X-ray study (EDX) of the samples (a) ZnO, showing Zn and O related peaks and corresponding amount detected in few nanostructures. (b) Co-1, (c) Co-3 and (d) Co-5: showing Zn, O and Co related peaks with their relative amount.

Figure: 4.22(a) represents EDX spectrum for pure ZnO sample, where Zn and O related peaks gives the evidence of purity of the sample. On the other hand, in the spectrum as presented from Figure: 4.22(b) to 4.22(d), we have noticed the presence of Zn, O and Co related peaks. It is to be noted that EDX investigation was performed with only few particles of each sample, which indicated that cobalt ion was distributed in the entire sample. One can note from the tables cited along with each spectrum that the amount (wt %) of Co is increasing linearly from Co-1 to Co-5 sample. Moreover, a slight deviation from the fixed amount as given during synthesis is observed during the study. This may be due to the reasons, (a) Only a few particles were exposed to the beam, (b) We cannot neglect the instrumental error, (c) Agglomeration may occur due to the period between synthesis and characterization.
(iv) Fourier Transform Infrared spectroscopy (FTIR) study

In the FTIR spectrum, as presented in the figure: 4.23, for the bare ZnO and Co doped samples shows similar feature for all samples. Pure ZnO and Co-doped ZnO have wurtzite structure and are further supported by FTIR. Undoped ZnO, Co doped, similar spectra and the corresponding broadening peaks at 3434 cm$^{-1}$ is due to OH Stretching vibrations (from NaOH, used as a precursor), the band at absorption of atmospheric CO$_2$ on the metallic cations at 2383 cm$^{-1}$; the band at 1632 cm$^{-1}$ represents to C = O stretching vibrations; the band at 1407 cm$^{-1}$ indicates oxide from ZnO peak and the band observed at 955 cm$^{-1}$ is attributed to C-H band [264, 265]. It is well known that for metal-oxide band stretching the identical absorption peak should present near 500 cm$^{-1}$. In our case we have observed this identical absorption peak for all samples at 419 cm$^{-1}$.
In figure: 4.24, a comparative FTIR plot is presented where IR peak positions for all samples (ZnO, Co-1, Co-3, Co-5) corresponding to O-H, C, H, Co\(^2\), ZnO, C=O, C-H and metal-oxide stretching and bending are shown with respective dash lines. In addition to this, from the FTIR spectrum (figure: 4.22 and figure: 4.23) it has been observed that Co-3 sample exhibit zero %transmittance at 419 cm\(^{-1}\) due to Zn-O and Co-O stretching and bending. From this, it can be concluded that Co-3 sample behave differently compared to any other sample. Moreover, the ZnO sample shows slight deviation (~57 cm\(^{-1}\)) for the IR peak corresponding to C=O stretching. Except this slight deviation no other peak shift has been observed. No shift of IR peaks indicates that the FTIR result is in good agreement with that of XRD [266].
(v) Luminescence spectroscopy

Figure 4.25: Photoluminescence spectra of different samples: ZnO, Co-1, Co-3 and Co-5.

Photo luminescent properties of bare ZnO and Co doped (Co-1 to Co-5) ZnO is presented in figure: 4.25. Photoluminescence investigation, performed on the bare ZnO specimen, at an excitation wavelength of ~325 nm showed two main PL bands: one in the UV region (~399 nm) and the other broad peak in the green region (~513 nm). An associated lowering of intensity of the doped samples indicates suppression of radiative recombination process.

For Co-1 and Co-3 doped samples red shifting is associated with suppression of the UV and green band emission peaks. For Co-1 doped ZnO nanorods, suppressed but broadened UV emission peak centered at around 440 nm were observed.

The UV peak is red shifted and suppressed about 46% as compared with the bare ZnO sample, for the Co-3 doped sample the suppression decreases by about 48% and the peak width was broadened further. However, when Co-5 was doped no characteristic peak for near band edge emission was observed. Similar feature has been observed by Y. X. Wang et al. [267].
In general, the intensity ratio of UV emission band to visible emission band is considered to be as an indicator of the crystallinity of ZnO materials [268]. For better crystallinity this ratio should be higher. In a similar work done by Z. W. Zhao and B. K. Taya et al. [269] have found decreased ratio of UV emission band to visible emission band which indicated inferior quality of corresponding sample. In our study the Co doped ZnO sample exhibited relatively lower peaks in the visible range while relatively higher peaks at UV region. This leads to increased ratio of UV emission to visible band emission, which in turn suggests good crystallinity of our samples. Generally higher order peak in the visible region arises due to defect states associated with oxygen vacancies or Zn interstitials or other defects induced by the dopant or dopant-related defects in the samples which further support the higher intensity in absorbance [270].

(v) **UV-Visible Spectroscopy**

UV-Visible spectroscopy is an important tool to determine band gap of as synthesized samples. The onset of absorption of each spectrum gives the signature of enhancement of individual band gap of the sample due to quantum confinement effect. Comparative reflectance spectra (%) obtained from UV-Vis study for all samples are presented in figure: 4.26. Bare ZnO indicates highest reflectance (%), while reflectance (%) of Co doped samples decreases with increasing Co concentration. Optical reflectance spectra for all samples reveal strong quantum confinement with increased band gap energies. The increase in the diffuse reflectivity with a definite linear region of the greatest slope is attributed to an exponential drop in the absorption coefficient. The onset of this exponential drop had been suggested as a more universal method of determining absorption edges from which the band gap can be deduced. For calculation of absorption edge a linear fit was given to the linear part of the increase in reflectivity [271].
Figure 4.26: Comparative UV-Vis spectra showing % Reflectance of different samples: ZnO, Co-1, Co-3 and Co-5.

Band gap of all Co doped and bare ZnO were calculated from the intersection of two linear portions of each spectrum which showed blue shift. For bare ZnO (figure: 4.27a) the enhancement is small (~0.02 ev), the enhancement energies estimated for (Co-1 to Co-5) were 0.05 eV, 0.04 eV and 0.06 eV respectively (Figure:4.27b to 4.27d). The band gap of all Co doped samples exceeds than pure ZnO, this feature agrees with the value reported earlier [272-275]. Enhancement of energy due to quantum confinement of the nanostructures has been indicated in the UV-Visible study.
Figure 4.27: Band gap is estimated from the absorption edges at the onset of exponential drop from the optical reflectance spectra for the samples (a) ZnO, (b) Co-1, (c) Co-3 and (d) Co-5.

4.3 Ni doped ZnO

Among the transition metal, Ni is an important dopant; since, Ni$^{2+}$ (0.69 Å) has the same valence as Zn$^{2+}$ and its radius is close to that of Zn$^+$ (0.74 Å), so it is possible for Ni$^{2+}$ to replace Zn$^{2+}$ in ZnO lattice. So far, the influence of Ni doping in the ZnO lattice host has been reported by several groups. Doping of Ni in ZnO matrix has been done by several techniques [276,277], we have fabricated Ni doped ZnO nanopstructures by adopting the same solid state chemical reaction route as described in chapter-2. The concentration of Nickel
acetate and Zinc acetate were varied within the range 1 at% Ni - 5 at% Ni and accordingly indexed as Ni-1, N-3 and Ni-5. In this chapter the structural and optical properties will be focussed. XRD. EDS. HRTEM were carried out to investigate structural properties, while PL and UV-Vis. Spectroscopy study were performed to investigate optical properties of Ni:ZnO nanostructures. XRD study ruled out the existence of additional phases in the sample due to Ni doping. HRTEM study showed the clear evidence of formation nanorods for Ni:ZnO system.

(i) X-Ray diffraction study

The XRD spectrum of Ni doped and undoped ZnO is presented in figure: 4.28. Like Mn and Co, Ni doped samples (Ni-1, Ni-3 and Ni-5) also exhibit hexagonal wurtzite structure of ZnO in their XRD patterns. The XRD pattern reveals the absence of any secondary phases due to Ni doping. Compared to undoped specimen Ni doped samples exhibit peak shift in the XRD spectra. The XRD peak shift for the Ni:ZnO system can be more clearly visualized from the figure: 4.29, which is obtained by plotting from the XRD data within the ‘2θ’ range 31°-37° for the reflections by the planes (100), (002) and (101).

![XRD pattern for the samples (ZnO, Ni-1, Ni-3 and Ni-5)](image)

**Figure 4.28:** XRD pattern for the samples (ZnO, Ni-1, Ni-3 and Ni-5)
Figure 4.29: Enlarged view of the XRD pattern for the samples (ZnO, Ni-1, Ni-3 and Ni-5) within diffraction angle (2θ) range 31° - 37° corresponding to the reflecting planes (100), (002) and (101), showing clear peak shift.

Table 4.9: ‘2θ’ values corresponding to the peak positions for diffracting planes (1 0 0), (0 0 2) and (1 0 1) for the samples (ZnO, Ni-1, Ni-3 and Ni-5)

<table>
<thead>
<tr>
<th>Plane</th>
<th>ZnO</th>
<th>Ni-1</th>
<th>Ni-3</th>
<th>Ni-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1 0 0)</td>
<td>31.68</td>
<td>31.87</td>
<td>31.72</td>
<td>31.83</td>
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<tr>
<td>(0 0 2)</td>
<td>34.32</td>
<td>34.5</td>
<td>34.39</td>
<td>34.48</td>
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<tr>
<td>(1 0 1)</td>
<td>36.14</td>
<td>36.36</td>
<td>36.22</td>
<td>36.33</td>
</tr>
</tbody>
</table>

The values for ‘2θ’ at the peak positions corresponding to the diffracting planes (1 0 0), (0 0 2) and (1 0 1) for the samples (ZnO, Ni-1, Ni-3 and Ni-5) are presented in the table: 4.9. Different values for ‘2θ’ corresponding to a particular peak clearly indicates the peak shift. The shift of peaks for the Ni doped samples take place towards the higher value of ‘2θ’ from the peak positions for pure ZnO sample. The change of XRD peak can be attributed for the change of size and strain of the Ni:ZnO nanostructures due to Ni doping.
Table 4.10(a): Lattice spacing for the diffracting planes (1 0 0), (0 0 2) and (1 0 1) for the samples (ZnO, Ni-1, Ni-3 and Ni-5) estimated from their respective ‘2θ’ values as shown in table: 4.9.

<table>
<thead>
<tr>
<th></th>
<th>ZnO</th>
<th>Ni-1</th>
<th>Ni-3</th>
<th>Ni-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1 0 0)</td>
<td>2.82</td>
<td>2.81</td>
<td>2.82</td>
<td>2.8</td>
</tr>
<tr>
<td>(0 0 2)</td>
<td>2.61</td>
<td>2.6</td>
<td>2.6</td>
<td>2.6</td>
</tr>
<tr>
<td>(1 0 1)</td>
<td>2.48</td>
<td>2.47</td>
<td>2.48</td>
<td>2.47</td>
</tr>
</tbody>
</table>

Table 4.10(b): Estimated crystallite size of as synthesized nanostructures for the samples (ZnO, Ni-1, Ni-3 and Ni-5) estimated from FWHM and 2θ values corresponding to (101) diffracting plane of each sample.

<table>
<thead>
<tr>
<th></th>
<th>FWHM (w) (degree)</th>
<th>2θ (degree)</th>
<th>crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>.53254</td>
<td>36.14</td>
<td>15.51</td>
</tr>
<tr>
<td>Ni-1</td>
<td>.55806</td>
<td>36.36</td>
<td>14.81</td>
</tr>
<tr>
<td>Ni-3</td>
<td>.54001</td>
<td>36.22</td>
<td>15.30</td>
</tr>
<tr>
<td>Ni-5</td>
<td>.58630</td>
<td>36.33</td>
<td>14.10</td>
</tr>
</tbody>
</table>

The lattice spacing ‘d’ for all samples were estimated from their respective ‘2θ’ values corresponding to the diffracting planes (1 0 0), (0 0 2) and (1 0 1) of the nanocrystals which are shown in the table: 4.10(a). From the table ‘d’ values were utilizes to estimate the lattice parameters ‘a’ and ‘c’ as 3.237 Å and 5.2 Å respectively according to the equation 4.1. For determination of size of the nanostructures, FWHM and 2θ values corresponding to the most intense peak (1 0 1) were considered for the Scherer formula (equation: 3.2) and the respective values are presented in the table: 4.10(b). From the estimated size,
we have observed that the crystallite size of the Ni doped ZnO slightly decreases due to Ni doping compared to undoped specimen. The size of the nanocrystals lies within the range 14.1 nm – 15.51 nm.

The size and strain of the nanostructures were also estimated from Williamson-Hall (W-H) plot as shown in figure: 4.30 for the sample Ni-5. In this plot we have considered first six peaks of the XRD pattern. From the intercept (\(\sim 0.0099\)) and the slope (\(\sim 7.488 \times 10^{-4}\)) of the plot the average size and strain of the Ni-5 nanostructures were estimated. In a similar way the size and strain of other samples were also estimated and presented in the table 4.11.

![Williamson-Hall plot](image)

**Figure 4.30:** Williamson- Hall plot for the sample Ni-5, from the slope and intercept of the straight line strain (7.488 \(\times 10^{-4}\)) and size (13.9 nm) of the Ni-5 nanostructures were estimated.

**Table 4.11:** Crystallite size and strain estimated from Williamson- Hall plot for the samples (ZnO, Ni-1, Ni-3 and Ni-5)

<table>
<thead>
<tr>
<th>sample</th>
<th>size (nm)</th>
<th>strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>16.17</td>
<td>2.58 (\times 10^{-3})</td>
</tr>
<tr>
<td>Ni-1</td>
<td>15.75</td>
<td>1.14 (\times 10^{-3})</td>
</tr>
<tr>
<td>Ni-3</td>
<td>15.90</td>
<td>1.44 (\times 10^{-3})</td>
</tr>
<tr>
<td>Ni-5</td>
<td>13.90</td>
<td>0.75 (\times 10^{-3})</td>
</tr>
</tbody>
</table>
From the above investigations it has been noticed that with decreasing size of the nanostructures the strain also decreases. The highest strain was exhibited by ZnO nanorod with size 16.17 nm, while the lowest strain was shown by Ni-5 with size 13.9 nm. The particle size, as obtained from both XRD data is in agreement with the sizes as calculated from W-H plot. This may be due to the limitations of Scherrer formula where particle strain is not considered.

(ii) Photoluminescence property

![Photoluminescence graph](image)

**Figure 4.31:** Luminescence response of Ni-3 nanorods and nanoparticles.

Few studies on Ni doped ZnO have been reported and several results showed that the luminescence properties of ZnO were changed after doping of Ni [278–281]. Photoluminescence response of Ni-3 sample is shown in figure: 4.31 The intense peak at 404 nm (~3.04 eV) is attributed due to the typical band edge (near ultra violet) emission peak, in addition to this other suppressed peaks are observed at 463 nm (~2.68 eV) and 511 nm (~2.4 eV), which are contributed due to defect states for e.g. the green peak (~511 nm) is due to substitution of O at Zn position [282,243]. The suppressed emission peak in the green region may be attributed due to less defect in the crystal structure of the Ni:ZnO system.

Figure: 4.32 shows the individual optical transmittance spectra for (A) ZnO, (B) Ni-1, (C) Ni-3 and (D) Ni-5 nanostructures. The observed transmittance (%) for the samples was recorded in between 58% to 73% in the UV region. The
sample Ni-3 exhibited highest transmittance (73%), while the Ni-1 sample exhibited the lowest transmittance (58%). The transmittance (%) for all samples in the visible region was recorded below 2.5%. The energy gaps (E_g) for the nanorods has been estimated from the spectra using the relation for a direct transition [283], which are 3.453 eV, 3.425 eV, 3.429 eV and 3.426 eV for the samples ZnO, Ni-1, Ni-3 and Ni-5 respectively. The comparative transmittance (%) spectra for all samples can be visualized from the figure: 4.33

Figure 4.32: % Individual transmitted spectra for (A) ZnO, (B) Ni-1, (C) Ni-3, and (D) Ni-5.

Figure 4.33: % Compared transmitted (%) spectra for (A) ZnO, (B) Ni-1, (C) Ni-3, and (D) Ni-5. The sample Ni-3 shows highest transmittance (%), while the sample Ni-1 shows minimum transmittance (%).
In the reflectance spectra, it has been observed that due to the strong quantum confinement effect all bare and Ni doped samples exhibited blue shift. There is a slight but noticeable variation in band gap energies among the samples. This slight variation is attributed due to their similar (almost) crystalline sizes.

(iii) Transmission electron microscopy study

(a) Ni-1

![Figure 4.34](image-url): (A) TEM image of Ni-1 showing formation of elongated nanostructures, (B) HRTEM image of two isolated nanorods, (C) High resolution image of an isolated nanorod with lattice spacing 2.2 Å. (D) SAED pattern focused on the nanorod shown in (C).
Formation of elongated nanostructures has been depicted by the TEM study which is presented in the figure: 4.34(A). TEM study confirmed the formation of nanorods with average length 60 nm and diameter 15 nm. High resolution TEM image of an isolated nanorod is shown in figure: 4.34(B) and 4.34(C). Clear lattice fringe indicates good crystalline nature of the sample. The lattice spacing ~2.2 Å corresponds to the crystal growth plane (102). SAED pattern (figure: 4.34D) shows uniform distribution of lattice points. Two inner rings corresponds to the diffracting planes (101) and (002).

(b) Ni-3

**Figure 4.35:** (A) TEM image of Ni-3 showing formation of elongated nanostructures, (B) High resolution TEM image of few Ni-3 nanorods, (C) SAED pattern focused on an isolated nanorod as shown in fig. (D) with lattice spacing ~2.46 Å corresponding to the plane (101).

HRTEM images of Ni-3 sample are presented in figure: 4.35. Most of the nanostructures are agglomerated and elongated in nature (figure: 4.35A). Using standard software the length and diameters of few distinct nanorods were
measured and average length and diameter were estimated 53 nm and 15.3 nm respectively. With increased resolution, clear formation of few Ni-3 nanorods were observed, which are shown in figure: 4.35(B). SAED pattern focussed on an isolated nanorod is presented in figure: 4.35(C), in which few lattice points corresponds to the diffracting planes (101), (002) and (100). The HRTEM image of an isolated nanorod with average length 25 nm and diameter 6 nm is shown in figure: 4.35D, the observed lattice spacing ~2.46 Å corresponds to the plane (101). It indicates the growth plane of the crystal is along (101) plane.

(c) Ni-5

Figure 4.36: Figure (A) and (B) depicts formation of nanorods with av. length 44.5 nm and av. Diameter 12 nm. For the sample Ni-5, (C) SAED pattern, Inset : an isolated nanorod of av. length 56 nm and av. diameter 14 nm, (D) HRTEM image, when beam was focussed on the isolated nanorod; showing lattice spacing 2.2 Å.
HRTEM study revealed the formation of nanorods with average length 44.5 nm and diameter 12 nm as observed in figure: 4.36A and 4.36B. Figure: 4.36C represents the SAED pattern focussed on the isolated nanorod of av. length 56 nm and av. diameter 14 nm (inset of figure: 4.36C). The lattice spacing 0.22 nm has been observed from the HRTEM image (figure: 4.34D) of the isolated nanorod as shown in the inset of figure: 4.36C. Clear lattice fringe pattern can be attributed due to the high crystalline nature of the as synthesised sample. In case of Ni-5, we have observed a large number of isolated nanorods. In this concentration of Ni the growth plane was confirmed along the (101) plane.

4.4 Significant observations

4.4.1 Structural

- It was observed that along with decrease in size, the strain also decreases. Thus, size and strain of the nanostructures can be simultaneously manipulated by changing doping concentration.
- HRTEM study for all samples exhibited clear fringe patterns; it was attributed due to high crystalline nature of the as-synthesised samples. The growth direction of the bare ZnO was found along (102), while for all TM doped samples it was found along (101) plane. In case of bare ZnO, we have noticed several lattice distortions on the surface of the nanocrystallites, this may play a significant role to influence optical and magnetic properties of the NSs.
- A significant change in lattice parameters (a and c) has been investigated from the structural study of the as-synthesised NSs. Increasing lattice parameters have been observed as a result of Mn doping. Out of three samples Mn-3 doped ZnO showed highest values of lattice parameters (a and c).
Pure ZnO and TM-doped ZnO have wurtzite structure and are further supported by FTIR. Undoped ZnO, TM doped ZnO exhibited similar FTIR broadening peaks due to stretching and vibration of different elements present.

The identical IR peak for metal-oxide band stretching is observed near 500 cm\(^{-1}\) for all bare and TM doped ZnO. It was noticed that all samples exhibited IR peak near 500 cm\(^{-1}\), but from the comparative FTIR plot it was evidenced that compared to other Mn:ZnO samples, Mn-3 sample exhibited minimum %transmittance at ~500 cm\(^{-1}\) due to Zn-O and Mn-O stretching and bending. Observing the intense nature of the IR peak broadening for the sample Mn-3, it can be speculated that TM concentration can influence to shift IR peak positions.

### 4.4.2 Optical

In the undoped ZnO specimen, mainly two asymmetrically broadened PL responses were observed: the first, in the UV region and the other in the green region. The UV-band is attributed to the near band edge emission, while the green band is reasonably attributed to the emission which has originated due to the intrinsic defect states of ZnO, such as oxygen vacancy, zinc interstitial and oxygen antisite. An associated lowering of intensity of the doped samples indicates suppression of radiative recombination process.

In case of Co:ZnO system, the UV peak is red shifted and suppressed about 46% as compared with the bare ZnO sample, for the Co-3 doped sample the suppression decreases by about 48% and the peak width was broadened further. However, when Co-5 was doped no characteristic peak for near band edge emission was observed. This investigation indicates that Co concentration is playing significant role in displaying PL intensities in both UV and visible region.
• The suppressed emission peak as observed in the green region exhibited by the PL spectra of Ni:ZnO system may be attributed due to the presence of less defect in the Ni:ZnO crystal structure.

• In the UV- Visible study, it was observed that the sample Ni-3 exhibited highest transmittance (73%), while the Ni-1 sample exhibited the lowest transmittance (58%). The transmittance (%) for all samples in the visible region was recorded below 2.5%. It opens a wide possibility to use the sample in transparent TM:ZnO DMS.

• From the %Reflectance spectra of Co:ZnO system, it was noted that with increasing Co concentration the %Reflectance decreases.

• It has been observed that due to TM doping, the intensities of UV peaks in PL spectra get lowered and additional defect related peaks were generated. It reveals substantial influence in the PL intensities due to TM doping in ZnO.