CHAPTER 4

Studies of ZnO Based DMSs Nanostructures Synthesized by Chemical Doping Routes

Here, we have tried and developed an easy approach toward the synthesis of long and uniform Zn$_{1-x}$TM$_x$O Nanostructures by a solvothermal and sol-gel route at ambient conditions. The structural characterization and phase identification are carried out by XRD, XPS, FESEM, TEM and EDS analysis. Further, the oxidation state of the TM dopants inside the ZnO lattice is revealed by XPS data analysis. The magnetic properties are measured by vibrating sample magnetometer (VSM). Photoluminescence (PL) and UV-Vis absorption measurements are done to check the doping related changes in band edge emission and absorption spectra, the kind of defects present and their changes with doping. Systemic structural, magnetic, and optical properties reveal that both the nature of the defects as well as TM$^{2+}$ ions are significant ingredients to attain high moment as well as high ordering temperature in the 1-dimensional ZnO NRs. These findings provide a better insight into the underlying mechanisms of high temperature ferromagnetism in Zn$_{1-x}$TM$_x$O NRs, magnetic interaction is quantitatively analysed and explained using a bound magnetic polaron model and expected to arise from the intrinsic exchange interaction of Co ions and V$_{Zn}$, O$_i$ related defects.
4.1 **Investigations on Co doped ZnO Nanostructures synthesized by a solvothermal route**

### 4.1.1 Highlights

Here, we have developed an easy approach toward the synthesis of long and uniform Zn$_{1-x}$Co$_x$O NRs by a solvothermal route at ambient conditions. The structural characterization and phase identification are carried out by XRD, XPS, FESEM, TEM and EDS analysis. Further, the oxidation state of the Co dopants inside the ZnO lattice is revealed by XPS data analysis. The magnetic properties are measured by vibrating sample magnetometer (VSM). Photoluminescence (PL) and UV-Vis absorption measurements are done to check the doping related changes in band edge emission and absorption spectra, the kind of defects present and their changes with doping. Systemic structural, magnetic, and optical properties reveal that both the nature of the defects as well as Co$^{2+}$ ions are significant ingredients to attain high moment as well as high ordering temperature in the 1-dimensional ZnO NRs. These findings provides a better insight into the underlying mechanisms of high temperature ferromagnetism in Zn$_{1-x}$Co$_x$O NRs, magnetic interaction is quantitatively analysed and explained using a bound magnetic polaron model and expected to arise from the intrinsic exchange interaction of Co ions and V$_{Zn}$ O$_i$ related defects.

### 4.1.2 Result and Discussions

#### 4.1.2.1 Microstructure and Morphology

Figure 4-1(a) shows a typical XRD pattern for the Zn$_{1-x}$Co$_x$O (x= 0, 0.05, 0.07) samples. All the diffraction peaks like (100), (002), (101) correspond well to the hexagonal wurtzite ZnO crystal structure, hence it shows that Zn$_{1-x}$Co$_x$O samples have single-phase hexagonal wurtzite structure, indicating good quality doping of Co ions throughout the ZnO lattice. It should be noted that no other secondary peaks related to Co clusters or other oxides of Co ions are observed in the XRD pattern. Also it shows clear shifting of the diffraction peaks towards the higher angle for the three most intense peaks of the
XRD pattern. The lattice parameters \(a\), \(c\) and the cell volume ‘\(v\)’ are calculated from the XRD peak positions and we find that lattice parameters decrease with doping; as a consequence, the lattice volume decreases with increasing doping concentration (details: in Table 4-1). This is consistent with the fact that the ionic radius of Co\(^{2+}\) is 0.58 Å, whereas that of Zn\(^{2+}\) is 0.60 Å.\(^{235}\) The shifting of XRD pattern and corresponding decrease of the lattice parameters suggest that Co\(^{2+}\) ions are successfully incorporated into the ZnO lattice at the Zn\(^{2+}\) sites.

![Figure 4-1](image)

**Figure 4-1** XRD pattern of Zn\(_{1-x}\)Co\(_{x}\)O (\(x = 0, 0.05, 0.07\)) samples, the corresponding diffraction peaks for ZnO are marked in the pattern.

The general morphologies of Zn\(_{1-x}\)Co\(_x\)O samples are shown in Figure 4-2. Nearly spherical nanoparticles (NPs) are formed for the undoped ZnO (see inset of Figure 4-2(a)) and NRs are formed for the high concentration of Co doped ZnO samples (Figure 4-2(b)). Note that low concentration of Co doped sample shows spherical shaped NPs. The difference of the crystal growth velocities in different directions is expected to cause the change of morphologies. The surface energies are different for different crystal faces for ZnO nanocrystals, C-axis exhibits the highest growth rate due to the structure and surface anisotropy.\(^{263}\) Further, the presence of Co ions in the precursor solution induces a thermodynamical barrier, which retards the formation of the nucleation, as well as the growth rate of the primary nuclei (Zn\(^{2+}\)). Effectively Co\(^{2+}\) ions have more time to deposit uniformly on the nuclei along the c-axis, as a result c-axis growth has a faster rate than...
that along other directions. Meanwhile, for pure ZnO and lower doping concentrations
the intermediate Zn(OH)$_2$ dissolves rapidly due to the relatively low energy barrier,
giving a high concentration of Zn$^{2+}$ ions in the precursor, resulting irregular crystal
formation. As the doping concentration increases, the aspect ratio of length to diameter
increases and it leads to the long length of the NRs. Similar findings of increasing
NR/NW length with c-axis doped ion accommodation have been observed for Ce-doped
ZnO NRs and Co doped ZnO NRs. This accommodation of Co ions along the C-axis also
facilitate in FM ordering in the Co doped ZnO NRs. Figure 4-2(a) shows FESEM image
of the 5% Co doped ZnO nanoparticles (NPs) of average sizes as 50-80nm, inset shows
undoped ZnO NPs of average size of 300nm. Figure 4-2(b) shows TEM images of the 7%
Co doped ZnO NRs.
Figure 4-2 (a) FESEM image of the 5% Co doped ZnO NPs, inset shows undoped ZnO NPs with relatively larger size. (b) TEM image of the 7% Co doped ZnO NRs, (c) SAED pattern & (d) HRTEM lattice image of the a single 7% Co doped ZnO NR showing c-axis growth. (e) EDS spectra of a single Co doped ZnO NRs, showing presence of Co inside the ZnO lattice.

TEM micrograph reveals clearly the formation of good quality Co doped ZnO NRs having a smooth surface with diameter of 50-90 nm and length of 0.3-0.6 µm. HRTEM lattice images and the SAED pattern illustrate that all the NRs are single crystalline. The d-spacing of the crystal plane is calculated as 2.6Å showing the preferable crystal growth plane (002). Energy-dispersive X-ray spectroscopy (EDS) analysis on a single NR confirms the presence of Co atoms in the ZnO matrix. EDS analysis shows 2.36 atomic % of Co doping in the ZnO NRs, corresponding to the 7 molar percentage of the initial cationic precursor, with consideration of the accuracy of the EDS analysis. We confirm
the presence of substituted Co ions inside the ZnO matrix by XPS analysis, as discussed below.

### 4.1.1.3 Local structure of dopants and defects

Figure 4-3 shows the XPS spectra of (a) Zn 2p, (b) Co 2p and (c) O 1s states of pure and 7% Co-doped ZnO NRs. Two strong peaks centered on 1021.54eV and 1044.61eV (Figure 4-3(a)), which are in agreement with the binding energies of Zn 2p\(3/2\) and Zn 2p\(1/2\) respectively, with a spin-orbital splitting of 23.07eV, confirm that Zn is present as Zn\(^{2+}\).

The Co 2p\(3/2\) and Co 2p\(1/2\) core levels are observed at 780.10eV and 795.55eV (Fig 3b) respectively, with a spin-orbital splitting of 15.45eV, indicating that Co ions have a valence of 2+ in the Co-doped ZnO NRs. Moreover, the presence of Co as metal cluster in the Co-doped NRs can be ruled out because the differences of the 2p\(3/2\) and 2p\(1/2\) for the metallic state should be 15.05 eV.\(^{42, 264}\) These results demonstrate that a proper substitution of Co\(^{2+}\) ions in the host ZnO lattice can be achieved via the present route without any impurity oxide phase. The O1s peak in the surface is coherently fitted by three Gaussian components, centered at 530.6, 531.3 and 532.6eV, respectively, as shown in Figure 4-3(c) and (d) for the undoped and doped samples. The lower binding energy peak of the O 1s spectrum around 530 eV comes from the binding between O\(^{2-}\) and Zn\(^{2+}\) (or substitutionalCo\(^{2+}\)) ions in the hexagonal ZnO.\(^{243}\) The higher binding energy peak around 531 eV corresponds to the oxygen-deficient regions within the matrix of ZnO.\(^{244}\) Next higher binding energy peak at 532.6eV usually corresponds to absorbed hydroxyl group (-OH) on the surface (preferable at the vacancy sites) of the NRs/NPs.\(^{42}\) From the relative intensity of the XPS peaks it is expected that presence of V\(_o\) and OH group is very less in all the samples. This is consistent with the PL findings. Also we have shown the detail elemental analysis of Zn, O and Co in Table 4-1, calculated from the XPS spectra. It indicates that the percentage O is higher in all the samples and thus presence of Zn vacancy (V\(_{Zn}\)) and O interstitials (O\(_i\)) are expected. Further, insertion of Co ions inside ZnO matrix is more efficient around 6.3% for the 7 % Co doped ZnO NRs enhancing FM ordering, supporting the importance of higher concentration of doping along the axial accommodation.
Figure 4-3 XPS spectra of the (a) Zn $2p_{3/2}$ and $2p_{1/2}$ states and (b) Co $2p_{3/2}$ and $2p_{1/2}$ states of 7% Co doped ZnO NRs, (c) O 1s states of undoped ZnO NPs and, (d) O 1s states of 7% Co doped ZnO NRs.

4.1.1.4 Optical Properties

The UV-Vis absorption spectra have been used primarily to find possible modification in the energy band structure of ZnO after Co doping. Figure 4-4(a) shows the UV-Vis absorption spectra taken at RT for the undoped and doped samples. Observed change in
absorption peak due to doping indicates a change in the band structure. It is showing blue shift in the UV-VIS absorption edge. Also we have used the Tauc’s plot \((a \nu)^2 \text{ versus } \nu\) showing the bandgap behavior, as shown in the insets of Figure 4-4(a) for the band gap calculation. Extrapolation of straight portion of the Tauc’s plot shows that the band energy is in the intermediate defect states, as absorption from the high density defect related states are dominating over the band edge absorption. The observed blue shift indicates a band gap widening in the Co doped ZnO NSTs due to the incorporation of Co ions. Since the dimensions of the synthesized NSTs are larger than excitonic Bohr radius in ZnO, size effect is unlikely to cause the observed blue shift. The \(sp-d\) exchange interaction between the ZnO band electrons and localized \(d\)-electrons associated with the doped Co\(^{2+}\) cations may cause the change in such band structure.\(^{18, 57}\) The interaction leads to a modification in the energy bands.

PL studies for the pure ZnO and Co doped ZnO samples at room temperature reveal strong UV emission peak and a broad green-yellow emission band ranging from 450 nm to 730 nm, as shown in Figure 4-5(b-d). Observed broad PL peaks in the UV as well as in the visible region indicate existence of multicomponents which are extracted after fitting with multiple Gaussian functions. The obtained individual peak positions are tabulated in Table 4-2. Undoped ZnO NPs exhibit an excitonic emission band centered on 3.25eV (Peak I). Co-doped ZnO NRs show a systematic blue shift in the above mentioned UV emission with increase of Co doping concentration. The near band-edge transition is generally attributed to the recombination of free excitons. The blue shift of the UV emission peak has been attributed to the strong exchange interaction between the \(d\)-electrons of Co ions and the s, p electrons of the host band. Along with the free excitonic UV emission, one additional peak (Pak II) centered at 3.15eV is observed from all of the samples near the tail region of the above UV emission. This emission may be due to the recombination of free carriers at band tail states of ZnO.\(^{265}\) Band tail states are caused by the presence of lattice disorder/defects on the surface of NSTs and in the present case, Co doping induced lattice disorder is expected.
Next, PL peak is the green emission peak (Peak III) centered on ~2.38 eV, which is commonly observed in the ZnO NSTs. The origin of this peak is considered as the presence of $V_{Zn}$ or antisite oxygen ($O_{Zn}$) related defects. Other sources, such as singly ionized oxygen vacancy states ($O^{+}$) on the surface of ZnO NSTs might also be possible. In a recent review, Janotti et al. presented strong arguments in favor of the Zn vacancies ($V_{Zn}$) instead of the oxygen vacancies ($V_{O}$) being the origin of the green luminescence. Also, as our samples are O rich, as found from XPS and EDS analysis, the presence of $V_{O}$ is expected to be very less. The intense yellow emission (Peak IV) is observed from all of the samples, centered on ~2.11eV. This emission peak may be attributed to the recombination process associated with the oxygen interstitials ($O_{i}$). Also there might be contributions from hydroxyl groups, as presence of small intensity $V_{O}$ and hydroxyl group are seen by XPS measurements. Most of the theoretical calculations agree that $V_{Zn}$ and $V_{O}$ are the lowest energy defects, while the zinc and oxygen interstitials to be high in energy. Generally the defects which are favored under Zn-rich conditions ($V_{O}$, $Zn_{i}$) act as donors, while those favored under O-rich conditions ($V_{Zn}$, $O_{i}$) act as acceptors.

The peak at around 1.81eV in Co-doped ZnO NRs signify the characteristic transition of the high-spin Co$^{2+}$ impurity level, namely $4T_{1}(P)\rightarrow 4A_{2}(F)$ d-d internal transition. Generally, the orange-red emission (1.81eV) is considered as the evidence of the incorporation of Co$^{2+}$ ions in ZnO crystal lattice. Here doped cations might provide competitive pathways for recombination, nonradiative process or charge transfer process which results in quenching of the overall green-yellow emission. Also participation of the defects in FM interaction as bound states might be the reason for decrease of defect related emission in the doped NR samples. Similar reduction effects of luminescence have been observed previously in nanocrystals. Thus doping of Co$^{2+}$ ions also can be used to tune the visible PL properties of the ZnO NSTs and this intern affects the magnetic properties of the doped ZnO NRs.
Figure 4-4 (a) UV-Vis absorption spectra for the undoped and Co doped ZnO samples, showing blue shift of band edge absorption with doping. (b), (c) and (d) show PL spectra of undoped, 5%, 7% Co doped ZnO samples respectively. Strong UV and visible PL bands related to defects can be seen. Different PL peaks (I up to V) are fitted with Gaussian functions. Note the scaling factors in respective data to enable comparison of intensity.

4.1.1.5 Magnetic Properties

We observe distinct ferromagnetic behavior at and above RT in the doped Zn$_{1-x}$Co$_x$O samples measured by VSM. Figure 4-5(a) shows the magnetic hysteresis (M-H) loop with magnetic moment of 1.83 emu/g for 2T field, coercivity of 53 G and retentivity of 160 memu/g for the 7% Co doped ZnO NRs, measured at RT. We have measured the M-H loop several times to check the reproducibility and we have found no alteration of moment with time, implying the intrinsic nature of the FM in the ZnCoO NRs. Further the low temperature M-H measurement we find symmetric nature in the coercivity and hysteresis loop. Note, that the magnetic moment value for the Co doped ZnO NRs, as observed here, is relatively high as compared to the other findings for the ZnO based
DMS NRs/NWs. Figure 4-4(b) shows the temperature dependent magnetization for the same sample in the temperature range 300-573 K for 1500 G field. From the differential plot of the M-T curve we obtain the $T_c$ as 398 K. A tiny hump around 380K can be seen, indicating some secondary phase might be present but its contribution is negligible, since it vanishes with slight increase in temperature. Also all other characterizations have shown absence of any secondary phases. $T_c$ value for Co metal is 1300 K which implies that the observed FM cannot be due to the Co clusters or it’s other phases. As seen from the M-T curve, at higher temperature the magnetization shows a rapid decrease with temperature, indicating continuous transition from FM ordered state to paramagnetic (PM) disordered state, supporting single phase nature of the NRs. Note that, we observe relative low moment value (70memu/g) and coercivity as185 G for the 5% Co doped ZnO samples with the presence of the hysteresis loop. As its growth and the morphology are entirely different, with spherical shaped NPs, the low moment occurs may be due to specific morphology and associated defect structures. In our earlier work of Co doped (low concentration) ZnO NWs synthesized by vapor deposition, we found very low magnetic moment and its nature as PM.

Also, despite the presence of intrinsic defects no measurable magnetic moment is observed in the undoped samples. This confirms that defects alone are not sufficient to account for the observed strong FM in case of our samples. Probably the particular slow reaction synthesis promotes the insertion of Co ions inside the ZnO matrix helping long range FM interaction. We believe that the C-axis growth of the NRs with the axial accommodation of Co ions and the presence of $V_{Zn}$, $O_i$ related defects promote the FM interaction to attain such a high moment value in $Zn_{1-x}Co_xO$ NRs. Other groups have reported about the role of axial accommodation of Co ions and size dependence due to axial growth of Co doped ZnO NRs for the enhancement of RTFM.
4.1.3 Possible FM interaction and its origin

Our systematic study shows that formation of defect ($V_{Zn}$, $O_i$) mediated BMPs and their percolation is one of the most promising candidates for the observed FM. To understand the suitability of the BMP model, we attempt to fit the $M$ versus $H$ data using the BMP model.\(^{168}\)

The formula used for the fitting of BMP model:

$$M = M_0 L(x) + \chi_m H$$  \hspace{1cm} (1)

The details of the Eq. (1) are mentioned earlier. We have analyzed the $M$–$H$ curve by using Eq. (1). The experimental data along with fitted data are shown in Figure 4-6 for the 7% Co doped ZnO NRs. The fitted data closely follows the experimental data and the
fitted parameters are tabulated in Table 4-3. The spontaneous moment per BMP, $m_{\text{eff}}$, is found to be of the order of $10^{-17}$ emu. By assuming $m_s = m_{\text{eff}}$, we have estimated the concentration of BMP to be of the order of $10^{17}$ cm$^{-3}$ considering the effective Bohr radius of the BMPs as 0.76 nm (see Table 4-3).

**Figure 4-6** Initial curve (0-H$_{\text{max}}$) of the M-H plot is fitted with BMP model (Eq. (1)) for the 7% Co doped ZnO NRs. Symbols are for experimental data and the solid line is a fit with the BMP model. Extracted parameters are shown in Table 4-3.

However, this number is relatively small compared to the necessary concentration of $10^{20}$ cm$^{-3}$ in order to have long range percolation. Thus, the calculated low concentration of BMPs cannot fully account for the observed high magnetic moment in the doped ZnO. Also, as the initial M-H curve has not reached up to saturation value due to limitation of magnetic field, thus BMP fitting is having a limitation on the BMP parameters. It would lead to higher concentration of BMPs for the fitting up to saturation value, as observed in our earlier work. Further, presence of O$_i$, in our samples is favorable to exhibit presence of holes due to the activation of acceptor states. The activation of acceptor states for hole formation might be partly responsible for the enhancement in HTFM in the Co doped ZnO NRs, and it is consistent with the Dietl’s prediction of hole mediated ferromagnetism in Mn doped ZnO system. Also defect related surface spins might contribute partly for the observed FM in the Co doped ZnO NRs. Due to a large surface
area, a lot of defect modes have been found in the XPS and PL spectra. Sanchez et al. have reported that the uncompensated surface spins enhance the spin polarization induced by substitute Co ions and even in the absence of magnetic ions, it might promote the formation of p-derived extended magnetic states.\textsuperscript{128}

Figure 4-7 shows a schematic diagram of BMP percolation with respect to the presence of $V_{\text{Zn}}$ $O_i$ defects and distribution of Co ions in the ZnO lattice. It explains that defect mediated BMP formation within its hydrogenic radius helps to promote long range FM ordering with the increase of BMP concentration. Case I shows percolation of two nearby BMPs and case II is that of an isolated BMP. Whereas isolated Co ions can have rare FM interaction without the presence of defects, since they would either align antiferromagnetically in case of short-range interaction or can hardly interact through the itinerant carriers due to their dilute concentration as compared to their metallic FM phases. The doped cations provide an extra random potential, which extends the localized region as its concentration increases. Overlap between a hydrogenic electron and the cations within its orbit leads to ferromagnetic exchange coupling between them, provided the hydrogenic orbital radius is sufficiently large.\textsuperscript{271} The number of cation sites $v_c$ within a sphere of radius $r_H$ ranges from ten to a hundred, depending on the value of $r_H$ (For ZnO, $r_H = 0.76\text{nm}$, $v_c=64$).\textsuperscript{13} Thus enhances long range FM interaction in the Co doped ZnO NRs.

Note that, we don’t find any measurable magnetization in the undoped ZnO NPs. Also, defect related FM moment reported in the literature for the undoped NSTs is of much lower magnitude (of the order of $10^{-3}$ emu/g) as compared to doped DMSs.\textsuperscript{135, 170} We observed at least three orders of higher moment in the doped ZnO NRs. Possibly, axial growth of the NRs with higher concentration of Co ion accommodation along C-axis enhances the FM interaction. Thus, it appears that both TMs as well as defects are important ingredients to attain high moment as well as high $T_c$, as observed here.
Figure 4-7 Schematic diagram of the bound magnetic polaron (BMP) formation. $V_{zn, O}$ trapped carriers couple with the 3d shell spins of Co ions within its hydrogenic orbit, forming a BMP. FM ordering prevails through BMP percolation. Citation sites are represented by solid circles. Oxygen is not shown; the defects are represented by rectangular boxes.

Table 4-1 Lattice parameters calculated from the XRD pattern; Elemental composition extracted from XPS spectra.

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Crystal structure from XRD</th>
<th>Elemental composition from XPS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20 (degree)</td>
<td>Lattice Constants</td>
</tr>
<tr>
<td></td>
<td></td>
<td>A (Å)</td>
</tr>
<tr>
<td>Undoped ZnO</td>
<td>31.73</td>
<td>3.253</td>
</tr>
<tr>
<td>5% Co doped ZnO NPs</td>
<td>31.78</td>
<td>3.249</td>
</tr>
<tr>
<td>7% Co doped ZnO NRs</td>
<td>31.95</td>
<td>3.232</td>
</tr>
</tbody>
</table>
Table 4-2 Summary of the PL peaks with UV and visible emission bands fitted with Gaussian line shapes. Absorption peaks are measured from the respective UV-visible absorption spectrum.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak I (eV)</th>
<th>Peak II (eV)</th>
<th>Peak III (eV)</th>
<th>Peak IV (eV)</th>
<th>Peak V (eV)</th>
<th>Absorption peak (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped ZnO</td>
<td>3.25</td>
<td>3.15</td>
<td>2.38</td>
<td>2.11</td>
<td>--</td>
<td>3.28</td>
</tr>
<tr>
<td>5% Co doped ZnO NPs</td>
<td>3.28</td>
<td>3.15</td>
<td>2.40</td>
<td>2.11</td>
<td>1.81</td>
<td>3.32</td>
</tr>
<tr>
<td>7% Co doped ZnO NRs</td>
<td>3.29</td>
<td>3.15</td>
<td>2.38</td>
<td>2.14</td>
<td>1.81</td>
<td>3.34</td>
</tr>
</tbody>
</table>

Peak identity: NBE, Band tail states, $V_{Zn}$, $O_{Zn}$, $V_o^+$, $O$, Hydroxyl groups, $Co^{2+}$ $d-d$ internal transition, Band edge absorption.

Table 4-3 Saturation magnetization ($M_s$), coercivity ($H_c$), and retentivity ($M_r$) determined from M-H curve; transition temperature ($T_c$) determined from differentiated M-T curve. $M_0$, $m_{eef}$, $\chi_m$, N are determined from the BMP fitting of the M-H curves for different Zn$_{1-x}$Co$_x$O ($x = 0, 0.05, 0.07$) samples.

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>M-H parameters</th>
<th>Fitting parameters extracted from BMP model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$M_s$ (emu/g)</td>
<td>$H_c$ (G)</td>
</tr>
<tr>
<td>Undoped ZnO</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>5% Co doped ZnO NPs</td>
<td>0.07</td>
<td>185</td>
</tr>
<tr>
<td>7% Co doped ZnO NRs</td>
<td>1.83</td>
<td>53</td>
</tr>
</tbody>
</table>

4.1.4 Summary
In summary, HTFM with high magnetic moment is reported in the Zn$_{1-x}$Co$_x$O NRs synthesized by a low temperature solvothermal route. TEM micrograph reveals the formation of long and uniform ZnO NRs with 50-90 nm diameters and 0.3-0.6 µm length. XRD, XPS, HRTEM and EDS analysis confirm the absence of Co clusters in the doped NRs. XPS spectra also confirm the presence of Co ions in 2+ states within host lattice. RT magnetic measurements exhibit FM behavior with high moment of 1.83 emu/g for 2T field and Curie temperature around 398K. The structural, optical, and magnetic properties are sensitively changed for the incorporation of Co$^{2+}$ ions in the Zn$^{2+}$ lattice site. PL and
XPS spectra confirm the nature of defects present in the doped and undoped samples. PL and UV-VIS measurements show doping induced modification in the band edge emission and absorption spectra. These findings suggest that Co$^{2+}$ ions are successfully incorporated into the wurtzite lattice at the Zn$^{2+}$ sites. The observed FM is explained on the basis of intrinsic exchange interaction of Co ions and V$_{Zn}$, O$_i$ defects, both the Co ions as well as defects are significant ingredients to attain high moment as well as high ordering temperature. This 1D DMS NRs can be a good source of spin-polarized carriers and they can be used for spin injection or spin transport in spintronic devices.

### 4.2 Investigations on Ni doped ZnO Nanostructures synthesized by a solvothermal route

#### 4.2.1 Highlights

Ni doped ZnO system with the study of diverse magnetic properties and its interaction with respect to the experimental findings have been explored less as compared to the Co doped ZnO counterpart. Moreover, synthesis of Ni doped ZnO NMs showing FM above room temperature with a high moment and high crystallinity still remains a significant challenge for future spintronic devices. Under this scenario, magnetism in Ni doped ZnO is still a subject of interest that demands careful investigations. In this paper, we have followed an easy approach toward the synthesis of long and uniform Zn$_{1-x}$Ni$_x$O NRs, NPs by a solvothermal route at ambient conditions. Synthesis by solvothermal route using autoclave offers better advantages, such as easy and effective control of synthesis parameters, like low synthesis temperature, short-long reaction time, low cost processing, economical, and environmentally kind too. The structural characterization and phase identification are carried out by XRD, Raman, XPS, FESEM, TEM and EDS analysis. Further, the oxidation state of the Ni dopants inside the ZnO lattice is revealed by XPS data analysis. Photoluminescence (PL) and UV-Vis absorption measurements are done to check the doping related changes in band edge emission and absorption spectra, the kind of defects present and their changes with doping. The magnetic properties are measured by vibrating sample magnetometer (VSM).
4.2.2 Results and Discussion

4.2.1.1 Microstructure and Morphology

Figure 4-8 (a-d) shows a typical XRD pattern for the Zn$_{1-x}$Ni$_x$O ($x=0$, 0.03, 0.05) samples with respect to different morphology and synthesis conditions. Observed peaks confirm the single crystalline ZnO wurtzite structure for the pure ZnO NPs and Ni doped ZnO NPs, NRs. One small intensity secondary phase related peak can be seen for the 1-ZnO NPs for lower reaction temperature of synthesis. It may appear due to some Ni nanoclusters or Ni(OH)$_3$ related phases. Overall crystallinity has been improved and the morphology has been changed from NPs to NRs with the increasing reaction temperature.

![Figure 4-8](image)

**Figure 4-8** (a-d) XRD pattern of Zn$_{1-x}$Ni$_x$O ($x=0$, 0.03, 0.05) samples, 0-ZnO-NPs, 1-ZnO-NPs, 2-ZnO-NPs, 3-ZnO-NRs respectively, showing wurtzite ZnO peaks. Doping induced peak shift is clearly seen for the intense peaks corresponding to (100), (002), and (101) planes.
and time for the Ni doped samples. Also it shows clear shifting of the diffraction peaks towards the higher angle with doping for the three most intense peaks of the XRD pattern. The lattice parameters \( a, c \) and the cell volume \( v \) are calculated from the XRD peak positions and we find that lattice parameters have decreased with doping; as a consequence, the lattice volume decreases (details: in Table 4-4). This is consistent with the fact that the ionic radius of \( \text{Ni}^{2+} \) is 0.55 Å, whereas that of \( \text{Zn}^{2+} \) is 0.60 Å.\(^{235}\) The shifting of XRD pattern and corresponding decrease of the lattice parameters suggest that \( \text{Ni}^{2+} \) ions are successfully incorporated into the \( \text{ZnO} \) lattice at the \( \text{Zn}^{2+} \) sites.

The general morphologies of the \( \text{Zn}_{1-x}\text{Ni}_x\text{O} \) samples are shown in Figure 4-9(a) shows the FESEM image of undoped \( \text{ZnO} \) nanoparticles (NPs). Figure 4-9(b) & (c) show TEM images of the 3\% and 5\% Ni doped \( \text{ZnO} \) nanoparticles (NPs) of average sizes as 50-100 nm & 200-300 nm respectively.

Figure 4-9(d) shows TEM image of the 5\% Ni doped \( \text{ZnO} \) NRs. TEM micrograph reveals clearly the formation of good quality Ni doped \( \text{ZnO} \) NRs having a smooth surface with diameter of 60-70 nm and length of 0.4-0.6 \( \mu \)m. Note that the Ni doped samples for lower reaction temperatures and times are of rectangular shaped NPs. While, with the higher reaction temperature and time, morphology leads to the long 1D NRs due to C-axis growth, as for the \( \text{ZnO} \) NSTs C-axis exhibits the highest growth rate due to the structure and surface anisotropy.\(^{263}\) The difference of the crystal growth velocities in different directions is expected to cause the change of morphologies as the surface energies are different for different crystal faces. Similar findings have been observed for Ce-doped \( \text{ZnO} \) NRs and Co doped \( \text{ZnO} \) NRs.\(^{268, 269, 272}\) Also the accommodation of Ni ions along the C-axis enhances FM interaction in the TMdoped \( \text{ZnO} \) NRs.\(^{273}\) HRTEM lattice images and the SAED pattern illustrate that all the NRs are single crystalline. The d-spacing of the crystal plane is calculated as 2.57 Å showing the preferable crystal growth plane (002). Energy-dispersive X-ray spectroscopy (EDS) analysis on a single NR confirms the presence of Ni ions in the \( \text{ZnO} \) matrix. EDS analysis shows 2.36 atomic \% of Ni doping in the \( \text{ZnO} \) NRs, corresponding to the 5 molar percentage of the initial cationic
precursor, with consideration of the accuracy of the EDS analysis. We also confirm the presence of substituted Ni ions inside the ZnO matrix by XPS analysis, as discussed below.

Figure 4-9 (a) FESEM image of the undoped ZnO NPs. (b-c) TEM image of the 3% & 5% Ni doped ZnO NPs respectively (d) TEM image of the 5% Ni doped ZnO NRs, (e) SAED pattern & (f) HRTEM lattice image of the a single 5% Ni doped ZnO NR showing c-axis growth. (g) EDS spectra of a single Ni doped ZnO NRs, showing presence of Ni inside the ZnO lattice.
4.2.1.2 Local Structure of Dopants and Defects

Figure 4-10 shows the XPS spectra of (1) Zn 2p, (2) Ni 2p and (3) O 1s states of pure and 3%, 5% Ni-doped ZnO NPs and NRs. Figure 4-10(a-c) shows two strong peaks centered around 1021.54eV and 1044.61eV which are in agreement with the binding energies of Zn 2p$_{3/2}$ and Zn 2p$_{1/2}$ respectively for all the Ni doped samples. Their spin-orbital splitting energy is around 23.07eV, confirming that Zn is present as Zn$^{2+}$. Figure 4-10(d-f) show that the peaks of Ni 2p$_{3/2}$ and Ni 2p$_{1/2}$ core levels are centered around 855.51 and 873.01 eV, respectively, whereas the corresponding satellite structures are clearly observed at 861.01 and 879.11 eV for all the Ni doped samples. The ionic state and the phase information of the Ni ions within the ZnO matrix can be explained on the basis of the energy difference between Ni 2p$_{3/2}$ and Ni 2p$_{1/2}$ core levels. For Ni$^{2+}$ states inside ZnO matrix, the spin-orbital splitting energy difference is around 17.50 eV, which is different from the value (17.27 eV) of the metallic Ni phase.\textsuperscript{240, 241} We observe the spin-orbital splitting energy as 17.51 and 17.50 eV for the 2-ZnO and 3-ZnO samples which show RT FM behavior. Whereas this energy difference is around 17.80 eV for the 1-ZnO sample which shows paramagnetic nature. This relative higher splitting energy is observed due to the presence of Ni related secondary phases, which is also evidenced from the XRD pattern. Also, observed Ni 2p$_{3/2}$ (855.51 eV) position is quite different from that of the metallic Ni (852.7 eV), NiO (853.8 eV) and Ni$_2$O$_3$ (856.7 eV)\textsuperscript{242}. Furthermore, the shape of peaks for Ni metallic with satellites structure is narrow and different from the observed spectrum of Ni-doped ZnO NPs.\textsuperscript{242} These results provide clear evidence, that Ni ions are successfully substituted into tetrahedral sites of the ZnO wurtzite structure without forming any detectable secondary phases.

Figure 4-10(g-i) show O 1s peak for the Ni doped ZnO NPs, NRs. The binding energy peak at nearly 530 eV is attributed to O atoms at regular lattice site (O$_L$), between O$^{2-}$ and Zn$^{2+}$ (or substitutional Ni$^{2+}$) ions.\textsuperscript{243} The small intensity peak at higher binding energy of 533 eV corresponds to interstitial O atoms (O$_i$) or surface oxygen in forms of –OH groups. Also we have shown the detail elemental analysis of Zn, O and Ni in Table 4-4,
calculated from the XPS spectra. It indicates that the percentage O is higher in all the samples and thus presence of Zn vacancy (Zn$_V$) and O interstitials (O$_i$) are expected. Further, insertion of Ni ions inside ZnO matrix is more efficient around 3.9% for the 5% Ni doped ZnO NRs enhancing FM ordering, supporting the importance of higher concentration of doping with the axial accommodation.

**Figure 4-10** XPS spectra of (a-c) Zn 2p$_{3/2}$ and 2p$_{1/2}$ states; (d-f) Ni 2p$_{3/2}$ and 2p$_{1/2}$ states; (g-i) O 1s states of 3%, 5% Ni doped ZnO NPs, NRs; (1-ZnO, 2-ZnO, 3-ZnO samples).

### 4.2.1.3 Optical Properties

PL studies for the undoped and Ni doped ZnO samples at room temperature reveal strong UV emission peak and a broad green-yellow emission band ranging from 425 nm to 725 nm, as shown in Figure 4-11(a-d). Observed broad PL peaks in the UV as well as in the visible region indicate existence of multicomponent which are extracted after fitting with multiple Gaussian functions. The obtained individual peak positions are tabulated in Table 4-5. Undoped ZnO NPs exhibit an excitonic emission band centered on 3.25eV (Peak I). Ni-doped ZnO NPs, NRs show slight blue shift in the above mentioned UV
emission. The near band-edge (NBE) transition is generally attributed to the recombination of free excitons. The blue shift of the UV emission peak has been attributed to the strong exchange interaction between the d-electrons of Ni ions and the s, p electrons of the host band. Along with the free excitonic UV emission, one additional peak (Pak II) centered at 3.15eV is observed from all of the samples near the tail region of the above UV emission. Band tail states are seen due to the surface effect of nanomaterials caused by the presence of lattice disorder/defects on the surface in the chemical synthesized ZnO NSTs.\textsuperscript{265,274}

Next, PL peak is the green emission peak (Peak III) centered on ~2.30-2.27 eV, which is commonly observed in the ZnO NSTs. This broad peak in the visible region is well known for the intrinsic defects in ZnO, such as zinc vacancy (Zn\textsubscript{V}) or Oxygen vacancy (O\textsubscript{V}) related defects\textsuperscript{248,250,275,276} or antisite oxygen (O\textsubscript{Zn}).\textsuperscript{107} Emre et al. also reported about Zn\textsubscript{V}, O\textsubscript{V} defects as the source of green luminescence through detail EPR analysis.\textsuperscript{277} However as our samples are O rich, as evidenced from XPS and EDS analysis, the presence of O\textsubscript{V} is expected to be very less. Thus origin of this peak is considered as the presence of Zinc vacancy (V\textsubscript{Zn}) and or antisite oxygen (O\textsubscript{Zn}). Next an intense yellow emission (Peak IV) is observed from all of the samples, centered on ~2.05eV. This emission peak may be attributed to the recombination process associated with the ionized oxygen interstitials (O\textsubscript{i}) induced transitions.\textsuperscript{250,267} Most of the theoretical calculations agree that Zn\textsubscript{V} and O\textsubscript{V} are the lowest energy defects, while the Zn\textsubscript{i}, O\textsubscript{i} are to be higher in energy. Generally the defects which are favored under Zn-rich conditions (O\textsubscript{V}, Zn\textsubscript{i}) act as donors, while those favored under O-rich conditions (Zn\textsubscript{V}, O\textsubscript{i}) act as acceptors.\textsuperscript{107} So the formation of Zn\textsubscript{V}, O\textsubscript{i} related defects are more expected in case of these chemical synthesized Zn\textsubscript{1-x}Ni\textsubscript{x}O NPs, NRs. It is important to note that the position and the intensity of the defect related emission band strongly depend on the synthesis, as the origin as well as the concentration of intrinsic defects is in close relation with the synthesis procedure.\textsuperscript{276,278,279}

Note that the relative intensity of the defect emission to NBE emission has increased for the doped samples as compared to the undoped ZnO NPs. Also the overall defect
density has increased for the doped NPs and NRs with increased C-axis growth. We can clearly see from the comparison of the PL intensity profile that the relative defect ($V_{\text{Zn}}, O_i$) band intensity has increased for the 5% Ni doped NPs and NRs as compared to the undoped ZnO sample.\textsuperscript{273} High defect density with the higher percentage of doped Ni ions has chances of high density BMP formation, thus producing high magnetic moment through long range FM interaction.\textsuperscript{170, 240} We observe the appearance of RT FM characteristic in the Ni doped ZnO NRs with the presence of relative higher concentration of $V_{\text{Zn}}, O_i$ defects. Whereas the Ni doped ZnO NPs with the presence of relative lower concentrations of defects shows PM or low moment of FM characteristic. It suggests that high concentration of $V_{\text{Zn}}, O_i$ related defects along with the Ni ions inside ZnO matrix
promote the FM interaction. Thus doping of Ni\(^{2+}\) ions also can be used to tune the visible PL properties of the ZnO NSTs and this intern affects the magnetic properties of the doped ZnO NPs.

### 4.2.1.4 Magnetic Properties

We observe distinct ferromagnetic behavior with high moment in the doped Zn\(_{1-x}\)Ni\(_x\)O NRs measured by VSM. Figure 4-12(b-c) shows the magnetic hysteresis (M-H) loop for the 5% Ni doped ZnO NPs and NRs respectively measured at room temperature. Ni doped ZnO NPs synthesized for lower reaction temperature show weak FM characteristics with low moment, while Ni doped ZnO NRs synthesized for higher reaction temperature shows strong FM characteristics. Observed saturation magnetic moment (Ms) is of the order of 1.13 emu/g for the 5% Ni doped ZnO NRs. Detailed variation of the coercivity, retentivity and other magnetic properties are mentioned in the Table 4-6. It is well known that for the wide range of applications, the DMS material should have a \(T_c\) enough above RT (300 K). It’s clear from the RT M-H loop that this material can retain FM characteristic far above room temperature, as a result \(T_c\) will be high. Note, that the magnetic moment value for the Ni doped ZnO NRs, as observed here, is relatively high as compared to the other findings for the Ni doped ZnO based DMS NRs/NWs.\(^{269, 270}\) But in general Ni doped ZnO nanostructure systems show lower magnetic moment as compared to the Co doped counterpart.\(^{280, 281}\)

While, Ni doped NPs synthesized for both lower reaction time and temperature we observe PM characteristic, as the substituted Ni concentration and defect concentration are low (Figure 4-12(a)). Also Ni related secondary phases are present. As the kind of magnetic interaction for the Ni related extrinsic phases and the Ni ions inside the ZnO matrix are different, as a result the overall magnetic moment is not favoring FM nature for the 1-ZnO NPs. As the relative concentration of Ni doping and defect density have increased, so it enhances stronger FM interaction through BMP formation. Also for the Ni doped ZnO NRs the axial accommodation of Ni ions is more favorable for the FM interaction, giving the higher value for FM moment.\(^{167, 268}\) We have observed in our earlier work of Co doped ZnO NRs the special importance of axial accommodation of
TM ions in FM interaction.\textsuperscript{280} Thus, the higher doping concentration, higher defect density and the 1D (NW/NR) growth of nanostructure might provide a better environment to yield FM interaction with high ordering temperature in solvothermal synthesis.\textsuperscript{273} Note that, despite the presence of intrinsic defects no measurable magnetic moment is observed in the undoped sample. This confirms that defects alone are not sufficient to account for the observed FM in case of as synthesized samples. Further, in our earlier work of Co doped (low concentration) ZnO NWs synthesized by vapor deposition, we found very low magnetic moment and its nature as PM, as the observed defect concentration was too low, hence the ferromagnetic coupling could not be favorable\textsuperscript{252}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4-12}
\caption{(a-c) Room temperature M-H plot showing the hysteresis loop for the 3\%, 5\% Ni doped ZnO NPs, NRs. The inset shows the magnified M-H loop showing clear ferromagnetic hysteresis behavior for the NRs with higher reaction temperature and time.}
\end{figure}
4.2.3 Origin of the FM Interaction

The presence of intrinsic defects (Zn\textsubscript{V}, Zn\textsubscript{i}, O\textsubscript{Zn}, O\textsubscript{i} etc.) play an important role in the FM interaction for Ni doped ZnO systems\textsuperscript{31,250,282}. The long-range interaction is necessary to obtain HT FM in dilute concentration of Ni doped ZnO DMS systems and it can be mediated by defect induced states.\textsuperscript{11} In an earlier work on Co doped ZnO NPs, NRs we have demonstrated the important role of BMPs to achieve HT FM with high moment for the ZnO based DMS system.\textsuperscript{57,280}

Intrinsic defects, such as Zn\textsubscript{V}, O\textsubscript{i}, O\textsubscript{Zn} are inherently present in the as synthesized Zn\textsubscript{1-x}Ni\textsubscript{x}O NPs, NRs due to the stabilization of structure. Zn vacancies promotes the FM ordering by affecting the occupancy of extended Ni ions, also the presence of holes with the V\textsubscript{Zn} make Zn\textsubscript{1-x}Ni\textsubscript{x}O NRs strongly FM, as O\textsubscript{i} defects contribute holes in the above samples.\textsuperscript{54} Further J.B. Yi have reported that Zn vacancies itself might introduce magnetic moments as well as additional holes and FM coupling of these local moments could be mediated by the high concentration of holes introduced by doping and defects, resulting in RTFM.\textsuperscript{54} Our systematic study shows that formation of defect (V\textsubscript{Zn}, O\textsubscript{i}) mediated BMPs and their percolation is one of the most promising candidates for the observed FM. To understand the suitability of the BMP model, we attempt to fit the M versus H data using the BMP model.\textsuperscript{168} The formula used for the fitting of BMP model:

\[ M = M_0 L(x) + \chi m H \]

Details of Eq. (1) are mentioned in earlier work.\textsuperscript{280} The experimental data along with fitted data are shown in Figure 4-13 for the 5% Ni doped ZnO NRs. The fitted data closely follows the experimental data and the fitted parameters are tabulated in Table 4-6. The spontaneous moment per BMP, \( m_{\text{eff}} \) is found to be of the order of \( 10^{-17} \) emu. By assuming \( m_s = m_{\text{eff}} \), we have estimated the concentration of BMP to be of the order of \( 10^{17} \) cm\textsuperscript{-3} considering the effective Bohr radius of the BMPs as 0.76 nm.

The calculated BMP concentration is relatively small compared to the necessary concentration of \( 10^{20} \) cm\textsuperscript{-3} in order to have long range percolation. Thus, the calculated
low concentration of BMPs cannot fully account for the observed high magnetic moment in the doped ZnO. Also defect related surface spins might contribute partly for the observed FM. Due to a large surface area, a lot of defects have been seen in the PL and XPS spectra. Sanchez et al. have reported that the uncompensated surface spins enhance the spin polarization induced by substitute Ni ions and even in the absence of magnetic ions, it might promote the formation of p-derived extended magnetic states. Further, presence of O\textsubscript{i}, in our samples is favorable to exhibit presence of holes due to the activation of acceptor states. The activation of acceptor states for hole formation might be partly responsible for the enhancement in HTFM in the Ni doped ZnO NRs, also it is consistent with the Dietl’s prediction of hole mediated ferromagnetism in Mn doped ZnO system.

![Figure 4-13](image-url)

**Figure 4-13** Initial curve (0-H\textsubscript{max}) of the M-H plot is fitted with BMP model (Eq. (1)) for the 5% Ni doped ZnO NRs. Symbols are for experimental data and the solid line is a fit with the BMP model. Extracted parameters are shown in Table 4-6.

Note that, we don’t find any measurable magnetization in the undoped ZnO NPs. Also, defect related FM moment reported in the literature for the undoped NSTs is of much lower magnitude (of the order of 10\textsuperscript{-3} emu/g) as compared to doped DMSs. We observed at least three orders of higher moment in the Ni doped ZnO NRs. Possibly, axial growth of the NRs with higher concentration of Ni ion accommodation along C-axis enhances the FM interaction. Thus, it appears that both TMs as well as defects are important ingredients to attain high moment as well as high T\textsubscript{c}, as observed here. More
detailed experimental work like might provide further insights into the origin of ferromagnetism in magnetically doped oxides and the possible way to improve its quality.

Table 4-4 Lattice parameters calculated from the XRD pattern; Elemental composition extracted from XPS spectra.

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Crystal structure from XRD</th>
<th>Elemental composition from XPS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20 (degree)</td>
<td>FWHM (31)</td>
</tr>
<tr>
<td>Undoped ZnO NPs</td>
<td>31.73</td>
<td>34.39</td>
</tr>
<tr>
<td>3%Ni-ZnO-120 C-10h-NPs</td>
<td>31.79</td>
<td>34.45</td>
</tr>
<tr>
<td>5%Ni-ZnO-120 C-15h-NPs</td>
<td>31.97</td>
<td>34.62</td>
</tr>
<tr>
<td>5%Ni-ZnO-150 C-20h-NRs</td>
<td>32.10</td>
<td>34.73</td>
</tr>
</tbody>
</table>

Table 4-5 Summary of the PL peaks with UV and visible emission bands fitted with Gaussian peaks.

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Peak I (eV)</th>
<th>Peak II (eV)</th>
<th>Peak III (eV)</th>
<th>Peak IV (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-ZnO NPs</td>
<td>3.25</td>
<td>3.16</td>
<td>2.28</td>
<td>2.05</td>
</tr>
<tr>
<td>1-ZnO NPs</td>
<td>3.26</td>
<td>3.15</td>
<td>2.30</td>
<td>2.05</td>
</tr>
<tr>
<td>2-ZnO NPs</td>
<td>3.29</td>
<td>3.15</td>
<td>2.28</td>
<td>2.06</td>
</tr>
<tr>
<td>3-ZnO NRs</td>
<td>3.28</td>
<td>3.16</td>
<td>2.27</td>
<td>2.06</td>
</tr>
</tbody>
</table>

Table 4-6 Saturation magnetization (M_s), coercivity (H_c), and retentivity (M_r) determined from M-H curve; M_0, m_eff, \( \chi_m \) N are determined from the BMP fitting of the M-H curves for different Zn_{1-x}Ni_xO (x = 0, 0.03, 0.05) samples.

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>M-H parameters</th>
<th>Fitting parameters extracted from BMP model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M_s (emu/g)</td>
<td>H_c (G)</td>
</tr>
<tr>
<td>0-ZnO</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>1-ZnO</td>
<td>0.16</td>
<td>...</td>
</tr>
<tr>
<td>2-ZnO</td>
<td>0.20</td>
<td>70</td>
</tr>
<tr>
<td>3-ZnO</td>
<td>1.13</td>
<td>150</td>
</tr>
</tbody>
</table>
4.2.4 Conclusion sample

In summary, RTFM with high magnetic moment is reported in the Zn$_{1-x}$Ni$_x$O NRs synthesized by a solvothermal route. The shape and size of the Ni doped ZnO NS have increased with increasing reaction temperature and time, leading to the C-axis 1D growth and stronger FM characteristic. TEM micrograph reveals the formation of long and uniform ZnO NRs with 60-70 nm diameters and 0.4-0.6 µm length. XRD, XPS, HRTEM and EDS analysis confirm the absence of Ni clusters in the doped NPs/NRs. XPS spectra also confirm the presence of Ni ions in 2+ states within host lattice. RT magnetic measurements exhibit FM behavior with moment of 1.13emu/g and coercivity of 150 G. The structural, optical, and magnetic properties are sensitively changed for the incorporation of Ni$^{2+}$ ions in the Zn$^{2+}$ lattice site. PL and XPS spectra confirm the nature of defects (Zn$_V$, O$_i$) present in the doped and undoped samples. PL spectra also demonstrate doping induced modification in the band edge emission. These findings suggest that Ni$^{2+}$ ions are successfully incorporated into the wurtzite lattice at the Zn$^{2+}$ sites. The observed FM is explained on the basis of intrinsic exchange interaction of Ni ions and Zn$_V$ and O$_i$ defects, both the Ni ions as well as defects are significant ingredients to attain high moment as well as high ordering temperature.