CHAPTER 3

TM (Co, Ni) Doped Oxide DMSs Synthesized by Ball Milling Technique

Here we attempt an easy approach toward the synthesis of uniform Zn$_{1-x}$TM$_x$O, Ti$_{1-x}$TM$_x$O$_2$ Nanostructures by a ball milling technique at ambient conditions. The structural characterization and phase identification are carried out by XRD, RAMAN, XPS, TEM and EDS analysis. Further, the oxidation state of the TM dopants inside the ZnO lattice is revealed by XPS analysis. Photoluminescence (PL) and UV-Vis absorption measurements are carried out to check the doping related changes in band edge emission and absorption spectra. The kind of defects present and their changes with doping are explored from the PL spectra. The field dependent and temperature dependent magnetic properties are studied by the measurement of a vibrating sample magnetometer (VSM). The variation of magnetic properties with growth condition, doping concentration and presence of defects are studied and possible origin of ferromagnetism has been explained.

3.1 High Temperature Ferromagnetism and Optical Properties of Co Doped ZnO Nanoparticles

3.1.1 Highlights

In this work, we report on the magnetic, structural and optical properties of Co-doped ZnO NPs synthesized by a ball milling technique. X-ray diffraction (XRD) and transmission electron microscopy (TEM) are used to examine phase segregation and morphological analysis. Micro Raman Scattering and photoluminescence spectrum are measured to confirm the presence of oxygen vacancy defects. UV–VIS optical absorption
is used to infer the substitution of cobalt inside the Zn lattice corresponding to the bandgap shift. RT magnetic measurement shows clear M-H hysteresis loop with relatively high magnetic moment of the order of 2-6 emu/g. The temperature variation of magnetization shows high transition temperature of ~ 790 K. The observed magnetization and its temperature dependence are discussed with reference to the role of defects and doping concentration in the ZnO sublattice.

3.1.2 Structural characterization

3.1.1.1 XRD data analysis

Figure 3-1 shows some typical XRD patterns of the Co doped ZnO NPs. Figure 3-1(a), (b) and (c) are for undoped, 3% doped and 5% doped NP1, respectively. Similarly, Figure 3-1(d), (e) and (f) are for undoped, 3% doped and 5% doped NP2, respectively. For each sample, all the observed diffraction peaks can be indexed to a ZnO wurtzite structure (space group P6\text{3}mc), and no other impurity phase was found, which indicates that the Co ions successfully occupy the lattice site rather than interstitial ones. In addition, very slow scans near the peaks of both hexagonal and cubic cobalt phases reveal no signatures of any kind of additional phases in the NPs. XRD Measurement of Co powder shows one intense peak around 44° which does not appear for the doped samples indicating Co is doped well in the ZnO sublattice. Compared to undoped ZnO, the doped samples show lowering of intensity and increase in full width at half maxima (FWHM) of the XRD pattern. Nanoparticle size is reduced considerably for the doped samples during milling compared to undoped NPs of two different initial sizes, as shown in Table 3-1. Interestingly, a slow scan comparison of the (101) peak of Co-doped and the undoped ZnO NPs show a higher 2θ value and lower intensity for the doped ZnO NPs, as shown in the inset of Figure 3-1. The peak shift is larger in case of NP1 as compared to NP2. The change in the XRD pattern in doped samples is attributed to size reduction and lattice strain induced by the ball milling. Since the ionic radius of Co and Zn 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.\textsuperscript{211} From the measured shift in
20 for (101) plane, we estimate a reduction in inter-planar spacing (d_{101}) of ~0.38% for NP1 and it is little lower for NP2. This strain in the NPs is expected to influence the electronic properties including band-structure of ZnCoO. Note that, one cannot exclude the possibility of formation of other precipitates or clusters small enough not to be detected in XRD measurement.

![Figure 3-1](image)

**Figure 3-1** XRD pattern of the Co-doped ZnO NPs: For NP1: (a) undoped (b) 3% Co doped (c) 5% Co doped; For NP2: (d) undoped, (e) 3% Co doped, (f) 5% Co doped. The insets show comparison of the (101) peak for undoped and doped ZnO NPs. Peak shift is evident in Co doped NPs in both cases.

**3.1.1.2 SEM, TEM images and morphology analysis**

Figure 3-2(a), (b) shows low-magnification SEM images of the undoped ZnO NPs and Figure 3-2(c), (d) shows low-magnification TEM of the 3% Co doped ZnO NPs prepared after 5hrs of milling. The micrograph reveals average particle size distribution in the range 80-100 nm for NP1 and 40-50 nm for NP2 before milling. For the doped ZnO, the
average size of the NPs is about 20-25 nm for NP1 as well as NP2. Different kinds of shapes of the NPs are discernible in Figure 3-2(a)-(d): irregularly shaped particle, larger rectangular platelets and hexagonally shaped particles. However, doped NPs are of regular shapes, mostly spherical. HRTEM lattice images are presented in Figure 3-2(e), which shows that all the NP2 are single crystalline. The d-spacing of the crystal plane is calculated as 0.244 nm which shows the preferable crystal growth plane is (101) and it is also the highest intensity peak in the XRD pattern shown in Figure 3-1. This shows a compressive strain of ~0.81% in the doped ZnO NPs. The crystallinity and preferential orientation of the NPs in the sample are confirmed from the selected area electron diffraction (SAED) patterns shown in Figure 3-2(f), confirming that the ZnCoO NPs are single crystals. The SAED pattern obtained by focusing the beam on a few nanoparticles of the sample clearly indicates the single crystalline nature of each NPs. Also, it confirms that the nanocrystals are indeed in the wurtzite phase. Due to low doping concentration, there is no cobalt clusters observed in the as-prepared NPs. Zn, Co, and O related peaks are seen in the EDS spectra measured on few single particle of the as-prepared ZnCoO, as shown in inset of Figure 3-2(e), besides Cu and C peaks from carbon coated Cu grid used in TEM. This indicates that cobalt ions were uniformly distributed in the entire ZnCoO samples.
3.1.1.3 Raman Spectra analysis

Raman scattering is a versatile technique for detecting the incorporation of dopants and the resulted defects and lattice disorder in the host lattice.\textsuperscript{212} The zone-center optical phonons of the wurtzite structure of ZnO can be classified according to the following irreducible representations: \( \Gamma_{\text{opt}} = A_1 + E_1 + 2E_2 + 2B_1 \). The \( B_1 \) modes are silent in Raman scattering, whereas \( A_1 \) and \( E_1 \) modes are polar and hence exhibit different frequencies for
the transverse-optical (TO) and longitudinal-optical (LO) phonons.\textsuperscript{213} The nonpolar $E_2$ modes have two frequencies, namely, $E_2$ (high) and $E_2$ (low) associated with the motion of oxygen (O) atoms and zinc (Zn) sublattice, respectively.\textsuperscript{214} Figure 3-3 shows the room-temperature Raman spectra of undoped and doped samples for NP1 and NP2 in the range 200 to 800 cm\textsuperscript{-1}. For the undoped ZnO, the sharpest and strongest peak at ~437 cm\textsuperscript{-1} can be assigned to $E_2$(high), which is the strongest mode in wurtzite crystal structure. In the doped NP1, $E_2$(high) is downshifted to 434.0 cm\textsuperscript{-1} and in NP2 it is observed at 436.25 cm\textsuperscript{-1}. This large downshift in NP1 compared to NP2 indicates higher tensile strain in NP1 than that in NP2. Note that XRD analysis showed a compressive strain in the doped NPs. Thus, presence of lattice strain in the doped NPs is confirmed from Raman and XRD analysis. The peaks at 330 and 379 cm\textsuperscript{-1} are assigned to the second-order vibration mode and $A_1$ (TO) mode, respectively. In the doped NPs, the broad peak at ~574 cm\textsuperscript{-1} is deconvoluted into two peaks, as shown in inset of Figure 3-3. The peak at 574 cm\textsuperscript{-1} is the $E_1$(LO) mode and can be attributed to defects due to O vacancies, Zn interstitial defect states.\textsuperscript{215}

![Figure 3-3](image.png)

**Figure 3-3.** Raman Spectra for the undoped and 3% Co doped ZnO NPs: (a) NP1 (b) NP2, The inset on the upper right corner in each case shows the magnified view of the defect related Raman bands in the in Co doped samples.
Compared with the undoped ZnO NPs, additional strong peaks can be observed at ~547 and ~574 cm\(^{-1}\) in the Raman spectra of the Zn\(_{1-x}\)Co\(_x\)O (\(x = 0.03, 0.05\)). Wang et al.\(^{212}\) and Cheng et al.\(^{216}\) also observed this mode in (Co, Al) and Ce-doped ZnO. According to the literature, this mode is induced by host lattice defects, such as oxygen vacancies and Zn interstitials. With the doping content, the host lattice defects in ZnO are activated and amplified and then this mode appears. In the present case, due to the smaller ionic radius of Co\(^{2+}\) than that of Zn\(^{2+}\), when Co\(^{2+}\) was doped into ZnO lattice, more oxygen vacancies and Zn interstitials are created. Therefore, the appearance of 547 and 574 cm\(^{-1}\) can be used to characterize Co\(^{2+}\) doped into ZnO lattice.\(^{217}\)

### 3.1.3 Optical absorption and photoluminescence studies

Many groups have confirmed that Co atomically substitutes on Zn sites using a variety of optical methods such as X-ray photoelectron spectroscopy\(^{218}\) and optical absorption.\(^{218, 219}\) The four-fold coordinated ionic radii of Co\(^{2+}\) (0.058 nm) and Zn\(^{2+}\) (0.06 nm) are very similar and results in a large solubility of Co\(^{2+}\) in the ZnO lattice.\(^{220}\) Evidence for Co substitution in the ZnO lattice can be inferred from optical UV-VIS absorption spectra. The UV-VIS absorption spectrum was used primarily to find possible change in the band gap. Figure 3-4(a) and (b) show the UV-VIS spectra taken at room temperature on different doped samples. The change in absorption peak due to doping indicates a change in the band structure. A blue-shift is observed in the bandgap energy for the cobalt doped samples compared to the undoped ZnO. Since the NP sizes are larger than excitonic Bohr radius in ZnO, size effect is unlikely to cause the observed blue shift. It is the strain that causes the change in the band structure of doped ZnO. The sp–d exchange between the ZnO band electrons and localized d-electrons associated with the doped Co\(^{2+}\) cations may cause the change in such band-structure. The interaction leads to corrections in the energy bands.\(^{221}\)
Figure 3-4. UV-Vis absorption spectra of (a) undoped and Co doped ZnO NPs (3%, 5%) for NP1; (b) undoped and Co doped ZnO NPs (3%, 5%) for NP2. Doped NPs show clear blue shifted band. (c) Comparison of PL spectra of undoped and Co doped ZnO NPs. High intensity of D band (520 nm) in doped NP1 is seen due to higher density of Zn\text{\textsubscript{i}}, O\text{\textsubscript{V}} defects. Inset shows low temperature PL spectra of NP2 exhibiting DBEs and AXs indicating presence of free carriers.

Photoluminescence (PL) spectroscopy is an effective method to investigate the presence of defects in semiconductors. The PL spectra of the undoped and Co-doped ZnO NPs recorded at room temperature are shown in Figure 3-4(c). There are two distinct emission bands in the spectra of the NPs, one peak is in the UV region (~380 nm) and another broad visible emission at 520 nm due to the intrinsic defect related band (D). As compared to the undoped NP1, the UV emission peak for the doped NP1 is found to be blue shifted and intensity reduced. The ~380 nm peak usually originates from the near band-edge (NBE) transition of ZnO and is generally attributed to the recombination of free excitons.\textsuperscript{222} The blue-shift indicates a higher band gap for the doped NP that may be
caused by strain\textsuperscript{211} since the NP sizes are much above the excitonic Bohr diameter of ZnO. The D band is centred at \textasciitilde520 nm and it is observed that the D band becomes broader and very intense with doping of Co in ZnO NPs. It is often attributed to the radiative recombination of photogenerated holes with electrons occupying the singly ionized oxygen vacancy ($V_o$).\textsuperscript{223, 224} Based on the band-structure calculations the visible emission has been assigned to $V_o$ and $Zn_{in}$.\textsuperscript{225} Therefore, it is believed that the observed strong visible emission in doped ZnO originates from the deep levels of Co-doped ZnO NPs and is due to the presence of $V_o$ and $Zn_{in}$ defects. The inset of Figure 3-4(c) shows a PL spectrum of NP2 recorded at low temperature (80K). The three peaks at 368, 374 and 382 nm are attributed to donor-bound excitons (DBE), acceptor bound excitons (AX) and 1\textsuperscript{st} order phonon replica of AX.\textsuperscript{226} Thus low temperature PL measurement shows that the ZnO NPs have free carriers that are important for the FM interaction in DMS materials.

3.1.4 Magnetic measurements

The magnetic properties of the Co-doped ZnO NPs were investigated using VSM. We observed distinct ferromagnetic behaviour at room temperature in the doped samples only. Despite the presence of some intrinsic defects in undoped ZnO NPs, no trace of FM was observed in the undoped and milled ZnO sample that was first tested under similar conditions using the VSM. This confirms that defects alone in ZnO NPs cannot account for the observed FM in the doped NPs. Figure 3-5 shows the magnetic hysteresis ($M$-$H$) loops for 3\% and 5\% doped NP1 and NP2 measured at 300 K. The saturation magnetizations ($M_s$) of the samples varied in the range of 3.95-7.02 emu/g with a coercive filed ($H_c$) of \textasciitilde260 G for the 5 hrs milled sample of different initial particle size and different doping concentration. Samples with higher milling time were also tested by M-H measurement that do not show any significant variation of $M_s$ with milling time indicating that doping is almost saturated for 5 hrs milling. The change of $M_s$ and $H_c$ for different starting ZnO NPs and doping concentration are compared for NP1 and NP2, as shown in Table 3-1. It is evident that $M_s$ value is higher for Co doped ZnO NP2 with smaller starting sizes of NPs, i.e., NP2 of size 42 nm than NP1 of size 80 nm, and the $M_s$ increases with the doping concentration. Higher $M_s$ in lower size starting nanopowder is
likely to be caused by enhanced doping and higher FM ordering in nanometer sized ZnO particles.

![Figure 3-5](image)

**Figure 3-5.** RT M-H loop showing hysteresis of the Co doped ZnO NPs: (a) 3% Co doped NP1, (b) 5% Co doped and NP1, (c) 3% Co doped NP2, (d) 5% Co doped NP2. The inset shows the magnified M-H loop showing clear ferromagnetic hysteresis behavior. Measured parameters are listed in Table 3.1.

These results indicate a particle size dependent doping and higher magnetization in nanopowder with lower initial size. Note that ZnO NP2 contains higher concentration of oxygen vacancy defects than the ZnO NP1 (as evident from stronger D band in PL) and these defects mediate the magnetic interactions in the doped NPs. Post growth annealing in air atmosphere at 250°C affects the magnetization. $M_s$ first increases for 250°C annealing and then it decreases to a low value for annealing at 500°C due to paramagnetic transition process (see Table 3-1). Same kind of variation in magnetization can be seen in the magnetization vs. temperature (M-T) data shown below where magnetization increases slowly before starting transition towards paramagnetic nature.

It is well known that for use in a wide range of applications without temperature control, the ferromagnet should have a $T_C$ enough above RT (300K). Figure 3-6 shows the temperature dependent magnetization of doped NP1 and NP2 in the temperature range 300 to 850 K. From the differential plot of the M-T curve we obtained the $T_C$ as ~791K.
for NP1 and 819K for NP2 source, which implies that the FM is not due to the Co metal ($T_c > 1300K$).

![Figure 3-6. Temperature dependent magnetization (M-T) curve of 3% Co doped ZnO NP1 and NP2 showing high transition temperature ($T_c$) and sharp FM to PM transition.](image)

As seen from the M-T curve, at higher temperature (>700K) the magnetization shows a rapid decrease with temperature. The magnetization measurement at 300K of the post M-T measurement, i.e., the Co: ZnO NPs annealed at 850 K in ambient condition shows that the magnetic moment is significantly reduced, which decreases to 0.59emu/g for the 5% Co doped sample. This magnetic transition suggests that high-temperature process causes a rapid destruction of ferromagnetic coupling. Note that compared to the 3% doped samples, 5% doped samples did not exhibit any sharp transition at higher temperature. The absence of a sharp FM to paramagnetic transition in M-T curve for higher doped (5% Co) ZnO NPs may be because of possible antiferromagnetic interaction due to the reduction in average interatomic distance of doped Co ions. Thus, 3% doping of small size NPs is found to yield best result for the observed high temperature FM.
Table 3-1. Co (3, 5 %) doped ZnO NPs of different initial sizes: Crystallite size determined from XRD profile; saturation magnetization ($M_s$), coercive filed ($H_c$); remanent magnetization ($M_r$) are determined from M-H curves; and transition temperature ($T_c$) are listed. $M_0$, $m_{\text{eff}}$, $\chi_m$, $N$ are calculated by BMP model fitting from the M-H curve with.

<table>
<thead>
<tr>
<th>Co-doped, ZnO source</th>
<th>Crystallite size (nm)</th>
<th>$M_s$ (emu/g)</th>
<th>$H_c$ (Gauss)</th>
<th>$M_r$ (emu/g)</th>
<th>Fitting parameters extracted from BMP model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Undoped</td>
<td>Doped</td>
<td></td>
<td></td>
<td>$M_0$ (emu/g)</td>
</tr>
<tr>
<td>3%, NP1</td>
<td>81.8</td>
<td>21.7</td>
<td>3.95</td>
<td>268</td>
<td>0.42</td>
</tr>
<tr>
<td>5%, NP1</td>
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<td>18.1</td>
<td>5.91</td>
<td>263</td>
<td>0.68</td>
</tr>
<tr>
<td>3%, NP2</td>
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<td>25.2</td>
<td>4.39</td>
<td>244</td>
<td>0.43</td>
</tr>
<tr>
<td>5%, NP2</td>
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<td>7.02</td>
<td>264</td>
<td>0.66</td>
</tr>
<tr>
<td>3%, Annealed</td>
<td>81.8</td>
<td>---</td>
<td>4.21</td>
<td>250</td>
<td>0.35</td>
</tr>
<tr>
<td>250°C post M-T</td>
<td>42.4</td>
<td>---</td>
<td>0.59</td>
<td>204</td>
<td>0.09</td>
</tr>
</tbody>
</table>

### 3.1.5 Possible FM interaction and it’s Origin

The origin of observed HT FM in these NPs could arise from a number of possibilities, such as the intrinsic property of the doped NPs, extended defects in the ZnO NPs, formation of some nanoscale Co-related secondary phase, Co precipitation and CoO. However, CoO phase can be easily ruled out, since CoO is antiferromagnetic with a Neel temperature of 293 K. Secondly, metallic Co is also an unlikely source of this FM, as XRD and HRTEM results show no metallic Co clusters in the NPs. Also undoped ZnO that were milled under identical conditions does not exhibit any measurable magnetization. Hence, defects alone cannot give such high magnetic moment as observed in the doped ZnO NPs. Thus, transition metals essentially plays the key role to the observed FM. UV-VIS absorption, photoluminescence (PL) spectra showed a band-gap modification which suggests Co$^{2+}$ ions were successfully incorporated into the wurtzite
lattice at the Zn\(^{2+}\) sites. Therefore FM is expected to arise from the intrinsic exchange interaction of magnetic moments mediated by the defects in doped NPs.

There are several mechanisms proposed in the literature regarding the origin of FM in DMSs. The exact mechanism of intrinsic FM in TM-doped oxides is still under debate. A diversity of theories has been proposed, such as RKKY interaction, super-exchange, double-exchange between the d states of TMs, free-carrier-mediated exchange and sp–d exchange mechanism, etc.\(^{227}\) The RKKY interaction is based on free electrons, but ZnO cannot transform into a metal at such a low doping. Direct interactions such as double-exchange or super-exchange cannot be responsible for the FM because the magnetic cations are dilute in our samples. All these proposed theories cannot well accord with the experimental results in DMSs.\(^{227}\) According to the literature, magnetic cations, carriers and defects can make up bound magnetic polarons (BMPs) that may be responsible for the room temperature FM. In addition to the magnetic doping effect, oxygen vacancy (\(V_\text{O}\)) defects have been suggested to play an important role in the magnetic origin for oxide DMSs.\(^{228}\) The theoretical studies suggest that \(V_\text{O}\) can cause an obvious change of the band structure of host oxides and makes a significant contribution to the FM.\(^{13, 229}\) The formation of BMPs, which include electrons locally trapped by oxygen vacancy, with the trapped electron occupying an orbital overlapping with the \(d\) shells of TM neighbors, has also been proposed to explain the origin of FM.\(^{13}\) Oxygen vacancies are inherently present in as grown ZnO NPs due to the stabilization of structure. On the basis of observed strong D band emission in PL and intense defect modes seen in Raman spectra, we presume that oxygen vacancies play a key role in the observed FM at room temperature and above. We notice that post growth air annealing at 250°C shows increase of \(M_s\) owing to the increase of O-vacancy or vacancy clusters that may help to create more BMPs and their percolation.\(^{30}\) Our systematic study shows that oxygen-vacancy defect constituted BMPs are one of the promising candidate for the origin of room-temperature FM in this system. Within the BMP model, the greater density of oxygen vacancy (\(V_\text{O}\)) and more doping help to produce more BMPs which yields a greater overall
volume occupied by BMPs, leading to the overlap of BMPs and enhancing FM. This evolution is observed in our case, increase of magnetization with the Co concentration indicating that the FM in our samples may be due to percolation of BMPs.

To understand the suitability of the BMP model to explain the observed data, we attempted to fit the M versus H data to the BMP model by following Chiorescu et al. 230 According to the BMP model, the measured magnetization can be fitted to the relation:

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

(1)

where the first term is from BMP contribution and the second term is due to paramagnetic matrix contribution. Here \( M_0 = N m_s \), \( N \) is the number of BMPs involved and \( m_s \) is the effective spontaneous moment per BMP. \( L(x) = \coth(x) - 1/x \) is the Langevin function with \( x = m_{\text{eff}} H / (k_B T) \), where \( m_{\text{eff}} \) is the true spontaneous moment per BMP, and at higher temperature it can be approximated to \( m_s = m_{\text{eff}} \). We have analyzed the M–H curve by using Eq. (1). The parameters \( M_0, m_{\text{eff}} \) and \( \chi_m \) are variable in the fitting process. The experimental data along with fitted data are shown in Figure 3-7 for the 3% Co doped Zn\(_{1-x}\)Co\(_x\)O sample at 300K. We notice that the fitted data closely follows the experimental data and the fitted parameters are tabulated in Table 3-1. The total BMP magnetization \( M_0 \) values are found to be in the order of 4-7 emu/g. For a given doping concentration, the \( M_0 \) values are found to be higher for lower initial size ZnO NPs, i.e., NP2, and this is thought to be due to the enhanced doping effect in lower size NPs. Also the \( M_0 \) value is found to increase with increase in doping concentration.

The paramagnetic susceptibility \( \chi_m \) is found to be of the order of \( 10^{-5} \) cgs unit and its value marginally changes with doping. The spontaneous moment per BMP, \( m_{\text{eff}} \) is found to be in the order of \( 10^{-17} \) emu. By assuming \( m_s = m_{\text{eff}} \), we have estimated the concentration of BMP, which was found to be in the order of \( 10^{18} \) cm\(^{-3}\) (see Table 3-1).
Figure 3-7. Initial portion of the M-H curve fitted with BMP model (Eq. 1): (a) 3% Co doped ZnO NP1 (b) 3% Co doped NP2. Extracted parameters are shown in Table 3.1.

However, this number is relatively small compared to the concentration necessary for percolation in ZnO. Assuming a realistic value of the effective Bohr radius of the donor orbitals forming the BMPs to be 0.76 nm, the required concentration of BMPs in order to percolate through the ZnO lattice is in the range of $10^{20}$ cm$^{-3}$ which is two orders of magnitude larger. Thus, the calculated low concentration of BMPs cannot fully account for the observed high magnetic moment in the doped ZnO. Therefore, BMP model does not satisfactorily explain the observed HT FM. Further, the model proposed in ref 13 cannot account for such high temperature FM. In order to have larger Curie temperatures one needs to assume artificially that a substantial amount of the carrier charge density is located on the magnetic impurity site. However, there is no direct experimental evidence to justify such an assumption. 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.
Furthermore, in the literature there exists controversy whether the FM observed in oxide DMS could be solely related to intrinsic defects. However, the magnetic measurement of the undoped and 5 hrs milled ZnO NPs did not produce any measurable hysteresis loop. Note that in the literature, defect related magnetization observed in the undoped NPs is of much lower magnitude \(10^{-3}\) emu/g as compared to doped DMSs. We observed at least three orders of higher value of magnetization in the doped ZnO NPs. Thus, it appears that both TMs as well as defects are important ingredients for the magnetic interactions and presence of TM is essential for the high magnetization value observed here. Pemmaraju et al. identified the Co-\(V_O\) pair defect as the most likely candidate for the near-room temperature FM in Co doped ZnO and demonstrated that such centre can indeed promote long-range coupling, if additional n-type doping is present. However, the required concentrations of such defects are extremely high and the predicted \(T_c\) is also below 300K.

It may be noted that a majority of the previous studies on Co doped ZnO NPs shows a relatively smaller \(M_s\) value at or above RT. It is likely that due to large density of point defects as well as extended defects such as dislocations associated with the strain in the ZnO lattice, ferromagnetic interactions has been enhanced in the doped NPs. It is expected that samples with higher concentration of defects would show higher magnetization.

### 3.1.6 Summary

In summary, nanocrystalline \(Zn_{1-x}Co_xO\) has been synthesized by a simple ball milling technique using two different initial sizes of ZnO NPs. Microstructure analysis shows that the NPs are of single crystalline ZnO wurtzite structure. XRD, HRTEM, EDS, UV-VIS absorption measurements indicate that Co\(^{2+}\) substitute into ZnO lattice at Zn\(^{2+}\) site. Raman scattering and PL studies confirm the presence of large amount strain and defects in the doped NPs. FM characteristics with high moment and high ordering temperature have been observed. Though the exact mechanism for the observed FM is not clear, possibly pairing of the Co\(^{2+}\) ions and extended defect (e.g. dislocations) may be responsible for the observed FM at and above room temperature. The observed FM is
occurring by the intrinsic exchange interaction of $\text{Co}^{2+}$ ions and $\text{V}_0$, $\text{Zn}_i$ defects through BMP formation and their percolation. Experimental M-H data have been fitted with the BMP model. As compared to the Co doping of bulk and thin film of ZnO, ZnO NPs exhibit enhanced ferromagnetic exchange interaction perhaps related to the weak confinement/size effect. Also, we have found that ZnO NPs of smaller initial size show higher $M_s$ value. Both the Co ions as well as defects are significant ingredients to attain high moment as well as high ordering temperature. The structural, optical, and magnetic properties are significantly changed for the incorporation of $\text{Co}^{2+}$ ions in the $\text{Zn}^{2+}$ lattice site. It is considered to be an important step for the development of semiconductor devices that can retain their FM properties above room temperature for the realization of practical commercial or mobile devices.

### 3.2 Structural, optical and magnetic studies of Ni doped ZnO Nanoparticles: correlations of magnetic moment with defect density

#### 3.2.1 Highlights

Here, we have followed an easy approach toward the synthesis of uniform $\text{Zn}_{1-x}\text{Ni}_x\text{O}$ NPs by a ball milling technique at ambient conditions. The structural characterization and phase identification are carried out by XRD, RAMAN, XPS, 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 a vibrating sample magnetometer (VSM). Ni doped ZnO system, in which diverse magnetic properties, kind of FM interaction with respect to the experimental findings have been explored quiet less as compared to the Co doped ZnO system. Moreover, synthesis of Ni doped ZnO NSTs 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.
3.2.2 Microstructure and Morphology

Figure 3-8(a-d) shows a typical XRD pattern for the Zn_{1-x}Ni_xO (x= 0, 0.03, 0.05) NPs for different milling time. Observed peaks confirm the single crystalline ZnO wurtzite structure for the 3% Ni doped sample. Though for the samples synthesized with lower milling time a small intensity secondary phase related peak is observed which have disappeared for higher milling time, as Ni ions have inserted inside ZnO matrix with higher milling time. Hence the the material has reached a single phase nature. Generally for the nickel content of x>5% it is beyond the solid solubility limit of Ni in ZnO, specialy for ball milling technique.\cite{57,233}

Figure 3-9 also shows clear shifting of the diffraction peaks towards the higher angle with the doping effect 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.\cite{234} This is expected as the ionic radius of Ni^{2+} is 0.55 Å, whereas that of Zn^{2+} is 0.60 Å.\cite{235} The shifting of XRD pattern and corresponding decrease of the lattice parameters suggest that Ni^{2+} ions are successfully incorporated into the ZnO lattice at the Zn^{2+} sites.
Figure 3-8. (a) XRD pattern of Zn$_{1-x}$Ni$_x$O ($x = 0, 0.03$) NPs for different milling times (4-12hr) showing wurtzite peaks. Doping induced peak shift is clearly seen for the intense peaks corresponding to (100), (002), and (101) planes.

Figure 3-9 (a) shows TEM image of the undoped ZnO NPs and Figure 3-9 (b) shows TEM image of the 3% Ni doped ZnO NPs synthesised for 12hrs of milling. The micrograph reveals average particle size distribution in the range 80 nm for the undoped NPs before milling. For the doped ZnO NPs, the average size is around 30-40 nm. Different kinds of shapes, like irregularly shaped particle, larger rectangular platelets and hexagonally shaped particles are visible for the undoped NPs. However, doped NPs are of regular shapes, mostly spherical, also its size is reduced due to the milling effect. HRTEM lattice images are presented in Figure 3-9(c), which shows that all the NPs are single crystalline. The d-spacing of the crystal plane is calculated as 2.47 Å which shows the preferable crystal growth plane is (101) and it is also the highest intensity peak in the XRD pattern shown in Figure 3-8. Also the crystallinity and preferential orientation of the NPs in the sample are confirmed from the selected area diffraction (SADE) patterns.
as shown in Figure 3-9 (d), confirming that the Zn$_{1-x}$Ni$_x$O NPs are single crystals. The SAED pattern is obtained by focusing the beam vertically on a single nanoparticle, hexagonal pattern indicates the single wurtzite structure of the ZnO NPs. EDS spectra attached with the TEM set-up taken on few single NPs of the as-synthesized Zn$_{1-x}$Ni$_x$O sample shows Zn, Ni, and O related peaks besides Cu from Cu grid used in the, as shown in Figure 3-9(e). This indicates that Ni ions are successfully inserted inside the ZnO matrix.

**Figure 3-9.** (a) TEM image of undoped ZnO NPs. (b) TEM image of the 2% Ni doped ZnO NPs, (c) HRTEM lattice image & (d) SADE pattern of a single 2% Ni doped ZnO NP showing c-axis growth. (e) EDS spectra taken on a few single Ni doped ZnO NPs.
Figure 3-10(a-d) shows the RT Raman spectra of the undoped and the 3% Ni doped ZnO NPs in the range 400 cm$^{-1}$ to 800 cm$^{-1}$. One sharp and strong peak at 437 cm$^{-1}$ can be seen for all the samples and it is assigned to E2 (high), which is the strongest mode in wurtzite crystal structure, associated with the motion of oxygen atoms in ZnO lattice. Note that as compared to undoped NPs, the doped NPs are showing strong Raman band around 547 and 574 cm$^{-1}$. The peak at 574 cm$^{-1}$ is the E1(LO) mode and can be attributed to defects due to O vacancies, Zn interstitial defect states.

The other peak is observed at 547 cm$^{-1}$. Wang et al. and Cheng et al. also observed this mode in (Co, Al) and Ce-doped ZnO. According to the literature, the additional modes are induced by host lattice defects; the host lattice defects in ZnO are activated and amplified with the doping content and then these modes appears. In the present case,
due to the smaller ionic radius of Ni²⁺ than that of Zn²⁺, more oxygen vacancies and Zn interstitials are created in the Ni²⁺ is doped into ZnO sample.²³⁹

3.2.3 Local structure of dopants and defects

The valance state and elemental contents of Ni doped ZnO NSTs can be determined from the binding energies of each element in the XPS spectra. The peak positions depend on the local structure of the different ions and can provide the information about the chemical state of different element. Figure 3-11 shows the XPS spectra of (1) Zn 2p, (2) Ni 2p and (3) O 1s states of pure and 3% Ni-doped ZnO NPs. Figure 3-11(a) shows two strong peaks centered around 1021.54eV and 1044.61eV which are in agreement with the binding energies of Zn 2p₃/₂ and Zn 2p₁/₂ respectively. Their spin-orbital splitting energy is around 23.07eV, confirming that Zn is present as Zn²⁺.

![XPS spectra of (a) Zn 2p₃/₂ and 2p₁/₂ states and (b) Ni 2p₃/₂ and 2p₁/₂ states of 3% Ni doped ZnO NPs, (c) O 1s states of undoped ZnO NPs and, (d) O 1s states of 2% Ni doped ZnO NPs.](image)

**Figure 3-11.** XPS spectra of the (a) Zn 2p₃/₂ and 2p₁/₂ states and (b) Ni 2p₃/₂ and 2p₁/₂ states of 3% Ni doped ZnO NPs, (c) O 1s states of undoped ZnO NPs and, (d) O 1s states of 2% Ni doped ZnO NPs.
Figure 3-11(b) shows that the peaks of Ni 2p\textsubscript{3/2} and Ni 2p\textsubscript{1/2} core levels are centered around 855.51 and 873.01 eV respectively, for the 3% Ni doped ZnO NPs, 12hr. milled. Whereas the corresponding satellite structures are clearly observed at 861 and 879 eV. 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\textsubscript{3/2} and Ni 2p\textsubscript{1/2} core levels. For Ni\textsuperscript{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 eV for the 3% Ni doped ZnO NPs. Also, as observed Ni 2p\textsubscript{3/2} (855.51 eV) position is quite different from that of the metallic Ni (852.7 eV), NiO (853.8 eV) and Ni\textsubscript{2}O\textsubscript{3} (856.7 eV).\textsuperscript{242} Furthermore, the shape of peaks for Ni metallic with satellites structure is narrow and different from the as observed spectrum of Ni-doped ZnO NPs.\textsuperscript{242} These results give evidence, that Ni ions are successfully substituted into tetrahedral sites of the ZnO wurtzite structure without forming any detectable secondary phases. The O1s peak in the surface is coherently fitted by Gaussian components, centered at 530.4, 531.5 and 532.7 eV, respectively, as shown in Figure 3-11(c-d) for the undoped and 3% Ni doped samples. The low binding energy curve at nearly 530.4 eV is attributed to O atoms at regular lattice site (O\textsubscript{L}), between O\textsuperscript{2−} and Zn\textsuperscript{2+} (or substitutional Ni\textsuperscript{2+}) ions.\textsuperscript{243} The medium binding energy curve at nearly 531.5 eV is associated with O atoms in the oxygen deficient regions (O\textsubscript{V}) within the ZnO matrix ZnO.\textsuperscript{244} The highest binding energy curve at nearly 532.7 eV corresponds to interstitial O atoms (O\textsubscript{i}) or surface oxygen in forms of −OH groups. From the relative intensity of the XPS peaks it is expected that presence of O\textsubscript{i} related defect is minimum in the both undoped and doped samples. This is consistent with the PL findings, where V\textsubscript{O} related green emission is dominant.

3.2.4 Optical Properties

Figure 3-12(a) shows the UV–Vis absorption spectra taken at RT for the undoped and doped samples. A distinct blue shift is observed in the absorption edge for the Ni doped ZnO NPs as compared to the undoped ZnO NPs. The observed blue shift indicates slight modification in the band structure in the Ni doped ZnO NSTs due to the incorporation of
Ni ions. Various ways have been used to determine the band gap \( E_g \) from optical absorption measurements.\(^{245}\) A practical method is to equate \( E_g \) with the wavelength at which the absorption is 50% of that at the excitonic peak (or shoulder). Since there is a lack of sharp edge in the doped samples, we followed the derivative method to extract the inflection point and calculate the \( E_g \). Calculated \( E_g \) are shown in Table 3-2.

It shows a blue shift in the as calculated band gap (\( E_g \)) with doping. The observed changes in the absorption edges indicate a change in the band structure due to doping and resulting defect.\(^{246}\) 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 Ni\(^{2+}\) cations may cause the change in such band structure.\(^{18, 57}\) The interaction leads to a modification in the energy bands.

PL spectra is very effective to characterize the presence of defects, which have been shown to play a crucial role in the development of FM ordering in ZnO based DMSs. Here, PL studies for the pure and Ni doped ZnO NPs at room temperature reveal a strong UV emission peak and a broad visible emission band ranging from 410 nm to 650 nm, as

![Figure 3-12.](image) (a) UV-Vis absorption spectra for the undoped and Ni doped ZnO NPs, showing blue shift of band edge absorption with doping.
shown in Figure 3-13(a-b). Observed broad PL peak in the visible region indicate existence of multicomponents which are extracted with multiple Gaussian peak fit. The obtained individual peak positions are tabulated in Table 3-2.

![Figure 3-13. (a-b) PL spectra of undoped and 3% Ni doped ZnO NPs. Strong UV and visible PL bands related to defects can be seen. Different PL peaks (I up to IV) are fitted with Gaussian functions.](image)

Undoped ZnO NPs exhibit an excitonic emission band centered on 380 nm (3.23eV) (Peak I). This near band-edge emission (NBE) is generally attributed to the recombination of free excitons present in the ZnO NSTs. Ni-doped ZnO NPs show a blue shift in this NBE as 3.26 eV. 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.

Next, PL peak (II) is a blue emission centered on ~ 425 nm (2.91 eV) and it is commonly observed in the ZnO NSTs, originating from the presence of Zn, related surface defects. As the emission attributed to O (in the red and near-infrared regions)
is not observed here and the blue emission corresponding to the Zn is observed, so our sample might be Zn rich. Hence, Zn and V\textsubscript{O} defect pairs are expected to be responsible for the visible emission. An intense green emission peak (III) is observed centered on ~515 nm (2.40 eV). The origin of this peak is considered as the presence of singly ionized oxygen vacancy states (V\textsuperscript{O}\textsuperscript{+}).\textsuperscript{247, 248} V\textsubscript{O} might have three different charge states, as F\textsuperscript{0} (doubly occupied), F\textsuperscript{+} (singly occupied), and F\textsuperscript{2+} (unoccupied) in the ZnO lattice.\textsuperscript{45, 59} However, the F\textsuperscript{0} and F\textsuperscript{2+} vacancies have spin-zero ground states; thus, they do not induce FM in ZnO.\textsuperscript{13, 59} The F\textsuperscript{+} vacancy contributes magnetic moment and can activate bound magnetic polarons (BMPs) in DMSs.\textsuperscript{45, 249} It is hard to distinguish V\textsubscript{Zn} and V\textsubscript{O} from the PL spectrum only due to the slight difference of their emission centers. So, lower density of V\textsubscript{Zn}, O\textsubscript{i} related defects might be present, as a long tail of visible emission have been observed upto higher wavelength. Next, a yellowish green emission peak (IV) centered on 550 nm (2.25 eV) is observed. It might appear from the antisite oxygen (V\textsubscript{Zn}) related defect states. Also small amount of O\textsubscript{i} defects and hydroxyl group might be present on the surface of ZnO NSTs as the same has been observed in the XPS spectra.\textsuperscript{250, 251} Note that the relative intensity of the UV emission to the visible emission peak has increased from 1.8 to 3.2 for the 3% Ni doped NPs as compared to the undoped ZnO NPs. So, the relative intensity of the defect modes have reduced in the doped NPs due to milling induced doping effect. Also magnetic moment value has reduced with the reduction of defect density for the Ni doped sample with higher milling time. So Defects are expected to play important role in the FM interaction of the doped Ni ions.\textsuperscript{234} But as both the milled and unmilled pure ZnO NPs are not showing any detectable FM moment in spite of the presence of defect modes, it indicates that the defects alone are not sufficient to promote FM ordering in the as synthesized sample. Thus doping of Ni\textsuperscript{2+} ions through milling effect 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.

### 3.2.5 Magnetic Properties

We observe distinct ferromagnetic behavior at and above RT in the doped Zn\textsubscript{1-x}Ni\textsubscript{x}O samples measured by VSM. Figure 3-14(a-f) shows the magnetic hysteresis (M-H) loop.
for the 3%, 5% Ni doped ZnO NPs for different milling times, measured at room
temperature. As observed saturation magnetic moment (Ms), are of the order of 2.6-1.6
emu/g and 2.9-2.8 emu/g for the 3% and 5% Ni doped samples respectively. Detailed
variation of the coercivity, retentivity and other magnetic properties are included in the
Table 3-3. It is well known that for the wide range of applications, the DMS material
should have a $T_c$, well above RT (300 K).

Figure 3-14. (a-f) Room temperature M-H plot showing the hysteresis loop for the 3% & 5% Ni doped
ZnO NPs for different milling times (4-12hr).

Figure 3-15 shows the temperature dependent magnetization for the 12hr. millied 3% Ni
doped ZnO NPs in the temperature range 300-700 K for 1500 G field. From the
differential plot of the M-T curve we obtain the $T_c$ as 597 K. 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 NPs. Note that compared to the 3% Ni doped
sample, 5% Ni doped sample does not exhibit any sharp transition in the M-T
measurement. The absence of a sharp FM to paramagnetic transition in the M-T measurement for higher percentage of doping may be for the partial antiferromagnetic interaction due to the reduction in average interatomic distance of doped Ni ions.

![Temperature dependent magnetization (M-T) curve of the 3% Ni doped ZnO NPs, 12hr. milled.](image)

Figure 3-15. Temperature dependent magnetization (M-T) curve of the 3% Ni doped ZnO NPs, 12hr. milled.

Note that for the 3% Ni doped sample $M_s$ value have decreased for higher milling time. As the contribution of Ni related extrinsic phase is disappearing with higher milling time, as evidenced from XRD pattern, hence more Ni ions are inserted inside the ZnO matrix. As the kind of FM interaction for the Ni ions in extrinsic phase and the Ni ions inside the ZnO matrix are different, as a result the overall FM moment value have decreased and the material have reached a single phase nature for the higher milling time. Also with further insertion of Ni ions inside ZnO matrix a preference of antiferromagnetic over ferromagnetic interactions might happen partially in the regions where the distance between adjacent Ni2+ ions decreases.²⁴⁶ Whereas, the change in magnetic moment value is not that much significant for the 5% Ni doped samples, as extrinsic phase remains even for higher milling time. Also the Ni related secondary phases have been observed in the XRD pattern for the 5% Ni doped samples. Further, the transition nature in the M-T measurement is not that sharp for the 5% Ni doped sample. This systematic study suggest that 3% doping is an optimum choice for the ball milling technique, as higher
concentration (5.7%) of doping shows impurity related XRD peak even for high milling time. Also we have reported in our earlier work about the choice of low concentration of magnetic doping and transition problem in the M-T curve for higher doping concentration. Thus, 3% doping of TM seems to yield an optimum choice for the observed high temperature FM in ball milling technique.

Note that, despite the presence of intrinsic defects no measurable magnetic moment is observed for the undoped sample. This confirms that the defects alone are not sufficient to account for the observed strong FM in case of our 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 due to the low defect concentration in that particular growth process. FM coupling could not occur due to the absence of defects. So we believe that the presence of TM ions and the defects (V\textsubscript{O}, Zn\textsubscript{i}, O\textsubscript{Zn}) promote the FM interaction to attain such a high moment value and high ordering temperature.

Table 3-2. 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>Relative peak intensity(\left(I_{\text{UV}}/I_{\text{D}}\right))</th>
<th>Absorption Band Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped ZnO NPs</td>
<td>3.23</td>
<td>2.85</td>
<td>2.45</td>
<td>2.25</td>
<td>1.8</td>
<td>3.28</td>
</tr>
<tr>
<td>3% Co doped ZnO NPs, 12h</td>
<td>3.26</td>
<td>2.88</td>
<td>2.45</td>
<td>2.25</td>
<td>3.2</td>
<td>3.32</td>
</tr>
<tr>
<td>Peak identity</td>
<td>NBE</td>
<td>Zn\textsubscript{i}</td>
<td>(O_{1}, F^+)</td>
<td>(O_{2\text{h}}, O_{i})</td>
<td>Hydroxyl groups</td>
<td></td>
</tr>
</tbody>
</table>
Table 3-3. 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. $M_0$, $m_{eff}$, $\chi_m$, N are extracted from the BMP fitting of the M-H curves for different $\text{Zn}_{1-x}\text{Ni}_x\text{O}$ ($x = 0, 0.03$) 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>Nil</td>
<td>Nil</td>
</tr>
<tr>
<td>4-ZnO</td>
<td>2.56</td>
<td>280</td>
</tr>
<tr>
<td>8-ZnO</td>
<td>1.84</td>
<td>260</td>
</tr>
<tr>
<td>12-ZnO</td>
<td>1.63</td>
<td>274</td>
</tr>
</tbody>
</table>

3.2.6 Possible FM Interaction

The presence of the intrinsic defects ($V_O$, $Zn_i$, $V_{Zn}$ etc.) play important role in the FM interaction for TM doped ZnO based DMS systems.\cite{240, 246, 253} The long-range interaction is necessary to obtain HT FM in dilute concentration of TM doped ZnO DMS systems and it can be mediated by defect induced states.\cite{11, 13, 60} According to the bound magnetic polaron (BMP) model, bound electrons (holes) in the defect states can couple with TM ions and cause the ferromagnetic regions to overlap, giving rise to long range FM ordering.\cite{13, 168} When donors or acceptors are present, the sp-d interaction often leads to the formation of BMPs. A BMP is a particular type of complex near an occupied donor or an acceptor. It consists of the bound electron (hole) together with the spins of the TM ions within a hydrogenic Bohr orbit of radius $r_H$ (for ZnO, $r_H=0.76$ nm). Due to the sp-d interaction the latter spins can have a significant net ferromagnetic alignment, in this case the BMP resembles a “ferromagnetic ball” embedded in the host lattice doped with TM ions that surround it.\cite{168} Percolation of these BMPs promotes high magnetic moment and high Curie temperature. In an earlier work on Co doped ZnO NPs, we have demonstrated the important role of BMPs to achieve HT FM with high moment for the ZnO based DMS system.\cite{57}

Intrinsic defects, such as $V_O$, $Zn_i$ are inherently present in the as synthesized $\text{Zn}_{1-x}\text{Ni}_x\text{O}$ NPs due to the stabilization of structure. Our systematic study shows that formation of defect ($Zn_i$, $V_O$) 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:

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

(1)

The details in 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 3-16 for the 3% Ni doped ZnO NPs. The fitted data closely follows the experimental data and the fitted parameters are tabulated in Table 3-3. 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 3-3).

However, the calculated BMP concentration is relatively small compared to the necessary concentration of \( 10^{20} \) cm\(^{-3} \) in order to have long range percolation as reported by Coey et al.\textsuperscript{13} Thus, the BMP concentration cannot fully account for the observed high magnetic moment in the doped ZnO NPs. Further some of the isolated Ni ions might interact by AFM interaction, resulting overall decrease of BMP concentration.\textsuperscript{246} Also defect related surface spins might contribute partly for the observed FM in the Ni doped ZnO NPs.\textsuperscript{249} 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}

Note that, the defect related FM moment for the undoped NSTs as well as for many reports on TM doped ZnO NSTs are of much lower magnitude (micro or mili emu/g).\textsuperscript{135, 170} We observed at least three orders of higher moment as well as high \( T_c \) value in the Ni doped ZnO NPs. 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. More detailed experimental work like AHE, magnetotransport measurements might provide further insights into the origin of ferromagnetism in magnetically doped oxides.\textsuperscript{170}
3.2.7 Summary

In summary, Ni doped ZnO (Zn$_{1-x}$Ni$_x$O) NPs showing HTFM with high magnetic moment have been synthesized for a low concentration (3%) of Ni doping. We observe through systematic study that 3% doping is an optimum choice for the ball milling technique, as higher concentration (5,7%) of doping shows appearance of secondary phases, further FM to PM transition is not sharp as seen in the M-T measurement. XRD, Raman, XPS, HRTEM and EDS analysis confirm the absence of extrinsic phases in the 3% Ni doped ZnO NPs for higher milling time. HRTEM lattice image and the SADE patterns show that all the NPs are of single crystalline phase. RT magnetic measurements exhibit FM behavior with saturation moment of 2.6-1.6 emu/g and $T_c$ around 597 K. XPS spectra also confirm the presence of Ni ions in 2+ states within the host lattice. PL and UV-VIS measurements show doping induced modification in the band edge emission and absorption spectra. These findings suggest that Ni$^{2+}$ ions are successfully
incorporated into the wurtzite lattice at the Zn$^{2+}$ sites. Also, PL and XPS spectra confirm the nature of defects present in the undoped and doped samples. The FM moment has decreased due to decrease of defect density with higher milling time. The observed FM is occurring by the intrinsic exchange interaction of Ni$^{2+}$ ions and V$_O$, Zn$_i$ defects through BMP formation and their percolation. Both the Ni ions as well as defects are significant ingredients to attain high moment as well as high ordering temperature. The structural, optical, and magnetic properties are significantly changed for the incorporation of Ni$^{2+}$ ions in the Zn$^{2+}$ lattice site.

3.3 Structural, Optical and Magnetic Properties of Co doped TiO$_2$ nanoparticles

3.3.1 Highlights

Here we try to grow Ti$_{1-x}$Co$_x$O$_2$ (x = 3%, 5%, 8%) NPs of single phase nature by a ball milling technique. We investigate on the detail structural, optical and magnetic properties of as grown NPs to indentify the phase formation, doping effect and the presence of defects which are believed to play key role in the ferromagnetic interaction at and above room temperature. The obtained NPs are identified as of the anatase TiO$_2$ structure with no signature of Co-cluster or any other oxides of Cobalt by XRD, Raman, HRTEM and EDS analysis. Raman scattering spectra is used to observe the defect related shifting and broadening of most intense peaks, E$_g$(1) at 142 cm$^{-1}$ and highest frequency E$_g$(3) at 638 cm$^{-1}$ Raman modes. Photoluminescence study further shows the band edge emission peak and oxygen vacancy defects in doped NPs. RT FM is observed in the doped samples with saturation magnetization ($M_s$) of 2.79 - 7.39 emu/g. Temperature dependence magnetization ($M$-T) shows sharp ferromagnetic to paramagnetic transition with a high Curie temperature ($T_c$) of ~ 793K for 3% doped NPs whereas higher percentage of doped samples does not exhibit a sharp magnetic transition.
3.3.2 Structural and morphology analysis

The XRD patterns of undoped and Co doped TiO$_2$ NPs are shown in Figure 3-17. All the diffraction peaks corresponded to the tetragonal anatase phase of TiO$_2$. There is no signature of any secondary phases such as rutile and brookite phase of TiO$_2$ or any Co-oxides phases and Co composites, which indicates that Co cations successfully occupy Ti cation sites in the anatase TiO$_2$ lattice. Slow scan comparison of (101) peaks for undoped and doped samples are shown in the inset of Figure 3-17, which indicates the slight shift of the peak to lower angle in doped samples. In addition, the doped samples show lowering of peak intensity and increase in FWHM of XRD patterns. The corresponding expansion of the lattice parameter could be expected, because the ionic radius of dopant Co$^{2+}$ ions (0.65 Å) was larger than that of host Ti$^{4+}$ ions (0.61 Å). Compared to undoped TiO$_2$, the nanoparticles size of doped samples is reduced considerably during milling. The average particle size of undoped and Co:TiO$_2$ NPs, determined from the XRD pattern are obtained as ~81 nm and 40 nm respectively. Note that, the existence of very small amount of Co clusters might be there, since they are hardly detectable by XRD measurement.

![Figure 3-17](image)

**Figure 3-17** XRD pattern of undoped, 3% and 8% Co-doped TiO$_2$ NPs. The inset shows comparison of the (101) peak for undoped and doped TiO$_2$ NPs.
The morphologies of doped NPs as obtained by FESEM and TEM are shown in Figure 3-18(a,b) and Figure 3-18(c,d) respectively, which reveals that the as grown NPs were almost spherical in size with average particle size in the range of 35 - 50 nm. The HRTEM study is applied to further analysis of lattice fringes for the doped samples, which are presented in the inset of Figure 3-18(c) and (d). The clear lattice fringes are obtained, implying that the as grown samples are highly crystalline. The d-spacing of the crystal plane is calculated as 3.28 Å and 3.38 Å for 3% and 8% doped samples, respectively indicating the preferable crystal growth plane is (101) and it is also the highest intensity peak in the XRD pattern shown in Figure 3-17. The crystalline nature further analyzed from selected area electron diffraction (SAED) pattern shown in the inset of Figure 3-18(d), indicating polycrystalline anatase TiO$_2$ NPs.

**Figure 3-18** SEM images of the morphology of the Co doped TiO$_2$ NPs: (a) 3% doped, (b) 8% doped. TEM images of the doped TiO$_2$ NPs: (c) 3% Co (d) 8% Co, The inset in (c) and (d) show HRTEM lattice images of 3% and 8% Co doped NPs, respectively. The inset in (d) also shows the corresponding SAED pattern of 8% doped sample.
3.3.1.3 Raman Spectra analysis

Figure 3-19 RT shows the Raman spectra of the Ti$_{1-x}$Co$_x$O$_2$ NPs. Oxygen deficiency within the material, however, strongly affects the Raman spectrum by producing shifting and broadening of some spectral peaks. All the Raman peaks of as grown Ti$_{1-x}$Co$_x$O$_2$ NPs are similar with the tetragonal anatase TiO$_2$ phase. However, the most intense E$_g$(1) Raman mode at 142 cm$^{-1}$ shows the maximum blue shift while E$_g$(3) Raman mode at 638 cm$^{-1}$ is red shifted in doped samples as compared to undoped TiO$_2$. Moreover, all the observed peaks for doped samples broaden and decrease in intensity with respect to undoped samples. Interesting change of the main E$_g$(1) Raman mode has been interpreted by different mechanism such as the non-stoichiometry due to oxygen vacancies or disorder induced defects and phonon confinement effects. The crystalline size in the nanoscale range may effects the frequency shifting and broadening of this peaks due to the phonon confinement, as reported for the small sized TiO$_2$ NPs by various authors.$^{254, 255}$ Similar examination regarding the phonon confinement, both in experimental and theoretical calculation was reported by Zhang et al.$^{256}$ They suggested that along with the phonon confinement, oxygen vacancies also play an important role for frequency shifting as well as broadening of Raman modes. To compare the phonon confinement, we also measure the Raman spectra of the 5h milled undoped TiO$_2$ NPs having nearly same crystallite size. Here, a small blue shift of E$_g$(1) Raman mode observed for undoped TiO$_2$ 5 h milled NPs which may be due to phonon confinement and/or defects, but considerable large blue shift for 5 h milled Co:TiO$_2$ NPs is attributed to the existence of more defects. Thus oxygen vacancies plays dominant role in Co:TiO$_2$ NPs in our samples. In addition, a red shift of E$_g$(3) Raman mode clearly observed for doped samples. This was also reported by C. Huag et al. for Co doped TiO$_2$ nanotubes.$^{257}$ Thus the introducing of Co into the TiO$_2$ lattice largely affects the Raman modes. The absence of characteristic vibrational modes of Co cluster, Cobalt-oxide or Co-Ti species in the Raman spectra in doped samples clearly indicates that Co occupied the substitutional sites in the host TiO$_2$ lattice, which is consistent the results of XRD pattern.
3.3.3 Optical absorption studies

Many research groups have confirmed incorporation of Co into the TiO$_2$ lattice using a different optical measurements such as XPS spectra\textsuperscript{258} and PL spectra\textsuperscript{259, 260}. Evidence for Co substitution in the TiO$_2$ can be further confirmed from the UV-Vis absorption spectra. Generally the bandage of Co doped samples are shifted to lower energy, Compared to undoped TiO$_2$. The red shift of absorption spectra with insertion of Co into TiO$_2$ has already been reported in Co doped TiO$_2$ thin films as well as the other transition metal doped oxide materials [34-36]\textsuperscript{261, 262}.

According to the energy band structure of TiO$_2$, the valence band (VB) top and the conduction band (CB) bottom correspond to mainly O$_{2p}$ and Ti$_{3d}$ states, respectively. The optical absorption around 380 nm for undoped TiO$_2$ is solely band-to-band (O$_{2p}$ – Ti$_{3d}$) transition while the slight red shift in Co:TiO$_2$ NPs can be explained as being mainly due to sp-d exchange interactions between the band electrons and the localized d electrons of the Co$^{2+}$ ions substituting Ti$^{4+}$ cations. The s-d and p-d exchange interactions give rise to

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**Figure 3-19.** Raman Spectra for the undoped and Co doped TiO$_2$ NPs: (a) undoped without milling, (b) undoped, (c) 3% doped and (d) 8% doped 5 hr milled NPs. The inset on the upper right side show the magnified view of the E$_g$(1) Raman modes.
downward shifting of the CB edge and an upward shifting of the VB edge, leading to a band gap narrowing. The indirect band gap of all samples were determined by extrapolating the tangent of the \((ahu)^{1/2}\) vs \(hu\) curves to \((ahu)^{1/2} = 0\) as shown in the inset of Figure 3-20. The observed band gap of undoped \(\text{TiO}_2\), 3% and 8% Co doped samples are 3.23 eV, 3.07 eV and 3.16 eV, respectively. The lowering in band gap energy for doped samples indicating Co cations have been successfully incorporated into the \(\text{TiO}_2\) crystal lattice.

![Figure 3-20. UV-Vis-DRS absorption spectra of undoped and Co doped TiO\(_2\) NPs: (a) undoped, (b) 3% 5 h (c) 3% 8 h and (d) 8% 5 h milled Co doped NPs. Doped NPs show clear red-shifted band. The inset shows \((ahu)^{1/2}\) vs \(hu\) plot, indicating reduction of band gap for doped NPs.](image)

The defect states can be well understood from the following relations: [39]

\[
\begin{align*}
\text{TiO}_2 & \rightarrow \text{TiO}_2^- (e^-/h^+) (e_{\text{CB}}^- + h_{\text{VB}}^+) \\
V_0^o + e_{\text{CB}}^- & \rightarrow V_0^- (e^- \text{ trapping in deep traps}) \\
V_0^o + h_{\text{VB}}^+ & \rightarrow V_0^o^- + h_0 \ (\text{radiative recombination})
\end{align*}
\]

Where \(V_0^o\) (Kroger notation) is an ionised oxygen vacancy level, which is rapidly traps a photogenerated CB electrons \((e_{\text{CB}}^-)\). This electron subsequently interacts with a VB hole \((h_{\text{VB}}^+)\) either radiatively or nonradiatively. The dominant but not exclusive route for charge carrier recombination in nanostructured semiconductor is the nonradiative path.
because of the strong coupling of wave functions of trapped electrons and holes with the lattice phonons.\textsuperscript{13}

3.3.4 Magnetic measurements

Distinct RT ferromagnetic behaviour has been observed in the doped samples only. While, no trace of FM is observed in the undoped and milled TiO\textsubscript{2} samples that are first measured under similar conditions using the VSM, despite the presence of some intrinsic defects in undoped TiO\textsubscript{2} NPs. This confirms that defects alone cannot account for the observed FM in the doped TiO\textsubscript{2} NPs. Figure 3-21 shows the RT magnetic hysteresis ($M$-$H$) loops for 3\% and 8\% doped 5 h milled NPs measured at 300 K. The saturation magnetizations ($M_s$) of 3\% and 8\% doped samples are 2.79 emu/g and 7.39 emu/g with a coercive field ($H_c$) 253 G and 259 G, respectively. Post growth annealing of both 3\% and 8\% doped samples in air atmosphere at 300°C for 2 hrs effects the magnetization. The saturation magnetization of post-growth annealed samples in air atmosphere is found to be decreased considerably which might be due to reduction of oxygen vacancy concentration while annealed in oxygen-rich environment.\textsuperscript{229}

\begin{figure}[h]
\centering
\includegraphics[width=0.7\textwidth]{M-H_loop.png}
\caption{RT M-H hysteresis loop for the Co doped TiO\textsubscript{2} NPs: 3\%, 8\% Co doped TiO\textsubscript{2} NPs. The insets show the magnified M-H loop, showing clear FM behaviour. Measured parameters are listed in Table 3.1.}
\end{figure}
It is well known that for use in a wide range of applications without temperature control, the DMSs should have a $T_c$ enough above RT (300K). Figure 3-22 shows the temperature dependent magnetization of 3% Co doped NPs in the temperature range 300 to 850 K. HT measurement is carried out in nitrogen atmosphere to avoid any oxidation effect which can affect the FM ordering of the material. From the differential plot of the M-T curve we obtained the $T_c$ as $\sim 793$K for 3% doped NPs, which implies that the FM is not due to the Co metal ($T_c > 1300$K). As seen from the M-T curve, at higher temperature ($> 750$K) the magnetization shows a rapid decrease with temperature for 3% doped sample. This magnetic transition suggests that high-temperature process causes a rapid destruction of ferromagnetic coupling. Note that compared to the 3% doped sample, 8% doped sample did not exhibit any sharp transition at higher temperature. The absence of a sharp FM to paramagnetic transition in M-T curve for higher doped (8% Co) TiO$_2$ NPs may be because of possible antiferromagnetic interaction due to the reduction in average interatomic distance of doped Co ions. Thus, lower concentration (3%) of doped NPs is found to yield best result for the observed high temperature FM.

![Figure 3-22](image)

**Figure 3-22.** RT Temperature dependent magnetization (M-T) curve for 3% Co doped TiO$_2$ NPs showing high transition temperature ($T_c$). It shows sharp ferromagnetic to paramagnetic transition.
Table 3-4 Detail of magnetic measurements for Ti$_{1-x}$Co$_x$O$_2$ (x = 3%, 8%) NPs: saturation magnetization ($M_s$), coercive filed ($H_c$); remanent magnetization ($M_r$) and transition temperature ($T_c$) are listed. $M_0$, $m_{eff}$, $\chi_m$, N are calculated from BMP model fitting of the M-H curve.

<table>
<thead>
<tr>
<th>Co doping concentration</th>
<th>$M_s$ (emu/g)</th>
<th>$H_c$ (Gaus)</th>
<th>$M_r$ (emu/g)</th>
<th>$T_c$ (K)</th>
<th>$M_0$ (emu/g)</th>
<th>$M_{eff} \times 10^{17}$ (emu)</th>
<th>$\chi_m \times 10^{-5}$ (cgs)</th>
<th>$N \times 10^{16}$ (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3%</td>
<td>2.79</td>
<td>253</td>
<td>0.21</td>
<td>793</td>
<td>3.31</td>
<td>2.56</td>
<td>1.16</td>
<td>0.504</td>
</tr>
<tr>
<td>8%</td>
<td>7.39</td>
<td>259</td>
<td>0.54</td>
<td>...</td>
<td>8.73</td>
<td>2.53</td>
<td>2.91</td>
<td>1.344</td>
</tr>
<tr>
<td>3% (300 C) annealed</td>
<td>1.42</td>
<td>324</td>
<td>0.12</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>8% (300 C) Annealed</td>
<td>4.58</td>
<td>282</td>
<td>0.37</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>

Figure 3-23 Initial portion of the M-H curve fitted with BMP model (Eq. 1): (a) 3% and (b) 8% Co doped NPs. Extracted parameters are shown in Table 3-5.
3.3.5 Possible FM interaction and it’s Origin

The origin of observed FM at room temperature in these Ti$_{1-x}$Co$_x$O$_2$ NPs could arise from a number of possibilities, such as the intrinsic property of the doped NPs, extended defects in the NPs, formation of some nanoscale Co-related secondary phase. Our systematic study shows that formation of defect (O$_V$) 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-H data using the BMP model.\textsuperscript{168} The formula used for the fitting of BMP model:

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

3.3.6 Summary

In summary, Ti$_{1-x}$Co$_x$O$_2$ (x = 3%, 5%, 8%) NPs are synthesized by a simple ball milling technique, a physical doping method. Ferromagnetic behaviour at and above RT is explored in Co doped TiO$_2$ NPs using XRD, Raman spectra, HRTEM, EDS, PL spectroscopy and VSM measurements. XRD, HRTEM and EDS analysis confirm the absence of any secondary phases other than the anatase TiO$_2$ structure. Micro-Raman studies show the defect related shifting and broadening of E$_g$(1) and E$_g$(3) Raman modes. The additional weak PL emission peak at 491 nm in Co:TiO$_2$ NPs indicating the defects like oxygen vacancies. From these observations we expect that the FM behaviour of as grown NPs is mediated by Oxygen vacancies created by the incorporation of Co into the TiO$_2$ crystal lattice, not originated from extrinsic phases, like metallic Co clusters or any other Co-oxides. Thus Co:TiO$_2$ NPs were found to exhibit effective high T$_c$ ferromagnetism and it is an important step for the development of practical spintronic devices.