PART-I

ENHANCEMENT OF MAGNETIC PROPERTIES OF RARE EARTH NEODYMIUM DOPED ZnO NANOPARTICLES

The synthesis of neodymium doped ZnO (Zn$_{1-x}$Nd$_x$O, x=0.0, 0.03, 0.06 and 0.09) nanostructures by co-precipitation method with improved optical and magnetic performance is reported. X-ray diffraction pattern indicates that most of Nd$^{3+}$ ions are incorporated in Zn$^{2+}$ ions of ZnO lattice and hence there is no secondary peak of NdO$_3$ in synthesized ZnO nanoparticles (NPs). The FTIR analysis of synthesized NPs exhibits similar patterns in Zn/Nd-O bands observed at 480 cm$^{-1}$. HRSEM images revealed the formation of spindle like morphology for pure and Nd doped ZnO with an average particle size of 200-300 nm. The incorporation of Nd ions is confirmed by EDS analysis. UV-Visible absorption spectra of pure and Nd doped ZnO NPs showed the variation of band gap in the range of 3.06 – 2.65 eV. Raman analysis confirmed the formation of wurtzite structure of NPs which is distorted due to Nd substitution in ZnO matrix. X-ray photoelectron spectroscopy (XPS) confirmed the Nd incorporation in ZnO lattice as Nd$^{3+}$. The results of PL and VSM showed that ferromagnetism of Nd doped ZnO NPs is originated from the oxygen vacancies.
SYNTHESIS AND MAGNETIC INVESTIGATIONS OF RE (Nd, Gd) DOPED ZnO NANOSTRUCTURES

CHAPTER-IV

4.1 INTRODUCTION

Recently, ZnO nanostructures are very much desirable materials because of their tremendous optical, electrical, magnetic, photo catalytic and biomedical properties [1]. Diluted Magnetic Semiconductors (DMS) have received extensive attention due to their promising applications in spintronic devices. Among various semiconductors, ZnO nanoparticles are particularly appealing because of their theoretically predicted room temperature ferromagnetism (RTFM) as well as their direct wide band gap (3.37 eV) and large exciton energy (60 meV), which may enable in integration of magnetic and optoelectronic properties in designing new devices [2]. In general, doping with certain ions is an efficient way to further enhance the properties of semiconductor nanostructures. In the past decade, ZnO doped with 3d transition metal (TM) ion has been intensively studied to obtain DMSs. In these type of TM doped ZnO, TM ion interactions play a vital role in controlling the excitation dynamics [3, 4] and also its magnetism is so weak that it is often buried by experimental artifacts and has always experienced problems in reproducibility or precipitation of secondary metallic phases.

Compared with 3d TMs, 4f rare earth (RE) elements have larger magnetic moments and may potentially enhance ferromagnetism (FM) in doped semiconductors [5, 6]. Theoretical investigations revealed that stable FM coupling between RE ions are mediated by the delocalized electrons. This is particularly beneficial to ZnO, since it exhibits n-type conductivity with a large population of ‘s’ electrons [7]. The influence of RE doping in ZnO mainly focuses on its optical properties. A fewer reports are available on RE doped ZnO nanostructures which provide information about the density of RE ions and also the response of the nanostructures to the applied magnetic field.
SYNTHESIS AND MAGNETIC INVESTIGATIONS OF RE (Nd, Gd) DOPED ZnO NANOSTRUCTURES

In the past, several researchers focused their attention on RE elements doped ZnO especially ZnO doped with Ce, Eu, Gd, Tb, Yb and Er [8, 9]. The present work mainly focuses on Nd doped ZnO NPs. Previously some experimental and theoretical researches were reported on Nd doped ZnO [10]. Doping method has been extensively used in modification of the electronic structure of ZnO NPs to achieve improved optical, magnetic and catalytic properties [11]. Recently, Wang et al reported an RTFM with a large magnetic moment of 4.1 μB per Nd in their Nd doped ZnO prepared by a vapor transport method [6].

Several methods for synthesis of ZnO are reported in the literature, such as co-precipitation, ultrasonic radiation using precipitation, microwave irradiation, mechanical ball milling, solution combustion and microwave assisted solvothermal methods [12, 13]. Among these methods, co-precipitation method attracts more attention due to its unique advantages including low cost, simple lab equipment, easy adjusting dopant concentration and synthesized huge amount of nanoparticles (NPs) etc. In the present paper, a simple co-precipitation method was applied in preparation of Nd doped ZnO nanostructures. The influence of various mole fractions of Nd$^{3+}$ ions in ZnO and their structural, optical and magnetic properties were discussed in detail.

4. 2 EXPERIMENTAL DETAILS

Synthesis of undoped and Nd doped ZnO was carried out using analytical grade zinc nitrate [Zn (NO$_3$)$_2$], neodymium nitrate [Nd (NO$_3$)$_2$] and sodium hydroxide (NaOH) in its received condition. In the synthesis process, a required amount of zinc nitrate was completely dissolved in deionized water and a required amount of aqueous NaOH solution was added drop by drop to the aqueous zinc nitrate. The solution was stirred and
SYNTHESIS AND MAGNETIC INVESTIGATIONS OF RE (Nd, Gd) DOPED ZnO NANOSTRUCTURES

maintained at room temperature for 30 min, and then kept at 80 °C for 5 hours. Later, a white precipitate was formed slowly. Next, the white precipitate was washed several times with double distilled water and ethanol. The precipitate was dried at 120 °C for one hour. The obtained ZnO samples were annealed at 300 °C in the air atmosphere for 2 hours. Thus, powder of ZnO was collected and used for further studies.

For the synthesis of Zn$_{1-x}$Nd$_x$O (x = 0.03, 0.06 and 0.09) NPs, the calculated amount of neodymium nitrate was mixed with zinc nitrate solution. The required amount of aqueous NaOH solution was added drop by drop to the homogenous mixture to get a white precipitate. The procedure adopted for the preparation of undoped ZnO NPs was followed in the synthesis of Nd doped ZnO NPs.

4.3 CHARACTERIZATION OF SAMPLES

The structural analysis of the synthesized samples was carried out by using a powder X-Ray diffractometer (PANalytical X’Pert Pro) with Cu-Kα radiation (wavelength: 1.5418 Å). The functional characterization was carried out using Fourier Transform Infra Red (FT-IR) spectroscopy which employs Thermo Nicolet 380 with KBr pellet method at room temperature in the range of 4000-400 cm$^{-1}$. The morphology of the samples was examined using an FEI QUANTA 250, Scanning Electron Microscope. A Cary Eclipse photoluminescence (PL) spectrograph was used to record PL spectra. The XPS measurements were performed with an XPS instrument (Carl Zeiss) equipped with Ultra 55 FESEM with EDS and all the spectra were recorded under ultra high vacuum with AlK$_\alpha$ excitation at 250 W. Raman spectra of the films were recorded using a micro Raman spectrometer (Acton SpectraPro 2500i, Princeton Instruments,
Acton Optics & Coatings). The magnetic measurements were carried out using a vibrating sample magnetometer (Lake Shore Model-7404, USA).

4.4 RESULTS AND DISCUSSION

4.4.1 Structural analysis

Figure 4.1 shows the X-ray diffraction patterns of undoped and different concentration of Nd doped ZnO nanostructures. All the diffraction peaks correspond to hexagonal wurtzite structure phase which is in agreement with the respective JCPDS card no.36-1451. It is worthy to note that no additional peaks due to Nd or NdO₂ phases are present in the prepared samples, thus indicating the phase purity of ZnO nanostructures. The absence of impurity peaks and close matching with the hexagonal phase structure of the synthesized samples also suggest that the samples are highly crystalline and most of Nd³⁺ ions are incorporated into ZnO lattice [14].
Figure 4.1 (A) XRD patterns of undoped ZnO and Nd doped ZnO NPs and (B) (100), (002) and (101) peaks shifting towards lower angle side and decreasing intensity with the increase of Nd concentration.

It is observed from Figure 4.1(B) that the position of the main peaks shifted to lower angle side, which indicates that Nd$^{3+}$ ions are incorporated into the ZnO crystal lattice [15]. This shift is caused by the strain developed due to the effect of different ionic radii of the respective metal ions. The crystallite size (D) for hexagonal ZnO doped with different concentration of Nd$^{3+}$ ions was estimated by using the formula available elsewhere [16-19]. The average crystallite size (D) was found to be in the range of 38-29 nm. The lattice strain and dislocation density was calculated using the relation given in chapter III and is tabulated in Table 4.1.
Table 4.1. Crystallite size, micro strain and dislocation density values of Nd doped ZnO NPs.

<table>
<thead>
<tr>
<th>Nd concentration</th>
<th>Crystallite size (D) (nm)</th>
<th>Micro-strain (ε) (10^{-3})</th>
<th>Dislocation density (δ) (lines/m^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>38.4</td>
<td>1.01</td>
<td>7.62052E+14</td>
</tr>
<tr>
<td>0.03</td>
<td>35.2</td>
<td>1.92</td>
<td>9.96827E+14</td>
</tr>
<tr>
<td>0.06</td>
<td>30.5</td>
<td>2.01</td>
<td>1.95283E+15</td>
</tr>
<tr>
<td>0.09</td>
<td>29.2</td>
<td>2.21</td>
<td>1.40834E+15</td>
</tr>
</tbody>
</table>

The lattice parameters of semiconductors usually depend on the foreign atoms, defects and the difference in ionic radii with respect to the substituted matrix ions. The difference in the ionic radii of Nd^{3+} with respect to Zn^{2+} gives the variations existing in the lattice constants.

For pure ZnO NPs, the values of the lattice parameters 'a' and 'c' are estimated to be 3.25 Å and 5.21 Å, respectively. The substitution of Nd^{3+} ions in the place of Zn^{2+} ions increases the values of the lattice constants 'a' and 'c' and the interplaner distance of 'd' for the doped ZnO NPs.

The volume (V) of the unit cell for hexagonal system is calculated from the equation [20] given in chapter III, the unit cell volume of ZnO also increases with the substitution of RE metal. The volume of the unit cell values are estimated as 47.508, 47.609, 47.666 and 47.729 Å^3 for ZnO, Zn_{0.97}Nd_{0.03}O, Zn_{0.94}Nd_{0.06}O and Zn_{0.91}Nd_{0.09}O respectively. This indicates that, Nd^{3+} ions reside partially in tetrahedral Zn positions.
The positional parameters, bond length and atomic packing factor were calculated by using the equations described in chapter III.

There is a strong correlation between c/a ratio and ‘u’. The c/a ratio decreases with increase in ‘u’ in such a way that those four tetrahedral distances remain nearly constant through a distortion of the tetrahedral angles due to the long-range polar interaction. In this case, the c/a ratio decreases in the Nd doped ZnO NPs. The values of c/a and ‘u’ parameters are given in Table 4.2. The Zn-O bond length of pure ZnO NPs is 1.9752 Å. The bond length values are found to increase with increase in the Nd concentrations (Table 4.2), due to the effect of the replacement of Zn$^{2+}$ ions in ZnO lattice.

**Table 4.2.** Structural parameters of Nd doped ZnO NPs.

<table>
<thead>
<tr>
<th>Nd concentration</th>
<th>Lattice parameter values (Å)</th>
<th>Atomic packing factor (c/a)</th>
<th>Volume (V) (Å$^3$)</th>
<th>Positional parameter (u)</th>
<th>Bond length (Zn-O) (L) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.247 5.205 1.603 47.508 0.3803 1.975</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.03</td>
<td>3.249 5.211 1.604 47.610 0.3797 1.978</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.06</td>
<td>3.249 5.209 1.603 47.667 0.3796 1.978</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.09</td>
<td>3.252 5.212 1.603 47.730 0.3798 1.979</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4.4.2 FT-IR analysis

The chemical compositions of the synthesized Nd doped ZnO samples were confirmed by FTIR spectroscopy. FTIR spectra shown in Figure 4.2 consist of various well defined peaks observed at 3448, 2372, 1492, 883 and 481 cm\(^{-1}\). The absorption peak which appeared at 3448 cm\(^{-1}\) corresponds to the stretching vibration of O-H band. This absorption peak appears due to the O-H stretching of surface absorption of water molecules [22]. The peaks found at 2860 and 2950 cm\(^{-1}\) are attributed for symmetric and asymmetric C-H bonds. The absorption band at 2372 cm\(^{-1}\) is attributed from the CO\(_2\) present in the samples. These CO\(_2\) bands may get increased due to some trapped CO\(_2\) in air ambient during the characterization measurements [23]. The peaks appearing at 1492 and 881 cm\(^{-1}\) represent the asymmetrical stretching of nitrate (NO\(_3\)) compounds. The absorption peak appeared below 480 cm\(^{-1}\) can be attributed to the metal-oxygen peak of Zn-O stretching mode in ZnO matrix [24].
No other absorption band was detected in the FTIR spectrum, which substantiates that the synthesized NPs are almost pure without any significant impurity. In Nd doped ZnO samples, the vibration mode which appeared at ~550 cm\(^{-1}\) represent the Zn-Nd-O stretching band which may be due to the substitution of Nd\(^{3+}\) ions in Zn\(^{2+}\) sites [25]. The existence of additional peak at 550 cm\(^{-1}\) and increased intensity of this peak with an increase in Nd concentration proves in the substitution of Nd ions in ZnO lattice.
4.4.3 Morphological analysis

Figure 4.3 shows the HRSEM images of Nd doped ZnO NPs with heterogeneous morphology. Spindle like particles with a horizontal diameter of 200-300 nm were obtained and it can be observed that there is a smooth surface over the particles. The average diameters of Nd doped ZnO NPs increases with an increase of Nd ion concentration. Hence, it is reasonable to mention that Nd doping favors faster growth of spindle particles.
Figure 4.3. HRSEM images for (a1, a2) undoped ZnO, (b1, b2) Zn$_{0.97}$Nd$_{0.03}$O,
(c1, c2) Zn$_{0.94}$Nd$_{0.06}$O and (d1, d2) Zn$_{0.91}$Nd$_{0.09}$O NPs.
4.4.4 Compositional analysis

The chemical compositions of synthesized ZnO NPs with different Nd concentrations were measured by EDS spectra as shown in Figure 4.4 (a-d). These spectra confirmed the presence of Zn, O and Nd in Nd doped ZnO NPs whereas the spectrum of undoped ZnO NPs exhibited the presence of only zinc and oxygen ions. The obtained EDS result confirms about the presence of Nd$^{3+}$ which is successfully substituted as a dopant in ZnO matrix.

**Figure 4.4.** EDS analysis for (a) undoped ZnO, (b) Zn$_{0.97}$Nd$_{0.03}$O, (c) Zn$_{0.94}$Nd$_{0.06}$O and (d) Zn$_{0.91}$Nd$_{0.09}$O NPs.
4.4.5 Photoluminescence studies

The photoluminescence (PL) properties for undoped and Nd doped ZnO NPs investigated at room temperature using a 320 nm excitation wavelength of Xe lamp is shown in Figure 4.5. A strong near-band-edge emission (NBE) in the UV region and weak band deep-level emission in visible region were detected. The undoped ZnO PL spectrum shows five emission peaks at 390, 411, 439, 489 and 523 nm, analysed by Gaussian deconvolution.

![Photoluminescence spectra](image)

**Figure 4.5.** Photoluminescence spectra of (a) undoped ZnO, (b) Zn$_{0.9}$Nd$_{0.05}$O, (c) Zn$_{0.94}$Nd$_{0.06}$O and (d) Zn$_{0.91}$Nd$_{0.09}$O NPs.
SYNTHESIS AND MAGNETIC INVESTIGATIONS OF RE (Nd, Gd) DOPED ZnO NANOSTRUCTURES

The PL peak at 390 nm is due to the recombination of photo generated holes and electrons occupying the oxygen vacancies in the ZnO crystalline photo catalyst [26]. During the recombination, the electron in the donor level jumps from the oxygen vacancy level of the valence band in ZnO NPs and the transition generates violet emission which appeared at 411 nm. The blue emission at 439 nm originated from the irradiative overlap of the electron transition from the shallow donor level of oxygen vacancies and the defect donor level is associated with ionized oxygen vacancies to the valence band. The green emission band around 489 and 523 nm is attributed to deep-level or traps state emission as well as the vacancies of zinc and oxygen, zinc interstitials in the crystal [27-29].

The Nd doped ZnO NPs showed NBE with higher intensity than the undoped ZnO as shown in Figure 4. 5 (b-d), but the violet emission intensity decreased with increase in the percentage of Nd. The continuous decrease of violet emission band intensity is due to the interaction between Nd atoms and the support oxide. With an increase in Nd doping concentration, the NBE peak shows a slight red shift from 390 to 392 nm. These results confirmed that the PL intensities highly depend on the concentration of Nd ions [9]. The enhancement of broad blue emission was influenced by the removal of electron captures on the surface of the nano crystals. This may be generated due to electronic transition from an interstitial Zn to a Zn vacancy. Two peaks near 490 and 520 nm correspond to the green emission which are clearly visible in various percentages of Nd doped ZnO and they normally originate from the single occupied oxygen vacancies or zinc interstitials because of the antisite oxygen which is induced as a result of the lattice distortion caused by incorporation of large ionic radius of Nd ions in the ZnO lattice [30].
4.4.6 XPS analysis

The XPS technique was used to investigate the chemical composition and oxidation state of synthesized ZnO samples. The binding energy (BE) is calibrated with carbon C1s peak (284.4 eV). The elements Zn, Nd, O and C of the Zn$_{0.94}$Nd$_{0.06}$O NPs are detected in the wide spectrum which is shown in Figure 4.6. The XPS spectra of Zn (2p), Nd (3d) and O (1s) species are further illustrated by using Figure 4.7 (a-c) respectively. As seen from Figure 4.7 (a), two strong peaks appeared at 1019.8 eV and 1042.9 eV and they are in good agreement with a binding energy value of Zn 2p$_{3/2}$ and Zn 2p$_{1/2}$ respectively. The energy difference of these two peaks is 23.1 eV and it agrees well with the standard value of 22.97 eV which reveals the presence of Zn$^{2+}$ bound to be oxygen in the ZnO matrix [31, 32].

![XPS wide survey spectrum of Zn$_{0.94}$Nd$_{0.06}$O NPs.](image)

**Figure 4.6.** XPS wide survey spectrum of Zn$_{0.94}$Nd$_{0.06}$O NPs.
SYNTHESIS AND MAGNETIC INVESTIGATIONS OF RE (Nd, Gd) DOPED ZnO NANOSTRUCTURES

The neodymium peaks Nd (3d) usually appear in the range of 980-1010 eV. The peaks located at 980.9 eV and 1003.7 eV in Figure 4.7 (b) can be assigned to Nd 3d_{5/2} and Nd 3d_{3/2} core levels respectively and 1009.4 eV is a satellite peak of Nd (3d) core level of NPs, which indicates that the Nd ions have a 3+ oxidation state in Nd doped ZnO NPs [33]. Based on XRD and XPS results, the Nd dopants are found to be incorporated into ZnO lattice. However, it is reported that for small doping concentration of Nd^{3+}, a large fractions of the Nd^{3+} atoms are substituted in Zn lattice sites within the wurtzite crystal structure [34].

Figure 4.7. XPS spectra of (a) Zn (2p), (b) Nd (3d) and (c) O (1s) level of Zn_{0.94}Nd_{0.06}O NPs.
SYNTHESIS AND MAGNETIC INVESTIGATIONS OF RE (Nd, Gd) DOPED ZnO NANOSTRUCTURES

The O (1s) spectrum revealed three distinct components as shown in Figure 4.7 (c). The peak centered at 528.8 eV is attributed to O\textsuperscript{2-} ions on wurtzite structure [35]. The middle energy level of the O1s signal at 530.2 eV may be associated with loosely bound oxygen on the surface or micropores belonging to adsorbed O\textsubscript{2} or H\textsubscript{2}O on the ZnO surface [36]. Finally, the peak located at higher energy level at 531 eV is attributed to the lattice oxygen’s in the Zn-O-Zn and Zn-OH on the surface [37].

4.4.7 Raman analysis

Wurtzite ZnO belongs to space group \textit{C\textsubscript{4}}\textit{6\textsubscript{v}} with two formula units per primitive cell. A primitive ZnO cell has four atoms and each atom occupies \textit{C\textsubscript{3\textsubscript{v}}} sites and leads to 12 phonon branches. The optical phonon irreducible representation is given by \( \Gamma_{\text{opt}} = A\textsubscript{1} + 2B\textsubscript{1} + E\textsubscript{1} + 2E\textsubscript{2} \). The \( A\textsubscript{1} \) and \( E\textsubscript{1} \) modes were polar and they can split into transverse-optical (TO) and longitudinal-optical (LO) phonons and both are infrared and Raman active, while \( B\textsubscript{1} \) modes are Raman inactive [38]. The \( A\textsubscript{1} \) phonon vibration is polarized parallel to the c-axis; the \( E\textsubscript{1} \) phonon is polarized perpendicular to the c-axis. Every mode corresponds to a band in the Raman spectrum. The intensities of the bands depend on the scattering cross-section of these modes. Nonpolar \( E\textsubscript{2} \) modes are Raman active and have two wave numbers, namely \( E\textsubscript{2L} \) and \( E\textsubscript{2H} \) associated with the motion of oxygen and zinc sub lattice respectively. Strong \( E\textsubscript{2H} \) modes are the characteristics of the wurtzite lattice and they indicate good crystallinity. The \( E\textsubscript{2L} \) mode is associated with the presence of oxygen vacancies and zinc interstitial. \( A\textsubscript{1L} \) phonon can appear only when the c-axis of wurtzite ZnO is parallel to the samples surface. Figure 4.8 shows the measured Raman spectra of Nd\textsuperscript{3+} doped ZnO at room temperature. The peaks at 162 cm\textsuperscript{-1} (\( E\textsubscript{2L} \) and
439 cm\(^{-1}\) (E\(_{2H}\)) are attributed to the non polar E\(_2\) vibration of Zn and O lattice in wurtzite ZnO. The band at 337 cm\(^{-1}\) is attributed to the multi phonon process. The band at 572 cm\(^{-1}\) is assigned as E\(_{1L}\) mode of ZnO nanoparticles [39].

![Raman spectra of Nd doped ZnO NPs.](image)

The sharp and strongest peak at 439 cm\(^{-1}\) can be assigned to a higher frequency branch of E\(_{2H}\) of ZnO, which indicates good crystallinity in the wurtzite crystal structure. With increased Nd\(^{3+}\) concentration, the intensities of E\(_{2H}\) and E\(_{2L}\) modes are found to decrease, which can be attributed to the lattice distortion in ZnO matrix. Doping is the main factor that causes lattice distortion of the crystals matrix by using different ionic
radii of doping elements. The crystalline quality of Nd$^{3+}$ doped ZnO is observed to be inferior to the undoped ZnO nanoparticles.

4.4.8 Magnetic properties

Magnetic measurements were carried out at room temperature on Nd$^{3+}$ doped ZnO nanoparticles. Figure 4.9 shows the magnetization versus magnetic field curves for undoped and Nd$^{3+}$ doped ZnO NPs. All the curves exhibited a well defined magnetization hysteresis thus implying a weak ferromagnetic behavior at room temperature and they have a qualitatively similar hysteresis loops except undoped ZnO which exhibits the diamagnetic behavior. From Figure 4.9, it can be inferred that magnetization increases with an increase in Nd$^{3+}$ concentration. The saturation magnetization is found to be 0.041, 0.051 and 0.069 emu/g for the samples Zn$_{0.97}$Nd$_{0.03}$O, Zn$_{0.94}$Nd$_{0.06}$O and Zn$_{0.91}$Nd$_{0.09}$O, respectively. The concentration of oxygen vacancies played an important role in mediating the ferromagnetic exchange interaction between Nd$^{3+}$ ions. In the sample with low Nd concentration (Zn$_{0.97}$Nd$_{0.03}$O), an appreciable ferromagnetic component is developed despite the sample containing lesser Nd$^{3+}$ ions compared to other samples. The results revealed that oxygen vacancies and zinc interstitials are generated with an increase in Nd$^{3+}$ doping which is responsible for the observed long range ferromagnetism. Moreover, the electrons or holes of the RE ions can mediate the ferromagnetism in RE doped ZnO, the s-f coupling between the RE ions (f) and the ZnO host (s) states contributed to the DMSs [40]. The coercivity also increased with Nd$^{3+}$ concentration.

From these results, the observed ferromagnetic behavior in the samples may be attributed to defects like oxygen vacancies and zinc interstitial, which is consistent with
the bound magnetic polarons (BMP) model [41]. According to the BMP model, bound electrons in defects like oxygen vacancies and zinc interstitial can couple Nd$^{3+}$ ions and create order in ferromagnetic samples.

**Figure 4.9.** Hysteresis curves of (a) undoped ZnO (b) Zn$_{0.97}$Nd$_{0.03}$O, (c) Zn$_{0.94}$Nd$_{0.06}$O and (d) Zn$_{0.91}$Nd$_{0.09}$O NPs [Inset: magnification part of hysteresis loops.]
4.5 CONCLUSIONS

Pure and Nd doped ZnO NPs were successfully synthesized by the co-precipitation method. The hexagonal wurtzite structure was identified for undoped and Nd doped ZnO through XRD analysis and it also confirmed the substitution of Nd$^{3+}$ ions into the lattice site of Zn$^{2+}$ ions in ZnO matrix. The presence of all functional groups was ascertained from FTIR analysis and this study confirmed that, Nd$^{3+}$ ions were occupied the Zn$^{2+}$ position. Spindle like morphologies were found for all ZnO NPs observed from HRSEM. The compositional analysis (EDS) confirmed the presence of Zn, O and also proved the presence of Nd ions as a successful dopant in ZnO. The optical band gap of pure and doped ZnO samples were found to vary from 3.06 to 2.65 eV. Raman analysis showed that wurtzite structure of Nd doped ZnO NPs was slightly distorted, which proves the incorporation of Nd ions in ZnO lattice. The diamagnetic behavior of pure ZnO was changed into the weak ferromagnetic nature for doped ZnO.
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SYNTHESIS AND MAGNETIC INVESTIGATIONS OF RE (Nd, Gd) DOPED ZnO NANOSTRUCTURES

PART-II
INFLUENCE OF GADOLINIUM DOPING ON STRUCTURAL AND MAGNETIC PROPERTIES OF ZnO NANOPARTICLES

Pure and Gd doped ZnO nanoparticles (NP) with hexagonal wurtzite structure were synthesized via co-precipitation method. The structural properties of synthesized pure and Gd doped ZnO nanoparticles were investigated by employing X-ray diffraction analysis and it showed smaller crystallite size for undoped than Gd doped ZnO. HRSEM analysis revealed about spindle like morphologies for the synthesized nanoparticles. Optical properties of the nanoparticles were investigated by photoluminescence study and it showed the band edge emission for all synthesized materials with additional emissions in visible region due to the presence of vacancy and interstitial defects. FTIR spectra provided the functional characteristics of pure and Gd doped ZnO nanoparticles. XPS measurement revealed about the composition of nanostructures. Room temperature magnetic measurement was carried out by using a vibrating sample magnetometer and it showed ferromagnetism in low level Gd doped ZnO nanoparticles, which switched into super paramagnetism due to the further increase in Gd concentration of ZnO matrix.
4.1 INTRODUCTION

Diluted Magnetic Semiconductors (DMS) represent a synergistic collaboration between charge based semiconductors and spin based magnetism [1-2]. Earlier, theoretical studies predicted and experiments verified that some wide band gap semiconductors such as ZnO and TiO$_2$ doped with transition metals (TMs) are effective DMS [3]. Zinc oxide (ZnO) has received much attention in recent years due to its unique physical properties and potential applications in ultraviolet photoconductive detectors, optoelectronic devices, light emitting diodes, solar cell transparent electrodes, etc. [4, 5]. ZnO nanoparticles are particularly appealing because of their theoretically predicted room temperature ferromagnetism (RTFM) as well as their direct wide band gap (3.37 eV) with tunable and high exciton binding energy of 60 meV [6]. ZnO nanoparticles (NPs) are synthesized using various methods, including ultrasonic radiation using precipitation, microwave irradiation, mechanical ball milling, solution combustion and microwave assisted solvothermal methods [7, 8]. Among these methods, co-precipitation method attracts more attention due to its unique advantages including low cost, simple lab equipment, easy adjustment of dopant concentration and large scale synthesis of nanoparticles.

In the past decade, ZnO doped with 3d TM ions have intensively been studied to obtain suitable DMS materials for device applications. In general, doping with certain ions is an efficient way to enhance the properties of semiconductor nanoparticles. In TM doped ZnO, TM ion interaction plays a vital role in controlling the excitation dynamics [9]. Also, the magnetism is so weak and in buried with experimental artifacts and is associated with problems of reproducibility or precipitation of secondary metallic phases.
SYNTHESIS AND MAGNETIC INVESTIGATIONS OF RE (Nd, Gd) DOPED ZnO NANOSTRUCTURES

Compared with 3d TM, 4f rare earth (RE) elements have larger magnetic moments and are likely to enhance the ferromagnetism (FM) in doped semiconductors [10]. Recently, RE doped DMS materials have attracted interest due to their unique optical properties and high emission quantum yield. In TM ions, magnetic moment arises from a partially filled outer most 3d electrons, whereas in RE ions magnetic moment arises from the inner 4f incomplete sub-shell. In TM ions, the strength of the spin-orbital coupling is much smaller than the crystal field energy and hence, the orbital momentum is quenched and only spin momentum contributes towards magnetism. In contrast, 4f electrons in RE ions are shielded by the 5d 6s electrons and the strength of the spin-orbital coupling is much greater than the crystal field energy [11]. These 4f electrons undergo indirect exchange interaction via 5d or 6s conduction electrons yielding high magnetic moment per atoms due to high orbital momentum [12]. Recent experimental results have shown that the incorporation of RE metals such as Gd\(^{3+}\) ion in wide band gap semiconductor GaN results in enhanced ferromagnetic property [13], which motivates the researchers towards RE metal ion doping in metal oxide materials for spintronics applications. In particular, Gd\(^{3+}\) is of greater interest due to its scintillation and optical devices in the place of other luminescent and large magnetic behavior materials [14].

In this work, the structural, optical and magnetic properties of gadolinium doped ZnO NPs are reported. The structural and morphological characterizations were performed by using X-ray diffraction (XRD), Raman and high resolution scanning electron microscope (HRSEM). The valence state of Gd in the host matrix is characterized by X-ray photoelectron spectroscopy (XPS). This work describes the paramagnetic nature in Gd doped ZnO NPs. It is observed that the unpaired spins in Gd 4f
do not undergo a direct exchange interaction with nearest Gd$^{3+}$ ions nor do they take part in carrier mediated ferromagnetism. It is observed that paramagnetism arises due to the presence of localized non-interacting spins present in 4f shell of Gd$^{3+}$.

4.2. EXPERIMENTAL DETAILS

Synthesis of undoped and Gd doped ZnO was carried out by using analytical grade zinc nitrate [Zn (NO$_3$)$_2$], gadolinium nitrate [Gd (NO$_3$)$_2$] and sodium hydroxide (NaOH) in as- received condition. In the synthesis process, a required amount of zinc nitrate was completely dissolved in deionized water and a required amount of aqueous NaOH solution was added drop by drop to the aqueous zinc nitrate. The solution was stirred and maintained at room temperature for 30 min, and then kept at 80 °C for 5 hours. Later, a white precipitate was formed. Then, the white precipitate was washed several times with double distilled water and ethanol. The precipitate was dried at 120 °C for one hour. The obtained ZnO samples in powder form were annealed at 300 °C in air for 2 hours and used for further studies.

For the synthesis of Zn$_{1-x}$Gd$_x$O ($x =$ 0.03, 0.06 and 0.09) NPs, a calculated amount of gadolinium nitrate was mixed with zinc nitrate solution. The required amount of aqueous NaOH solution was added drop by drop to the homogenous mixture to get a white precipitate. Further, a similar procedure adopted for the preparation of undoped ZnO NPs was followed for the synthesis of Gd doped ZnO NPs.
4.3 RESULTS AND DISCUSSION

4.3.1 Structural analysis

X-ray diffraction (XRD) measurements were carried out to determine the crystalline nature of pure and Gd doped ZnO NPs. The diffraction peaks of all synthesized samples in the XRD patterns (Figure 4.10(A)) can be unambiguously indexed and assigned to the typical wurtzite structure ZnO phase with a hexagonal crystal system (space group P63mc; JCPDS card no. 36-1451) [10]. XRD pattern of undoped ZnO shows eleven peaks at 2θ = 31.76°, 34.39°, 36.24°, 47.52°, 56.59°, 62.83°, 66.42°, 67.93°, 69.07°, 72.51° and 76.87° and were respectively indexed to the (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202) planes. For the lightly doped sample Zn$_{0.97}$Gd$_{0.03}$O, the XRD pattern is found to be similar to that of pure wurtzite ZnO structure. Further increase in the Gd doping concentration [Zn$_{0.94}$Gd$_{0.06}$O and Zn$_{0.91}$Gd$_{0.09}$O samples] causes absence in higher 2θ peaks which correspond to the planes (004) and (202) compared to pure ZnO. No reflection peaks from Gd or Gd$_2$O$_3$ can be noticed in the diffraction patterns. The absence of impurity peaks and close matching with the hexagonal structure of synthesized samples also suggest that the samples are highly crystalline and most of Gd$^{3+}$ ions are incorporated into the ZnO lattice [15]. The plane of the (100), (002) and (101) corresponding to 2θ, 32.81°, 34.46° and 36.29° for pure ZnO phase were found to be gradually shifted to the lower diffraction angles with respect to the Gd$^{3+}$ ion concentration until reaching at 31.76°, 34.39° and 36.25° by doping with (0.09 mol %) of Gd (Figure 4.10 (B)). This observation confirms in possible substitution of ZnO ions by Gd$^{3+}$ ions in Gd doped ZnO. The reflection peak intensity becomes weaker apparently as FWHM value increases, which indicates in the decrease in crystalline
nature of the samples. Furthermore, the calculated average crystallite size ‘D’, micro strain (ε) and dislocation density (δ) were tabulated in Table 4.3 using the relation given in chapter III. The calculated average crystallite size was found to be in the range of 31-24 nm.

![XRD patterns of ZnO and Gd doped ZnO NPs](image)

**Figure 4.10** (A) XRD patterns of ZnO and Gd doped ZnO NPs, (B) (100), (002) and (101) peaks shifted towards lower angle side and decreased intensity with the increase of Gd concentration.

Based on the hexagonal structure, the lattice parameters of ZnO at different contents of Gd were determined. The lattice parameters, unit cell volume (V), positional parameters (u) and bond length were calculated using the equations as described in chapter III and the calculated values are tabulated in Table 4.4.

A slight increase in ZnO lattice parameters due to Gd doping may be due to the expansion of ZnO lattice caused by the possible substitution of Gd$^{3+}$ (radius 0.938 Å) into Zn$^{2+}$ (radius 0.74 Å) lattice of ZnO [17, 18].
Table 4.3. Crystallite size, micro strain and dislocation density values of pure and Gd doped ZnO NPs.

<table>
<thead>
<tr>
<th>Gd concentration</th>
<th>Crystallite size (D) (nm)</th>
<th>Micro-strain (e) x 10^{-3}</th>
<th>Dislocation density (δ) x 10^{15} (lines/m^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>31.8</td>
<td>1.11</td>
<td>1.046</td>
</tr>
<tr>
<td>0.03</td>
<td>28.5</td>
<td>1.30</td>
<td>1.511</td>
</tr>
<tr>
<td>0.06</td>
<td>25.8</td>
<td>1.38</td>
<td>1.660</td>
</tr>
<tr>
<td>0.09</td>
<td>24.7</td>
<td>1.46</td>
<td>1.855</td>
</tr>
</tbody>
</table>

The unit cell volume of ZnO is observed due to increase in the substitution of RE metal ions. The unit cell volumes are estimated as 47.442, 47.661, 47.675 and 47.705 Å³ for ZnO, Zn_{0.97}Gd_{0.03}O, Zn_{0.94}Gd_{0.06}O and Zn_{0.91}Gd_{0.09}O respectively. This observation indicates that these ions reside partially in tetrahedral Zn positions. It is interesting to note that the incorporation of Gd ion causes observed changes in Zn-O bond length.

Table 4.4. Structural parameters of pure and Gd doped ZnO NPs.

<table>
<thead>
<tr>
<th>Gd concentration</th>
<th>Lattice parameter values (Å)</th>
<th>Atomic packing factor (c/a)</th>
<th>Positional parameter (u)</th>
<th>Volume (V) (Å³)</th>
<th>Bond length (Zn-O) L (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>e</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>3.245</td>
<td>5.200</td>
<td>1.602</td>
<td>0.3798</td>
<td>47.442</td>
</tr>
<tr>
<td>0.03</td>
<td>3.250</td>
<td>5.210</td>
<td>1.603</td>
<td>0.3797</td>
<td>47.661</td>
</tr>
<tr>
<td>0.06</td>
<td>3.250</td>
<td>5.210</td>
<td>1.603</td>
<td>0.3797</td>
<td>47.675</td>
</tr>
<tr>
<td>0.09</td>
<td>3.251</td>
<td>5.211</td>
<td>1.603</td>
<td>0.3797</td>
<td>47.705</td>
</tr>
</tbody>
</table>
SYNTHESIS AND MAGNETIC INVESTIGATIONS OF RE (Nd, Gd) DOPED ZnO NANOSTRUCTURES

From Table 4.4, it is observed that Gd substituted in ZnO lattice distorted the wurtzite crystal structure which is confirmed from a monotonous increase in lattice parameters ‘a’ (Å) and ‘c’ (Å) and the corresponding unit cell volume ‘V’ (Å³) with an increase in the Gd content in ZnO phase.

4.3.2 FTIR analysis

In order to identify the presence of a small amount of impurity phase in Zn₁₋ₓGdₓO NPs, FTIR spectroscopy was utilized. The FTIR measurements for all the samples were performed using the KBr pellet method in the wave number range 400-4000 cm⁻¹ at room temperature as shown in Figure 4.11.

![FTIR Spectra](image)

**Figure 4.11.** (A) FTIR spectra of (a) undoped ZnO, (b) Zn₀.₉₇Gd₀.₀₃O, (c) Zn₀.₉₄Gd₀.₀₆O and (d) Zn₀.₉₁Gd₀.₀₉O NPs. (B) The enlarged FTIR spectra in the wave number range 1000-400 cm⁻¹ at room temperature.
SYNTHESIS AND MAGNETIC INVESTIGATIONS OF RE (Nd, Gd) DOPED ZnO NANOSTRUCTURES

The presence of nitrate phase in all ZnO NPs is confirmed by observing two bands around the wave number 1633 and 1335 cm\(^{-1}\) [19]. But, the presence of nitrate phase impurity was not detected in the XRD patterns of all the synthesized samples. Normally, the absorption band within the range of 1000 cm\(^{-1}\) is attributed to the bands corresponding to inorganic elements. The peak appeared at 515 cm\(^{-1}\) can be attributed to the metal-oxygen (Zn-O) bonds and they verified about the formation of doped ZnO [20]. The broadband around 3459 cm\(^{-1}\) represents the stretching vibrations of the O-H group, whereas the bands around 2342 cm\(^{-1}\) correspond to CO\(_2\) mode. These CO\(_2\) bands may arise due to some trapped CO\(_2\) in the air ambience during the FTIR characterization [21]. The absorption band appearing around 1670 cm\(^{-1}\) is due to the bending vibrations of the inter layered H\(_2\)O molecule in Gd doped ZnO NPs. Various higher wave number impurity bands are due to the surface adsorbed water from precursors during the synthesis process or during the characterization.

Figure 4.11(B) depicts the FTIR spectra below 1000 cm\(^{-1}\) which shown the presence of Zn-O/Zn-Gd-O bonds and their functional groups. In doped samples, the absorption band shows new peak, which appeared at 852 cm\(^{-1}\) and it correspond to Gd-O [22]. The metal oxide peak for doped samples bear testimony to the broad absorption nature around the low wavenumber region due to increased lattice distortion produced by initial doping of Gd into Zn-O. In further doping of Gd, the metal oxide absorption peak shifts towards higher wave number side due to the change in bond length caused by replacement of Gd ions instead of Zn ions. No other absorption band was detected in the FTIR spectrum which substantiates that the synthesized NPs are almost pure without any significant impurity.
4.3.3 Morphological analysis

Figure 4.12 shows the HRSEM images of Gd doped ZnO NPs with heterogeneous morphology. Spindle like particles with a horizontal diameter of 150-300 nm were observed. It is also seen that all the particles are embedded on a smooth surface. The average diameter of Gd doped ZnO NPs increase with an increase in Gd ion concentration. Hence, it is predicted that Gd doping favors faster growth of spindle particles.

![HRSEM images](image)

**Figure 4.12.** HRSEM images of (a) undoped ZnO, (b) Zn$_{0.97}$Gd$_{0.03}$O, (c) Zn$_{0.94}$Gd$_{0.06}$O and (d) Zn$_{0.91}$Gd$_{0.09}$O NPs.
4.3.4 Compositional analysis

The chemical compositions of synthesized ZnO NPs with different Gd concentrations were measured by EDS spectra and are shown in Figure 4.13 (a-d). These spectra displayed the presence of Zn, O and Gd in Gd doped ZnO NPs whereas the spectrum of undoped ZnO NPs showed the presence of only zinc and oxygen ions. The obtained EDS result confirms the presence of Gd$^{3+}$ which is successfully substituted as a dopant in ZnO matrix.

![Figure 4.13](image_url)

**Figure 4.13.** EDS analysis of (a) undoped ZnO, (b) Zn$_{0.97}$Gd$_{0.03}$O, (c) Zn$_{0.94}$Gd$_{0.06}$O and (d) Zn$_{0.91}$Gd$_{0.09}$O NPs.
4.3.5 Photoluminescence (PL) spectra

Photoluminescence (PL) is one of the important characterization tools to study the structural defects and quality of crystalline structure which plays a crucial role in development of diamagnetic properties in ZnO based DMSs. Figure 4.14 shows the room temperature PL spectra of Zn$_{1-x}$Gd$_x$O (0<x<0.09) samples recorded between 350 nm and 550 nm. It is noticed from Figure 4.14 that pure ZnO sample have four emission bands, (i) low intense peak at 388 nm corresponding to ultra-violet (UV) emission, (ii) high intense peak centered at 410 nm corresponding to violet emission, (iii) low intense and sharp peaks centered at 439 nm and 489 nm representing the blue emission.

![Photoluminescence spectra of Gd doped ZnO NPs from 350 nm to 550 nm for different Gd concentrations Zn$_{1-x}$Gd$_x$O (X=0, 0.03, 0.06 and 0.09) at room temperature.](image)

**Figure 4.14.** Photoluminescence spectra of Gd doped ZnO NPs from 350 nm to 550 nm for different Gd concentrations Zn$_{1-x}$Gd$_x$O (X=0, 0.03, 0.06 and 0.09) at room temperature.
UV and violet emissions are assigned to the near-band-edge (NBE) transition from the conduction band to valence band [23]. A strong and sharp UV emission peak around 385-400 nm was observed for both TM and RE doped ZnO, which corresponds to the recombination radiation due to the exciton [24]. In the present work, a UV band intensity of Gd doped ZnO samples is always higher than what is observed for pure ZnO sample. The suppression of violet band at higher Gd concentrations represents the increase of non-radiative recombination transition.

The emission of visible light such as blue and green is generally believed to be generated by deep level defects such as oxygen vacancies (V_o), zinc vacancies (V_{Zn}), oxygen interstitials (O_i), Zinc interstitials (Zn_i) and oxygen antisites (O_{Zn}) [25]. The observed blue emission bands between 480 and 490 nm is due to a radiative transition of an electron from the deep donor level of Zn_i to an acceptor level of neutral V_{Zn} [26]. The decreased intensity in blue band (~ 440 nm) indicates that deep donor level of Zn_i is decreased by Gd doping which is supported by EDS results.

The appearence of new and intense green emission around 530 nm confirms about the incorporation of Gd into ZnO lattice. It is found from Figure 4.14(b-d) that the intensity of green band increases with an increase in Gd concentration. The green emission is ascribed to the defects of oxygen vacancies created in the ZnO.
4.3.6 XPS analysis

XPS is a selective and sensitive surface characterization technique to determine the chemical composition of materials and it is also effective in investigating the characteristics (valence) of the constituent atoms (ions) by monitoring their binding energies. The survey spectrum of Zn$_{0.94}$Gd$_{0.06}$O NPs mainly shows carbon, oxygen, gadolinium and zinc species [Figure 4.15(a)]. Besides, high-resolution spectra were also recorded to study the electronic states of the elements. In the Zn 2p high resolution XPS spectrum, two peaks at 1023.1 eV and 1046.1 eV correspond to the binding energies of Zn 2p$_{3/2}$ and Zn 2p$_{1/2}$ respectively, which is consistent with the emission of 2p photo electrons from ZnO [27]. Furthermore, the Gd 3d spectrum (Figure 4.15(c)) consists of a spin orbit doublet located at 1222.6 eV for Gd 3d$_{3/2}$ and 1198.2 eV for Gd 3d$_{5/2}$ respectively, and three satellite peaks (1232.3eV, 1238.7 eV and 1243 eV) of Gd 3d$_{3/2}$ were also observed. This indicates that the Gd ions in the NPs consist of +3 states and they exist in the form of Gd$_2$O$_3$ [28]. Hence, this spectrum further demonstrated that the doping of Gd$^{3+}$ ions was successfully achieved.
The O 1s core level spectrum of Gd doped ZnO is shown in Figure 4.15(d). The O 1s spectrum of ZnO shows a sharp peak centered at 533 eV, which is mainly assigned to the oxygen atoms coordinated with Zn atoms. In case of Gd doped ZnO, a slight shift in the value of the binding energy of the sharp peak (534.3 eV) as well as an additional shoulder centered on 531.1 eV was observed [29, 30]. These peaks may be attributed to the coordination of oxygen in Gd-O-Gd and Gd-O-Zn, respectively.
4.3.7 Raman analysis

According to the group theory, wurtzite type ZnO belongs to the space group $C_{6v}^4$ with two formula units in the primitive cell. At the central point of the Brillouin zone, group theory predicts about the existence of the following phonon modes:

$$\Gamma = 2A_1 + 2B_1 + 2E_1 + 2E_2$$

Among these modes, there are acoustic modes with $\Gamma_{ac0} = A_1 + E_1$ and optical modes with $\Gamma_{opt} = A_1 + 2B_1 + E_1 + 2E_2$. For optical modes, $B_1$ modes are Raman silent. Both $A_1$ and $E_1$ are polar and are split into transverse (TO) and longitudinal optical (LO) phonons. A nonpolar phonon mode with symmetry $E_2$ has two frequencies: $E_{2H}$ associated with oxygen atoms and $E_{2L}$ associated with Zn sublattice. Among the optical modes, $A_1$, $E_1$ and $E_2$ are Raman active [31, 32]. Figure 4.16 shows Raman spectra of pure and Gd doped ZnO using 514.5 nm wavelength of an argon green laser. Five Raman modes are observed at 182, 241, 387, 438 and 586 cm$^{-1}$. 
Figure 4.16. Micro-Raman spectra of (a) undoped ZnO, (b) Zn$_{0.97}$Gd$_{0.03}$O,
(c) Zn$_{0.94}$Gd$_{0.06}$O and (d) Zn$_{0.91}$Gd$_{0.09}$O NPs.

The peak located at 438 cm$^{-1}$ is attributed to the ZnO nonpolar optical phonons of
E$_{2H}$ mode, one of the characteristic peaks of wurtzite ZnO [33]. The peak at 387 cm$^{-1}$ is
associated with A$_1$ (TO) which is also the first-order optical mode of wurtzite ZnO [34].
The small peak observed at 241 cm$^{-1}$ is attributed to E$_{2L}$ which is the second-order feature
caused by multiphonon processes [35]. The peaks at 182 cm$^{-1}$ (E$_{2L}$) and 438 cm$^{-1}$ (E$_{2H}$)
are attributed to the non polar E$_2$ vibration of Zn and O lattice in wurtzite ZnO. The band
at 586 cm$^{-1}$ is assigned as E$_{1L}$ mode of ZnO nanoparticles [36, 37]. E$_{2L}$ and E$_{2H}$ represent
the wurtzite structure with good crystallinity. The intensity of both E$_{2H}$ and E$_{2L}$ modes
decreased gradually with an increase in Gd$^{3+}$ concentration, which may be attributed to the lattice distortion in ZnO matrix.

Doping is the main factor that causes the lattice distortion of the crystal matrix with different ionic radii of dopants. The crystalline quality of Gd$^{3+}$ doped ZnO is observed to be inferior to the undoped ZnO nanoparticles. The sharp and strongest peak at 438 cm$^{-1}$ can be assigned to a high frequency branch of E$_{2H}$ of ZnO, which indicates about good crystallinity in the wurtzite crystal structure.

4.3.8 VSM analysis

Figure 4.17 shows the M-H curves of Gd doped ZnO NPs in the magnetic field range of ± 15 kOe. Pure ZnO sample exhibited diamagnetic nature at room temperature as shown in Figure 4.17(a) which is consistent with previous reports [10]. The lower concentration (0.03 mol%) of Gd doped ZnO sample exhibits a clear ferromagnetic behavior. The conversion of diamagnetic nature of undoped ZnO sample into the ferromagnetic nature of Gd doped ZnO sample indicates about the successful incorporation of Gd atoms in ZnO lattice. In further increase in Gd concentration (0.06 mol%), the behavior was further changed from ferromagnetic to super paramagnetic or weak ferromagnetic. The magnetization of the sample increased with an increase in Gd concentration up to 0.09 mol%. The observed paramagnetism may be due to the presence of isolated Gd$^{3+}$ ions, whereas the reduction in the magnetization is most likely due to the presence of antiferromagnetic interaction in the system. When Gd ions are incorporated into ZnO, room temperature ferromagnetism with high magnetization was expected in the system. The notion behind this expectation is that Gd is ferromagnetic in nature with persistence of ferromagnetic ordering up to ~289 K [38].
Figure 4.17. (A) Diamagnetism for undoped ZnO, (B) Magnetic behavior of
(a) Zn$_{0.97}$Gd$_{0.03}$O, (b) Zn$_{0.94}$Gd$_{0.06}$O and (c) Zn$_{0.91}$Gd$_{0.09}$O NPs and inset figure
shows their magnified loop.

The RT ferromagnetism arises as a result of exchange interaction between the free
delocalized charge carrier initiating from the oxygen vacancies and zinc interstitial in the
crystal structure as a result of the dopant. Further increase in dopant content increases the
oxygen vacancy, that eventually changes the magnetic ordering of the sample from
ferromagnetic to paramagnetic due to ferromagnetic competition in oxides [39].

The electronic configuration of Gd$^{3+}$ is [Xe] 6s$^2$5d$^1$4f$^7$ with 7 unpaired electrons in
the 4f shell. These unpaired 4f electrons polarize the 6s and 5d valence electrons resulting
in a magnetic moment of 7.63 µB/Gd$^{3+}$ [40]. However, because of the shielding of this
4f shell by 6s 5d valence shell electrons, the interaction of these unpaired spins with the
outermost ligands or other Gd$^{3+}$ is expected to be weak. These non-interacting and
localized magnetic spins of Gd$^{3+}$ induces paramagnetic moment only [38]. Paramagnetic
nature at room temperature has been reported in pure Gd$_2$O$_3$ as well as in Gd doped oxide
semiconductors such as TiO$_2$, SnO$_2$ and ZnO [41].
Ney et al., [42] reported the paramagnetic behavior of Gd doped ZnO with magnetic moment of 7.63 μB/Gd³⁺ with a small lattice distortion and the results were in agreement with the first-principle density functional theory calculations. They detected the presence of secondary oxide phases of Gd₂O₃ or other antiferromagnetic phase of Gd³⁺ contributing in the reduction in the paramagnetic behavior. The origin of magnetism in Gd doped ZnO sample was reported due to the carrier mediate oxygen vacancies created in RE dopants [43]. In this case, there is no secondary peak of Gd₂O₃ and also a high concentration of Gd doping exhibits paramagnetic behavior at room temperature.

The XRD and micro-Raman studies clearly show that an increase in doping concentration increases the large number of Gd³⁺ incorporated in ZnO lattice. More oxygen vacancies are generated by an increase in Gd³⁺ dopant content, which may be responsible for changing the ferromagnetic into paramagnetic behavior and result in antiparallel alignment of the magnetic spin of Gd 4f shell present in the nearest neighbour.
4.4 CONCLUSION

In the present work, ZnO NPs is synthesized with different Gd ion doping concentrations by applying co-precipitation method. X-ray diffraction and XPS results revealed that the doping of Gd ions has a minor influence on the internal structure of ZnO. Crystal structure and surface morphology were studied by using XRD and HRSEM analyses. The presence of small impurity phase is detected in the FTIR spectra of doped ZnO samples. The conversion of diamagnetic behavior of pure ZnO to ferromagnetic for lightly doped (Gd-0.03) ZnO sample and further increase in doping concentration changes the ferromagnetic into paramagnetic behavior (weak ferromagnetic) which is confirmed from VSM analysis. The dominant paramagnetic ordering with increasing Gd concentration suppressed the ferromagnetic nature of Zn_{0.97}Gd_{0.03}O sample.
REFERENCES


