Chapter 5

Doped ZnO nanostructures grown by hydrothermal method

5.1 Introduction

Methods for introducing new magnetic, optical, electronic, photophysical or photochemical properties to semiconductor nanocrystals are attracting intense interest as prospects for nanotechnological applications emerge in the areas of spintronics, optoelectronics, quantum computing, photocatalysis and luminescence labeling. Introduction of impurity atoms into semiconducting materials is the primary method for controlling the properties of the semiconductors, such as band gap, electrical conductivity etc. II-VI and III-V semiconductors that have been doped with transition metals are currently generating much research interest, principally for their novel magnetic properties. These semiconductors are commonly called as di-
lute magnetic semiconductors (DMS) and are envisioned to be the suitable candidate for spintronic devices. Materials for spintronics (spin based electronics) combine complementary properties of ferromagnetic material and semiconductor structures. In DMS, a stoichiometric fraction of the host semiconductor atoms is randomly replaced by magnetic atoms and resulting solid solution is semiconducting, but can possess well defined magnetic properties (paramagnetic, antiferromagnetic, ferromagnetic) that conventional semiconductor do not have. Dilute magnetic semiconductor based on ZnO have attracted a great deal of attention because their application in magnetic semiconductor devices. To date, the origin of ferromagnetism in oxide DMSs remain controversial topic. For ZnO based DMSs, oxygen vacancies ($V_O$) and zinc vacancies ($V_{Zn}$) play important roles in the magnetic origin.

The optical properties of doped semiconductor nanoparticles has given rise to intriguing science in nanoresearch in the new millennium. With emerging interest in the field emission display (FED) as one of the promising candidates for flat panel display devices, extensive research on the low voltage phosphors for FED have been carried out. In particular, the use of oxide phosphors has been preferred for LED application due to higher stability in a high vacuum environment and less emission of contaminating gases. Much attention has been paid to the optical properties of II-VI semiconductor nanocrystals such as CdSe, CdS and ZnS because their optical properties depend strongly on the nanocrystal size and shape. But sulfide based phosphor is known to easily degrade at high current densities. High quality II-IV semiconductor nanocrystals also become materials for doping of optically active impurities. The II-VI semiconductor nanocrystals doped with luminescent centers exhibit efficient luminescence even at room
temperature. There are many reports on the synthesis and optical properties of II-VI semiconductor nanocrystals doped with luminescence centers such as transition metals, rare earth ions and donor acceptor pair. Rare earth ions are good luminescence centers due to their narrow and intense emission lines originating from 4f intrashell transitions. These rare earth doped nanocrystals have wide variety of applications including phosphors, display monitors, x-ray imaging, scintillators, optical communications and fluorescence imaging.

This chapter is divided into two parts: first part deals with the synthesis and characterization of cobalt doped ZnO nanostructures for magnetic applications and the synthesis and characterization of europium doped ZnO nanostructures for the luminescent applications are discussed in the second part of the chapter.

5.2 Co$^{2+}$ doped ZnO nanoflowers grown by hydrothermal method

Dilute magnetic semiconductors (DMS) have become a new area of research interest due to its potential application in the field of spintronics [229, 230]. The basic requirement for practical applications is to achieve Curie temperature ($T_c$) well above the room temperature [231]. Transition metal doped semiconductors, namely ZnO, SnO$_2$ etc., have attracted a great research interest due to the prediction of room temperature ferromagnetism (RTFM) in them [232, 233]. However the origin of RTFM is not yet clearly understood. The preparation method and growth conditions play an important role in determining the magnetic behaviour of ZnO based DMS materials.
Zinc oxide (ZnO) is a wide band gap (3.3 eV) II-VI compound semiconductor and having an exciton binding energy of 60 meV. The magnetic studies of the pure ZnO shows well known diamagnetic behavior [234, 235]. Hydrothermal method is one of the most cost effective methods and flexible in terms nature of substrates due to its significantly low growth temperature employed. The low growth temperature prevents the diffusion of dopants to form metal clusters.

This chapter deals with the synthesis of undoped and Co$^{2+}$ doped ZnO nanostructures by hydrothermal method and their structural, morphological, optical properties and magnetic properties were studied using x-ray diffraction (XRD), scanning electron microscopy (SEM), photoluminescence (PL), diffuse reflectance (DRS) measurements and superconducting quantum interference device (SQUID) magnetometry.

### 5.2.1 Experimental

Undoped ZnO and cobalt doped ZnO nanostructures were grown by hydrothermal method. An appropriate quantity of ammonium hydroxide was added to the mixture of zinc acetate (1M-0.3M) and cobalt nitrate (0.01M-0.001M) solution to adjust the pH value between 9 and 11. The Co content was changed by altering the molar ratio of zinc acetate and cobalt nitrate. The mixture was stirred vigorously for 20 min to form a homogeneous solution with the colour changing from pink to brown. The resulting solution was then transferred into a teflon-lined autoclave, which was sealed and maintained at 100°C for 3 to 6 h, before being left to cool to room temperature naturally. A light green precipitate was obtained. After washing with distilled water several times, these samples were finally dried at 60°C.
for 2 h for further characterization. The experiment is repeated by varying process parameters such as duration of growth, molar concentration of precursors and growth temperature. The undoped ZnO nanoparticles were also synthesized in a similar manner described above but without adding Co(NO$_3$)$_2$.

The synthesized nanostructures were structurally characterized by x-ray diffraction technique using Rigaku D max-C x-ray diffractometer with Cu K$_\alpha$ radiation (1.5418 Å). Morphology of the samples was analyzed using scanning electron microscopy (SEM) using JEOL model JSM - 6390LV. The exact amount of cobalt that is incorporated in the ZnO nanostructures was determined using inductively coupled plasma- atomic emission spectra (ICP-AES) obtained using thermo electron IRIS INTREPID II XSP DUO. The optical band gap $E_g$ was estimated from the UV-Vis-NIR diffuse reflectance spectra (DRS) recorded with JASCO V-570 spectrophotometer. The samples for this study were used in the form of powder and pure BaSO$_4$ used as the reference. Room temperature photoluminescence (PL) of the samples was measured on Horiba Jobin Yvon Fluoromax-3 spectrofluorimeter using Xe lamp as the excitation source. Magnetic measurements were taken with superconducting quantum interference device (SQUID) magnetometer (QD MPMS-XL)
5.2.2 Results and discussion

Figure 5.1: XRD patterns of Co doped ZnO nanostructures grown by hydrothermal method with different concentration of Zn (Ac)$_2$, the Co(NO$_3$)$_2$ concentration fixed at 0.01 M and the growth temperature as 100°C for 3 h.

Figure 5.1 shows the powder x-ray diffraction patterns of cobalt doped ZnO nanostructures prepared at different molarity of zinc acetate and a growth temperature of 100°C for 3 h with a fixed cobalt nitrate concentration of 0.01M. Figure 5.2 shows the XRD pattern of cobalt doped ZnO nanostructures prepared at different molarity of cobalt nitrate, the zinc acetate was fixed at 1 M and the growth temperature being 100°C and for a duration of 3 h. All the peaks in the x-ray diffraction profile could be assigned to the typical wurtzite structure of ZnO [216]. There are no characteristic peaks of impurity phases regardless of the dopant concentrations. Thus the wurtzite structure is not modified by the addition of Co into the ZnO matrix. The wurtzite structure of the ZnO is not obtained as the concent-
tration of the Co(NO$_3$)$_2$ precursor increases beyond 0.1 M. With increase of dopant concentration, the peak positions of cobalt doped ZnO shift towards high angles because Co ions have the smaller ionic radius (0.72 Å) than Zn ions (0.74 Å) [236]. It is found that the lattice parameters of Co doped ZnO nanostructures increases with molar concentration of cobalt nitrate. The increase in the lattice parameters is attributed to the cobalt substitution in zinc site of zinc oxide nanostructures.

Figure 5.2: XRD patterns of Co doped ZnO nanostructures grown by hydrothermal method with different concentration of Co(NO$_3$)$_2$, Zn(Ac)$_2$ concentration fixed at 1 M and the growth temperature is 100°C for 3 h

Figure 5.3 shows the SEM image of the cobalt doped ZnO nanostructures synthesized at 100°C for a duration of 6 h from 0.3 M zinc acetate and 0.01M cobalt nitrate. SEM image confirms the formation of hexagonal shaped rods and the rods assemble like a flower. The cobalt doped
ZnO structures has an average diameter of about 0.56 µm and a length of about 13 µm. Figure 5.4 shows the SEM image of the cobalt doped ZnO nanostructures synthesized at 100°C, but for a duration of 3 h from 0.3 M zinc acetate and 0.001M cobalt nitrate. It confirms that the width of the nanorods decreases as the time of growth decreases from 6 h to 3 h, however there is not much change in the length of these rods which is about 13 µm. Thus the doping of cobalt in ZnO matrix may generate some active sites around the circumference of ZnO nuclei, so that ZnO will preferentially grow on the active sites. Flower like ZnO nanostructures can be grown by varying the process parameters such as time of growth, temperature, pH etc [237].

Figure 5.3: SEM image of the cobalt doped ZnO nanorods grown by hydrothermal method at a growth temperature of 100°C for 6 h
Results and discussion

Figure 5.4: SEM image of the cobalt doped ZnO nanorods grown by hydrothermal method at a growth temperature of 100°C for 3 h

The exact amount of cobalt that is incorporated in the ZnO nanostructures was determined using ICP-AES data. The ICP-AES shows that cobalt incorporated into the nanostructures is about 0.11 atomic % for lower concentration of cobalt nitrate (0.001M) and about 1.06 atomic % for higher concentration (0.01M) of cobalt nitrate in the precursor solution. It is found that the Co content in the ZnO nanostructures increases with cobalt nitrate concentration.

The successful incorporation of Co$^{2+}$ on Zn sites in the ZnO nanostructures is further confirmed by electron paramagnetic resonance (EPR) studies. A broad spectrum observed for these nanostructures due to their random orientation with respect to the magnetic field. The measured spectrum is broader for several reasons. First, Co$^{2+}$ located near the surface of the nanostructures will see a different crystal field compared to Co$^{2+}$
core of the nanostructures. Furthermore Co-Co interactions can also cause a broadening of the spectrum. The g value of Co$^{2+}$ doped ZnO nanocrystals, $g = 4.6109$ is comparable with reported values [238]. The EPR spectrum of ZnO:Co$^{2+}$ samples are shown in figure 5.5.

**Figure 5.5:** EPR spectra of Co doped ZnO nanostructures grown by hydrothermal method at 100$^0$C for 6 h

Figure 5.6 shows the room temperature photoluminescence emission spectra of ZnO nanostructures and cobalt doped ZnO nanostructures prepared at 100$^0$C using 0.3 M zinc acetate for a growth duration of 6 h. Blue emission at 437 nm was observed for an excitation wavelength of 350 nm in the ZnO nanostructures and it may be due to Zn interstitial related defects [224, 225]. The dominant transition at 1.88 eV due to the d-d transitions of Co$^{2+}$ in tetrahedral crystal fields is not seen in the room temperature PL spectra. Low temperature PL studies are necessary to observe the d-d transitions of Co$^{2+}$ ions [239].
Results and discussion

**Figure 5.6:** Room temperature photoluminescence emission spectra of ZnO and Co doped ZnO nanostructures grown by hydrothermal method at 100°C for a duration of 6 h

Figure 5.7 shows the diffuse reflectance spectra (DRS) of undoped ZnO and cobalt doped ZnO nanostructures synthesized by hydrothermal method at a growth temperature of 100°C for 3 h. Figure 5.7(a) corresponds to the DRS of undoped ZnO synthesized from 0.3 M Zn(Ac)$_2$ and figure 5.7(b), (c) and (d) corresponds to that of Co doped ZnO synthesized from 0.3 M, 0.5 M and 1 M Zn(Ac)$_2$ respectively for a particular concentration of Co(NO$_3$)$_2$ of 0.01 M. Two bands of absorption are observed for the Co doped ZnO samples: an intense absorption peak in the ultraviolet region and a weak band in the visible region (1.8-2.3 eV). The absorption at high energies is due to the band to band transition of ZnO and the visible band is due to
the Co\textsuperscript{2+} d-d internal transitions. The three peaks observed at positions 1.89 eV, 2.03 eV, 2.19 eV have been identified as the internal transitions \(^{4}A_{2}\) to \(^{2}T_{1}(G)\), \(^{4}T_{1}(P)\) and \(^{2}A_{1}(G)\) of substitution of Co\textsuperscript{2+} on Zn sites in ZnO, respectively [225]. The band gap of the material can be obtained from the figure 5.7 and it shows that the band gap of the Co doped ZnO nanostructures increases from 3.32 eV to 3.44 eV as the concentration of zinc acetate precursor decreases from 1 M to 0.3 M while other growth parameters were kept constant. The band gap of undoped ZnO is found to be 3.42 eV. This blue shift in the band gap of undoped ZnO and Co doped ZnO nanostructures are due to the quantum confinement effects.

\textbf{Figure 5.7:} Diffuse reflectance spectra of (a) undoped ZnO and cobalt doped ZnO nanostructures grown by hydrothermal method at a growth temperature of 100\(^{\circ}\)C for 3 h using Zn(Ac)\textsubscript{2} precursors of various molarity (b) 0.3 M (c), 0.5 M (d) and 1 M
The magnetic moment of Co doped ZnO nanostructures, synthesized from 0.01 M cobalt nitrate, measured in the field range 0 to ± 20 kOe at 5 K is shown in the figure 5.8. The hydrothermally synthesized Co doped ZnO nanostructures were showing paramagnetic behaviour since the curve do not show any hysteresis and no remanence. According to Blasco et. al [240] the ferromagnetism at room temperature is always due to the presence of secondary phases and not due to the doping of ZnO, whereas single phases behave as paramagnetic semiconductors. XRD patterns of Co doped ZnO nanostructures synthesized by hydrothermal method shows no significant peaks of secondary phases which may explain the absence of ferromagnetism in Co doped Zno nanostructures.

Figure 5.8: Magnetic hysteresis loop of Co doped ZnO nanostructures synthesized from 0.01 M cobalt nitrate at 5 K
The ferromagnetism in dilute magnetic semiconductors is originated from the exchange interaction between free delocalized carriers and localized d spins of the cobalt ions [241]. So the presence of free carriers is essential for the appearance of ferromagnetism in DMS. Free carriers can be induced either by doping or by defects or by cobalt ions in another oxidation state like Co$^{3+}$. The samples prepared by hydrothermal method have limited number of impurities or defects, which may explain the absence of free carriers and consequently the ferromagnetism.

Figure 5.9: Temperature dependant magnetic moment of Co doped ZnO nanosstructures synthesized from 0.01 M cobalt nitrate in a magnetic field of 200 Oe

The steep increase in the magnetic moment with decreasing temperature below 50 K as shown in the figure 5.9 is a characteristics of all DMS materials and probably related to the defects structure and possible fraction of Co atoms which are not participating in the long range ferromagnetic
ordering [242]. As the temperature falls below 50 K, the paramagnetic properties dominates and the magnetization increases.

Figure 5.10 shows the inverse susceptibility ($\chi^{-1}$) of Co doped ZnO nanostructures synthesized from 0.01 M cobalt nitrate as a function of temperature. The result is consistent with the Curie-Weiss equation [243]

$$\chi = \frac{C}{(T + \Theta)} \quad (5.1)$$

where $\chi$ is the magnetic susceptibility, $C$ is the paramagnetic Curie constant and $\Theta$ is the Curie-Weiss temperature. It can be observed from the figure that the curve passes through the origin indicating nanostructures are paramagnetic in nature, giving no evidence for antiferromagnetic coupling.

**Figure 5.10:** Temperature dependent inverse susceptibility of Co doped ZnO nanostructures synthesized from 0.01 M cobalt nitrate under a magnetic field of 200 Oe
5.2.3 Conclusion

Cobalt doped zinc oxide (ZnO) and undoped ZnO nanostructures were synthesized by low temperature hydrothermal method by varying the process parameters such as molarity of precursors and time of growth. The structural studies of these Co doped ZnO and undoped ZnO nanostructures were characterized by x-ray diffraction technique. SEM images show that width of the nanorods decreases with decrease in the duration of hydrothermal growth. Blue PL emission at 437 nm were observed from the ZnO nanostructures at an excitation wavelength of 350 nm which corresponds to Zn interstitial related defects. Three peaks observed at positions 1.89 eV, 2.03 eV, 2.19 eV in DRS spectrum confirms the presence of substitutional incorporation of Co$^{2+}$ on the Zn site in the ZnO matrix. The spectrum also shows that the band gap of ZnO nanostructures is blue shifted from that of bulk ZnO powder due to quantum confinement effects. ICP AES studies confirm the incorporation of cobalt in the ZnO nanostructures. The g value obtained from the EPR measurements is comparable with theoretical values which confirm the Co$^{2+}$ incorporation in ZnO matrix. The magnetic studies of Co doped ZnO nanostructures shows paramagnetic behaviour and is attributed to the absence of secondary phases.

5.3 Red luminescence from hydrothermally synthesized Eu doped ZnO nanoparticles under visible excitation

Phosphor which has high efficiency and low degradation is required for the development of lighting technology and for flat panel displays such as field
emission displays (FEDs) and plasma display panels (PDPs) [244, 245]. The use of oxide phosphors in place of conventional sulfide phosphors has been preferred for FED applications due to higher stability in high vacuum environment and less emission of contaminating gases [105].

High quality II-VI semiconductor nanocrystals and their luminescence properties have been studied recently both experimentally and theoretically [246–248]. The II-VI semiconductor nanomaterial are unique host materials for doping optically active impurities, and these semiconductor doped with luminescence centers exhibit efficient luminescence even at room temperature [101, 249].

In recent years, rare earth (RE) doped wide band gap semiconducting nanomaterials finds various applications such as thin-film electroluminescent (TFEL) devices [250], optoelectronic or cathodoluminescent devices [251]. RE-doped insulators are used in telecommunications, lasers and amplifiers [252], medical analysis and phosphors [244], etc.

CdSe and CdS are the most widely studied among the II-VI semiconductor nanoparticles [246–248, 253, 254]. However these materials contain toxic elements such as Cd and Se. Zinc oxide (ZnO) is a wide band gap (3.3 eV) II-VI compound semiconductor with large exciton binding energy (60 meV). ZnO is an environmentally friendly material and is one of the suitable candidates for practical use as a nanodevices. It has a stable wurtzite structure with lattice spacing $a = 0.325$ nm and $c = 0.521$ nm. Most of the ZnO: RE$^{3+}$ crystals have been synthesized by traditional high temperature solid state reaction [250, 255] which is energy consuming and difficult to control the particle properties.

Rare-earth (RE) ions are better luminescent centers than the transition metal elements because their 4f intrashell transitions originate narrow and
intense emission lines. The synthesis of Eu doped ZnO nanoparticles by low temperature hydrothermal method and their photoluminescence emission characteristics were discussed in this chapter.

5.3.1 Experimental

The Eu doped ZnO nanoparticles were synthesized from the stock solutions of Zn(CH$_3$COO)$_2$.2H$_2$O (0.1 M) prepared in 50 ml methanol under stirring. To this solution Eu$_2$O$_3$ varying from 0.005 gm to 0.03 gm was added. This leads to europium concentration variation from 1.2 at.% to 5.27 at.% in the ZnO nanoparticle. 25 ml of NaOH (0.3 M) solution prepared in methanol was mixed with the above solution under continuous stirring in order to get the pH of reactants between 8 to 11. These solutions was transferred into teflon lined sealed stainless steel autoclaves and maintained at 150°C for 12 h under autogenous pressure. It was then allowed to cool naturally to room temperature. After the reaction was complete, the resulting white solid products were washed with methanol, filtered and then dried in air in a laboratory oven at 60°C. The undoped ZnO nanoparticles were also synthesized in similar manner described above but without adding Eu$_2$O$_3$.

The synthesized samples were characterized for their structure by x-ray diffraction (Rigaku D max-C) with Cu K$_\alpha$ radiation (1.5418 Å). Transmission electron microscopy (TEM), selected area electron diffraction (SAED) and high resolution transmission electron microscopy (HRTEM) were performed with a JEOL JEM-3100F transmission electron microscope operating at 200 kV. The sample for TEM was prepared by placing a drop of the ZnO suspension in methanol onto a 200 mesh carbon coated copper grid. The grids were dried before recording the micrographs. The elemental composition of the Eu doped ZnO nanoparticles were determined using
energy dispersive x-ray spectroscopy (EDX). Room temperature photoluminescence (PL) of the samples was measured using the Horiba Jobin Yvon Fluoromax-3 spectrofluorimeter with Xe lamp as the excitation source.

5.3.2 Results and discussion

The x-ray diffraction pattern were recorded with Cu K\textsubscript{\alpha} radiation (1.5418 Å). The intensity data were collected over a 2\theta range of 20-80°.

![XRD pattern](image)

**Figure 5.11:** XRD pattern of undoped ZnO and Eu doped ZnO nanoparticles of varying Eu dopant concentration

All the peaks in the x-ray diffraction pattern (Figure 5.11) can be assigned to the typical wurtzite structure of ZnO [216]. There are no char-
acteristic peaks of Eu$_2$O$_3$ regardless of the Eu dopant concentration. Thus the wurtzite structure is not modified by the addition of Eu into the ZnO matrix. The average grain size (D) of the samples was estimated with the help of Scherrer equation using the diffraction intensity of (101) peak [217].

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$  \hspace{1cm} (5.2)

Where $\lambda$ is the wavelength (Cu K$_{\alpha}$), $\beta$ is the full width at half maximum (FWHM) of the ZnO (101) line and $\theta$ is the diffraction angle.

The broadening of the diffraction peaks is an indication that the synthesized materials are in nanometer regime. The grain size was found to be in the range of 8-12 nm depending on the growth condition. The lattice parameters calculated were also in agreement with the reported values.

EDX results shows that the elemental percentage of the Eu ions incorporated in the Eu doped ZnO nanoparticles are 1.2, 2.3, 4.53 and 5.27 at.% as 0.005, 0.01, 0.02 and 0.03 gm Eu$_2$O$_3$ were used in the precursor solution.

Figure 5.12(a) shows the TEM image and corresponding SAED pattern (inset of figure 5.12(a)) of 2.3 at.% Eu doped ZnO synthesized by hydrothermal method. TEM image confirms the formation of nanoparticles and it has an average size of 8 nm and they are spherical in shape. This result is consistent with what we had obtained from XRD analysis. From the diffraction rings of the SAED pattern, (002), (102) and (110) planes of ZnO were identified.

Figure 5.12(b) shows the TEM image and corresponding SAED pattern of 3.78 at.% Eu doped ZnO grown by hydrothermal method. TEM image confirms the size of the particles is in the nanoregime. These are not spherical in shape and it has a length of 20 nm and diameter of 7 nm. From
the diffraction rings in the SAED pattern, (002), (102) and (110) planes of ZnO were identified.

**Figure 5.12:** TEM image of Eu doped ZnO nanoparticles with (a) 1.2 at.% and (b) 3.78 at.% Eu dopant concentration. SAED pattern of the ZnO:Eu with (a) 1.2 at.% and (b) 3.78 at.% Eu dopant concentration are shown in the inset.

Figure 5.13 shows the photoluminescent emission spectra of Eu doped ZnO nanoparticles at an excitation wavelength ($\lambda_{ex}$) of 397 nm. The excitation energy almost coincides with the energy of $^7F_0 \rightarrow ^5L_6$ transitions of Eu$^{3+}$ ions, which is 3.147 eV [198]. Excitation at 397nm yields the characteristic emissions of Eu$^{3+}$ corresponding to $^5D_j (j=0, 1) \rightarrow ^7F_j (j=0, 1, 2, 3$ and 4). The direct excitation of Eu$^{3+}$ enhances the PL due to Eu$^{3+}$ ions. The emission at 596 nm originates from the magnetic- dipole allowed $^5D_0 \rightarrow ^7F_1$ transition, indicating that Eu$^{3+}$ ions occupy a site with inversion symmetry and 617 nm from electric- dipole allowed $^5D_0 \rightarrow ^7F_2$ transition, which results in a large transition probability in the crystal field with inversion antisymmetry. The intensity of emission corresponds to the $^5D_0 \rightarrow ^7F_2$ transition is stronger than that of $^5D_0 \rightarrow ^7F_1$ transition. It is suggested
that the Eu$^{3+}$ ions mainly take a site with inversion antisymmetry in the ZnO host. The emission at 701 nm is from $^5D_0 \rightarrow ^7F_4$ transition and at 653 nm is from $^5D_0 \rightarrow ^7F_3$ transition. The emission peaks at 583 nm corresponds to $^5D_0 \rightarrow ^7F_0$ transition. The observation of forbidden $^5D_0 \rightarrow ^7F_0$ transition indicates that some of the Eu ions are at low site symmetry. The emission at 543 nm is from $^5D_1 \rightarrow ^7F_1$ transition.

![Figure 5.13](image.png)

**Figure 5.13:** Room temperature photoluminescence emission spectra of Eu doped ZnO nanoparticles excited for various Eu dopant concentrations at an excitation wavelength of 397 nm

The luminescent intensity of Eu doped ZnO nanoparticles increases with increase in the Eu dopant concentration at first and then it decreases. When the activator concentration increases above a certain level, luminescence be-
gins to quench. Thus the emission intensity of $^5D_0 \rightarrow ^7F_j$ ($j=0-4$) depends on Eu dopant concentration. In this case, the pairing or aggregation of activator atoms at high concentration may change a fraction of the activators into quenchers and induce the quenching effect. The migration of excitation by resonant energy transfer between the Eu$^{3+}$ activators can sometimes be so efficient that it may carry the energy to a distant killer or to a quenching centre existing at the surface of the crystal.

Figure 5.14: Room temperature photoluminescence emission spectra of Eu doped ZnO nanoparticles excited for various Eu dopant concentrations at an excitation wavelength of 466nm

Figure 5.14 shows the photoluminescent emission spectra of Eu doped
ZnO nanoparticles excited at 466 nm. The peaks at 583, 596, 617, 653 and 701 nm corresponding to the $^5D_0 \rightarrow ^7F_j$ ($j=0-4$) transitions of Eu$^{3+}$ ions which is dominated by the $^5D_0 \rightarrow ^7F_2$ transition at 617 nm. In addition, the emission intensity increases with increasing Eu dopant concentration up to 4.53 at.% and then it decreases due to the concentration quenching.

Figure 5.15: Room temperature photoluminescence spectrum of ZnO nanoparticle excited at $\lambda_{ex} = 362$ nm. The inset shows the corresponding photoluminescent excitation spectra

Figure 5.15 shows the room temperature photoluminescence spectrum of the undoped ZnO nanoparticles excited at 362 nm. Green emission at
545 nm was observed from the hydrothermally synthesized ZnO nanoparticles. It can be attributed to the transition between singly charged oxygen vacancy and photo excited hole or Zn interstitial related defects [191, 224, 225]. The inset in the figure 5.15 shows the photoluminescent excitation spectra of the ZnO nanoparticles ($\lambda_{em} = 545$ nm) which indicates that the excitation is at 362 nm. The excitation peak corresponds to the band to band transition which shows a blue shift in the band gap of ZnO nanoparticles due to quantum confinement effects.

![Figure 5.16: Variation of PL integral intensity with amount of Eu dopant concentration under 397 nm and 466 nm excitation](image)

Figure 5.16 shows the variation of PL integral intensity, at an excitation
wavelength of 397 nm and 466 nm, as the Eu dopant concentration in ZnO increases from 1.2 at.% to 5.27 at.%. The PL integral intensity increases with increasing amount of Eu dopant concentration up to 4.53 at.% and then it decreases due to the concentration quenching.

When the nanoparticles are excited with wavelength of 325 nm, no intra-\(4f\) \(\text{Eu}^{3+}\) related emission is observed. The disappearance of the red emission excited at 325 nm wavelength is probably related to the shielding effect due to the existence of the \(\text{Eu}_{\text{Zn}}^*\) level \([256]\). Thus 325 nm photon is not in resonance with any transitions of \(\text{Eu}^{3+}\) ions.

Figure 5.17: Room temperature photoluminescent excitation spectra of Eu doped ZnO nanoparticles (\(\lambda_{em} = 617\) nm)

Figure 5.17 shows the photoluminescent excitation (PLE) spectra of the Eu doped ZnO nanoparticles (\(\lambda_{em} = 617\) nm) which indicates that the
excitation is at 397 and 466nm. The excitation peaks at 397 nm and 466 nm corresponds to the $^7F_0 \rightarrow ^5L_6$ and $^7F_0 \rightarrow ^5D_2$ transitions of Eu$^{3+}$ ions. The peak at 418nm corresponds to the 4f-5d transition of Eu$^{2+}$ ion [257]. It also shows that the PLE intensity increases with increase in the Eu dopant concentration up to 4.53 at.% and then it decreases. Figure 5.18 shows a schematic representation of the main energy levels identified in the studied samples [198].

Figure 5.18: Simplified energy diagram of Eu$^{3+}$ in Eu doped ZnO nanoparticles. The energies of absorption and emission lines are also shown.

The CIE color coordinates measured from the photoluminescent emission of Eu doped ZnO nanoparticles by varying the Eu dopant concentration
are shown in the figure 5.19. For the case of the Eu doped ZnO nanoparticles with Eu dopant concentration of 1.2 at.%, 2.3 at.%, 4.53 at.% and 5.27 at.%, the CIE coordinates are (0.43, 0.54), (0.46, 0.52), (0.49, 0.49) and (0.47, 0.51) respectively and these show the colors in yellowish-orange and yellow region.

Figure 5.19: CIE diagram of Eu doped ZnO nanoparticles synthesized by varying the Eu dopant concentration (1.2 at.% to 5.27 at.%)

5.3.3 Conclusion

Europium doped ZnO nanoparticles were synthesized by hydrothermal method by varying the Eu dopant concentration. XRD and SAED results show these nanoparticles have wurtzite structure and the particle size distribu-
lations were studied from the TEM. The red PL emissions from the intra-4f transition of Eu$^{3+}$ ions are observed under an excitation of 397 and 466 nm. Luminescence quenching is observed in the nanoparticles as the Eu dopant concentration increases. Incorporation of Eu in the nanoparticles was confirmed by the EDX studies. Thus Eu doped ZnO nanostructures can be used in UV to red converting applications.
Synthesis of Eu doped ZnO nanoparticles