Chapter 6

Investigations on structural, optical and magnetic properties of Cu$^{2+}$ doped ZnO-CdS composite nanopowder
6.1 Introduction

Doping of transition metal (TM) ions is an effective method to the energy level surface states of host materials. Photocatalytic and spectroscopic properties are influenced by doping of TM ions. Among the TM ions copper (Cu) is the most promising dopant, because of its catalytic activity. The catalytic properties are mainly attributed to the position and coordination of TM ions into the framework. Therefore, the characterization of TM ion states is very important issue of present investigations. Copper is a shiny reddish-brown metal. It is malleable, ductile and a good conductor of heat. It is second only to silver in electrical conductivity. The atomic number of Cu is 29 with the electronic configuration [Ar] 3d^{10}4s^{1}. Copper can have +1, +2, +3 and +4 oxidation states inclusively. The +1 and +2 oxidation states are the most common. It forms a rich variety of compounds with oxidation states, +1 and +2, which are often called cuprous and cupric respectively [1]. It exhibits d^9 and d^{10} configurations for +2 and +1 oxidation states respectively. The compounds exhibit a wide range of geometries including cubic, tetrahedral, octahedral and various distorted geometries. Cu^{2+} is observed to fluctuate between tetragonally distorted octahedral, square pyramidal and trigonal bipyramidal coordination. In the octahedral coordination, the axial ligands are elongated (John-Teller distortion) and exhibit large amplitude motions. The coordination number of Cu^{2+} is 5-7, lying between the traditionally accepted six-fold coordination [2, 3] and recent results suggesting five-fold coordination [4, 5].

Copper (Cu) is a typical nonmagnetic transition metal dopant, because metallic Cu and Cu related oxides are non-ferromagnetic materials. Theoretical and experimental studies have confirmed that there is room temperature ferromagnetism in Cu^{2+} doped frame works [6]. For this reason, Cu^{2+} doped ZnO-CdS composite nanopowder is considered as an ideal candidate to study the mechanism of ferromagnetism in ZnO based composite nanostructures. Cu^{2+} is a prominent luminescence activator, which can modify the luminescence of ZnO-CdS composite
by creating localized impurity/defect levels and it behaves as an acceptor in ZnO with its energy level locating at 0.17 eV below the bottom of the conduction band, making itself a good candidate for creating p-type ZnO [7]. Copper has many physical and chemical properties similar to those of Zn, and it can change microstructure and optical properties of ZnO based system. The overall scenario about room temperature ferromagnetism (RTFM) in Cu-doped systems still remains controversial, though in most of studies the observed RTFM is considered as an intrinsic property of a sample [8].

To the best of our knowledge, there are no reports has been dealt with the local structural characteristics of TM ions into ZnO-CdS nanocomposites. The geometric site symmetry, bonding nature and distribution of the incorporated elements in the framework are investigated by using spectroscopic techniques. In the present investigation, synthesis of undoped and Cu$^{2+}$ doped ZnO-CdS composite nanopowder by chemical precipitation method and structural, morphological, spectroscopic properties were studied in detail. These materials may potential for solar cell applications and lighting devices.
6.2 Experimental procedure

6.2.1 Materials

All the chemical reagents used were analytical grade without further purification. All the chemicals are above 99% in purity. Zinc acetate [Zn(CH\(_3\)COO)\(_2\)·2H\(_2\)O], cadmium acetate [Cd(CH\(_3\)COO)\(_2\)·4H\(_2\)O], sodium hydroxide [NaOH], sodium sulfide [Na\(_2\)S], Cupper oxide (CuO) and ethanol were used as precursors. Deionized water was used for all dilution and sample preparation. All the glassware used in this experimental work was acid washed.

6.2.2 Synthesis of Cu\(^{2+}\) doped ZnO-CdS composite nanopowder

For the synthesis of Cu\(^{2+}\) doped ZnO-CdS composite nanopowder, 0.01 mol% of CuO dissolved in 20 mL of water-ethanol matrix was added to the ZnO-CdS composite solution in the similar procedure as mentioned in the chapter 3 with continues stirring up to 4 h. The obtained dispersions were washed several times with deionized water and ethanol to remove impurities. After washing, the solution was centrifuged and the settled powder was dried in a hot air oven at 120 °C for 2 h. The synthesized Cu\(^{2+}\) doped ZnO-CdS composite nanopowder was further characterized by different spectroscopic techniques.

6.2.3. Characterization

Powder X-ray diffraction was done on PANalytical XPert Pro-diffactometer with CuK\(\alpha\) radiation (1.5406 Å). Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Spectroscope (EDS) images were taken from ZEISS EVO 18. Transmission Electron Microscope (TEM) images are recorded on HITACHI H-7600 and CCD CAMERA system AMTV600 by dispersing the samples in ethanol. Fourier Transformed Infrared (FT-IR) spectrum was recorded using KBr pallets on Thermo Nicolet 6700 spectrometer in the range of 4000–400 cm\(^{-1}\). Optical absorption spectrum was taken from JASCO V-670 Spectrophotometer in the
wavelength region of 200–1400 nm. The EPR spectrum was obtained from JEOL JES-TE100 ESR spectrometer operating at X-band frequencies and having a 100 kHz field modulation. Photoluminescence (PL) spectrum was obtained from Horiba Jobin-Yvon Fluorolog-3 Spectrofluorimeter with Xe continuous (450 W) and pulsed (35 W) lamps as excitation sources. The magnetic hysteresis loop was obtained from a Lake Shore 7407 Vibrating Sample Magnetometer (VSM).
6.3 Theory

Divalent copper has an electronic configuration [Ar] 3d⁹. The ground state electronic configuration in an octahedral crystal field is t⁶₂ge³⁶ and yields 2E₉g state. On excitation, one of the electrons in the t₂g orbital is promoted to the e₉ orbital and configuration t⁶₂ge⁴g gives 2T₂g state. Thus, only one single electron transition 2E₉g → 2T₂g is expected for Cu²⁺ in regular octahedral symmetry. The ground state, 2E₉g is Jahn-Teller unstable in regular octahedral field. Generally the degeneracy of the ground state 2E₉g is lifted by lowering in symmetry. The degeneracy of 2E₉g cannot be lifted in trigonal fields. Hence, the site symmetry can either be tetragonal or rhombic.

In octahedral crystal field, the free ion term for Cu²⁺ (d⁹) is 2D and it splits into 2E₉g and 2T₂g and 2E₉g being in lower level. Generally, ground state 2E₉g splits due to Jahn-Teller effect, which causes distortion in octahedral symmetry. In tetragonal symmetry 2E₉g level splits into 2B₁g(dₓ²−ᵧ²) and 2A₁g(dₓz) levels. The upper state 2T₂g splits into 2B₂g(dₓᵧ) and 2E₉g(dₓz, dᵧz) levels, the ground state being 2B₁g. In rhombic field (D₂h) the lower state 2Eg splits into 2A₁g(dₓ²−ᵧ²) and 2A₂g(dₓz) whereas the upper level 2T₂g splits into 2B₁g(dₓᵧ), 2B₂g(dₓz) and 2B₃g(dᵧz) states [9]. The number of bands expected for Cu²⁺ ion is four in rhombic and three in tetragonal fields respectively. The three bands are expected [10] for the following transitions in the tetragonal field:

\[
\begin{align*}
2B₁g & \rightarrow 2A₁g : 4 \text{ Ds} + 5\text{ Dt} \\
2B₁g & \rightarrow 2B₂g : 10 \text{ Dq} \\
2B₁g & \rightarrow 2E₉g : 10 \text{ Dq} + 3 \text{ Ds} - 4 \text{ Dt}
\end{align*}
\]

where Dq, Ds and Dt are crystal field (Dq) and tetragonal field (Ds and Dt) parameters. Octahedral molecules involve the lowering of symmetry (O₆ to D₄h) due to the result of lengthening or shortening two transition metal ligand bonds with
respect to the other four. The correlation of different electronic states in octahedral (O_h), tetragonal (C_{4v}) and rhombic (C_{2v}) symmetries are shown in Fig. 6.1.

Fig. 6.1 The splitting of the energy levels for Cu^{2+} in octahedral, tetragonal and rhombic symmetries

Either in octahedron or in tetragonally distorted octahedron, the ligands are treated as point charges surrounding the central metal ion. Here Dq, Ds and Dt are defined as:

\[ D_q = \frac{1}{6} e^2 \left( \frac{r^4}{a^5} \right) \]
\[ D_t = \frac{2}{21} Ze^2 \left( \frac{r^4}{l/a^5} \pm \frac{r^4}{l/b^5} \right) \]
\[ D_s = \frac{2}{7} Ze^2 \left( \frac{r^2}{1/a^3} \pm \frac{r^2}{1/b^3} \right) \]

where \( r^2 \) and \( r^4 \) are interpreted as mean square and mean fourth power radii of the metal orbitals. a and b are represented in terms of bond length differences for axial and equatorial bonds [11]. Here Dq is the cubic crystal field parameter and is a measure of the separation between the t_{2g} and e_{g} orbital. Actually 10Dq gives the magnitude of the splitting. When the cubic symmetry of the ligand environment is distorted tetragonally to specify the amount of distortion, two parameters Ds and Dt are used. Dt and Dq will have the same sign in the case of axial elongation and opposite sign in the case of axial contraction.
6.4 Results and discussion

6.4.1 Powder X-ray diffraction analysis

X-ray diffraction patterns of Cu$^{2+}$ doped ZnO-CdS composite nanopowder is shown in Fig. 6.2. All the diffraction peaks can be indexed to a mixed phase of hexagonal wurtzite structured ZnO (JCPDS: 36-1451) and CdS (JCPDS: 65-3414). No additional peaks corresponding to any secondary or impurity phase were observed which indicates that impurity ions do not change the structure of host lattice. Broadening of diffraction peaks shows the formation of nanosized particles.

![X-ray diffraction pattern of Cu$^{2+}$ doped ZnO-CdS composite nanopowder](image)

All the diffraction peaks at $2\theta = 31.90$, 34.55, 36.38, 47.68, 56.72, 62.97, 66.50, 68.08, 69.25, 72.60 and 76.99 are indexed to the planes (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (2 0 0), (1 1 2), (2 0 1), (0 0 4) and (2 0 2) of hexagonal wurtzite ZnO ($a = 0.3253$, $c = 0.5197$ nm) and $2\theta = 25.19$, 26.68, 28.87, 44.01 and 52.12 are corresponding to the diffraction planes (1 0 0), (0 0 2), (1 0 1), (1 1 0), (1 1 2) of hexagonal CdS ($a = 0.4112$, $c = 0.6692$ nm). A small shift in the position of diffraction peaks is observed towards higher angles and broadening of XRD peaks increases as compared to undoped sample. Shifting in peak position and
line broadening of the XRD pattern arises due to the presence of micro strains in the sample. The average crystallite size was calculated from FWHM of maximum intensity peak of ZnO i.e. (1 0 1). The average crystallite size is calculated using Debye-Scherrer’s formula,

$$D = \frac{0.9 \lambda}{\beta \cos \theta}$$

Where $\lambda$ is wavelength (CuK$\alpha$), $\beta$ is full width at half maximum (FWHM), $\theta$ is diffraction angle. The dislocation density ($\delta$) and micro strain ($\varepsilon$) were calculated using equations, $\delta = \frac{1}{D^2}$ and $\varepsilon = \frac{\beta \cos \theta}{4}$. The crystallite size, dislocation density and micro strain are evaluated as 27 nm, $1.32 \times 10^{15}$ lines/m$^2$ and $1.28 \times 10^{-3}$. Williamson and Hall suggested a method to evaluate the crystallite size and micro strain of the powder sample using the following expression

$$\beta \cos \theta = (0.9 \ \lambda / D) + 4\varepsilon \sin \theta$$

W-H equation represents a straight line between $4\sin \theta$ (X-axis) and $\beta \cos \theta$ (Y-axis). The slope of the line gives micro strain ($\varepsilon$) and intercept $(k\lambda / D)$ of the line represents crystallite size (D). The calculated values of crystallite size (D) and micro strain ($\varepsilon$) are 28 nm and $0.61 \times 10^{-3}$ respectively. W-H plot of Cu$^{2+}$ doped ZnO-CdS composite nanopowder is shown in Fig. 6.3. The crystallite sizes and micro strain values calculated using W-H plots are very close to the values obtained from Debye-Scherrer’s formula.

![Fig. 6.3 W-H plot of Cu$^{2+}$ doped ZnO-CdS composite nanopowder](image)
6.4.2 Morphological studies

SEM micro graphs of Cu\textsuperscript{2+} doped ZnO-CdS composite nanopowder at different magnifications are presented in Fig. 6.4. From low resolution SEM images, it can be clearly observed that, the prepared nanopowder shows many agglomerates with spherical like morphology. The agglomeration could be induced by densification resulting from the narrow space between particles. The grain sizes observed in SEM micrographs are different from the crystallite size evaluated from powder XRD studies, it is due to segregation among the crystal nucleus [12].

Fig. 6.4 SEM images of Cu\textsuperscript{2+} doped ZnO-CdS composite nanopowder

The chemical compositional details of the prepared samples were obtained from EDS. Fig. 6.5 shows the EDS spectrum of (a) undoped and (b) Cu\textsuperscript{2+} doped ZnO-CdS composite nanopowder. It is clearly indicates the presence of Zn, O, Cd, S and Cu species. Fig. 6.6 shows the typical TEM images of Cu\textsuperscript{2+} doped ZnO-CdS composite nanopowder. The TEM images shows spherical like structures with little agglomeration. The particle size is greater than the average size calculated by XRD because of agglomeration of the particles during drying process or non-distinguishable interfaces of the crystallites [13].
Fig. 6.5 EDS pattern of Cu$^{2+}$ doped ZnO-CdS composite nanopowder

Fig. 6.6 TEM images of Cu$^{2+}$ doped ZnO-CdS composite nanopowder
6.4.3 FT-IR analysis

FT-IR spectrum of Cu$^{2+}$ doped ZnO-CdS composite nanopowder is shown in Fig. 6.7. The characteristic bands observed at 519 and 619 cm$^{-1}$ are attributed to the fundamental vibrational modes of Zn-O [14] and Cd-S [15]. These vibrational modes are indicative of successive synthesis of ZnO-CdS nanocomposite. The structural changes are observed at 687, 897 cm$^{-1}$. The absorption band at 1114 and 1384 cm$^{-1}$ are assigned to stretching vibrational modes of O-H and C=O. The symmetric bending mode of vibrations of H-O-H is served at 1632 cm$^{-1}$. The band at 2341 cm$^{-1}$ represents the C-O symmetric bending vibrations of CO$_2$ molecule [16]. The bands observed at 2856 and 2926 cm$^{-1}$ are attributed to C-H stretching mode of vibration [17] and the band at 3455 cm$^{-1}$ is corresponding to O-H stretching vibration [18].

Fig. 6.7 FT-IR spectrum of Cu$^{2+}$ doped ZnO-CdS composite nanopowder
6.4.4 Optical absorption study

Fig. 6.8 depicts the optical absorption spectrum of Cu$^{2+}$ doped ZnO-Cds composite nanopowder. The optical absorption spectrum consists three bands at 665 nm (15033 cm$^{-1}$), 823 nm (12147 cm$^{-1}$) and 1192 nm (8387 cm$^{-1}$) attributed to the transitions $^2$B$_{1g} \rightarrow ^2$E$_g$, $^2$B$_{2g}$ and $^2$A$_{1g}$ respectively. The wavenumbers of the different transitions are given by the following formulae [19].

$$^2B_{1g} \rightarrow ^2A_{1g} : 4D_s + 5D_t$$
$$^2B_{1g} \rightarrow ^2B_{2g} : 10D_q$$
$$^2B_{1g} \rightarrow ^2E_g : 10D_q + 3D_s - 5D_t$$

Evaluated crystal field and tetragonal field parameters are Dq = 1214, Ds = 1610 and Dt = 389 cm$^{-1}$. Dq and Dt will have same sign in case of axial elongation and opposite sign in axial contraction. Hence Dq and Dt indicates a tetragonally elongated distorted octahedral site symmetry.

![Optical absorption spectrum of Cu$^{2+}$ doped ZnO-Cds composite nanopowder](image)

**Fig. 6.8 Optical absorption spectrum of Cu$^{2+}$ doped ZnO-Cds composite nanopowder**
6.4.5 EPR study

Electron paramagnetic resonance (EPR) provides a simple and accurate way to analyze concentration and distribution of doped paramagnetic ions within the host crystals [13]. EPR spectrum of Cu$^{2+}$ doped ZnO-CdS composite nanopowder exhibits four lines corresponding to the parallel hyperfine splitting of the copper nucleus ($I = 3/2$) and it gives single broad EPR signal due to exchange interaction. EPR spectrum of Cu$^{2+}$ doped ZnO-CdS composite nanopowder is shown in Fig. 6.9.

Fig. 6.9 EPR spectrum of Cu$^{2+}$ doped ZnO-CdS composite nanopowder

The spin-Hamiltonian and hyperfine splitting parameters are evaluated as

$g_\parallel = 2.3391$, $g_\perp = 2.0550$ and $A_\parallel = 130 \times 10^{-4}$ cm$^{-1}$, $A_\perp = 36 \times 10^{-4}$ cm$^{-1}$

The fact that $g_\parallel > g_\perp$ suggests that Cu$^{2+}$ ions are subjected to tetragonally elongated octahedral distortion, which is also confirms from the optical absorption
studies. These values are well consistent with previously reported Cu\(^{2+}\) doped frame works. Sathish et al., reported that Cu\(^{2+}\) ions entered into ZnCdO lattice as tetragonally elongated octahedral site symmetry and similar results are observed by Rama Krishna et al. [20, 21]. From the spin-Hamiltonian parameters, the Fermi contact term (\(\kappa\)) was calculated using the following expressions

\[
\kappa = \left(\frac{A_\circ}{P}\right) + \Delta g_o
\]

where P is the dipolar contribution to the hyperfine splitting value, A is a negative quantity and usually assigned to the free ion value of 0.036 cm\(^{-1}\). 

\[
A_\circ = \frac{(A_\parallel + 2A_\perp)}{3}, \quad \text{where } A_\parallel \text{ and } A_\perp \text{ are the hyperfine coupling constants in the parallel and perpendicular directions to the field.}
\]

\[
g_\parallel \text{ and } g_\perp \text{ are the } g \text{-values parallel and perpendicular to the field and } \Delta g_o = g_o - g_e, \quad \text{where } g_o = \frac{(g_\parallel + 2g_\perp)}{3} \text{ and } g_e (2.0023) \text{ is the free ion value. The Fermi contact term is a measure of the polarization produced by the uneven distribution of d-electron density on the inner core s-electron. The evaluated value of } \kappa = 0.33. \text{ The covalency parameter for the in plane } \sigma \text{-bonding is evaluated from the expression } [22]:
\]

\[
\alpha^2 = \frac{A_\parallel}{0.036} + (g_\parallel - g_e) + \frac{3}{7} (g_\perp - g_e) + 0.04
\]

where \(\alpha^2\) represents the covalency of the in-plane \(\sigma\)-bonding between copper and its ligands. The evaluated value of \(\alpha^2\) is 0.76 which indicates that the bonding is less covalent in nature. \(\alpha'\) can be evaluated from the normalization conditions on the ground state \(^2\)B\(_{1g}\) orbital as:

\[
\alpha' = (1 - \alpha^2)^{1/2} + aS
\]

In the above equation, S is the overlap integral between d\(_{x^2-y^2}\) orbital and normalized ligand orbital. The value of S (0.076) is used for of oxygen ligands [23]. The evaluated parameter for \(\alpha'\) is 0.55. The axial symmetry of g and A tensors can be explained in terms of the slightly distorted octahedral coordination around the Cu\(^{2+}\) ion. An octahedral complex with a tetragonal elongation would give g\(_\parallel\) > g\(_\perp\) > g\(_e\) and the tetragonality measure (g\(_\parallel\) – g\(_e\))/( g\(_\perp\) – g\(_e\)) with the ground state is \(^2\)B\(_{1g}\).
The EPR results can be correlated with optical data to obtain orbital reduction parameters using the following formulae

\[
g_{\parallel} = 2.0033 \pm (8K_{\parallel}^2 \lambda / \Delta E_1) \\
g_{\perp} = 2.0023 \pm (2K_{\perp}^2 \lambda / \Delta E_2)
\]

where \(K_{\parallel}\) and \(K_{\perp}\) are the parallel and perpendicular components of orbital reduction factor (K). \(\lambda\) is the spin orbit coupling constant and is equal to \(-830\) cm\(^{-1}\) for a free Cu\(^{2+}\) ion. \(\Delta E_1\) and \(\Delta E_2\) are corresponds to the transitions of \(^2B_{1g} \rightarrow ^2B_{2g}\) and \(^2B_{1g} \rightarrow ^2E_g\) respectively. From the above relations, orbital reduction factors (K, \(K_{\parallel}\) and \(K_{\perp}\)) which are a measure of covalency [24-27]. K = 1 for an ionic environment and for a covalent environment K < 1. The lower the value of K, the greater is the covalent nature. By using \(\Delta E_1 = 12147\) cm\(^{-1}\) and \(\Delta E_2 = 15033\) cm\(^{-1}\), the orbital reduction parameters are evaluated. They are \(K_{\parallel} = 0.78\), \(K_{\perp} = 0.69\) and \(K = 0.72\). These values of K are in tune with other copper complexes in distorted octahedral coordination [21]. The evaluated values of bonding and orbital reduction parameters suggest the partial covalent nature with Cu\(^{2+}\) in the host lattice.

6.4.6 Photoluminescence study

Photoluminescence spectrum is very sensitive to the electronic structure of the materials. PL spectra were shown four characteristic emission peaks in both UV and visible regions. Fig. 6.10 shows the room temperature PL spectrum of Cu\(^{2+}\) doped ZnO-CdS composite nanopowder under the excitation wavelength of 325 nm. It is well known that surface defects play an important role in the luminescence properties of nanostructure. PL spectrum of Cu\(^{2+}\) doped ZnO-CdS composite nanopowder consists four emission bands at UV and visible regions. The UV emission peaks centered at 367, 380 nm are attributed to near-band-edge emission. A sharp blue emission peak at 425 nm can be assigned to surface vacancies like oxygen vacancies and zinc vacancies, i.e. to the recombination of electron-hole pairs at the valance band [28].
A strong broad green emission peak in the range of 450-570 nm is attributed to the electron transfer from CdS to ZnO on excitation. On the other hand, comparison of PL spectra of both undoped and Cu$^{2+}$ doped sample indicates that the green emission intensity increases in presence of Cu$^{2+}$. The significant increase in the luminescence of Cu$^{2+}$ doped ZnO-CdS composite nanopowder should be mainly attributed to the defect states and surface vacancies.

The CIE 1931 chromaticity diagram of Cu$^{2+}$ doped ZnO-CdS composite nanopowder is shown in Fig. 6.11. The calculated chromaticity coordinates of Cu$^{2+}$ doped ZnO-CdS composite nanopowder are (x, y) = (0.1751, 0.4075), which indicates the colour vision of the sample. The spots on the chromaticity diagram represent the bluish-green region. Due to colour tenability with excitation wavelength of Cu$^{2+}$ doped ZnO-CdS composite nanopowder can be useful for optical display applications [29].
From CIE 1931 chromaticity coordinates \((x, y)\), correlated colour temperature (CCT) is calculated using McCamy equation [30].

\[
\text{CCT} = -449 \, n^3 + 3525 \, n^2 - 6823.3 \, n + 5520.33
\]

Where \(n = (x-x_e)/(y-y_e)\) is inverse slope line with \(x_e = 0.3320, y_e = 0.1858\). The CCT is an indication of colour appearance of light emitted by the light source. In the present study, CCT is evaluated as 12274 K, which represents orange light emission.

Fig. 6.11 CIE diagram of Cu\(^{2+}\) doped ZnO-CdS composite nanopowder
6.4.7 Magnetic study

Magnetization measurement was carried out to understand the magnetic behaviour of Cu$^{2+}$ doped ZnO-CdS composite nanopowder at room temperature. The hysteresis loop of the sample is shown in Fig. 6.12. The shape of hysteresis loop and noticeable coercivity of M-H curve could be attributed to strong ferromagnetism at room temperature. Cu$^+$ does not possess any magnetic moment. It is believed that ferromagnetic interactions arise due to substitution of Cu$^{2+}$ ions in host lattice because in the case of Cu$^{2+}$ ions with d$^9$ configuration, there is an unpaired electron, which can bring about a net magnetic moment [31].

Fig. 6.12 M-H hysteresis loop of Cu$^{2+}$ doped ZnO-CdS composite nanopowder
The most common mechanism for observed ferromagnetism in Cu-doped ZnO based nanostructures is the carrier induced ferromagnetism [32]. The saturation magnetization (Ms), remnant magnetization (Mr) and coercive field (Hc) of Cu$^{2+}$ doped ZnO-CdS composite nanopowder are estimated to be $17.076 \times 10^{-3}$ emu/g, $1.834 \times 10^{-3}$ emu/g and 117.47 Oe respectively. From the XRD analysis of the sample, the absence of secondary phase or the metallic copper clusters are confirmed and optical studies also confirm the substitution of copper into ZnO-CdS nanocomposite. Thus, ferromagnetism in the prepared sample could be considered as the exchange interaction between local spin-polarized electrons and conductive electrons.
6.5 Conclusion

Cu$^{2+}$ doped ZnO-CdS composite nanopowder was successfully synthesized by simple chemical precipitation method.

- XRD pattern of the prepared samples exhibited hexagonal phase of ZnO as well as hexagonal phase of CdS. The average crystallite size is found to be 29 nm.
- SEM and TEM micrographs shows non-uniformly distributed spherical shaped structures with average diameter of 20 nm. EDS spectrum confirmed the presence of Zn, O, Cd, S and Cu in the prepared sample.
- FT-IR spectrum shows symmetric stretching vibrations of Zn-O, Cd-S and other functional groups.
- From optical and EPR studies, it is concluded that Cu$^{2+}$ is entered into the host lattice as tetragonally elongated octahedral site symmetry and partially covalent bonding nature was observed between Cu$^{2+}$ and its ligands.
- PL spectrum illustrate the quenching of UV with enhanced visible emission for Cu$^{2+}$ doped ZnO-CdS composite nanopowder.
- The synthesized composite nanopowder may use in visible light emitting devices and development of solar cell applications.
- The observed RT ferromagnetism in Cu$^{2+}$ doped ZnO-CdS composite nanopowder is due to the exchange interaction between local spin-polarized electrons and conductive electrons.
6.6 References


