Chapter 4

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

ZnO-CdS nanocomposites have been extensively investigated due to their distinguished performance in optics, electronics, light emitting devices, photocatalysts and photovoltaic cells [1-4]. Inorganic materials having high luminous efficiency, energy saving and environmental protection are long-lasting pursuits of researchers. Luminescent centres in a nanocomposite material can be excited either via direct pumping the centres or indirectly through energy transfer from the host materials.

At room temperature, ZnO nanostructures often exhibit sharp near band edge emission (NBE) in the ultraviolet (UV) region and broad deep level emission (DLE) in the green region that is related to oxygen/zinc vacancies [5-7]. While CdS nanostructures with smaller bandgap energies always show green (DLE) luminescence which arising from cadmium or sulfur vacancies [8, 9]. In ZnO/CdS nanocomposites, both ZnO and CdS can contribute to the green DLE luminescence. It is also possible that the luminescence of one component is quenched by the other [10, 11]. Due to the large number of defects present at the ZnO/CdS interface that will also lead to luminescence. Therefore, it is difficult to probe using conventional techniques the origin of luminescence in such ZnO/CdS nanocomposites, which is important for their application in solar cells [12-14].

Nowadays, the synthesized luminescent materials in nanoscale are essential for ongoing device development and miniaturization. Among these inorganic luminescence materials, ZnO-CdS nanocomposites widely applied in light emitting displays and biomedicine [15, 16]. In the recent past, many composite nanomaterials doped with manganese have been studied due to its interesting optical properties [17, 18]. Manganese is a pinkish-gray element, exists naturally in the environment and has chemically active nature. It is a key component of iron, steel production and widely used in alloys and fertilizers as catalyst. Manganese ions has d⁵ configuration.
Divalent manganese ion is a well-known paramagnetic ion and plays an important role as luminescence activator in several inorganic materials. EPR spectrum of paramagnetic Mn$^{2+}$ exhibits six resonance lines due to zero field and the hyperfine splitting. While hyperfine splitting of Mn$^{2+}$ is scarcely sensitive to structural changes, but highly sensitive to zero-field splitting and hence they are capable of reflecting symmetries and structural changes of host lattices [19]. The luminescent properties of Mn$^{2+}$ activated phosphors have various practical applications in lighting and electronic displays. The tetrahedral coordinated Mn$^{2+}$ usually exhibits green emission, whereas octahedrally coordinated Mn$^{2+}$ exhibits orange to red emission. Mn$^{2+}$ doped phosphors generally show intense broad-band emissions due to spin-forbidden d-d transition from $^4T_{1g} \rightarrow ^6A_{1g}$ within the 3d shell in which the electrons are strongly coupled to lattice vibration [20]. Because of spin and parity selection rules, Mn$^{2+}$ luminescence in a host lattice has relative long lifetime (~10 ms).

In the present study, Mn$^{2+}$ doped ZnO-CdS composite nanopowder was synthesized using chemical precipitation method. The prepared sample was characterized by XRD, SEM with EDS, TEM, optical absorption, EPR, PL, FT-IR and vibrating sample magnetometer (VSM). Mn$^{2+}$ doped ZnO-CdS composite nanopowder exhibits good structural, optical and magnetic properties. The prepared samples may useful for future applications such as photocatalyst, light emitting devices and solar cells.
4.2 Experimental procedure

4.2.1 Materials

To synthesize Mn$^{2+}$ doped ZnO-CdS composite nanopowder, the following materials were used. All the chemical reagents used were analytical grade without further purification. Zinc acetate [$\text{Zn(\text{CH}_3\text{COO})_2\cdot2\text{H}_2\text{O}}$], cadmium acetate [$\text{Cd(\text{CH}_3\text{COO})_2\cdot4\text{H}_2\text{O}}$], sodium hydroxide [$\text{NaOH}$], sodium sulfide [$\text{Na}_2\text{S}\cdot\text{xH}_2\text{O}$], manganese oxide [$\text{MnO}$] and ethanol were used as precursors. Deionized water was used for all dilution and sample preparation. All the chemicals are above 99% in purity. All the glassware used in this experimental work was acid washed.

4.2.2 Synthesis of Mn$^{2+}$ doped ZnO-CdS composite nanopowder

In typical procedure, 0.01 mol% of manganese oxide [$\text{MnO}$] dissolved in 20 mL of water-ethanol matrix was added to the ZnO-CdS composite solution as mentioned in the chapter 3 and then stirred for 4 h. The obtained dispersions were washed several times with deionized water and ethanol to remove impurities. After washing, the solution was centrifuged at 10,000 rpm about 30 min. The settled powder was collected and dried in a hot air oven at 120 °C for 2 h. The synthesized Mn$^{2+}$ doped ZnO-CdS composite nanopowder was characterized using different techniques.

4.2.3 Characterization

Powder X-ray diffraction pattern was recorded on PANalytical XPer Pro-diffractometer with CuKα radiation (1.5406 Å). Scanning Electron Microscope (SEM) images were taken from ZEISS EVO 18. The chemical composition was determined with an Oxford EDS analyzer attached with SEM instrument. Transmission Electron Microscope (TEM) images are recorded on HITACHI H-7600 and CCD CAMERA system AMTV600 by dispersing the samples in ethanol.
Optical absorption (UV-vis) spectrum was taken from JASCO V-670 spectrophotometer in the wavelength region of 200–1400 nm. The EPR spectrum was obtained from JEOL JES-TE 100 EPR spectrometer operating at X-band frequencies and having a 100-kHz field modulation. PL spectrum was obtained from Horiba Jobin-Yvon Fluorolog-3 Spectrofluorimeter with Xe continuous (450 W) and pulsed (35 W) lamps as excitation sources. Fourier Transformed Infrared (FT-IR) spectrum was recorded using KBr pallets on Shimadzu IRAffinity-1 in the range of 4000–400 cm\(^{-1}\). The magnetic hysteresis loop was obtained from a Lake Shore 7407 vibrating sample magnetometer (VSM).
4.3 Theory

The electronic configuration of Mn$^{2+}$ is (Ar) 3d$^5$. It gives rise to $^2$S, $^2$P, $^2$D, $^2$F, $^2$H, $^4$P, $^4$D, $^4$F, $^4$G and $^6$S terms. The ground multiplet of Mn$^{2+}$ is $^6$S (3d$^5$). Therefore, any crystalline field does not directly affect this state. To explain the ground level splitting, it is necessary to consider an admixing to $^6$S of higher multiplets and configurations which are split under the action of crystalline field. In a cubic crystalline field of low to moderate strength, five d-electrons of Mn$^{2+}$ are distributed in t$_{2g}$ and e$_g$ orbitals with three in the former and two in the later. Thus the ground state configuration is t$_{2g}^3$e$_g^2$. This configuration gives rise to the electronic states $^6$A$_{1g}$, $^4$A$_{1g}$, $^4$E$_g$, $^4$T$_{1g}$, $^4$T$_{2g}$ and to a number of doublet states of which $^6$A$_{1g}$ lies lowest according to Hund’s rule. The energy level for Mn$^{2+}$ in octahedral environment is as follows: $^6$S $\rightarrow$ $^6$A$_{1g}$, $^4$G $\rightarrow$ $^4$T$_{1g}$ + $^4$T$_{2g}$ + $^4$E$_g$ + $^4$A$_{1g}$, $^4$D $\rightarrow$ $^4$T$_{2g}$ + $^4$E$_g$, $^4$P $\rightarrow$ $^4$T$_{1g}$. The $^4$E$_g$ - $^4$A$_{1g}$ (4G) and $^4$E$_g$ (4D) levels have relatively less influence compared to other levels by crystal filed [21]. Since, all excited states of Mn$^{2+}$ (belonging to d$^5$ configuration) will be either quartets or doublets. Energy level diagram of Mn$^{2+}$ in a free ion state is shown in Fig. 4.1.

Crystal field (CF) is termed weak when its influence is lesser than that of spin orbit interaction and electronic repulsion, whereas it is strong when its influence is greater. If the CF influence is in between that of spin orbit and electronic repulsion, it is treated as intermediate field. The transitions $^6$A$_{1g}$ $\rightarrow$ $^4$T$_{1g}$ and $^6$A$_{1g}$ $\rightarrow$ $^4$T$_{2g}$ depends on the crystal field strength Dq and give rise to broad bands. For the transition like $^6$A$_{1g}$ $\rightarrow$ $^4$E$_g$, which are independent of Dq the bands would be less broadened [22]. Splitting of EPR line in Mn$^{2+}$ is shown in Fig. 4.2. Tanabe-Sugano diagram for d$^5$ configuration is shown in Fig. 4.3.
Fig. 4.1 Energy level diagram of Mn$^{2+}$ in a free ion state

Fig. 4.2 Splitting of EPR line of Mn$^{2+}$ owing to hyperfine interaction
Fig. 4.3 T-S diagram for octahedral d⁵ electron configuration
4.4 Results and discussion

4.4.1 Powder X-ray diffraction analysis

The X-ray diffraction pattern of Mn$^{2+}$ doped ZnO-CdS composite nanopowder is shown in Fig. 4.4. All the diffraction peaks marked in circles are indexed to a hexagonal wurtzite structure of ZnO (JCPDS: 36-1451) with lattice cell parameters $a = 0.3254$, $c = 0.5210$ nm. The peaks marked in triangles are indexed to the wurtzite structure of CdS (JCPDS: 65-3414) with lattice cell parameters $a = 0.4129$, $c = 0.6728$ nm. This result confirms the successful synthesis of ZnO-CdS composite nanopowder. No other peaks corresponding to any impurity phase were detected, which suggests the sample is in good purity and well crystallinity.

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

Fig. 4.4 X-ray diffraction pattern of Mn$^{2+}$ doped ZnO-CdS composite nanopowder

The average crystallite size of Mn$^{2+}$ doped ZnO-CdS composite nanopowder is calculated using Debye-Scherrer’s formula [23],

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

where $D$ is the average crystallite size, $\lambda$ is incident wavelength (CuK$\alpha$), $\beta$ is full width at half maximum (FWHM) and $\theta$ is diffraction angle. The average
crystallite size was estimated from most intense diffraction peak as 18 nm. The micro strain (\( \varepsilon \)) was calculated using the expression [24],

\[ \varepsilon = \beta \cos\theta / 4 \]

The micro strain is evaluated as \( 1.9576 \times 10^{-3} \). The Scherer’s formula gives information about the average size of crystallite but it neglects the effect of strain in the crystal. Thus using the Williamson–Hall formula [25], we have estimated the contribution of crystalline domain size effect and micro strain effect on the diffraction pattern as,

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

W-H equation represents a straight line between \( 4\sin\theta \) on X-axis and \( \beta \cos\theta \) on Y-axis. The slope of the line gives micro strain (\( \varepsilon \)) and intercept (\( k\lambda / D \)) of the line represents crystallite size (\( D \)). W-H plot of Mn\(^{2+}\) doped ZnO-CdS composite nanopowder is shown in Fig. 4.5. The evaluated values of crystallite size (\( D \)) and micro strain (\( \varepsilon \)) are 19 nm and \( 2.3485 \times 10^{-3} \) respectively. These values are in good constituent with the values obtained from Debye-Scherer’s formula.

![Fig. 4.5 W-H plot of Mn\(^{2+}\) doped ZnO-CdS composite nanopowder](image)
4.4.2 Morphological studies

The morphologies of Mn$^{2+}$ doped ZnO-CdS composite nanopowder were investigated by SEM and TEM. Fig. 4.6 shows the SEM micrographs of Mn$^{2+}$ doped ZnO-CdS composite nanopowder at different magnifications. The SEM images shows uniformly distributed spherical like structures with small agglomeration. The agglomeration could be induced by densification resulting from the narrow space between particles.

Fig. 4.6 SEM micrographs of Mn$^{2+}$ doped ZnO-CdS composite nanopowder

In order to verify the stoichiometric chemical composition, further performed EDS analysis on Mn$^{2+}$ doped ZnO-CdS composite nanopowder and is shown in Fig. 4.7. The characteristic peaks in the spectrum can be identified only the target elements (Zn, O, Cd, S and Mn) without any impurities. These results indicate the incorporation of manganese ions into the ZnO-CdS composite nanopowder.

The microstructures of the as-prepared samples are further demonstrated by their TEM images. Fig. 4.8 depicts the typical TEM images of Mn$^{2+}$ doped ZnO-CdS composite nanopowder. The TEM micrographs reveal that the prepared sample has sphere like and spherical like structures with average size of 20 nm.
Fig. 4.7 EDS pattern of Mn$^{2+}$ doped ZnO-CdS composite nanopowder

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>O K</td>
<td>21.97</td>
<td>55.85</td>
</tr>
<tr>
<td>S K</td>
<td>10.49</td>
<td>13.31</td>
</tr>
<tr>
<td>Mn K</td>
<td>0.93</td>
<td>0.69</td>
</tr>
<tr>
<td>Zn K</td>
<td>23.25</td>
<td>14.46</td>
</tr>
<tr>
<td>Cd L</td>
<td>43.36</td>
<td>15.69</td>
</tr>
<tr>
<td>Totals</td>
<td>100.00</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 4.8 TEM images of Mn$^{2+}$ doped ZnO-CdS composite nanopowder
4.4.3 FT-IR analysis

Fig. 4.9 shows FT-IR spectrum of Mn\textsuperscript{2+} doped ZnO-CdS composite nanopowder, which exhibits the characteristic bands of ZnO and CdS. In addition to this, the spectrum exhibits fundamental vibrations O-H groups. The band observed at 467 cm\textsuperscript{-1} is corresponds to metal oxide bond (Zn–O), which confirm the formation of ZnO [26]. The band appeared at 620 cm\textsuperscript{-1} is attributed to the stretching vibrational mode of Cd-S [27]. The band observed at 1114 cm\textsuperscript{-1} is assigned to O-H stretching mode of H\textsubscript{2}O molecule. The band at 1384 cm\textsuperscript{-1} corresponds to the C=O stretching vibration [2]. The vibrational band observed at 1619 cm\textsuperscript{-1} is a characteristic of symmetric bending vibration of H\textsubscript{2}O molecule. A broad peak in the range of 3200 - 3500 cm\textsuperscript{-1} corresponds to the vibrational mode of O-H bond [28].
4.4.4 Optical absorption study

The analysis of optical absorption spectrum is one of the most abundant tools for understanding and developing the electronic band structure of crystalline and non-crystalline materials. Electronic configuration of Mn$^{2+}$ (d$^5$ configuration) gives rise to free ion terms $^6S$, $^4P$, $^4F$, $^4G$ and number of doublet states of which $^6S$ occupies the ground state. In crystal field, $^6S$ and $^4P$ terms split as $^6A_{1g}$ and $^4T_{1g}$ respectively. $^4D$ and $^4G$ splits into $^4E_g$+$^4T_{2g}$ and $^4A_{1g}$+$^4E_g$+$^4T_{1g}$+$^4T_{2g}$ respectively. Fig. 4.10 predicts the optical absorption spectrum of Mn$^{2+}$ doped ZnO-CdS composite nanopowder.

![Fig. 4.10 Optical absorption spectrum of Mn$^{2+}$ doped ZnO-CdS composite nanopowder](image)

The spectrum shows four characteristic bands at 360 (27770 cm$^{-1}$), 404 (24745 cm$^{-1}$), 447 (22365 cm$^{-1}$) and 556 nm (17980 cm$^{-1}$) are assigned to the transitions $^6A_{1g}(S) \rightarrow ^4T_{2g}(D)$, $^6A_{1g}(S) \rightarrow ^4A_{1g}(G)$ + $^4E_g(G)$, $^6A_{1g}(S) \rightarrow ^4T_{2g}(G)$ and $^6A_{1g}(S) \rightarrow ^4T_{1g}(G)$ respectively. The nature and position of the bands shows the
characteristic of Mn$^{2+}$ in octahedral symmetry. The energy matrices for d$^5$ configuration with Tree’s correction factor ($\alpha = 76$ cm$^{-1}$) are solved for various values of crystal field parameter (Dq) and Racah parameters (B and C), a good fit is obtained for Dq = 830, B = 825 and C = 3000 cm$^{-1}$. These values are in well consistent with previous reports [29]. The observed and calculated values are presented in Table 4.1. The evaluated crystal field and Racah parameters suggest that the Mn$^{2+}$ ions entered into the host lattice as octahedral site symmetry.

<table>
<thead>
<tr>
<th>Transition From $^6A_{1g}$ $\rightarrow$</th>
<th>Wavelength nm</th>
<th>Band position Wavenumber (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^4T_{1g}(G)$</td>
<td>556</td>
<td>17980 17983</td>
</tr>
<tr>
<td>$^4T_{2g}(G)$</td>
<td>447</td>
<td>22365 22348</td>
</tr>
<tr>
<td>$^4A_{1g}(G) + ^4E_g(G)$</td>
<td>404</td>
<td>24745 24756</td>
</tr>
<tr>
<td>$^4T_{2g}(D)$</td>
<td>360</td>
<td>27770 27719</td>
</tr>
</tbody>
</table>

### 4.4.5 EPR study

The EPR spectrum of Mn$^{2+}$ doped ZnO-CdS composite nanopowder is shown in Fig. 4.11. The EPR spectrum of powder sample was analyzed in order to obtain spin-Hamiltonian parameters. It is clear that the EPR spectrum exhibit well resolved six line hyperfine structure at $g = 1.9924$, characteristic of octahedral site symmetry of Mn$^{2+}$ within the host material with an average hyperfine splitting constant $A = 94.93$ cm$^{-1}$ [30]. The hyperfine structure originates from the interaction between the Mn$^{2+}$ electron cloud and $^{55}$Mn nucleus with spin I = 5/2. This indicates the presence of paramagnetic Mn$^{2+}$ ions in the prepared sample. Mn$^{2+}$, is unique
among d⁰ configurations and there is only one state with maximum spin multiplicity (⁶S₅/₂) which splits into three Kramer’s doublets (±5/2, ±3/2 and ±1/2). In the presence of magnetic field, the degeneracy is completely removed and five fine structure transitions are possible. Each fine structure transition will be split into six hyperfine components due to ⁵⁵Mn hyperfine coupling and may give in all 30 allowed transitions. The sextets belong to the transitions 5/2↔3/2, 3/2↔1/2, 1/2↔−1/2, −1/2↔−3/2, −3/2↔−5/2. The sextet (g = 1.9924) observed in the present study is corresponding to 1/2↔−1/2 transition.

Fig. 4.11 EPR spectrum of Mn²⁺ doped ZnO-CdS composite nanopowder

In general, the g-value for the hyperfine splitting is indicative of the nature of bonding. If the g-value shows a negative shift with respect to the free electron value (2.0023) then the bonding is ionic and conversely, if the shift is positive, then the bonding is more covalent [31]. In the present case, the g-value shows negative shift (0.01558), indicative of ionic bonding between Mn²⁺ and ligands.
4.4.6. Photoluminescence study

It is well known that surface defect states play key role in the luminescence properties of nanostructure [32]. Fig. 4.12 shows the room temperature PL spectrum of Mn$^{2+}$ doped ZnO-CdS composite nanopowder under the excitation wavelength of 325 nm. The luminescence of Mn$^{2+}$ ions is known to be affected by the host crystal field and site symmetry, which can vary the emission colour from green to orange/red. Generally, Mn$^{2+}$ emits green light when it located in a tetrahedral coordination by forming a weak crystal field and orange to red light in an octahedral one by forming a strong crystal field [33].

![Fig. 4.12 PL spectrum of Mn$^{2+}$ doped ZnO-CdS composite nanopowder](image)

In the present study, PL spectrum exhibits four characteristic bands at UV, blue, green and red regions. UV emission peak centered at 367 nm is attributed to near band edge emission arising from energy loss due to strong electron–phonon interactions at room temperature [34]. The blue emission band centered at 425 nm
is due to the host related defect states like Zn vacancies [35]. The suppressed green emission in the region 480-570 nm is due to sulfur vacancies, cadmium vacancies, sulfur interstitial or cadmium interstitial defects [36]. The sharp red emission band at 627 nm is due to the incorporation of Mn$^{2+}$ ions. The emission process is attributed to a d-level spin-forbidden transition for Mn$^{2+}$ ions acting as an activating center. In particular, the transition from lowest excited state to ground state, $^4T_1 \rightarrow ^6A_1$, is directly responsible for the red light emission and is arising from the octahedrally coordinated Mn$^{2+}$ sites.

Fig. 4.13 shows the CIE 1931 chromaticity diagram of Mn$^{2+}$ doped ZnO-CdS composite nanopowder. Chromaticity coordinates were calculated from the corresponding PL spectrum as $(x, y) = (0.460, 0.379)$, which indicates colour vision of the sample. The dark spot on the chromaticity diagram represents orange-red region. From CIE 1931 chromaticity coordinates $(x, y)$, correlated colour temperature (CCT) is calculated using McCamy equation [37].

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

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 2423 K, which represents orange light emission.
Fig. 4.13 CIE diagram of Mn$^{2+}$ doped ZnO-CdS composite nanopowder
4.4.7 Magnetic study

To study the effect of Mn-doping on the magnetic properties of ZnO-CdS composite nanopowder, the M-H hysteresis loop carried out at room temperature on VSM and is shown in Fig. 4.14.

![M-H hysteresis loop of Mn²⁺ doped ZnO-CdS composite nanopowder](image)

**Fig. 4.14** M-H hysteresis loop of Mn²⁺ doped ZnO-CdS composite nanopowder

It can be seen from Fig. 4.14 that the prepared sample exhibit clear magnetic hysteresis loop, which indicates the room temperature ferromagnetism with saturated coercivity and magnetization values. The saturation magnetization (Ms), coercive field (Hc) and retentivity (Mr) of prepared sample are $32.802 \times 10^{-3}$ emu/g, 89.466 Oe and $1.8138 \times 10^{-3}$ emu/g respectively. The observed magnetic behavior may be attributed to the exchange interaction between the localized magnetic dipole moments of the magnetic ions and the free delocalized charge of current carriers. The impurities/defects play a major role of these free carriers and strongly related to the oxygen vacancies and processing conditions [38].
4.5 Conclusion

In summary, Mn$^{2+}$ doped ZnO-CdS composite nanopowder was synthesized by chemical precipitation method.

- X-ray diffraction pattern reveals well crystallinity and the average crystallite size is found to be 18 nm.
- SEM and TEM analysis showed non-uniformly distributed spherical like structures with diameter of 20 nm. The agglomerate in the prepared sample could be induced by dencification resulting from the narrow space between particles.
- FT-IR spectrum exhibited bands related to the presence of Zn-O and Cd-S vibrational modes.
- Optical absorption spectrum exhibits four characteristic bands of Mn$^{2+}$ ions in distorted octahedral sites. The crystal field and racah parameters evaluated as $D_q = 830$, $B = 825$ and $C = 3000$ cm$^{-1}$.
- EPR spectrum showed sextet at $g = 1.9924$, which confirms octahedral site symmetry and the nature of bonding between the doping Mn$^{2+}$ ions and its ligands is ionic.
- PL spectrum show UV and visible emission bands. The strong red emission band is the characteristic of Mn$^{2+}$ ions with octahedral coordination. This was also confirmed from optical and EPR studies.
- Hysteresis loop show clear ferromagnetism at room temperature.
4.6 References


