CHAPTER-3

Cu Doped Cd_{1-x}Zn_xS Alloy: Synthesis, Structural, Optical and Thermal Investigations

3.1 Introduction

Nanomaterials in various forms such as quantum dot, nanowires, nanorods and nanotubes have been attracted the researchers for various promising applications, noval properties as compared to their bulk form. The semiconductor quantum dot material of group II-VI have been found highly useful due to their wide spread applications in photovoltaic, electroluminescence devices, solar cells, light emitting diodes and sensors [1-4]. In the last two decades, the binary semiconducting nanomaterials of II-VI group as CdS, ZnS, CdSe and CdTe with and without doping have been extensively investigated due to their number of applications in optoelectronic devices [5-6]. ZnS is a semiconducting material which has a wide band gap of 3.7eV, due to which these sulfides doped with transition metal ions and rare earth ions were studied extensively [3]. Now a days, ternary type semiconductors like CdZnS alloy shows excellent physical properties and their wide energy band-gap lies between CdS (2.4eV) and ZnS (3.68eV) [7-8]. The material CdZnS has been widely investigated due to its potential use for various device applications such as window layers for solar cells, low voltage cathode luminescence, blue and ultraviolet laser diodes, electro-luminescence displays and antireflection coating for infrared devices [9-10]. Further, this material has high capability by covering the wavelength from yellow to green which is infact very difficult to be covered by other semiconductors [11]. Furthermore, the ternary type semiconductor nanomaterials were investigated by many scientists by band gap tuning with their composition [12-15]. Moreover, with doping we can tailor the properties of these semiconductors especially for optical and electrical properties. Doping in these materials has been carried out by transition metal and rare earth ions [16]. However, more successful doping has been done by using transition metal ions like Mn and Cu due to the fact that chemical properties of these dopants are similar with the host materials [17]. Although, there have many type of work reported on the thin films prepared by CdZnS but their work on doped alloy nanostructures are still limited. The Cu doped CdZnS material is seen highly useful for quantum confined nanocrystals known as quantum dot semiconductor material. Due to large value of surface to volume
ratio, the surface energy of the nanocrystal increases and thus directing such materials highly useful for photonic and optoelectronic devices [18]. In fact with the decrease of particle size in a material more atoms are lying at the surface rather than in the interior side. The promising applications of such quantum dot nanomaterials might have been seen in heterojunction solar cells and photoconductive devices [19]. As CdZnS has also lead to a decrease in losses by window absorption and hence increase of short circuit current in the solar cells. The desirable optical and physical properties are expected from of these quantum dot semiconductors which may be obtained by changing the host constituents and doped materials.

In present course of research work our main aim is to synthesize Cu doped Cd$_{1-x}$Zn$_x$S (0≤ x ≤1) semiconductor nanocrystals by using chemical co-precipitation technique and analysis of their structural properties by XRD, FTIR, TEM, AFM and EDX methods. The optical properties have also been investigated by using UV-visible absorption spectra and photoluminescence spectra. The thermal properties are analyzed by the thermal gravimetric (TG) and differential thermal analysis (DTA). Moreover, the effect of Zn concentration on the structural behavior of alloy nanocrystals has also been investigated and discussed.

### 3.2 Experimental Details

#### 3.2.1 Chemicals used

Cadmium acetate dihydrate (Cd(CH$_3$COO)$_2$.2H$_2$O), Triethylamine (N(CH$_2$CH$_3$)$_3$), copper acetate monohydrate (Cu(CH$_3$COO)$_2$.H$_2$O) and urea (NH$_2$CONH$_2$) were purchased from Sigma Aldrich. Zinc acetate dihydrate (Zn (CH$_3$COO)$_2$.2H$_2$O) and thiourea (NH$_2$CSNH$_2$) consumed as the source material for Zn and S ions and they were purchased from the Loba Chemie.

#### 3.2.2 Precursors preparations

All the consumed chemicals have been used as such without further purification. Double distilled water was taken as a solvent in all chemical reactions. We are using acetate as a precursor group. Nearly about 0.5 M cadmium acetate and zinc acetate were taken according to their molar ratio in a beaker and add 100 ml double distilled water and stirred for about half an hour at a temperature 60°C. In another beaker or conical flask (500ml) 1M urea, 1M thiourea were taken, dissolved in 100 ml of double distilled water and stirred it for half an hour under normal stirring rate 450 rpm.
3.2.3 Synthesis of Cu doped Cd$_{1-x}$Zn$_x$S ($0 \leq x \leq 1$) nanomaterials

First we take at x=0 i.e there was no addition of zinc, we prepare 100% CdS. In the precursors solution (Ist beaker) there is only one precursor i.e cadmium acetate, 0.01M of copper acetate monohydrate as a dopant had been added. In the conical flask solution 8 ml triethylamine added under vigorous stirring at 60°C for half an hour. After 10 minute stirring precursor’s solution of first beaker was taken in a burette and then it was added drop wise into second beaker under vigorous stirring condition at 60°C. The drop rate were kept minimum (20 drops per minute) so that the drop completely mix in the solutions under stirring rate 990 rpm (revolution per minute). Consequently, the color of the solution changes from light yellow to deep yellow during the reaction. After that completion of the stirring, the precipitates were left undisturbed for one day and then washed and filtered. Then the precipitates were dried in air oven at 90°C for 8 hours. Finally, they were crushed in powder form using a pestle mortar and used for their various characterizations. By following the same procedure we prepare all the samples taking different mole fraction of x (x=0.1, 0.3, 0.5, 0.7, 0.9, 1). We observe that the color of precipitates at particular concentration of zinc changes. The yellowness of the precipitates decreases as we increase the concentration of zinc and at x=1 we obtained white color precipitates, which confirms the formations of ZnS. This also confirms the introduction of Zn in the CdS and formation of CdZnS series. The complete synthesis process has been shown in Fig. 3.1 by a flow chart.

![Flow chart for synthesis of Cu doped Cd$_{1-x}$Zn$_x$S ($0 \leq x \leq 1$).](image)

Fig. 3.1: Flow chart for synthesis of Cu doped Cd$_{1-x}$Zn$_x$S ($0 \leq x \leq 1$).
3.2.4 Characterization

Experimental setups related to their specifications are given under this section. The XRD patterns of powdered samples were measured on Rigoku Powder X-ray diffractometer with CuKα (λ=0.15406 nm) radiation. The XRD information of prepared samples were obtained at an operating voltage 40 kV and current at 30 mA with a fix scanning rate 2 degree min\(^{-1}\) from 20 = 20° to 80°. The Nicolet 5700 type FTIR spectrometer was employed in the range 700-4000 cm\(^{-1}\) for analysis of the functional groups present in the precursors. For FTIR recording, the samples were mixed homogeneously with KBr and pellets of desired dimensions were prepared. Morphology of the prepared samples was also observed on a FEI TECNAI G\(^2\) high resolution transmission electron microscope (HRTEM) operated at 200 kV. For preparations of samples for TEM measurements, nanoparticles were dispersed in ethanol and kept in a sonicator up to five minutes. Thus the solution was dripped onto a carbon coated copper grid and after this dried at room temperature. For the compositional analysis EDX spectra were recorded on JEOL JBM 6510LV. The AFM studies have been carried out on a Multimode Bruker 8 model. The sample was prepared by dissolving 1gm of powder in 5ml of ethanol and dried it on a glass made substrate in air at clean room temperature. These substrates are taken in form flat and must be extremely clean to avoid artifacts and to improve resolution of the images. We can use mica, silicon, graphite and gold as a substrate for taking AFM images. The optical absorption spectra of the prepared samples have been recorded by using a UV-VIS-NIR spectrophotometer (Varian Cary-5000) in the wide range 200-800 nm. In order to record absorption spectra, samples were finally used by dissolving 0.011 gm powder of the synthesized materials in 5 ml of ethanol. To record the emission spectra Varian/ Perkin Elmer, Model: CARY-Eclipse/ LS-50B were used. The excitation light wavelength was taken as 250 nm to observe the emission in 400-600 nm range. The thermal analysis of the powder sample was obtained by thermo gravimetric and differential thermal analysis (TGA and DTA) on Perkin Elemer, STA 6000 at heating rate 20°C/min in nitrogen atmosphere.

3.3 Results and Discussion

3.3.1 XRD analysis

Fig. 3.2 demonstrates XRD patterns of Cu doped Cd\(_{1-x}\)Zn\(_x\)S (0 ≤ x ≤ 1) nano crystals with different values of mole fraction x (0, 0.1, 0.3, 0.5, 0.7, 0.9). From extracted
information, the synthesized nano crystals have exhibited main peaks at 2θ ~25.02°, 26.62°, 27.88°, 43.86°, 47.78° and 52.22° corresponding to the hkl planes (100), (002), (101), (110), (103) and (200) respectively. The presence of peaks in the XRD spectra confirms about the crystalline nature of our prepared samples and the obtained structure is hexagonal. The observed peaks have been well matched with the JCPDS (Joint Committee on Powder Diffraction Standard) data file no.40-0836. The XRD data of all the samples have shown the same (002) crystal plane for the preferential orientation. The broadening of XRD peaks confirms about the formation of nanoparticles known as quantum dots. As seen from the Fig.3.2 the XRD peaks are found slightly shifted towards higher 2θ angles as with the increase of mole fraction of zinc. In our samples formation of secondary phases is not observed in the XRD study.

![XRD pattern](image)

**Fig. 3.2:** XRD pattern of Cu: Cd₁₋ₓZnₓS alloy at different values of mole fraction (x).

From the XRD data different d-values for the various samples of Cu doped Cd₁₋ₓZnₓS (0 ≤ x ≤ 1) were determined by using the well known Bragg’s relation and obtained results have been given in the table 3.1. Further, the experimental values of lattice constants ‘a’ and ‘c’ for hexagonal phase of Cu: CdZnS alloy are calculated using the equation (3.1) as mentioned in the table 3.1.

\[
\frac{1}{d^2} = \frac{4}{3} (h^2 + hk + k^2) / a^2 + l^2 / c^2
\]  

(3.1)
Table 3.1: Structural parameters of the prepared samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak Position (2θ)</th>
<th>a(Å)</th>
<th>c(Å)</th>
<th>d (Å)</th>
<th>Volume of unit cell (Å)³</th>
<th>Lorentz Factor(L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cdₐ₀.₉Znₐ₀.₁S:Cu</td>
<td>26.62</td>
<td>4.117</td>
<td>6.687</td>
<td>3.345</td>
<td>98.15</td>
<td>4.848</td>
</tr>
<tr>
<td>Cdₐ₀.₇Znₐ₀.₃S:Cu</td>
<td>26.98</td>
<td>4.084</td>
<td>6.608</td>
<td>3.304</td>
<td>95.44</td>
<td>4.727</td>
</tr>
<tr>
<td>Cdₐ₀.₅Znₐ₀.₅S:Cu</td>
<td>26.92</td>
<td>4.093</td>
<td>6.636</td>
<td>3.318</td>
<td>96.27</td>
<td>4.747</td>
</tr>
<tr>
<td>Cdₐ₀.₃Znₐ₀.₇S:Cu</td>
<td>27.02</td>
<td>4.062</td>
<td>6.591</td>
<td>3.296</td>
<td>94.17</td>
<td>4.721</td>
</tr>
<tr>
<td>Cdₐ₀.₁Znₐ₀.₉S:Cu</td>
<td>27.28</td>
<td>4.000</td>
<td>6.552</td>
<td>3.276</td>
<td>90.78</td>
<td>4.627</td>
</tr>
</tbody>
</table>

Unit cell volume [20] for hexagonal structure is determined by using the equation (3.2).

\[ V = \sqrt{\frac{3}{2}a^2c} \]  

(3.2)

Fig.3.3: (a) Variation of particle size and (b) lattice parameters with Zn (x) composition.

In the Fig.3.3 (a & b), the change in lattice parameters and particle size with composition of Zn (x) has been demonstrated. It can be seen that there is a gradual decrease in particle size and lattice parameters with the increase in Zn concentration. Although a slight decrease in the values of lattice parameters was obtained with the increase in Zn content as mentioned in the table 3.1. The smaller value of atomic radii of Zn²⁺ ion (0.74 Å) than the Cd²⁺ ion (0.97 Å) seems to be reason for this variation [21] and Zn ion are substituted in the lattice by replacing Cd ion. The distribution of diffraction planes in the powder samples is given by Lorentz factor; this factor is a function of diffraction geometry and Bragg angle [22]. The following relation was used for calculation Lorentz factor (3.3).

\[ L = \frac{1}{4}\sin^2\theta \cos\theta \]  

(3.3)
3.3.1.1 Nanocrystallite size, microstrain and dislocation density

The broadening of XRD peak includes both size and strain broadenings and it is simply expressed by relation (3.4). The strain induced in powder samples is due to crystal defect and distortion; it was calculated using the formula (3.5). The lattice strain and crystallite size present in the sample was determined. The Williamson-Hall relation [23] has been used for calculation as given by equation (3.6).

\[
\beta_{\text{size + strain}} = \beta_{\text{size}} + \beta_{\text{strain}} \tag{3.4}
\]

\[
\varepsilon = \frac{\beta_{\text{hkl}}}{4 \tan \theta} \tag{3.5}
\]

\[
\beta_{\text{hkl}} \cos \theta = \frac{K\lambda}{D_{\text{W-H}}} + 4\varepsilon \sin \theta \tag{3.6}
\]

The notation \(K = 0.9\) is for uniform small size crystals, \(\lambda\) denotes the wavelength of X-ray, \(\theta\) denotes for the Bragg angle, \(\varepsilon\) is the strain distribution and \(D_{\text{W-H}}\) represents the average crystallite size. Although contribution of crystallite size and lattice strain effect to the broadening of peaks are independent of each other [24]. The XRD peak broadening due to the small crystallite size and lattice strain present in the material, can be distinguished with the help of W-H plot as exhibited in Fig.3.4. The variation of \(\beta \cos \theta\) with \(\sin \theta\) gives linear fit that yields the slope \(\varepsilon\) and the crystallite size has been estimated from the intercept on y-axis.

![W-H Plots](image)

**Fig. 3.4:** W-H plot of Cu: Cd\(_{1-x}\)Zn\(_x\)S alloy at different values of mole fraction (x).

For strain analysis W-H method seems to be better rather than Debye-Scherrer method comparatively [25]. It has been noticed from the Fig.3.2 a decrease in size of
nanocrystallite there is a gradual reduction in microstrain as given in the table 3.2. However, influence on the broadening of XRD peak may be negligibly small due to very small values of strain. With this considerations (ε = 0), Williamson-Hall relation transforms to Debye-Scherrer relation [26] as given by equation (3.7)

\[ D = \frac{K \lambda}{\beta \cos \theta} \]  

(3.7)

The mean value of crystalline size \((D_{W,H})\) of Cu doped \(Cd_{1-x}Zn_xS\) samples was obtained 11.58, 11.49, 8.43, 6.53, 5.38 and 2.60 nm for the mole fraction value \(x = 0.0, 0.1, 0.3, 0.5, 0.7\) and 0.9 respectively and the results have been summarized in the table 3.2.

**Table 3.2: Size, microstrain and dislocation density at different concentration of zinc.**

<table>
<thead>
<tr>
<th>Samples</th>
<th>(D_{W,H}) (nm)</th>
<th>(D_{D-S}) (nm)</th>
<th>(D_{TEM}) (nm)</th>
<th>Strain (\varepsilon)</th>
<th>Dislocation density (1/&lt;D&gt;^2 (\rho) * 10^{-3} (cm^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS:Cu</td>
<td>10.2</td>
<td>11.58</td>
<td>10</td>
<td>0.000502</td>
<td>7.45</td>
</tr>
<tr>
<td>(Cd_{0.9}Zn_{0.1}S:Cu)</td>
<td>5.92</td>
<td>11.49</td>
<td>-</td>
<td>-0.008085</td>
<td>7.57</td>
</tr>
<tr>
<td>(Cd_{0.7}Zn_{0.3}S:Cu)</td>
<td>5.88</td>
<td>8.43</td>
<td>8</td>
<td>-0.003952</td>
<td>14.07</td>
</tr>
<tr>
<td>(Cd_{0.5}Zn_{0.5}S:Cu)</td>
<td>4.05</td>
<td>6.53</td>
<td>-</td>
<td>-0.00866</td>
<td>23.45</td>
</tr>
<tr>
<td>(Cd_{0.3}Zn_{0.7}S:Cu)</td>
<td>4.43</td>
<td>5.38</td>
<td>5</td>
<td>-0.010075</td>
<td>34.54</td>
</tr>
</tbody>
</table>

From data analysis of table 3.2 it may be interpreted as the particle size by W-H analysis has been found to be less as compared to Scherrer method for the samples under study. Relatively a value of smaller particle size may be found due to the negative strain in our samples. Although, negative strain has been obtained by the addition of Zn concentration in CdS:Cu. However, Zn free sample of CdS:Cu has a positive value of strain. It may be pointed out that possibility reason for the occurrence of negative strain may be believed due to of smaller ionic radii of zinc ion compared to cadmium ion [21].

**3.3.2 FTIR analysis**

The FTIR analysis reveals for the presence of functional groups as well as vibrational frequency of chemical bonds in organic and inorganic materials. In this technique infrared light interacts with the sample then chemical bond of the functional group absorbs IR radiation and consequently stretching, bending and contraction at specific wave number start. The IR spectroscopy analysis demonstrates absorption of light by the samples in the range from 700-4000 cm\(^{-1}\).
The FTIR spectra of Cu doped Cd$_{1-x}$Zn$_x$S at different values of x (0, 0.1, 0.3, 0.5, 0.7, 0.9) have been exhibited in the Fig 3.5. In the higher wave number regions a peak at 3310-3380 cm$^{-1}$ is assigned corresponding to O-H stretching of absorbed water molecules [15]. Our measurement shows strong absorption that centered at 1420, 1550, 2350 and 1630 cm$^{-1}$ which may be from the symmetric stretching of acetate COO-group [20]. Further, it has been observed that the deepness of the absorbance is reduces with enhancement in the concentration of zinc.

### 3.3.3 TEM analysis

TEM analysis has been used to find size and shape of crystallites and also to confirm about nano crystalline nature of our prepared samples. Fig.3.6 demonstrates the TEM micrographs of Cu doped Cd$_{1-x}$Zn$_x$S (x = 0, 0.3, 0.7) samples. Micrographs of our prepared samples revealed about the compact arrangement of almost homogeneous nanoparticles with approximately spherical shape. These TEM images shows the agglomerated nanoparticles and their comparison proves that agglomeration increases as the Zn concentration increases that may be believed due decrease in the particle size and consequently surface to volume ratio increases. With this there is increase in neighboring interaction of particles by the increase of zinc concentration in our samples. TEM and XRD analysis give the particle size which is given in the table 3.2. The TEM measurement has given particle size about 5 nm and 10 nm as the smallest
and largest size respectively. However, the particle size from two TEM images has been seen closer to their respective values determined by Debye-Scherrer’s XRD method rather than W-H method. Hence, it may be mentioned from the two different XRD data analysis of particle size, the Debye Scherrer’s analysis is indicating for relatively in good agreement with TEM analysis. The TEM images examine high crystalline nature of the prepared material. TEM histograms of the samples demonstrated about distribution of particles size have been shown in the Fig.3.7. The Histograms gives a bar graph that indicates frequency of occurrence against the particle size range [27].

Fig. 3.6: TEM micrographs of Cu: Cd$_{1-x}$Zn$_x$S at (a) $x = 0$ (b) $x = 0.3$ and (c) $x = 0.7$.

![TEM micrographs of Cu: Cd$_{1-x}$Zn$_x$S](image)

Fig. 3.7: Histograms of Cu: Cd$_{1-x}$Zn$_x$S at (a) $x = 0$, (b) $x = 0.3$ and (c) $x = 0.7$.

3.3.4 Energy dispersive spectrum (EDS)

The EDX analysis provides the compositional type analysis of powder samples. The EDX-spectra of Cu doped Cd$_{0.7}$Zn$_{0.3}$S have been shown in Fig.3.8. The spectrum shows
the successful doping of Cu in the lattice of CdZnS. However the presence of O in samples was also depicted in the spectrum which shows that O from acetate group was left in samples that were not removed by washing the samples. Further, the existence of Cd, Zn and S in our samples is also confirmed from energy dispersive X-ray spectrum. The atomic and weight percentage (%) of these content have also been given in the table 3.3, which confirms the alloying composition of sample Cd$_{0.7}$Zn$_{0.3}$S:Cu by weight (%) clearly.

![EDAX spectrum of Cu doped Cd$_{0.7}$Zn$_{0.3}$S nanomaterials.](image)

**Fig. 3.8: EDAX spectrum of Cu doped Cd$_{0.7}$Zn$_{0.3}$S nanomaterials.**

**Table 3.3: Compositional analysis of Cu doped Cd$_{0.7}$Zn$_{0.3}$S nanomaterials.**

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight (%)</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>13.55</td>
<td>40.14</td>
</tr>
<tr>
<td>S</td>
<td>17.58</td>
<td>25.98</td>
</tr>
<tr>
<td>Cu</td>
<td>0.45</td>
<td>0.34</td>
</tr>
<tr>
<td>Zn</td>
<td>15.54</td>
<td>11.26</td>
</tr>
<tr>
<td>Cd</td>
<td>52.87</td>
<td>22.29</td>
</tr>
<tr>
<td><strong>Totals</strong></td>
<td><strong>100.00</strong></td>
<td></td>
</tr>
</tbody>
</table>

**3.3.5 AFM analysis**

In order to investigate surface morphology and roughness, AFM technique was used in tapping mode and 2μm × 2μm areas of sample surfaces was imaged. The two and three dimensional surface morphology images of Cd$_{0.1}$Zn$_{0.9}$S:Cu quantum dots have been shown in the Fig. 3.9. The tip-position of AFM informs about the three dimensional topographic image. The AFM images of Cu doped Cd$_{0.1}$Zn$_{0.9}$S in 2 D also show the spherical shape of prepared nanomaterials that is in close agreement with our TEM (Fig.3.6) measurements. Images by AFM were observed in the tapping mode.
Roughness is the measurement of closely spaced irregularity or uneven which is broken by prominences and other similar types [29]. Surface roughness feature value depends on the scale of measurement. It is quantified by the vertical spacing or height of a real surface from its original form. Large spacing gives more surface roughness; if the spacing is small the surface is smooth. The roughness is obtained from the profile that is by measurement of the height of peak to the trough of a wave produced by the vibration of a cantilever. The bar graph in the Fig.3.10(b) gives the RMS value of roughness that is equal to 33.5 nm and the profile gives the roughness height is determined around 200 nm. The effect of dopant Cu on the 3D image in Fig.3.9 (b) is also clearly observed.

![Fig. 3.9: AFM images (a) 2D and (b) 3D of Cd$_{0.1}$Zn$_{0.9}$S:Cu nanomaterials.](image)

![Fig. 3.10: (a) 2D scanned AFM image (b) profile extraction and root mean square roughness (bar graph) analysis of Cd$_{0.1}$Zn$_{0.9}$S:Cu nanomaterials.](image)
3.3.6 UV-visible analysis

The spectra of UV-visible absorption of prepared Cd$_{1-x}$Zn$_x$S:Cu (x ≤ 1) quantum dots are shown in the Fig.3.11 (a). The maximum absorption peak value for the sample CdS (x=0) is at 238 nm which indicates the beginning of absorption and blue shift absorption is found in comparison to the bulk form of CdS. Next absorption peak in the same sample was observed at 278 nm and another absorption at shoulder appeared at 484 nm. As the zinc concentration increases from (x=0, 0.1, 0.3, 0.5, 0.7, 0.9) absorption peak are observed at 278, 244, 242, 231, 221 and 220 nm respectively. It has been observed that there is a blue-shift absorption peak by the increase in Zn concentration and also found blue shifted in comparison to the spectra bulk form materials because of quantum size effect. As the size of nanoparticles is found comparable to the Bohr excitonic radius of same sample then quantum confinement effect changes the electronic structure of the nanomaterials and widens the band gap $E_g$. Consequently, the absorption, emission and band gap are observed blue shifted [30]. The value of band edge absorption are 294, 263, 261, 255, 249, 237 with respect to Zn ion concentration x = 0, 0.1, 0.3, 0.5, 0.7, 0.9 respectively. Hence, we observe that the band edge absorption also shifted towards the shorter wavelength side with increase in Zn concentration as shown Fig.3.11(a). On the basis of already published results, an absorption peak occurring between 225 and 230 nm has been assigned with the formation of nanosized ZnS [31]. Hence, it also confirms the formation of CdZnS series as sample at x=0.7 and x=0.9 give absorption in 225-230 nm range.

In our study, the absorption is found to decrease with increase in wavelength. For a direct band gap type material the absorption coefficient is given by the Tauc relation of equation (3.8). According to Tauc’s relation [32] the absorption coefficient is expressed by

$$\alpha h\nu = A(h\nu - E_g)^n$$

(3.8)

Here A denotes as a constant and $E_g$ denotes band gap of the materials. However, value of exponent n vary with the type of the transition; n with values 1/2, 2, 3/2 and 3 corresponds allowed direct, allowed-indirect, forbidden-direct and forbidden-indirect type transitions respectively [33].
Fig. 3.11: (a) Absorption spectra and (b) band-gap energy of the Cu doped Cd$_{1-x}$Zn$_x$S ($0 \leq x \leq 1$).

In our case, the materials used CdZnS is a direct wide band gap semiconducting material, so transitions are direct band gap type transitions, therefore we have taken $n = 1/2$. But, in the case of nanocrystalline materials, transitions have been found very much different as compared to the bulk material like transition. From the above equation, it is obvious that, plot of $(\alpha h\nu)^2$ vs. $h\nu$ has indicated a divergence at an energy value, $E_g$ for occurrence of the transition. Considering the values at discontinuities for the band-gap, the nature of transition (i.e., the $n$ value) is determined. The exact value of energy band gap is determined by extrapolating the straight line portion of $(\alpha h\nu)^2$ vs. $h\nu$ graph to the $h\nu$ axis as shown in the Fig.3.11(b). The energy band gap of these particles is also found to vary from 3.75 to 5.44 eV. From the graph of Tauc-plot the energy band gap value for our prepared samples with Zn concentration at different values of $x$ like 0, 0.1, 0.3, 0.5, 0.7, 0.9 were found as 3.8, 3.75, 4.17, 4.39, 5.04, 5.44 eV respectively. Further, it has been observed that band gap energy has almost increased with the increase in concentration of zinc except for $x=0.1$ sample. The large band gap shifting as compared to bulk form with addition of Zn indicates formation of semiconducting nanomaterials. Our results are also found in good agreements with the Zubeda et al. [34]. In this case band gap energy value also varies with the particle size $R$ that is increasing with decrease in particle size. This may also be explained on the basis of quantum confinement effect. As the confinement increases in three dimension (quantum dot), there is discretization in the energy levels and with this band gap of the materials has more increased. At a fixed doping Cu concentration, an effective band gap increment is seen by increase in the concentration of Zn.
With the use of quantum confinement model for effective-mass approximation and analyzing these optical absorption spectra, taking the value of band gap in nanoform of the prepared nanomaterials, one may estimate average value of radius \( R \) for prepared quantum dot samples with the help of expression [35]

\[
E_{g\text{(nano)}} - E_{g\text{(bulk)}} = \frac{\hbar^2}{8\mu R^2} - 1.8\left(\frac{e^2}{\epsilon R}\right)
\]  

(3.9)

where \( E_g \) denotes the energy band gap for the bulk/nano, material \( \mu \) is effective mass of the hole and electron, \( R \) is the diameter of the nanomaterials, \( e \) is the electron charge, \( \epsilon \) is the relative dielectric constant of the materials. The first term represents the kinetic term, corresponding to quantum localization energy because of the quantum confinement effect which depends on \( 1/R^2 \). The second term represents Columbic term seen proportional to \( 1/R \), [36] and this term is neglected and equation (3.9) is reduces as effective-mass approximation (EMA). In our present work, only 1st term is used in the calculation of particle size because only effective mass was used in this term. The same has also been considered by Sharma et al. for CdZnS nanomaterials [37]. The size of the quantum dot is determined 1.33 nm for CdS (\( x=0 \)) that has been calculated from the EMA equations. However, the particle size from the XRD and TEM is found larger than the UV-visible analysis for this sample. This difference may be believed due to that we are taking approximate effective mass of electron and hole as almost similar way of interpretation in case of without dopant reported by Sharma et al [37] or there may be other factors.

![Optical band gap vs concentration of zinc(x) in Cd\(_{1-x}\)Zn\(_x\)S:Cu (x<1) nanomaterials.](image)

Fig. 3.12: Variation of band gap vs concentration of zinc\( (x) \) in Cd\(_{1-x}\)Zn\(_x\)S:Cu (x<1) nanomaterials.
Further, it has been noticed that at x=0, the energy band-gap value determined from the Tauc plot is found higher than the bulk value of CdS (2.42eV) that may be due to size quantization effect [38]. Change in energy band-gap with x (Zn concentration) is found to be almost linear nature and increases with x as shown in Fig.3.12. This increase in band gap value clearly indicates for Zn$^{2+}$ ions were successfully substituted by Cd$^{2+}$ ions in our CdZnS host lattice and formation of a continuous series of solid solution has been confirmed by increase value in band-gap energy [39] by addition of Zn. The similar type of results has been observed by Narasimman et al. in case of thin films of CdZnS [40].

**3.3.7 Photoluminescence spectroscopy (PL)**

In photoluminescence electron are excited by radiation of suitable frequency that undergoes radiative recombination by de-excitation either at valence band (band edge emission) or trap states within the band gap. In this work, we record excitation and emission spectra. The samples were excited by xenon source at a wavelength of 250 nm at room temperature. Since more defect states are introduced by doping of Cu (1%) in to CdZnS nanoparticles. At this excitation wavelength, direct excitation of dopant levels within band gap of host is achieved. Electrons are excited from the valence band to the conduction band and thus holes are created in the valence band. Fig. 3.13 (a) exhibits emission spectra of Cu doped Cd$_{1-x}$Zn$_x$S:Cu (x ≤1) samples centered at 600-602 nm. The emission spectra of all our samples give a orange-red emission originating due to electronic transition from the lowest excited states of CdZnS matrix to the copper induced t$_2$ level. The similar type of results were also reported by the Rathore et al. [30]. The broadening in the photoluminescence have been observed in all the samples which are, in fact, due to the recombination of the defects states induced by Cu$^{2+}$ modified surface trap states created by doping [41]. It may be pointed out that larger QDs having size 5–6 nm, emit longer wavelengths resulting the emission of orange or red colors. In our research work we have also larger size of quantum dots except at x=0.9, so the emission is found in orange or red region. On the other hand, relatively smaller QDs (radius of 2–3 nm) give shorter wavelengths of light by emitting blue and green color, although specific colors and size may depends on the exact composition of the QDs material [42]. With the decrease in size of the nanoparticles the density of surface states increases that result in to increase surface-to-volume ratio.
Consequently, there is a reduction in the probability of excitonic or band-edge emission via non-radiative type surface recombination and the nanoparticles shows PL emission from energy levels lower than the band gap [43]. As emission peak and peak width of all our samples have exhibited results at almost same wavelength. Hence no significant change in the emission spectra of the samples under study was observed. This type of behavior may be understand due to the radiative type defects exist in the cores of CdZnS nanocrystals and the energy levels of the defects are not changed by the concentration of Zn. PL peak emission of this type of surface defects are usually existed in the range of 500-600 nm wavelength [44].

It has also been observed that the intensity of emission for CdZnS:Cu (Zn=0.9) increases and this may be understood due to creation of more electron-hole pairs and hence the fluorescence intensity increases. In order to calculate band gap, we have used the equation \( E = \frac{hc}{\lambda} \) for a peak position and found to be 2.04 eV which also confirms the light emission from the deep trap states (shown in Fig. 3.13). Further, it was observed that all PL spectra shows asymmetry shape in the PL peaks which may be because of structural and morphological disorders present in our prepared samples. Luminescence characteristics also depend on defect levels of different type of nanoparticles and prepared samples have exhibited stokes-shifted and broad luminescence peaks arise from deep surface states [45,43].

![Figure 3.13](image.png)

Fig. 3.13: (a) Photoluminescence spectra (b) schematic energy level diagram of Cd\(_{1-x}\)Zn\(_x\)S:Cu ternary alloy at different values of mole fraction (x).
3.3.8 Thermo gravimetric (TGA) and differential thermal analysis (DTA)

TGA and DTA are important for thermal analysis of prepared samples for knowing physical and chemical behavior of the materials at different temperatures. Under this work the material has been examined by a controlled temperature program. In DTA, either energy is released or absorbed by the sample produce a phase transition [46].

TGA was investigated from room temperature to 1000°C with a heating rate 20°C/min in nitrogen atmosphere. Fig. 3.14 (a) shows the TG-DTA curve of the CdS:Cu nanomaterials. TGA curve shows a very smooth linearly weight loss from 29°C to the 1000°C temperature. However, there was observed 5% weight-loss from 175°C to the 332°C due to some water and organic residuals present in the materials [47]. The 1st exothermic peak was observed in the DTA curve at 64°C and next at 172°C attributed to the evaporation of water and organics [48]. Further at 230°C, a small endothermic peak may correspond to the evaporation and lattice deformation [49]. After this, it goes exothermally 614°C with a small endothermal peak at 648°C. In the last, a broad exothermic peak at 871°C goes to the 947°C was observed.

![Fig. 3.14: TGA and DTA curves of (a) CdS:Cu(x=0) and (b) Cd_{0.1}Zn_{0.9}S:Cu nanomaterials.](attachment:fig314.png)

Fig. 3.14 (b) shows the thermal analysis of Cd_{0.1}Zn_{0.9}S:Cu nanomaterials. In TGA curve, there is found a slightly weight loss up to 620°C and after that, a smooth downward weight loss has been observed up to 992°C temperature. This weight loss of the sample may be believed by the release of residual sulfur ions [49]. In DTA, there is
smooth exothermic feature was found up to the 922°C and after that an endothermic peak is started. Rajesh kumar et al. has observed stability at 250°C for CdS:Mn nanoparticles [50]. Hence, from the TGA-DTA plots it has been observed that there is no phase transition occurs because there was no sharp endo or exotherms present in our prepared samples. This shows that our prepared samples were thermally stable which can be used in engineered plastic materials and pigments in paints [51].

3.4 Conclusions

With co-precipitation method, desirable samples of copper doped Cd$_{1-x}$Zn$_x$S (0≤x≤1) nanomaterials were synthesized successfully. The XRD measurement of our prepared samples shows crystalline nature of the material with hexagonal structure. From XRD results, it is concluded that average particle size corresponds to the highest peak of all the samples has been obtained in the size range 2 to 12 nm. Further, it is also concluded that there is a decrease in particle size with the increase in Zn concentration. Furthermore, the W-H plot indicates the presence of negative strain in the prepared samples having Zn concentration. The presences of O-H and COO- groups in the samples have been confirmed by the FTIR spectroscopy. Moreover, the TEM results also confirmed the formation of nanomaterials in the same size range as reported by XRD method. The nearly spherical shape and agglomeration of the nanoparticles has been observed by the TEM images. The EDX spectrum shows the presence of Cd, Zn, S and Cu which confirms the composition of the series and doping of Cu in the lattice of CdZnS. AFM gives the two and three dimensional surface morphology in 2μm area show the spherical particles. RMS roughness was observed 33.5 nm and roughness height is found around 200 nm. The UV-visible spectra show a blue shifting in absorption spectra with Zn concentration and also in comparison of bulk form. A band gap tuning with Zn composition were observed 3.75 to 5.44 eV using the Tauc’s plot. The photoluminescence investigation reveals broad and asymmetric emission spectra in the orange-red region at 600 nm wavelength which may be due to the recombination of Cu$^{2+}$ related defects states. Hence, Cu doped ternary CdZnS materials increase the photocurrent which makes it more suitable for optoelectronic devices. Thermal properties indicate that the prepared nanomaterials are confirmed almost thermally stable.
References


