4.0 INTRODUCTION

Nanoparticles of Zn$_{1-x}$Cu$_x$S ($x = 0.0, 0.1, 0.2, 0.3$ and $0.4$) and Zn$_{1-x}$Fe$_x$S ($x = 0.0, 0.1, 0.2, 0.4$ and $0.6$) were synthesized using chemical co-precipitation method described in chapter II. The design and fabrication details of these techniques and procedure adopted for the synthesis of nanoparticles have already been given in the same chapter. The nanoparticles were characterized by SEM, EDAX, X-ray diffraction (XRD), TEM, Optical absorption, Photoluminescence, Electron spin resonance (ESR), Magnetization (VSM), FTIR, DSC and TGA analysis as described in chapter III. The optimum preparation parameters maintained to obtain good nanoparticles and the results of various characterization studies on Zn$_{1-x}$Cu$_x$S and Zn$_{1-x}$Fe$_x$S are presented in this chapter. The results are discussed and interpreted in the light of existing theories and available data on Zn$_{1-x}$Cu$_x$S and Zn$_{1-x}$Fe$_x$S and other similar DMS nanoparticle systems. This chapter comprises two parts, Part – I presents the results on Cu doped ZnS while Part – II is devoted to Fe doped ZnS nanoparticles.

4.1 PART – I: Cu DOPED ZnS NANOPARTICLES

Sample A (ZnS:Cu)

Zn$_{1-x}$Cu$_x$S with $x = 0.0, 0.1, 0.2, 0.3$ and $0.4$ was prepared by chemical co-precipitation method as discussed in chapter-2.

Preparation of Zn$_{1-x}$Cu$_x$S nanoparticles

Starting materials:

(a) ZnCH$_3$COOH (zinc acetate)
(b) Na$_2$S (sodium sulphide)
(c) Dopant = CuCH$_3$COOH (copper acetate)

Capping agent: Thiophenol

Stirring duration: 20h

Annealing temperature and duration: 300°C/2h in vacuum

Sample colour: Green (after annealing)
The compositional analysis of $\text{Zn}_{1-x}\text{Cu}_x\text{S}$ by EDAX confirmed that the samples were around the nominal compositions ($x=0.0, 0.1, 0.2, 0.3$ and $0.4$). The EDAX spectra are shown in Fig. 4.1. Table 4.1 gives the target and the estimated compositions. There are small variations, maximum of 3% around the exact stoichiometry, which could be due to the random alloying nature of Cu in ZnS. Hence, in all the following discussions only the target compositions are used. The representative SEM micrographs taken for nanocrystalline $\text{Zn}_{1-x}\text{Cu}_x\text{S}$ ($x=0.1, 0.2, 0.3$ and $0.4$) are shown in Fig. 4.2 – Fig. 4.5. All the samples have irregular shaped particles with size larger than a micrometer, which might be due to the agglomeration of the particles as a result of annealing. Kim et al [1] reported synthesis of $\text{ZnS}:\text{Cu}$ nanoparticles using SPP (sodium polyphosphate) as a capping agent under identical synthesis conditions by varying SPP input amount. They also could not clearly identify individual particles size in the SEM images.

**Table 4.1: Elemental compositions of $\text{Zn}_{1-x}\text{Cu}_x\text{S}$ samples from EDAX**

<table>
<thead>
<tr>
<th>Target composition ($x$)</th>
<th>Estimated composition in at. %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zn</td>
</tr>
<tr>
<td>0.0</td>
<td>69.94</td>
</tr>
<tr>
<td>0.1</td>
<td>66.28</td>
</tr>
<tr>
<td>0.2</td>
<td>56.96</td>
</tr>
<tr>
<td>0.3</td>
<td>49.14</td>
</tr>
<tr>
<td>0.4</td>
<td>41.89</td>
</tr>
</tbody>
</table>
Fig. 4.1. EDAX for elemental composition analysis of Zn$_{1-x}$Cu$_x$S ($x = 0.0, 0.1, 0.2, 0.3$ and $0.4$) annealed at 300°C/2h in vacuum.
Fig. 4.2. SEM micrograph of ZnS:Cu (x = 0.1) annealed at 300°C/2h in vacuum

Fig. 4.3. SEM micrograph of ZnS:Cu (x = 0.2) annealed at 300°C/2h in vacuum
Fig. 4.4. SEM micrograph of ZnS:Cu (x = 0.3) annealed at 300°C/2h in vacuum

Fig. 4.5. SEM micrograph of ZnS:Cu (x = 0.4) annealed at 300°C/2h in vacuum
4.1.2 STRUCTURAL STUDIES

The asprepared Zn$_{1-x}$Cu$_x$S samples were found to be amorphous in nature, where ‘x’ indicates the concentration of Cu$^{2+}$. Annealing at 100°C and 200°C in vacuum did not induce crystallinity (Fig. 4. 6 and 4.7). However, crystallization was induced on annealing the samples in vacuum at 300°C/2h. The X-ray diffraction patterns of annealed (300°C/2h) Zn$_{1-x}$Cu$_x$S samples (x=0.0, 0.1, 0.2, 0.3 and 0.4) obtained using Cu K$_\alpha$ radiation (λ= 1.5418 Å) in the range 20° - 65° are shown in Fig. 4. 8. The line broadening of the XRD pattern indicates the nanocrystalline nature of the samples. All the lines could be indexed to the cubic structure of ZnS (JCPDS card No. 80-0020) and no extra peaks were found indicating the single phase nature of the samples. Particle size was calculated from the FWHM of the peaks in the XRD spectrum, using the Debye-Scherrer formula [2]. The grain size is found to lie in the range 14 – 24nm. The particle sizes of Cu doped and undoped ZnS are given in Table. 4.2. As the composition (x) is increased the grain size increased indicating that the crystallinity increased with increasing ‘x’. The lattice parameter of cubic ZnS:Cu samples of all compositions are shown in Table 4.3. The variation of the lattice parameter ‘a’ with composition ‘x’ is shown in Fig. 4.9. It is obvious from the figure that the lattice parameter decreases linearly with composition following Vegard’s law [3]. There are no reports on the lattice parameter of the present system in nano form for comparison. In bulk ZnS, the solubility limit of Cu is only x = 0.3 [4], whereas, in nanophosphors a solubility limit of x = 0.5 is reported by Manzoor et al. [5]. The absence of extra peaks in the XRD of present samples confirms the complete solubility of Cu (x = 0.4) in nanophase ZnS. Khosravi et al [6] have reported for X-ray diffraction analysis, which shows that the diameter of the particles is ~21± 2 Å which is smaller than the Bhor exciton diameter for zinc sulphide.

4.1.3 TEM ANALYSIS

The TEM (Transmission Electron Microscope) measurements were also performed to confirm the nanocrystalline nature and to study the morphology of the particles. The TEM micrographs of ZnS:Cu (x = 0.1, 0.2, 0.3 and 0.4) are shown in Figs. 4.10(a) – 4.13 (a) respectively. The grains in all the samples are found to be well
Fig. 4.6. XRD pattern of Zn_{1-x}Cu_xS (x = 0.1) annealed at 100°C/2h in vacuum.

Fig. 4.7. XRD pattern of Zn_{1-x}Cu_xS (x = 0.1) annealed at 200°C/2h in vacuum.
Fig. 4.8. XRD pattern of Zn$_{1-x}$Cu$_x$S (x = 0.0, 0.1, 0.2, 0.3 and 0.4) annealed at 300°C/2h in vacuum.

Table: 4.2 Grain sizes of ZnS:Cu samples with composition (x)

<table>
<thead>
<tr>
<th>Composition (x)</th>
<th>Average Grain Size (nm)</th>
<th>From XRD</th>
<th>From TEM</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>14</td>
<td>--------</td>
<td>---------</td>
</tr>
<tr>
<td>0.1</td>
<td>16</td>
<td>7.0</td>
<td>---------</td>
</tr>
<tr>
<td>0.2</td>
<td>18</td>
<td>7.5</td>
<td>---------</td>
</tr>
<tr>
<td>0.3</td>
<td>21</td>
<td>8.2</td>
<td>---------</td>
</tr>
<tr>
<td>0.4</td>
<td>24</td>
<td>9.0</td>
<td>---------</td>
</tr>
</tbody>
</table>
Table. 4.3: Lattice parameters of $\text{Zn}_{1-x}\text{Cu}_x\text{S}$ nanoparticles

<table>
<thead>
<tr>
<th>Composition (x)</th>
<th>Lattice parameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>5.3354</td>
</tr>
<tr>
<td>0.1</td>
<td>5.3267</td>
</tr>
<tr>
<td>0.2</td>
<td>5.3144</td>
</tr>
<tr>
<td>0.3</td>
<td>5.3102</td>
</tr>
<tr>
<td>0.4</td>
<td>5.2986</td>
</tr>
</tbody>
</table>

Fig. 4.9. Variation of lattice parameter with composition (x)

isolated and nearly spherical in shape. The grain size is found to have a narrow distribution in size. The SAED patterns of ZnS:Cu samples are shown in Fig. 4.10 (b) – 4.13 (b). From the inter planar spacing determined from the SAED rings, it is noticed that the ZnS:Cu samples of all compositions have zinc blende structure with
diffraction planes corresponding to (111), (200), (220), (311), (331) and (400) (JCPDS card No. 80-0020). No planes corresponding to any impurity phase could be identified. This also confirms the single phased nature of the present nanocrystalline samples. Earlier authors [5 - 7] also reported only zinc-blende (cubic) structure for ZnS:Cu nanoparticles formed by chemical methods. Sang et al [8] reported a grain size of 5.7 nm from TEM images in Cu doped ZnS films formed by ion complex transformation method using PVA as a capping agent.

4.1.4 OPTICAL ABSORPTION STUDIES

The optical absorption spectra of ZnS and ZnS:Cu nanoparticles for varying copper dopings are shown in Fig. 4.14. It is well known that bulk ZnS possesses a band gap of 3.5 eV corresponding to the absorption peak at 350 nm. In the present study, nanoparticles of ZnS:Cu show the absorption peak around 330 nm corresponding to an energy gap of ~3.7 eV, characterizing the nanocrystalline nature, showing a small blue shift with increasing Cu ion content. The trend of band gap variation observed in the present study is similar to that reported by Wang et al.[9] and Kohrsravi et al.[6] in ZnS:Cu nanoparticles of average grain size of 4 nm and 2.1 nm prepared using glycine and sodium hexametaphosphate, respectively, as capping agents. In the present work, the band gap value of about 3.7 eV obtained for Cu doped ZnS nanoparticles with an average grain size of ~8 nm. This is relatively lower compared to the earlier reported band gap values of 4.3 - 4.5 eV with Cu content of 0.2 – 2.0 % [9] and 4.1 eV with Cu content of 6 at. % [6]. This difference could be attributed to the different capping agents used and also to the difference in the particle sizes. As expected for nanoparticles, in the present study (Fig. 4.14) the absorbance decreases with wavelength beyond the absorption maximum. The decrease in absorbance between 330 and 550 nm is assigned to d-d transitions of Cu$^{2+}$. Above 550 nm an increase in absorbance is noticed with increasing wavelength. In undoped ZnS nanoparticles the absorbance increases at a faster rate compared to Cu doped ZnS nanoparticles above 550 nm. Thus the observed dependence of absorbance on wavelength reflects the characteristics of zero-phonon absorbance [10]. Yang et al. [11] the absorption band edge and absorption shoulder of Cu$^{2+}$ doped ZnS samples do not change with increasing the impurity mole ratio of Cu$^{2+}$ ions.
Fig. 4.10 (a). TEM micrograph of ZnS:Cu (x = 0.1) annealed at 300°C/2h in vacuum

Fig. 4.10 (b) SAED pattern of ZnS:Cu (x = 0.1) annealed at 300°C/2h in vacuum
Fig. 4.11 (a). TEM micrograph of ZnS:Cu (x = 0.2) annealed at 300°C/2h in vacuum

Fig. 4.11 (b) SAED pattern of ZnS:Cu (x = 0.2) annealed at 300°C/2h in vacuum
Fig. 4.12 (a). TEM micrograph of ZnS:Cu (x = 0.3) annealed at 300°C/2h in vacuum

Fig. 4.12 (b) SAED pattern of ZnS:Cu (x = 0.3) annealed at 300°C/2h in vacuum
Fig. 4.13 (a). TEM micrograph of ZnS:Cu (x = 0.4) annealed at 300°C/2h in vacuum

Fig. 4.13 (b) SAED pattern of ZnS:Cu (x = 0.4) annealed at 300°C/2h in vacuum
Fig. 4.14. Optical absorption spectra of Zn$_{1-x}$Cu$_x$S ($x = 0.0, 0.1, 0.2, 0.3$ and $0.4$) annealed at 300°C/2h in vacuum.
4.1.5 PHOTOLUMINESCENCE STUDIES

The excitation spectra of ZnS and ZnS:Cu$^{2+}$ were recorded between 320 and 420 nm and are shown in Fig. 4.15. The excitation spectrum of undoped ZnS shows a series of excitation maxima. The first excitation maximum is located at 340 nm and appears relatively broader and more intense. The second excitation maximum located at 370 nm is less intense. However, the peaks around 393 nm and 410 nm are poorly resolved for undoped ZnS. This observation suggests the presence of different groups of particles with different sizes, each group being characterized by its characteristic and distinguishable band positions in ZnS. However the excitation spectrum of ZnS:Cu$^{2+}$ exhibits single excitation maximum at 370 nm indicating the suppression of growth of particles of different sizes due to the presence of Cu$^{2+}$ dopant. Its entry into the lattice of ZnS appears to modify the surface free energy of ZnS particles so that the size of particles could be controlled nearly within a narrow range.

The emission spectra (excited at 370 nm) of Zn$_{1-x}$Cu$_x$S (x=0.0, 0.1, 0.2, 0.3 and 0.4) samples are shown in Fig. 4.16. Undoped ZnS gives an intense broad emission band covering a major part of the visible region peaking at 491 nm. Such green emission in ZnS:Cu nanoparticles has also been reported by others [9, 61]. The emission spectra of ZnS:Cu (x = 0.1) and ZnS:Cu (x = 0.2) are found to be similar to that of undoped ZnS, but there is a gradual decrease in intensity with the increase in copper doping. This observation confirms the entry of copper into the lattice of ZnS which was also evident from the XRD spectra which showed no extra peaks. No appreciable shift in emission maximum is noticed with increase in Cu content. The decrease in intensity with increasing Cu content is attributed to repeated excitation within the copper sites of the samples. Such a decrease in intensity with increasing copper loading was also reported by Wang et al. [9]. Yang et al. [11] reported two emission peaks at 460 and 507 nm, in Cu doped ZnS nanocrystals. Cu in ZnS bulk crystal has two main well-known emission bands, namely the blue band and the green band [12]. Recent work on Cu doped bulk ZnS crystals has reported orange emission also in addition to the blue and green light emissions. [13].
Fig. 4.15. PL excitation spectra of ZnS and ZnS:Cu (x = 0.1) nanoparticles annealed at 300°C/2h in vacuum.
Fig. 4.16. PL emission spectra of ZnS and Zn$_{1-x}$Cu$_x$S ($x=0.0, 0.1, 0.2, 0.3$ and $0.4$) nanoparticles annealed at 300°C/2h in vacuum.
4.1.6 **ESR ANALYSIS**

No resonance signal is detected in the ESR spectrum of un-doped ZnS. When Cu$^{2+}$ ions are introduced into the ZnS lattice, the ESR spectra of different dopant concentrations of Cu$^{2+}$ ions exhibit absorption lines at liquid nitrogen temperature. The ESR spectra of Zn$_{1-x}$Cu$_x$S ($x = 0.0, 0.1, 0.2, 0.3$ and $0.4$) at $77$ K are shown in Fig. 4.17. The ESR signal is weak for low concentrations. Hence, a spectrum of ZnS:Cu$^{2+}$ doped (with $x = 0.4$) is used for evaluating the spin-Hamiltonian parameters. The spin-Hamiltonian for a Cu$^{2+}$ ion in a ligand field of tetragonal symmetry as given by Kivelson and Neiman [14] is:

$$H = g_H \beta H S_z + g_S \beta (H S_x + H S_y) + A \, C^+ S_z + A \, C^- (I_x S_z + I_y S_y),$$

where $\beta$ is the Bohr magneton and $H$ is the applied magnetic field.

The evaluated $g$ and $A$ values for the present ZnS:Cu$^{2+}$ (Cu concentration at $x = 0.4$) samples are,

$$g_H = 2.34; \quad A_H = 42 \times 10^4 \text{ cm}^{-1}; \quad g_\perp = 2.05$$

The present value of $g$ is in the order of $g_H > g_\perp$, suggesting that Cu$^{2+}$ ions are subjected to tetragonal elongations. The ratio of $g_H/A_H$ indicates a rough estimate of coordination geometry of the central metal ion to its ligands. Its value ranging from $110 - 120$ being typical of planar complexes, while the range of $130 - 150$ is characteristic of slight to moderate distortion and the range $180 - 250$ indicates considerable distortion [15]. The present high value of this ratio suggests that the Cu$^{2+}$ ions are in a highly distorted tetrahedral environment of ZnS. This could be due to high dopant concentration ($x = 0.4$).

For samples of all copper concentrations, the number of spins ($N_s$) and the line width ($\Delta H$) are calculated using Rubbins and Bleanny relation [16] and are given in...
Table 4.4. It is obvious from the table that as the concentration of Cu increases the line width ($\Delta H$) increases (Fig. 4.18) as a result of increased dipole-dipole interaction between Cu$^{3+}$ ions and inhomogeneities in the internal field due to random distribution of Cu$^{2+}$ ions. A linear relation was established between the concentration ($x$) and the number of spins ($N_s$) and is shown in Fig. 4.19.

![ESR spectra of Zn$_{1-x}$Cu$_x$S (x=0.0, 0.1, 0.2, 0.3 and 0.4) annealed at 300°C/2h in vacuum.](image)

Fig. 4.17. ESR spectra of Zn$_{1-x}$Cu$_x$S (x=0.0, 0.1, 0.2, 0.3 and 0.4) annealed at 300°C/2h in vacuum.
Table 4.4 Number of spins ($N_s$) and line width ($\Delta H$) of Zn$_{1.5}$Cu$_x$S nanoparticles

<table>
<thead>
<tr>
<th>Composition (x)</th>
<th>Line width $\Delta H$ (Gauss)</th>
<th>Number of spins ($N_s \times 10^4$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>13.3</td>
<td>4.2</td>
</tr>
<tr>
<td>0.2</td>
<td>13.8</td>
<td>4.7</td>
</tr>
<tr>
<td>0.3</td>
<td>14.5</td>
<td>5.1</td>
</tr>
<tr>
<td>0.4</td>
<td>15.1</td>
<td>5.6</td>
</tr>
</tbody>
</table>

Fig. 4.18 Variation of line width ($\Delta H$) as a function of Cu ion concentration (x).
Concentration

Fig. 4.19. Plot showing the number of spins \(N_s\) as a function of Cu ion concentration \(x\).

4.1.7 FTIR ANALYSIS

FTIR spectra of Zn\(_{1-x}\)Cu\(_x\)S \((x = 0.1, 0.2, 0.3\) and 0.4\) samples are shown in Fig. 4.20. This FTIR analysis is undertaken in order to establish whether there is any chemisorbed thiophenol on the surface of nanoclusters. This analysis provides evidence to infer that thiophenol functions as a ligand to control the size of nanoclusters. In the spectrum there is a broad band in the higher energy region, assigned to S-H stretch corresponding to thiophenol. The less intense peak appearing above 3000 cm\(^{-1}\) is assigned to aromatic C-H vibrations. The skeletal vibration of thiophenol ring gives its characteristic peaks at 1575, 1474 and 1435 cm\(^{-1}\) in end plane bending vibration of aromatic ring. Carbon-hydrogen give peaks at 733 and 684 cm\(^{-1}\). The above discussion clearly confirms surface covering of ZnS:Cu clusters by thiophenol. Hence, the main function of thiophenol is to control the size of nanoclusters by absorption on its surface.
Fig. 4.20. FTIR spectra of Zn$_{1-x}$Cu$_x$S ($x = 0.1, 0.2, 0.3$ and $0.4$) nanoparticles
4.1.8 TGA ANALYSIS

The TGA trace of ZnS, derived between 50 and $600^\circ$C for ZnS is shown in Fig. 4.21. There is a weight loss between 50 and $160^\circ$C due to loss of absorbed water on the surface of material. It is followed by a small weight loss up to $200^\circ$C. From $200^\circ$C to $300^\circ$C there is a major weight loss, and is ascribed to decomposition of covalently bound organic, particularly thiophenol on the surface, above $300^\circ$C there is no significant weight loss and the resulting residue is found to be nearly 85%.

TGA of Cu doped ZnS was carried out between 50 and $80^\circ$C in air at a heating rate of $10^\circ$C/min in argon atmosphere. The resulting TGA traces are shown in Fig. 4.21. This analysis was undertaken to check the presence of absorbed compound if any on the surface of ZnS:Cu$^{2+}$ nanoparticles. If there are no absorbed compounds the TGA trace does not indicate any weight loss. Actually in the TGA trace there are about four stages of weight loss up to $700^\circ$C. The weight loss below $127^\circ$C is due to loss of water from the surface of materials. All the other weight losses above $140^\circ$C might be due to absorbed organics. Initially a major weight loss between $127^\circ$C-260$^\circ$C and the resulting residue decomposes in a sequence at higher temperatures. Hence based on this analysis, it could be said that the organics particularly thiophenol might be chemically bound to the surface of ZnS:Cu particles. Again, it might play a definite role on the control of the size of the particles during growth. It also supports the details provided in the FTIR analysis discussed previously.
4.1.9 DSC ANALYSIS

The DSC trace of ZnS, derived between 50 and 600°C are shown in Fig. 4.22. There is an intense endothermic peak between 50 and 150°C coinciding with the weight loss in its TGA trace as shown in Fig. 4.21. It is due to desorption of water from the surface of the nanoparticles. The endothermic peak lying between 200 and 320°C is due to decomposition and desorption of thiophenol covalently bound at 300 and 450°C. Both the decomposition between 200 and 500°C coincide with the weight loss in its TGA trace.

The DSC trace of ZnS:Cu is shown in Fig. 4.23 – 4.26. Here, the endothermic peak at 50 and 150°C coincides with weight loss in its TGA trace as shown in Fig. 4.21. This is due to desorption of water from the surface of ZnS:Cu. There is an intense sharp weight loss between 150 and 200°C but it is not observed in the TGA.
trace of ZnS. It is due to covalently bound water on the surface of ZnS:Cu. It is also evident from the FTIR spectrum discussed above. It is an evidence for the presence of Cu along with ZnS, but this is followed by one sharp and broad endotherm between 220 and 500°C, which appears similar to that observed in ZnS. Hence, it is concluded that thiophenol in both the undoped and doped samples may decompose between 220 and 500°C. Comparison of this trace with that of ZnS illustrates shift in the endotherms due to decomposition of thiophenol at higher temperatures. Hence, thiophenol might be strongly bound to the surface of ZnS:Cu nanoparticles.

Fig. 4.22. DSC analysis of Zn_{1-x}Cu_xS (x = 0.0) nanoparticles
Fig. 4.23. DSC analysis of $\text{Zn}_{1-x}\text{Cu}_x\text{S}$ ($x = 0.1$) nanoparticles

Fig. 4.24. DSC analysis of $\text{Zn}_{1-x}\text{Cu}_x\text{S}$ ($x = 0.2$) nanoparticles
Fig. 4.25. DSC analysis of Zn$_{1-x}$Cu$_x$S (x = 0.3) nanoparticles

Fig. 4.26. DSC analysis of Zn$_{1-x}$Cu$_x$S (x = 0.4) nanoparticles
4.2  PART – II:  Fe DOPED ZnS NANOPARTICLES

Sample B (ZnS:Fe)

Nanoparticles of Zn$_{1-x}$Fe$_x$S with $x = 0.0, 0.1, 0.2, 0.4$ and $0.6$ were prepared by chemical co-precipitation method as described in chapter - II.

Preparation of Zn$_{1-x}$Fe$_x$S nanoparticles

Starting materials:
- (a) ZnCH$_3$COOH (zinc acetate)
- (b) Na$_2$S (sodium sulphide)
- (c) Dopant = FeCH$_3$COOH (iron acetate)

Capping agent: Thiophenol

Stirring duration: 20h

Annealing temperature and duration: 300°C/2h

Sample colour: Yellowish (after annealing)

4.2.1 CHEMICAL ANALYSIS AND SEM MORPHOLOGY

The EDAX spectra of Zn$_{1-x}$Fe$_x$S ($x = 0.0, 0.1, 0.2, 0.4$ and $0.6$) are shown in Fig. 4.27. The variation in the relative intensity of ‘Fe’ lines with respect to Zn for varying percentage of ‘Fe’ is clearly evident. The estimated ‘Fe’ compositions are given in Table. 4.5 and are very close to the target compositions. The observed variation is very small and is within ± 1%. The SEM micrographs of nanocrystalline ZnS:Fe (0.1, 0.2, 0.4 and 0.6) annealed at 300°C/2h in vacuum are shown in Figs. 4.28 – 4.31. The Fe doped ZnS is found to have bigger particles with relatively smooth surface and less agglomeration. The $x = 0.6$ ‘Fe’ doped ZnS (Fig. 4.31) clearly shows the spongy agglomerated particles with relatively smaller sized particles.
Fig. 4.27. EDAX for elemental composition analysis of $\text{Zn}_{1-x}\text{Fe}_x\text{S} \ (x = 0.0, 0.1, 0.2, 0.4 \text{ and } 0.6)$ annealed at $300^\circ\text{C}/2\text{h}$ in vacuum.
Table 4.5: Elemental compositions of Zn$_{1-x}$Fe$_x$S samples from EDAX

<table>
<thead>
<tr>
<th>Composition (x)</th>
<th>at % of elements from EDAX</th>
</tr>
</thead>
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<td></td>
<td>Zn</td>
</tr>
<tr>
<td>0.0</td>
<td>69.94</td>
</tr>
<tr>
<td>0.1</td>
<td>63.16</td>
</tr>
<tr>
<td>0.2</td>
<td>55.30</td>
</tr>
<tr>
<td>0.4</td>
<td>37.96</td>
</tr>
<tr>
<td>0.6</td>
<td>24.15</td>
</tr>
</tbody>
</table>

Fig. 4.28. SEM micrograph of ZnS:Fe ($x = 0.1$) annealed at 300°C in vacuum
Fig. 4.29. SEM micrograph of ZnS:Fe (x = 0.2) annealed at 300°C in vacuum.

Fig. 4.30. SEM micrograph of ZnS:Fe (x = 0.4) annealed at 390°C in vacuum.
4.2.2 STRUCTURAL STUDIES

The asprepared \( \text{Zn}_{1-x}\text{Fe}_x\text{S} \) samples were found to be amorphous in nature as revealed by XRD, where \( x \) indicates the concentration of Fe. Annealing up to \( 200^\circ \text{C} \) did not induce crystallinity. However, crystallization was induced on annealing the samples in vacuum at \( 300^\circ \text{C}/2\text{h} \). The X-ray diffraction patterns of annealed \( (300^\circ \text{C}/2\text{h}) \) \( \text{ZnS:Fe} \) samples \( (x = 0.0, 0.1, 0.2, 0.4 \text{ and } 0.6) \) obtained using Cu \( \text{K}_\alpha \) radiation \( (\lambda = 1.5418 \text{ A}) \) in the range \( 20^\circ - 65^\circ \) are shown in Fig. 4.32. The line broadening of the XRD pattern also indicates the nanocrystalline nature of the samples. All the lines could be indexed to the cubic structure of \( \text{ZnS} \) in the entire range of composition studied and no extra peaks were found indicating the single phased nature of the samples confirming the complete solubility of Fe in \( \text{ZnS} \). The average diameter of the nanoparticles obtained from FWHM of XRD lines was in the
range 14 – 17.3 nm, which is in agreement with the average grain size obtained from TEM images (6.9 – 9.7). The variation of the lattice parameter ‘a’ with composition ‘x’ is shown in Fig. 4.33. It is obvious from the figure that the lattice parameter decreases linearly with composition ‘x’ following Vegard’s law [3] indicating the substitutional nature of the samples. Feng et al. [17] have reported hexagonal phase for lower ‘Fe’ concentrations (x < 0.4) and cubic phase for higher ‘Fe’ concentrations (x = 0.4 and 0.5) in ZnFeS thin films grown on sapphire by MOCVD. Further an increase in lattice parameters with increasing ‘Fe’ content has also been reported in both the phases. Borse et al. [18] have reported the coexistence of cubic and hexagonal phases in Fe doped ZnS nanoparticles formed by chemical precipitation method with Fe contents of 0.12, 1.20 and 5.85 wt%. However, these authors have not reported lattice parameters. There is no other lattice parameter data on ZnS:Fe nanoparticles for comparison.

Fig. 4.32. XRD pattern of ZnS:Fe (x =0.0, 0.1, 0.2, 0.4 and 0.6) annealed at 300°C/2h in vacuum.
Table 4.6: Lattice parameters of Zn$_{1.4}$Fe$_{0.6}$S nanoparticles

<table>
<thead>
<tr>
<th>Composition (x)</th>
<th>Lattice parameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>5.3251</td>
</tr>
<tr>
<td>0.1</td>
<td>5.3154</td>
</tr>
<tr>
<td>0.2</td>
<td>5.3152</td>
</tr>
<tr>
<td>0.4</td>
<td>5.3045</td>
</tr>
<tr>
<td>0.6</td>
<td>5.2972</td>
</tr>
</tbody>
</table>

Fig. 4.33. Variation of lattice parameter with composition (x)
Table. 4.7: Grain sizes of ZnS:Fe samples with ‘Fe’ composition (x)

<table>
<thead>
<tr>
<th>Composition (x)</th>
<th>Average Grain Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>From XRD</td>
</tr>
<tr>
<td>0.0</td>
<td>14</td>
</tr>
<tr>
<td>0.1</td>
<td>15.2</td>
</tr>
<tr>
<td>0.2</td>
<td>15.9</td>
</tr>
<tr>
<td>0.4</td>
<td>16.4</td>
</tr>
<tr>
<td>0.6</td>
<td>17.3</td>
</tr>
</tbody>
</table>

4.2.3 TEM ANALYSIS

TEM measurements were performed to confirm the nanocrystalline nature of the samples and to study the morphology of the particles. The TEM micrographs of ZnS:Fe (x=0.1, 0.2, 0.4 and 0.6) are shown in Figs. 4.34 (a) – 4.37 (a). The grains in the samples were found to be well isolated and nearly spherical in shape. The SAED pattern of Zn_{1-x}Fe_{x}S is also shown in Figs. 4.34 (b) – 37 (b). From the inter planar spacing determined from the SAED rings, it is identified that they have zinc blende structure with diffraction planes corresponding to (111), (220) and (311). No planes corresponding to any impurity phase could be identified. This also confirms the single phased nature of the nanocrystalline samples.
Fig. 4.34 (a). TEM micrograph of ZnS:Fe (x = 0.1) annealed at 300°C/2h in vacuum.

Fig. 4.34 (b). SAED pattern of ZnS:Fe (x = 0.1) annealed at 300°C/2h in vacuum.
Fig. 4.35 (a). TEM micrograph of ZnS:Fe (x = 0.2) annealed at 300°C/2h in vacuum

Fig. 4.35 (b). SAED pattern of ZnS:Fe (x = 0.2) annealed at 300°C/2h in vacuum
Fig. 4.36 (a). TEM micrograph of ZnS:Fe (x = 0.4) annealed at 300°C/2h in vacuum

Fig. 4.36 (b). SAED pattern of ZnS:Fe (x = 0.4) annealed at 300°C/2h in vacuum
Fig. 4.37 (a). TEM micrograph of ZnS:Fe (x = 0.6) annealed at 300°C/2h in vacuum

Fig. 4.37 (b). SAED pattern of ZnS:Fe (x = 0.6) annealed at 300°C/2h in vacuum
4.2.4 OPTICAL ABSORPTION STUDIES

The optical absorption spectra of ZnS and Fe doped ZnS nanopowders are shown in Fig. 4.38. The host ZnS shows two absorbance maxima between 300 and 400 nm in the near ultraviolet region. The band gap values corresponding to the maxima are 3.7 eV (328 nm) and 3.3 eV (367 nm). Since XRD showed only a single phase and no impurity peaks, the two different absorbance maxima are illustrative of two groups of particles with different sizes. ZnS:Fe (x = 0.1) also shows two absorbance maxima but slightly shifted to shorter wavelengths compared to the host. However, nanoparticles of higher 'Fe' content give only one absorbance maximum. This suggests that introduction of Fe in ZnS lattice might assist formation of particles with grain size in a narrow range. In addition, the particle size also decreases as a result of Fe loading and this is evident from the shift of the absorbance maximum towards shorter wavelength with increasing Fe content. Again there is no separate absorbance maximum for Fe, hence, there might not be any independent iron or iron
oxide or 'FeS' phase. It is also supported by XRD spectra which showed only ZnS peaks and no other impurity peaks. The band gap values corresponding to the absorbance maximum with varying 'Fe' composition are presented in Table 4.8. Feng et al. [17] have reported a shift in the absorption edge to longer wavelength (Red shift) with increasing Fe content in ZnFeS thin films. There is no other data on optical absorption of ZnS:Fe nanoparticles for comparison.

Table 4.8: Band gap as a function of composition (x) in Zn_{1-x}Fe_x S samples

<table>
<thead>
<tr>
<th>Composition (x)</th>
<th>Energy gap eV (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>3.7 (328)</td>
</tr>
<tr>
<td>0.1</td>
<td>3.8 (324)</td>
</tr>
<tr>
<td>0.2</td>
<td>3.9 (311)</td>
</tr>
<tr>
<td>0.4</td>
<td>4.1 (298)</td>
</tr>
<tr>
<td>0.6</td>
<td>4.2 (289)</td>
</tr>
</tbody>
</table>

Fig. 4.39. Variation of band gap with composition of ZnS:Fe samples
4.2.5 PHOTOLUMINESCENCE STUDIES

The excitation spectra of undoped and Fe doped ZnS nanoparticles in the wavelength range 320 - 420 nm are shown in Fig. 4.40. Typical excitation spectrum for ZnS:Fe with Fe concentration (x = 0.1) is only shown. The excitation spectrum of undoped ZnS nanoparticles shows a series of excitation maxima. The first excitation appears broader and more intense with a maximum at 340 nm. The second excitation maximum at 370 nm is less pronounced and not well resolved. Similarly, the maxima at about 393 nm and 410 nm are poorly resolved. This observation suggests the presence of different groups of particles with different sizes, each group being characterized by its own band gap excitation. On the other hand, the excitation spectrum of ZnS:Fe exhibits only one peak at 370 nm. This suggests that suppression of growth of particles with different sizes is favoured by the dopant Fe. Its entry into the lattice of ZnS might modify the surface free energy of ZnS particles so that the particle size could be confined to a narrow range.

The emission spectra of ZnS and Fe doped ZnS nanoparticles are shown in Fig. 4.41. The emission maximum for ZnS host occurs at 500 nm but for Fe doped ZnS the maxima are shifted to higher wavelength. Again, the emission intensity for Fe doped ZnS is less than that of the ZnS host. Hence, in all the Fe doped ZnS samples, the iron size must act to quench the fluorescence emission of host. For Fe (x = 0.1) loading, there is less fall in emission intensity whereas for other higher loading of iron there is much higher fall in intensity. Hence, the emission of ZnS might be absorbed/wasted due to repeated scatterings between Fe$^{3+}$ states, in the ZnS lattice. Since Fe$^{3+}$ possesses 3d$^{5}$ electron configurations with weak sulfide anions in its coordination sphere, there might not be crystal field splitting in Fe$^{3+}$. Hence, the emission of host ZnS might be used for the activation of forbidden electronic transitions in Fe$^{3+}$. Borse et al [18] have reported PL spectra of ZnS:Fe prepared by chemical coprecipitation method using mercaptoethanol as a capping agent. They also reported that the blue light emission ~ 425 nm in zinc sulphide host was completely quenched when doped with iron metal ions. It is known in bulk material [19] that iron gets doped substitutionally in ZnS. They act as electron trapping centers resulting in nonradiative recombination. This means that photo-excited electrons are preferentially transferred to iron metal ion induced trapping centers compared to anion vacancy.
defect centers. Quenching of photoluminescence peak at ~425 nm in ZnS colloidal particles by Cd$^{2+}$ ions was investigated by Weller et al. [20]. They observed that addition of Cd$^{2+}$ ions shifted the luminescence peak to 580 nm and the intensity of the peak kept on reducing with increased amount of Cd$^{2+}$ ion concentration. They have attributed this behaviour to the formation of co-colloids. It is speculated that Zn$^{2+}$ ions are being replaced by Cd$^{2+}$ ions at the surface of the particles. These are considered to be responsible for the fluorescence observed at 580 nm. However, it is possible to quench the luminescence peak at 500 nm by doping of iron in ZnS network if there is more positive charge relative to the lattice.

Fig. 4.40. PL excitation spectra of ZnS and ZnS:Fe ($x = 0.1$) nanoparticles annealed at 300°C/2h in vacuum.
Fig. 4.1. PL emission spectra of ZnS and Zn_{1-x}Fe_xS (x = 0.0, 0.1, 0.2, 0.4 and 0.6) nanoparticles annealed at 300°C/2h in vacuum.
As $\text{Fe}^{3+}$ possesses five unpaired electrons in its d-shell it can very well be studied by ESR spectroscopy. If $\text{Fe}^{3+}$ is present in smaller amounts there must be characteristic ESR signal for $\text{Fe}^{3+}$ and the intensity of the signal might also be high. If $\text{Fe}^{3+}$ content gradually increases there will be interaction between two adjacent $\text{Fe}^{3+}$ sites leading to decrease in intensity of ESR signal. This interaction occurs through the intervening sulphide bridges. In order to establish this view the ESR study was undertaken at room temperature for all the samples and the spectra are shown in Fig. 4.42. There is a gradual decrease in intensity of the signal with the increase in the content of $\text{Fe}^{3+}$. Hence, there might be a gradual increase in interaction between $\text{Fe}^{3+}$ sites with the increase in its content. In addition 'g' value given in Table. 9 decreases with the increase in Fe content. Hence, the free electron in Fe sites might not be delocalized over a long distance in samples with high Fe content. The total number of unpaired spins, shown in the same Table. 9, illustrates increase with increase in Fe content but the increase is not proportional to the number of spins for $x = 0.6$, that is, not six times that of ($x = 0.1$). It therefore confirms our view that there is interaction between two adjacent $\text{Fe}^{3+}$ sites through the sulphide bridges leading to suppression of free spins.

The line width, $\Delta H$, shown in Table. 4.9 increases with increase in Fe content due to chemical shift anisotropy. The chemical shift anisotropy that arises with high Fe content also supports the observation of large decrease in luminescence for high Fe loading. That is for increase in Fe content, the probability of suppressing emission could be enhanced. Borse et al [18] have also reported the presence of iron ions in the substitutional sites of $\text{Zn}^{2+}$ and observed to be in the $\text{Fe}^{3+}$ state.
Fig. 4.42. ESR spectra of Zn$_{1-x}$Fe$_x$S ($x = 0.1, 0.2, 0.4$ and $0.6$) annealed at $300^\circ$C/2h in vacuum.
Table 4.9. Lande’s $g$’ factor, Line width (ΔH) and number of spins (Ns) of ZnS:Fe samples

<table>
<thead>
<tr>
<th>Composition (x)</th>
<th>g-values</th>
<th>Line width (ΔH(G))</th>
<th>Number of spins (Ns) (X104)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>1.970</td>
<td>205</td>
<td>24.91</td>
</tr>
<tr>
<td>0.2</td>
<td>1.966</td>
<td>225</td>
<td>31.30</td>
</tr>
<tr>
<td>0.4</td>
<td>1.963</td>
<td>270</td>
<td>35.73</td>
</tr>
<tr>
<td>0.6</td>
<td>1.957</td>
<td>290</td>
<td>51.29</td>
</tr>
</tbody>
</table>

4.2.7 MAGNITIZATION MEASUREMENTS

The magnetization measurements on nanocrystalline Zn$_{1-x}$Fe$_x$S (x = 0 to 0.6) samples were performed at 300 K in EG & G Princeton Applied Research VSM 4500 equipment. The magnetization versus applied field plots are shown in Figs. 4.43 – 4.45 for samples of all compositions. The undoped ZnS sample exhibited diamagnetic behaviour (not shown here), whereas for the x = 0.1 and 0.2 ‘Fe’ doped ZnS samples the magnetization properties could not be extracted distinctly due to the weak ferromagnetic behaviour which may be due to the lower concentration of the magnetic dopants. On the other hand, samples with x = 0.4 and 0.6 showed stronger ferromagnetic behaviour with clear hysteresis loops. Among these two, the x = 0.4 ‘Fe’ doped ZnS samples were found to have more pronounced magnetization than the x = 0.6 ‘Fe’ doped ZnS samples. The retentivity of Zn$_{0.94}$Fe$_{0.06}$S samples was higher with a value of 0.174 emu/g than 0.110 emu/g of the Zn$_{0.94}$Fe$_{0.06}$S sample. Similarly, relatively higher magnetization ($M_{\text{max}} = 0.659$ emu/g) was observed for samples with x = 0.4 compared to $M_{\text{max}} = 0.452$ emu/g of the samples with x = 0.6. However, the coercivity was nearly equal for samples of these two ‘Fe’ concentrations. There is no data on magnetization of ZnS:Fe in literature for comparison.
Fig. 4.43. Magnetization measurements on ZnS:Fe \((x = 0.1)\) annealed at 300°C/2h in vacuum.

Fig. 4.44. Magnetization measurements on ZnS:Fe \((x = 0.2)\) annealed at 300°C/2h in vacuum.
4.2.8 FTIR ANALYSIS

The middle infrared FTIR spectra of thiophenol capped ZnS:Fe (x = 0.1, 0.2, 0.4 and 0.6) are shown in Fig. 4.46. In all these spectra there is a broad intense absorption between 3000 and 3700 cm$^{-1}$ due to O-H vibration of water molecules. It is also confirmed by its bending vibration occurring at about 1600 cm$^{-1}$. The weak vibration, assigned to peaks between 1300 and 1500 cm$^{-1}$, are due to aromatic ring vibration of capped thiophenol. The S-H vibration of thiophenol gives intense peaks between 1000 and 1250 cm$^{-1}$. The aromatic ring C-H bending vibrations give the peaks between 550 and 750 cm$^{-1}$. Hence, from this analysis it is concluded that ZnS:Fe particles after reaching a particular size, strongly absorbs thiophenol on their surface which results in effective control of the particle size.
4.2.9 TGA ANALYSIS

The TGA of Fe doped ZnS nanoparticles was carried out between 50 and 600°C and the results are illustrated in Fig. 4.47. All the samples show a weight loss between 50 and 125°C. It is ascribed to loss of adsorbed water in the sample. This is followed by another weight loss between 150 and 300°C. It is due to degradation and desorption of the template, thiophenol, used during the preparation. Presence of template on the surface of the particles was also evident from the FTIR analysis. The third weight loss that occurs between 350 and 500°C is due to decomposition of the residue of the previous decomposition. All the samples show nearly similar thermal behaviour.
Fig. 4.47. TGA analysis of Zn$_{1-x}$Fe$_x$S ($x = 0.1, 0.2, 0.3$ and $0.4$) nanoparticles
4.2.10 DSC ANALYSIS

The DSC analysis of all the ZnS:Fe nanoparticles was carried out between 50 and 600°C and the results are illustrated in Fig. 4.48. The endotherm lying between 50 and 150°C matches with the first weight loss in TGA discussed above. The endotherm due to decomposition of template lies between 200 and 300°C. The minor endotherm above 300°C, observed for all the samples, also match with the final weight loss in TGA.

![DSC Analysis of Zn$_{1-x}$Fe$_x$S nanoparticles](image)

*Fig. 4.48. DSC analysis of Zn$_{1-x}$Fe$_x$S (x = 0.1, 0.2, 0.4 and 0.6) nanoparticles*
REFERENCES


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