CHAPTER IV

PHOTOLUMINESCENCE STUDIES
OF Mn DOPED ZnS
NANOPARTICLES
4.1 INTRODUCTION

Since the first report of Mn-doped ZnS semiconductor nanocrystals by Bhargava et al. (1994a, 1994b) in 1994, many studies on doped semiconductor nanoparticles have been studied by many workers. During the past, doped II-VI semiconductor nanocrystals such as CdS:Mn (Levy et al. 1999, Counio et al. 1998, Tanaka et al. 2000), CdS:Eu (Morita et al. 2000), ZnO:Co,Ni (Radovanovic et al. 2002), ZnSe:Mn (Norris et al. 2001), ZnS:Cu (Sangwook et al. 2003, Jayanthi et al. 2007), ZnS:Pb,Cu (Yang et al. 2001), ZnS:Mn (Hajisalem et al. 2009, Biswas et al. 2008, Maity et al. 2004, Warad et al. 2005, Sapra et al. 2003, Bhattacharjee et al. 2002, Cao et al. 2002, Tanaka et al. 2000, Chen et al. 2002), etc. have attracted the attention of a large number of researchers. ZnS has attracted enormous interest because it has been commercially used for a variety of applications such as light-emitting diodes (LEDs), electroluminescence devices, flat panel displays, sensors, lasers, infrared windows, solar cells, bio-devices, and other optoelectronic devices. In addition, because of its wide band gap ZnS is suitable for use as a host material for a variety of dopants. It was reported by Bhargava et al. (2005) that the doping with Mn into ZnS nanocrystals results in the luminescence efficiency enhancement and the lifetime shorting in comparison with that of the bulk material. Such results were explained on the basis of the interaction of the sp electron hole of the host (ZnS) and the 3d electrons of the impurity (Mn) under condition of the quantum confinement for the sp states. Tanaka et al. (2005) and Chen et al. (2002) have analyzed photoluminescence excitation (PLE) spectra in the ultraviolet- and visible-regions for the ZnS:Mn nanoparticle samples with different sizes and they have proposed a model for the energy transfer from the host ZnS lattice to Mn$^{2+}$ d levels. It was concluded (Tanaka et al. 2005) that the Mn$^{2+}$ luminescence under the inter-band excitation occurs mostly by the energy transfer from the electron–hole pairs delocalized inside the ZnS host nanocrystals.
Because the chemical similarity between $\text{Zn}^{2+}$ and $\text{Mn}^{2+}$ facilitates the incorporation of the dopant ion, a lot of study has been made on doped ZnS:Mn nanoparticles. Since a significant part of the $\text{Mn}^{2+}$ ions resides near the surface of the nanoparticle the incorporated concentration of $\text{Mn}^{2+}$ is consistently lower than the intended dopant concentration (Yang et al. 2005). Whereas Bhargava et al. (1945a) have reported a considerable shortening of the lifetime Bharagava et al. 1945a), Bol et al. (Bol et al. 2001, 1998) have concluded that the lifetime of $\text{Mn}^{2+}$ in ZnS:Mn$^{2+}$ quantum dots is very similar to the bulk lifetime. Also the emission spectrum in ZnS:Mn$^{2+}$ is almost size-independent (Yang et al. 2005, Bol et al. 1998). Consequently, the growth of an inorganic (ZnS) shell around ZnS:Mn effectively reduces non-radiative decay paths whereby the enhancement in the luminescence (Quan et al. 2007) takes place more efficiently as compared to the organic passivation of the surface (Chen et al. 2004). The preparation techniques, luminescence properties, possible applications, etc. of ZnS:Mn nanoparticles can be found in the Reviews by Chen et al. (2004), Yang et al. (2005), Chander (2005), and Chandra et al. (2015).

In fact, ZnS is one of the first semiconductors discovered (Davidson et al. 1948) and it has traditionally shown remarkable fundamental properties, versatility and a promise for novel diverse applications. The atomic structure and chemical properties of ZnS are comparable to more popular and widely known ZnO semiconductor. However, certain properties of ZnS are unique and advantageous compared to ZnO. For example, ZnS has a larger bandgap of $\sim 3.72$ eV and $\sim 3.77$ eV (for cubic zinc blende (ZB) and hexagonal wurtzite (WZ) ZnS, respectively) as compared to ZnO ($\sim 3.4$ eV), and consequently, it is more suitable for visible-blind ultraviolet (UV)-light based devices such as sensors/photodetectors, etc. On the other hand, ZnS is traditionally the most suitable candidate for electroluminescence devices.
The important, unique properties and potential applications of semiconductor of Group II-VI compounds attracted the interest of many researchers (Weller et al. 1993, Alvisatos et al. 1996, Nirmal et al. 1999, Murray et al. 1993, Peng et al. 2002). ZnS is an important group II-VI semiconductor material having a wide band gap of 3.54 eV at room temperature (Kumbhojkar et al. 2000). It has attracted a lot of research not only due to its excellent properties at nanoscale and low toxicity when compared to other chalcogenides (Yamaguchi et al. 1999, Liu et al. 2006, Lee et al. 2007, Kulkarni et al. 2006), but it has also been extensively studied due to its potential for device applications like optical coatings, field effect transistor, optical sensors, electroluminescence displays, phosphors and other light emitting materials (Hullavarad et al. 2008, Chandramohon et al. 2009). Due to its wide band gap, ZnS has a high index of reflection and high transmittance in the visible range particularly suitable for host material for a large variety of dopants. The synthesis of Mn$^{2+}$ doped ZnS nanoparticles have been primarily investigated because of the luminescence of manganese ions inside the ZnS host. In fact, in Mn$^{2+}$ doped ZnS nanoparticles, the luminescence quantum efficiency is expected to increase as a result of greater interaction between the electron and hole of the host ZnS nanoparticles with localized dopant levels (Gaponeko et al. 1998). Basically, in photoluminescence, the electrons are excited from the ZnS valence band to conduction band by absorbing the energy equal to or greater than their band gap energy and subsequent relaxation of these photo-excited electrons to some surface states or levels is followed by radiative decay enabling luminescence in the visible region.

Hoa et al. (2011) have studied the optical properties of Mn-doped ZnS semiconductor nanoclusters synthesized by a hydrothermal process. Various samples of the ZnS:Mn with 0.5, 1, 3, 10 and 20 at.% Mn dopant have been prepared and characterized using X-ray diffraction, energy-dispersive analysis of X-ray, high
resolution electron microscopy, UV–VIS diffusion reflection, photoluminescence (PL) and photoluminescence excitation (PLE) measurements. All the prepared ZnS nanoclusters possess cubic sphalerite crystal structure with lattice constant $a = 5.408 \pm 0.011$ Å. The PL spectra of Mn-doped ZnS nanoclusters at room temperature exhibit both the 495 nm blue defect-related emission and the 587 nm orange Mn $^{2+}$ emission. Furthermore, the blue emission is dominant at low temperatures; meanwhile the orange emission is dominant at room temperature. The Mn$^{2+}$ ion-related PL can be excited both at energies near the band-edge of ZnS host (the UV region) and at energies corresponding to the Mn$^{2+}$ ion own excited states (the visible region). An energy scheme for the Mn-doped ZnS nanoclusters has been proposed to interpret the photoluminescence behaviour.

Konishi et al. (2001) have studied the enhancement of PL of ZnS:Mn nanocrystals by hybridizing with polymerized acrylic acid. By using either acrylic acid (AA) monomer or poly(acrylic acid) (PAA) polymer as a starting material, differences in optical and chemical properties of hybrid nanocrystals are compared. The enhancement of PL at 580 nm due to the d–d transition of Mn$^{2+}$ is larger for ZnS:Mn nanocrystals modified by AA and aged at $808^\circ$C for $t_{\text{age}}$ (aging time) hours for polymerization (the sample ZSAA5-$t_{\text{age}}$, $0 < t_{\text{age}} < 24$), as compared with that modified by PAA (the sample ZSPAA). The C=O groups and ZnS are excited simultaneously by a light of 350 nm to stimulate energy transfer to Mn$^{2+}$ ions jointly. In the samples ZSAA5-$t_{\text{age}}$, oxygen atoms of carboxyl groups form –S–O–C(=O)– bonds and the valence number of sulfur increases from -2 to +6, as confirmed by infrared absorption and X-ray photoelectron spectra. As a result, electrons of sulfur atoms are pushed toward carboxyl groups to enhance the emissions from both C=O groups and Mn$^{2+}$ ions. In contrast, the sample ZSPAA exhibits predominant interaction of C=O groups with metallic ions to form –C–O–Me– bonds (Me=Zn$^{2+}$ and Mn$^{2+}$). This decrease in the amount of C=O groups reduces energy transfer to Mn$^{2+}$ ions.
Bodo et al. (2012) have reported the synthesis and characterization of ZnS: Mn nanoparticles. They prepared ZnS:Mn nanoparticles by chemical co-precipitation method at room temperature and the structural and optical properties of the ZnS:Mn nanoparticles were determined by XRD, SEM, UV-Visible and FL analyses. XRD analysis showed the sample prepared were in cubic phase with particle size in the ranges 12 nm-25 nm. The SEM analysis revealed the growth of nanoparticles agglomerated in different shapes and orientations. In UV-visible study the band gap energy corresponding to the absorption edge estimated are found to be 4.4~ 4.3eV which shows the large blue shifting from the bulk band gap 3.6eV of ZnS. The FL peak analysis reveals the strongest absorption at around 329nm which is fairly blue shifted from the absorption edge of the bulk (345nm). They have concluded that the Mn incorporated into ZnS nanoparticles results in changing its morphological, structural and optical properties.

Bacherikov et al. (2012) have reported the factors influencing luminescent properties of ZnS:Mn nanoparticles obtained by the method of one-stage synthesis. They have proposed a model that combines appearance of defects responsible for self-activated (SA) emission in ZnS with its piezoelectric properties. Being based on analysis of the luminescence spectrum, they demonstrated the influence of mechanical destruction, impact of ultrasound, microwave radiation and pulsed magnetic field on the emission efficiency for centers of luminescence connected with intrinsic defects in ZnS:Mn prepared using the method of self-propagating high temperature synthesis (SHS). It has been shown that downsizing the ZnS:Mn crystals prepared according to the above method as well as more discrete differentiation of phases present in this material due to development and growth of inner boundaries and surface under external actions leads to quenched SA-photoluminescence with λ ~ 400–525 nm.
Peng et al. (2005) have reported the structural and optical investigation of Mn-doped ZnS:Mn nanocrystals. Using a solution-based chemical method, they have synthesized ZnS nanocrystals doped with high concentration of Mn$^{2+}$, in which the X-ray analysis confirmed a zinc blende structure. The average size obtained was about 3 nm. Photoluminescence spectrum showed room temperature spectrum in the visible region, which consisted of the defect-related emission and the $^4T_1 - ^6A_1$ emission of Mn$^{2+}$ ions. As compared to the undoped sample, the luminescence of the ZnS:Mn phosphor is enhanced by more than an order of magnitude, which indicated that the Mn$^{2+}$ ions can efficiently boost the luminescence of ZnS:Mn nanoparticles.

Rahdar et al. (2013) have reported effect of different capping agents on the structural and optical properties of Mn doped ZnS nanostructures, in which the phosphors were prepared by co-precipitation method using the solution of ZnCl$_2$, and Na$_2$S as sources for zinc and sulfur, respectively and MnCl$_2$ as doping agent, and thioglycerol(TG), mercaptoethanol (ME), sodium hexaetaphosphate (SHMP) were used as capping agents for controlling the particles size. The optical absorption spectra of the samples obtained using UV-Vis spectrophotometer shows the blue-shift with decreasing particle size. The value of band gap energy has been found to be in range 4.07-4.57 eV. This behavior is related to size quantization effect due to the small size of the particles. The ZnS:Mn nanoparticles were then characterized by using X-ray diffraction (XRD), in which the size of the particle is found to be in 2.20-2.67 nm range. TEM image showed the morphology of TG and ME- capped ZnS:Mn nanostructures.

Ummartyotin et al (2012) have investigated the synthesis and luminescence properties of ZnS and metal (Mn, Cu)-doped-ZnS ceramic powder. ZnS and metal (Mn, Cu)-doped-ZnS were successfully prepared by wet chemical synthetic route. The understanding of substituted metal ions (Mn, Cu) into ZnS leads to transfer the luminescent centre by small amount of metal dopant (Mn, Cu). Fourier transform
infrared and X-ray diffraction were used to determine chemical bonding and crystal structure, respectively. It is shown that small amount of metal (Mn, Cu) can be completely substituted into ZnS lattice. X-ray fluorescence was used to confirm the existence of metal-doped ZnS. Scanning electron microscope revealed that their particles exhibit blocky particle with irregular sharp. Laser confocal microscope and photoluminescence spectroscopy showed that ZnS and metal-doped-ZnS exhibited intense, stable, and tunable emission covering the blue to red end of the visible spectrum. ZnS, Mn-doped-ZnS and Cu-doped-ZnS generated blue, yellow and green color, respectively. Till now, the PL of ZnS:Mn nanoparticles have been studied by many other workers (Chander 2005, Chandra et al. 2015).

There are several methods to synthesize ZnS nanoparticles with various Mn$^{2+}$ concentrations such as sol-gel, chemical vapour deposition, chemical co-precipitation method, hydrothermal method (Karan et al. 2004, John et al. 2010, Ghosh et al. 2006, Tamrakar et al. 2008), etc. So among the different synthesis processes, chemical co-precipitation method is used because of its manifold advantages like simple, easy handling, economical and capability for large scale production. Till now, there are many reports on the synthesis and characterization of capped ZnS nanoparticles doped with various concentration of Mn$^{2+}$. But, it still requires further investigation so as to study more on the structural, optical and electrical properties with due emphasis given on the luminescence property for its use as a suitable candidate for various device applications.

The semiconductor nanoparticles are themselves highly unstable and in the absence of the capping agent, they agglomerate very rapidly (Waggon et al. 1996). Due to this reason, bonding of capping agent to nanoparticles is necessary to provide chemical passivation and also to improve the surface state which has substantial influence on the optical and electronic properties of nanoparticles (Ekimov et al.
As the surface of the nanoparticle is very high, agglomeration takes place which causes increase in the size of the particle. So in order to control the agglomeration, we have used mercaptoehanol as a capping agent especially during synthesis. Furthermore, the viscosity of the polymer solution will be helpful in controlling the growth of the nanoparticles and thus prevent particles from aggregating, and therefore, no stabilizers will be needed.

The dependence of PL of ZnS:Mn nanoparticles on the particle size is not satisfactorily understood to date. The present paper reports the synthesis, characterization and photoluminescence studies of Mn doped ZnS nanoparticles prepared by chemical precipitation method, in which mercaptoethanol has been used as an capping agent and discusses the salient features of PL in detail.

**4.2. EXPERIMENTAL**

Synthesis is the most important step in the studies of nanoparticles. The chemical precipitation method is used in the present investigation. For synthesis of ZnS:Mn nanoparticles 1M aqueous solution of ZnCl$_2$ and 1 M aqueous solution of Na$_2$S were mixed in presence of various concentrations of mercaptoethanol solution, and MnCl$_2$ was also mixed in required amount, while stirring the solution continuously. Five different samples of ZnS:Mn nanoparticles were prepared, namely, ZnS:Mn-I, ZnS:Mn-II, ZnS:Mn-III, ZnS:Mn-IV, and ZnS:Mn-V by changing the capping agent concentration to 0 M, .01 M, .025 M, 0.040 M, and 0.060M, respectively. The obtained precipitates were washed thoroughly three to four times in double distilled water and they were separated by centrifugation at 3500 rpm and finally air dried. Special care was taken to maintain the same physical condition during the synthesis of the samples.
The morphologies and sizes of the mercaptoethanol capped ZnS:Mn nanoparticles were determined by X-ray diffraction(XRD) studies with Cu K$_\alpha$ radiation ($\lambda=1.5418\text{Å}$). XRD data were collected over the range 20-70$^0$ at room temperature. X-ray diffraction patterns were obtained using a Rigaku Rotating Anode (H-3R) diffractometer. In XRD the particle size was determined using the Debye-Scherrer formula. The particle size was also calculated using the field emission gun scanning electron microscope (FEGSEM) and high resolution transmission electron microscope (HRTEM) methods.

The absorption spectra were recorded with the help of a Perkin Elimer $\lambda$-12 spectrophotometer. The photoluminescence were recorded with the help of a Shimadzu spectrofluorophotometer RF 5301PC.

4.3 RESULTS AND DISCUSSION

4.3.1 X-Ray Diffraction (XRD) Study

The XRD patterns for the samples are shown in Fig. 4.1 and Fig. 4.2 for ZnS:Mn nanocrystals for two different capping agent concentrations (merceptoethanol), Three different peaks are obtained at 20 values of 29.36$^0$, 48.77$^0$, 57.77$^0$ (for Fig. 4.1) and 28.72$^0$, 48.60$^0$, 57.68$^0$ (for Fig. 4.2), respectively. This shows that the samples have Zinc blende structure and the peaks correspond to diffraction at (111), (220) and (311) planes, respectively (Guinier 1963). The lattice parameter has been computed as 5.31Å, which is very close to the standard value (5.42Å). It is also seen from Fig. 4.1 and Fig. 4.2 that peaks are broadened for higher concentration of capping agent. The broadening of peaks indicates nanocrystalline behavior of the particles. The size of the particle has been computed from the width of the first peak using Debye-Scherrer formula (Mahamuni et al. 1993) given below:
\[ D = \frac{K\lambda}{\beta \cos \theta} \]  

(4.1)

where \( K \) is constant \((K = 0.9)\), \( \lambda \) the wavelength of X-ray, \( \beta \) the full width at half maximum and \( \theta \) is Bragg angle. The particle sizes obtained from XRD were in the range 2 nm - 3 nm. The Debye-Scherrer equation has a few limitations. The value of the constant used in the equation changes with the shape of the particles. It does not take into account the existence of a distribution of the size and the presence of defects in the crystalline lattice. Therefore, the calculation of diameter of grain from FWHM of the peak can overestimate the real value since the larger grains give strong contribution to the intensity, while the smaller grains form the base of the peak. Moreover, the presence of defects in a significant amount causes an additional enlargement of the diffraction line. These problems can be overcome by measuring the particle size by FEGSEM and HRTEM.

Fig. 4.1XRD pattern of ZnS:Mn nanocrystals for 0 M concentration of capping agent (merceptoethanol).
Fig. 4.2 XRD pattern of ZnS:Mn nanocrystals for 0.01 M concentration of capping agent (merceptoethanol).

### 4.3.2 EDX (Energy Dispersive X-ray)

Fig. 3 shows that energy dispersive X-ray (EDX) of ZnS:Mn nanoparticles. The sample (ZnS:Mn) gives the atomic %Zn=72.26 and %S=26.73, % Mn=1.01.
Fig. 4.3 EDX spectra of ZnS:Mn nanoparticle.

4.3.3 Field emission gun Scanning electron microscope (FEGSEM)

Fig. 4.4 shows the Field emission gun scanning electron microscope (FEGSEM) of ZnS:Mn nanoparticles. It is evident that the particle size is in the range of nanosize.
4.3.4 High resolution transmission electron microscope (HRTEM)

A typical HRTEM image of ZnS:Mn nanoparticles is shown in Fig. 4.5 and Fig. 4.6. The particle size obtained from HRTEM image is found to be in the range of 1 nm to 3 nm. HRTEM image clearly shows that the particles size is not spherical. The lattice fringes visible in the HRTEM micrograph are indicative of the crystalline nature of the particles. The tree diffraction rings in the EDX patterns correspond to the (111), (220) and (311) reflections, confirming the cubic zinc blende structure, which is in accordance with XRD results.
Fig. 4.5 HRTEM SAED image of ZnS:Mn nanoparticle

Fig. 4.6 HRTEM image of ZnS:Mn nanoparticles.
4.3.5 Fourier transforms infrared Spectra (FTIR)

Fig. 4.7 shows the typical spectra of synthesized ZnS:Mn nanoparticles. The spectra show characteristic peaks to 501, 640, 1019, 1058, 1286, 1406, 1460, 1618, 2011, 2848, 2951, 3450 cm\(^{-1}\) and some other associated peaks. The bands around 501 and 640 cm\(^{-1}\) are assigned to the Mn-O band. A strong intensity band at 1019 cm\(^{-1}\) may be due to S-O-C stretching. The stretching vibrations assigned to the C-S linkage occur in the region of 700-600 cm\(^{-1}\). The peaks at 640 cm\(^{-1}\) is assigned to the ZnS band (i.e., corresponding to sulphides). Bands around 900 - 1500 cm\(^{-1}\) are due to the oxygen stretching and bending frequency. The peaks at 2951, 2848 and 1406 - 1460 cm\(^{-1}\) are assigned to the characteristic vibrations of the methylene groups in merceptoethanol. The stretching vibration bands of the C-O groups on merceptoethanol located at 1000 -1300 cm\(^{-1}\) also bands around 1200 and 1100 cm\(^{-1}\) are due to the characteristic frequency of inorganic ions. The FTIR spectra showed peak at 1618 cm\(^{-1}\) representing the nitrogen – oxygen interaction. Band around 3000-3600 cm\(^{-1}\) are due to the hydrogen Stretching frequency (OH stretching). The band at 3450 cm\(^{-1}\) corresponds to characteristic vibration band of hydroxyl groups of merceptoethanol molecules.
4.3.6 Absorption Spectra Study

Optical absorption study plays an important to understand the behavior of semiconductor nanocrystals. A fundamental property of semiconductors is the band gap, which is the energy separation between the filled valance band and the empty conduction band. In fact, optical excitation of electrons across the band gap is strongly allowed, producing an abrupt increase in absorption at the wavelength corresponding to the band gap energy. Such feature in the optical spectrum is known as the optical absorption edge. Fig. 4.8 shows the optical absorption spectra of ZnS:Mn nanoparticles in the range of 400 nm-200 nm. Absorption edge was obtained at shorter wavelength in UV region at 290 nm, 278 nm, 260 nm, 233 nm, and 225 nm for ZnS:Mn-I, ZnS:Mn-II, ZnS:Mn-III, ZnS:Mn-IV and ZnS:Mn-V samples respectively. This result clearly
shows that the absorption edge shift towards the shorter wavelengths as the capping agent concentration is increased. The appearance of blue shift in the absorption edge is reflection of the band gap increase owing to quantum confinement effect. Fig. 4.8 shows the optical absorption spectra for the samples. ZnS:Mn is direct band gap materials, which has the band gap energy ~ 3.60 eV. It is clear from the figure that the absorption edge for the all the samples is blue-shifted. The blue-shift in the absorption edge indicates increase in effective band gap of the sample. The band gap energy of the samples corresponding to the absorption edge is found to 4.27 eV, 4.46 eV, 4.76 eV, 5.32 eV and 5.51 eV, respectively with increasing with increasing the capping agent concentration. It is observed that no optical absorption occurs at surface states and therefore they do not affect the absorption spectra. In fact, only the widening of the band gap is indicated. Similar results have been reported by Warada et al. (2005) on luminescent nanoparticles of Mn doped ZnS passivated with sodium hexametaphosphate. They have obtained a broad futureless and small absorption peak at 252 nm (4.9 eV). Lu et al. (2001) have investigated the absorption spectra of ZnS:Mn nanoparticles and they have obtained peak at 303 nm (4.09eV). Rahdar et al. (2013) have obtained absorption peak at 304 nm (4.07 eV) and 285 nm (4.35 eV) and 271 nm (4.57 eV) for Mn doped ZnS nanoparticles of sizes 2.67 nm, 2.35 nm and 2.20 nm. This result is in agreement with our results.
In the past, some theoretical models have been proposed (Guinier 1963, Suyver et al. 2001), relating the effective band gap of materials with the particle size. The simple model predicting the variation of exciton energy with the particle size is based on the effective mass approximation (EMA). In fact, the lowest excited state of the crystalline is assumed to be the ground state of an electron hole pair. The ground state energy of exciton or the increase in effective band gap as a function of crystalline size can be expressed as (Mahamuni et al. 1993).

\[
\Delta E = \frac{\hbar^2 \pi^2}{2r^2} \left[ \frac{1}{m_e^*} + \frac{1}{m_h^*} \right] - 1.786 \frac{e^2}{\varepsilon r} - 0.124 \frac{e^4}{\hbar^2 \varepsilon^2} \left[ \frac{1}{m_e^*} + \frac{1}{m_h^*} \right]^{-1} \quad \text{...(4.2)}
\]

where \(\Delta E\) is the blue-shift of the band gap, \(m_e^*\) effective mass of electron, \(m_h^*\) the effective mass of the hole, \(r\) the radius of the particles and \(\varepsilon\) the dielectric constant.
of semiconductor. In this equation the first term is the kinetic energy of the electrons and holes, the second is their coulomb attraction and the last term corresponds to the correlation between the two particles. The second and third terms are much smaller than the first term, and therefore, they can be neglected and thus Eq. (4.2) may be expressed as

\[ \Delta E = \frac{\hbar^2 \pi^2}{2r^2} \left[ \frac{1}{m_e^*} + \frac{1}{m_h^*} \right] \]  

\[ \text{...(4.3)} \]

The values of effective mass of the electrons and holes for ZnS are 0.41m_e and 0.61m_h (Lippens et al. 1991). Table 4.1 shows the particle size calculated from this model. It is to be noted that particle size estimated from absorption edge is of the same order as that obtained from broadening of XRD peaks. Increase in band gap corresponds to the smallest dimension of the nanocrystals, whereas XRD corresponds to average size. The values of particle size obtained by effective band gap model are nearly same and these results and XRD reveal that the nanoparticles are spherical in nature. The variation of particles size with capping agent concentration is illustrated in Fig. 4.9. Fig. 4.10 illustrates the dependence of band gap with particle size of ZnS:Mn nanoparticles.
Fig. 4.9 Dependence of particle size on the concentration of caping agent (merceptoethanol).

Fig. 4.10 Dependence of energy band gap on the particle size of nanoparticles.
Table 4.1 Comparison of particle size estimated by EMA formula and XRD of ZnS:Mn nanoparticles

<table>
<thead>
<tr>
<th>S.N</th>
<th>Sample</th>
<th>concentration of mercaptoethanol (mM)</th>
<th>Absorption edge (nm)</th>
<th>Effective Band Gap (eV)</th>
<th>Particle size (in nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>XRD</td>
<td>EMA</td>
</tr>
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<td>1</td>
<td>ZnS:Mn-I</td>
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<td>4.27</td>
<td>2.98</td>
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<td>2.80</td>
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<td>260</td>
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<td>2.61</td>
</tr>
<tr>
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<td>2.20</td>
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<td>ZnS:Mn-V</td>
<td>60</td>
<td>225</td>
<td>5.51</td>
<td>2.10</td>
</tr>
</tbody>
</table>

4.4 PHOTOLUMINESCENCE STUDY

Fig. 4.11 shows the PL spectra of ZnS:Mn nanoparticles. Two peaks are obtained in the PL of ZnS:Mn nanoparticles, in which the first peak shifts from 400 nm to 388 nm with decreasing size of the nanocrystals, and the second peak lies at 583 nm and it does not shift with reducing size of the nanocrystals. The photoluminescence spectra of ZnS:Mn nanoparticles with different capping agent concentrations reveals that the emission becomes more intensive with reducing size of the nanoparticles. The emission spectra related to the peak-I shift towards blue side with reducing size of nanoparticles; however, there is no such shift for the peak-II of the nanoparticles. The PL spectra of ZnS:Mn nanoparticles were measured for different concentrations of mercaptoethanol, in which the excitation wavelength was 220 nm for all the samples. The concentrations of capping agent were 0 M, 0.01M, 0.025M, 0.040 M, and 0.060 M and the concentration of Mn was kept 1.2 %. The experiment was performed at room temperature. Two peaks were found for each sample. The intensity of first peak in the PL spectra increases with increase in the concentration of capping agent i.e with the decrease in the particles size. The intensity
of second peak does not show any remarkable change. The PL emission centered at 583 nm is the characteristics emission of Mn$^{2+}$ ion which can be attributed to a $^4T_1 \rightarrow {}^6A_1$ transition. The blue emission around 400 nm is very broad and originates from the radiative recombination involving defect states in the ZnS nanocrystals.

![PL Spectra of ZnS:Mn for Different Sizes of Nanoparticles](image)

Fig. 4.11 The PL spectra of ZnS:Mn for different sizes of nanoparticles.

The dependence of PL intensities for PL peak-I and PL peak-II on the size of nanoparticles is shown in Fig. 4.12. It is seen from the figure that the intensities corresponding to both PL peak-I and PL peak-II decrease with the increasing size of nanoparticles.
Fig. 4.12 Dependence of PL intensities for PL peak-I and PL peak-II on the size of nanoparticles.

Fig. 4.13 Dependence of PL intensities for PL peak-I and PL peak-II on 1/r of nanoparticles, where r is the radius of nanoparticles.
Fig. 4.14 shows energy transfer scheme depicting different electronic transitions leading to emission in mercaptoethanol capped Mn\(^{2+}\) doped –ZnS nanoparticles. In this case, the incident light of wavelength 220 nm (5.63 eV) causes electrons to jump from valence band to the conduction band, i. e., the band-to-band transition, in which the energy released during the electron-hole recombination is transferred to Mn\(^{2+}\) centers causing the d–d excitation where in the \(^{4}T_{1} \rightarrow ^{6}A_{1}\) radiative relaxation gives rise to the orange emission at 583 nm (see Fig. 4.14 (b). In the case of mercaptoethanol-capped ZnS:Mn, as shown in Fig. 14.4 (a), the incident light of wavelength 220 nm (5.63 eV) causes electrons to jump from valence band to the conduction band, i. e., the band-to-band transition whereby some of the electrons reaching the conduction band are transferred to the nanoparticle surface states, and the subsequent transition of electrons from surface states to the valence band gives rise to the light emission of blue colour (Tamarkar et al. 2008). Some of the photons emitted from the surface states to the valence band transition may also transfer their energy directly to the Mn\(^{2+}\) centres. Thus, two different excitation paths prevail for the luminescence in mercaptoethanol capped -ZnS:Mn nanoparticles. The enhanced photoluminescence has been observed from the doped ZnS nanocrystals due to efficient energy transfer from the surface states to dopant centers in nanocrystals. The energy transfer efficiency has been found to increase with the concentration of mercaptoethanol or dopants.
4.5 MATHEMATICAL APPROACH TO THE SIZE DEPENDENCE OF PHOTOLUMINESCENCE INTENSITY OF ZnS:Mn NANOPARTICLES.

If \( r \) is the radius of nanoparticles, then the volume of nanoparticles can be expressed as

\[
V = \frac{4}{3} \pi r^3
\]

\( \text{...(4.4)} \)

The surface \( S \) of nanoparticles is given by

\[
S = 4\pi r^2
\]

\( \text{...(4.5)} \)

From Eq. (4.4) and (4.5), we get
\[
S/V = \frac{3}{r} \quad \text{....(4.6)}
\]

The blue emission around 400-388 nm, called PL peak I or PL type I, is very broad and originates from the radiative recombination involving defect states in the ZnS nanocrystals. The PL emission centered at 583 nm, called PL peak II or PL type II, is the characteristics emission of Mn\(^{2+}\) ion which can be attributed to a \(^4T_1 \rightarrow {}^6A_1\) transition. If \(\alpha\) is the absorption coefficient for the wavelength of light used for luminescence excitation and \(\Phi\), the photon flux of incident light, that is, the number of photons per unit area per second, then the rate of generation of excited charge carriers per unit surface is given by, \(\alpha\Phi\). As the rate of generation \(G_1\) of excited luminescence centres of type-I will be proportional to the product of surface to volume ratio \(3/r\) and \(\alpha\Phi\), we can write

\[
G_1 = \frac{3C_1 \alpha \Phi}{r} \quad \text{....(4.7)}
\]

where \(C_1\) is a proportionality constant.

Similarly the rate of generation \(G_2\) of excited luminescence centres of type-II can be expressed as

\[
G_2 = \frac{3C_2 \alpha \Phi}{r} \quad \text{....(4.8)}
\]

where \(C_2\) is a proportionality constant for luminescence centres of type-II.

If \(\tau_1\) is the lifetime of the excited luminescence centres of type-I, then we can write the following rate equation

\[
\frac{dn_1}{dt} = G_1 - \frac{n_1}{\tau_1}
\]

or,

\[
\frac{dn_1}{dt} = \frac{3C_1 \alpha \Phi}{r} - \beta_1 n_1 \quad \text{....(4.9)}
\]
where $\beta_1=1/\tau_1$, and $n_1$ is the number of excited luminescence centres of type-I at any time $t$.

Integrating Eq. (4.9) and taking $n=0$, at $t=0$, we get

$$n_1 = \frac{3C_1 \alpha \phi}{\beta_1 r} [1 - \exp(-\beta_1 t)] \quad \ldots (4.10)$$

Similarly the number $n_2$ of excited luminescence centres of type-II at any time $t$ can be expressed as

$$n_2 = \frac{3C_2 \alpha \phi}{\beta_2 r} [1 - \exp(-\beta_2 t)] \quad \ldots (4.11)$$

where $\beta_2=1/\tau_2$, in which $\tau_2$ is the lifetime of excited luminescence centres of type-II.

If $\eta_1$ and $\eta_2$ are the efficiencies for radiative light emission for type-I PL and type-II PL, then the PL intensities of PL peak-I and PL peak-II can be expressed by the following equations, respectively.

$$I_1 = \eta_1 \beta n_1 = 3\eta_1 C_1 \alpha \phi \frac{1}{r} [1 - \exp(-\beta_1 t)] \quad \ldots (4.12)$$

and,

$$I_2 = \eta_2 \beta n_2 = 3\eta_2 C_2 \alpha \phi \frac{1}{r} [1 - \exp(-\beta_2 t)] \quad \ldots (4.13)$$

For $\beta_1 t >> 1$, and $\beta_2 t >> 1$, saturation will occur in the PL intensities, and Eqs. (4.12) and (4.13) can be written as

$$I_{1s} = 3\eta_1 C_1 \alpha \phi \frac{1}{r} \quad \ldots (4.14)$$

and,

$$I_{2s} = 3\eta_2 C_2 \alpha \phi \frac{1}{r} \quad \ldots (4.15)$$

where $I_{1s}$ and $I_{2s}$ are the saturation values of the peak PL intensities of type-I and type-II, respectively.
It is evident from Eqs.(4.14) and (4.15) that the PL intensities $I_1$ and $I_2$ of the PL peak-I and peak-II, respectively, should depend on the surface to volume ratio as well as on the efficiencies for radiative decay $\eta_1$ and $\eta_2$, respectively.

When the light will be turned off, from Eq. (4.9) we get, $G = \frac{3C\alpha\phi}{r} = 0$. In this case, the decay of PL intensity will take place, and the decay of PL intensities for type-I and type-II PL can be respectively expressed as

$$I_{1d} = \frac{3\eta_1C_1\alpha\phi}{r}\exp[-\beta_1(t-t_c)]$$  \hspace{1cm} \cdots (4.16)

$$I_{2d} = \frac{3\eta_2C_2\alpha\phi}{r}\exp[-\beta_2(t-t_c)]$$  \hspace{1cm} \cdots (4.17)

where $t_c$ is the time at which the light used for PL excitation is turned off.

Equations (4.16) and (4.17) indicate the exponential decay of the PL intensity both for type I PL and type II PL.

It is seen from Fig. 4.13 that for larger size of nanocrystals, the relation between PL intensities $I_{1s}$ and $1/r; \mbox{ and } I_{2s}$ and $1/r$ are linear. However for small size of nanoparticles, the relation between $I_{1s}$ and $1/r; \mbox{ and } I_{2s}$ and $1/r$ are nonlinear. This result clearly shows that for small size of nanocrystals, in addition to the increase to surface to volume ratio, also $\eta_1$ and $\eta_2$ increase. Such experimental results have been obtained by Bharagva et al. for ZnS:Mn nanoparticles (Bharagava et al. 1945a,1945b). Furthermore, exponential decay of the PL intensity has also been reported (Bharagava et al. 1945a,1945b).
4.4. Conclusions

The important conclusions drawn from the present study are as given below:

(i) The nanoparticles of ZnS:Mn were grown by the chemical route in which mercaptoethanol was used as a capping agent.

(ii) From the XRD patterns, the sizes of the nanocrystals were found to be 2 nm - 3 nm. From the FEGSEM and HRTEM the average size of nanoparticles was also found to be 2 nm – 3 nm.

(iii) The size of nanoparticles decreases with increasing concentration of the capping agent, and the energy band gap increases with reducing size of the nanoparticles. This is an indication that the capping agent plays an important role in controlling the nanoparticle size.

(iv) The measurement of PL spectra of ZnS:Mn nanoparticles suggests two peaks in each sample. The blue emission around 400-388 nm, called PL peak I, is very broad and originates from the radiative recombination involving defect states in the ZnS nanocrystals. The PL emission centered at 583 nm, called PL peak II, is the characteristics emission of Mn$^{2+}$ ion which can be attributed to a $^4T_{1} \rightarrow ^6A_{1}$ transition.

(v) The intensity of first peak in the PL spectra increases with increase in the concentration of capping agent i.e with the decrease in the particles size. The intensity of second peak also increases with the reducing size of nanoparticles.

(vi) Expressions derived for the dependence of PL intensities of peak-I and peak-II on the size of nanoparticles indicate that the intensities of PL peaks should increase with the reducing size of nanoparticles; firstly due to the increase in the surface to volume ratio, and secondly, due to the increase in the efficiency of radiative decay with reducing size of nanoparticles.
(vii) The expressions derived indicate the exponential decay of the PL intensities.