APPENDIX

(A) Calculation of sample concentration:

Molecular weight of cadmium sulphate hydrate $3CdSO_4.8H_2O$ = 769.51 gm

1000 ml of 1 M of $3CdSO_4.8H_2O$ requires 769.51gm

$\therefore$ 100 ml of 0.3 M of $3CdSO_4.8H_2O = \frac{0.3 \times 769.51 \times 100}{1000}$ gm = 23.085 gm

Molecular weight of sodium sulphide flakes (Na_2S) = 78 gm

1000 ml of 1M of Na_2S requires 78 gm

$\therefore$ 100 ml of 0.3M of $Na_2S = \frac{0.3 \times 78 \times 100}{1000}$ gm = 2.340 gm

Molecular weight of zinc acetate dihydrate $Zn(CH_3COO)_2.2H_2O$ = 219.50 gm

1000 ml of 1M of $Zn(CH_3COO)_2.2H_2O$ requires 219.50 gm

$\therefore$ 100 ml of 0.3M of $Zn(CH_3COO)_2.2H_2O = \frac{0.3 \times 219.5 \times 100}{1000}$ gm = 6.585 gm

(B) Calculation of doping concentration:

General formula for Mn^{2+} doped CdS is $(Cd_{1-x}Mn_x)S$

$\therefore$ for 0.3 M, we can write as $(Cd_{0.3-x}Mn_x)S_{0.3}$

10% i.e. $(Cd_{0.27}Mn_{0.03})S_{0.3}$

$$Cd = \frac{0.27 \times 769.51 \times 100}{1000} = 20.777 \text{ gm}$$

$$Mn = \frac{0.03 \times 245.08 \times 100}{1000} = 0.735 \text{ gm}$$

(molecular weight of manganese acetate tetrahydrate $Mn(CH_3COO)_2.4H_2O$= 245.08 gm)

8% i.e. $(Cd_{0.276}Mn_{0.024})S_{0.3}$

$$Cd = \frac{0.276 \times 769.51 \times 100}{1000} = 21.238 \text{ gm}$$

$$Mn = \frac{0.024 \times 245.08 \times 100}{1000} = 0.588 \text{ gm}$$

6% i.e. $(Cd_{0.282}Mn_{0.018})S_{0.3}$

$$Cd = \frac{0.282 \times 769.51 \times 100}{1000} = 21.700 \text{ gm}$$

$$Mn = \frac{0.018 \times 245.08 \times 100}{1000} = 0.441 \text{ gm}$$

4% i.e. $(Cd_{0.288}Mn_{0.012})S_{0.3}$

$$Cd = \frac{0.288 \times 769.51 \times 100}{1000} = 22.162 \text{ gm}$$

$$Mn = \frac{0.012 \times 245.08 \times 100}{1000} = 0.294 \text{ gm}$$

2% i.e. $(Cd_{0.294}Mn_{0.006})S_{0.3}$

$$Cd = \frac{0.294 \times 769.51 \times 100}{1000} = 22.624 \text{ gm}$$

$$Mn = \frac{0.006 \times 245.08 \times 100}{1000} = 0.147 \text{ gm}$$

0% i.e. $(Cd_{0.3}Mn_{0})S_{0.3}$

$$Cd = \frac{0.3 \times 769.51 \times 100}{1000} = 23.085 \text{ gm}$$

$$S = \frac{0.3 \times 78 \times 100}{1000} = 2.340 \text{ gm}$$

(C) Determination of crystallite size by using Debye-Scherrer formula:

The crystallite size of CdS nanoparticles doped with different concentration of Mn^{2+} were calculated from the full width at half maximum (FWHM) of the most prominent diffraction peak using Debye-Scherrer formula

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

Here, D = average crystallite size

K = proportionality constant which is taken to be 0.94

λ = the wavelength of the Cu.Kα = 1.540598 Å β = Full width at half of the maximum intensity in radians

θ = the angle of diffraction.

For 0% CdS

$2\theta = 26.9325$ i.e. $\theta = 13.466$

$$\beta = \text{FWHM} \times \frac{\pi}{180}$$

$$D = \frac{0.94 \times 1.540598 \times 180}{2.5859 \times 3.142 \times \cos(13.466)} \text{ Å}$$

$$= \frac{260.6691816}{7.901530372} \text{ Å}$$

= 32.9 Å

= 3.3 nm [as 1 Å = 10^{-1} nm]

(D) Strain:

The strain in the synthesized sample is calculated by using the relation

$$\varepsilon_{hkl} = \frac{\beta\cos\theta}{4}$$

Here, $\beta = \text{FWHM} \times \frac{\pi}{180}$

$$= \frac{2.5859 \times 3.142}{180} = 0.045138321$$

$2\theta = 26.9325$ i.e. $\theta = 13.4662$

$\cos\theta = 0.972508278$

$$\therefore\ \varepsilon = \frac{0.972508278 \times 0.045138321}{4} = \frac{0.04389739}{4} = 0.01097 = 10.97 \times 10^{-3}$$

(E) Dislocation density:

Dislocation density in the sample is defined by using the relation

$$\delta = \frac{n}{D^2}$$

where *D* = crystallite size

n = minimum dislocation density and is equal to unity.

For 0% CdS, crystallite size = 3.3 nm

$$\therefore\ \delta = \frac{1}{(3.3)^2 \times 10^{-18}} \text{ m}^{-2} = \frac{1 \times 10^{18}}{10.89} \text{ m}^{-2} = 0.0918 \times 10^{18} \text{ m}^{-2} = 9.18 \times 10^{16} \text{ m}^{-2}$$

(F) Determination of energy band gap:

Energy band gap of the synthesized sample is determined by using wave-energy equation

$$E_g^{nano} = h\nu_g^{nano} = \frac{hc}{\lambda_g^{nano}}$$

where h = Planck's constant

$= 6.63 \times 10^{-34}$ J.s $= \frac{6.63 \times 10^{-34}}{1.6 \times 10^{-19}}$ eV.s [as 1 eV= 1.6 × 10^{-19} J]

$c = 3 \times 10^8$ m/s

$hc = 4.14375 \times 3 \times 10^{-15} \times 10^8$ eV.m $= 12.43125 \times 10^{-7}$ eV.m

For 0% CdS, $\lambda = 436$ nm $= 436 \times 10^{-9}$ m

$$\therefore E_g^{nano} = \frac{12.43125 \times 10^{-7}}{436 \times 10^{-9}} \text{ eV} = \frac{12.43125 \times 10^{2}}{436} = \frac{1243.125}{436} \text{ eV} = 2.85 \text{ eV}$$

(G) Determination of radius of particle size using EMA formula:

Effective mass formula is given by the relation

$$\Delta E_g = E_g^{nano} - E_g^{bulk} = \frac{h^2}{8R^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - \frac{1.8e^2}{4\pi\varepsilon_0\varepsilon R}$$

$$\Rightarrow (E_g^{nano} - E_g^{bulk})R^2 = \frac{h^2}{8}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - \frac{1.8e^2 R}{4\pi\varepsilon_0\varepsilon}$$

$$\Rightarrow (E_g^{nano} - E_g^{bulk})R^2 + \frac{1.8e^2 R}{4\pi\varepsilon_0\varepsilon} - \frac{h^2}{8}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) = 0$$

$$\therefore R = \frac{-\frac{1.8e^2 R}{4\pi\varepsilon_0\varepsilon} + \sqrt{\left(\frac{1.8e^2}{4\pi\varepsilon_0\varepsilon}\right)^2 + (E_g^{nano} - E_g^{bulk})\frac{h^2}{2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right)}}{2(E_g^{nano} - E_g^{bulk})}$$

where E_g^{nano} = energy band gap of the synthesized nanoparticle determined from UV-visible absorbance spectra = 2.85 eV (for 0% CdS)

E_g^{bulk} = energy band gap for bulk CdS =2.42 eV

h = Planck's constant = 6.63×10^{-34} J.s

m_e^* = effective mass of a conduction band electron in CdS= 1.73×10^{-31} kg

m_h^* = effective mass of a valence band hole in CdS = 7.29 × 10^{-31} kg

e = elementary charge = 1.6 × 10^{-19} J

ε = relative permittivity of CdS =5.7

ε_0 = permittivity of a vacuum = 8.854 × 10-12 C. J/m^2

$E_g^{nano} - E_g^{bulk}$ = (2.85 – 2.42) eV = 0.43 eV = 0.43 × 1.6 × 10^{-19} J = 0.688 × 10^{-19} J

$$\frac{1.8e^2}{4\pi\varepsilon_0\varepsilon} = \frac{1.8 \times (1.6 \times 10^{-19})^2}{4 \times 3.142 \times 5.7 \times 8.854 \times 10^{-12}} = \frac{4.608 \times 10^{-38}}{633.875568 \times 10^{-12}}$$

$$= 0.00726956 \times 10^{-26} = 0.726956 \times 10^{-28}$$

$$\left(\frac{1.8e^2}{4\pi\varepsilon_0\varepsilon}\right)^2 = 0.528465 \times 10^{-56} = 5.28465 \times 10^{-57}$$

$$\frac{h^2}{2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) = \frac{6.63 \times 10^{-68}}{2}\left(\frac{1}{1.73 \times 10^{-31}} + \frac{1}{7.29 \times 10^{-31}}\right)$$

$$= \frac{43.9569 \times 10^{-68}}{2}\left\{\frac{7.29 - 1.73}{(1.73 \times 7.29) \times 10^{-31}}\right\}$$

$$= \frac{43.9569}{2} \times \frac{5.56 \times 10^{-68}}{12.6117 \times 10^{-31}} = \frac{244.400364 \times 10^{-37}}{25.2234}$$

$$= \frac{244.400364 \times 10^{-37}}{25.2234} = 9.6894 \times 10^{-37}\ J^2.s^2.kg^{-1}$$

$$\therefore R = \frac{-0.726956 \times 10^{-28} + \sqrt{5.28465 \times 10^{-57} + 0.688 \times 10^{-19} \times 9.6894 \times 10^{-37}}}{2 \times (0.688 \times 10^{-19})}$$

$$= \frac{1.955351253 \times 10^{-28}}{2 \times (0.688 \times 10^{-19})} = \frac{1.955351253 \times 10^{-9}}{1.376} = 1.43 \times 10^{-9}\ m = 1.43\ nm$$

So, particle size for 0% CdS (diameter) = 2.86 nm ≈ 2.9 nm