

CHAPTER 7

GENERAL CONCLUSIONS AND AVENUES FOR FUTURE WORK

7.1. Summary of Conclusions:

This chapter contains the overall conclusion of the results obtained from PVA capped CdS:Mn and ZnS:Mn nanoparticles doped with different concentrations of Mn²⁺ (Mn= 0%, 2%, 4%, 6%, 8% and 10%) as well as the avenues for future work regarding this research study.

This thesis reports the synthesis of PVA capped CdS:Mn and ZnS:Mn with different doping concentration by adopting chemical co-precipitation method at room temperature. The results obtained on the crystal structure, particle size, surface morphology and chemical composition, absorption properties and band gap, photoluminescence properties and FTIR of these synthesized samples are discussed. The similarities and differences on the results obtained between CdS:Mn and ZnS:Mn nanoparticles are also stated.

The crystal structure and particle size of PVA capped CdS:Mn and ZnS:Mn nanoparticles with different doping concentrations are determined using X-ray diffraction (XRD) and Transmission electron microscope (TEM).

XRD studies clearly show the formation of cubic zinc blende structure for both PVA capped CdS:Mn and ZnS:Mn nanoparticles. The broadening in the diffraction peaks with different molar concentrations of Mn²⁺ suggest the presence of Mn²⁺ on the surface of CdS and ZnS host lattice. The crystallite sizes for PVA capped CdS:Mn and ZnS:Mn for the different concentrations are also estimated using Debye Scherrer formula and found to be in the range of 3.3 nm - 2.3 nm and 2.3 nm - 2.1 nm respectively.

The values of lattice constant for both CdS:Mn and ZnS:Mn with different doping concentrations have been obtained from Nelson-Riley plot and its value decreases

from the bulk value of 5.820 Å to 5.804 Å - 5.712 Å for CdS:Mn and from 5.345 Å to 5.339 Å - 5.288 Å for ZnS:Mn. Strain and dislocation densities have been calculated for the different doping concentrations which show that with the decrease in particle size, strain and dislocation density increases.

TEM results clearly show the formation of spherical shaped nanoparticles having sizes in the range of 3.95 nm - 5 nm for CdS:Mn and 3.45 nm - 4.85 nm for ZnS:Mn. HRTEM images also clearly show the formation of lattice fringes indicating the crystalline nature for both the synthesized samples. The selected area electron diffraction (SAED) pattern of the synthesized samples confirm the cubic zinc blende structure which is in good agreement with the XRD pattern of CdS:Mn and ZnS:Mn for the different doping concentrations.

The morphology of the synthesized samples is determined using Scanning electron microscope (SEM). SEM images for both the CdS:Mn and ZnS:Mn samples with different doping concentrations have shown a rough and spongy surface which is mainly due to the passivation of polyvinyl alcohol (PVA) and hence makes it difficult to estimate the particle size. The chemical composition is analyzed using Energy dispersive X-ray (EDX) spectroscopy which show the presence of strong peaks of Cd, S for the CdS:Mn nanoparticles and Zn, S for the ZnS:Mn nanoparticles but for both the samples, the Mn^{2+} peak is not observed clearly which is due to the low doping concentration.

The energy band gap of the synthesized samples is calculated from UV-vis absorption spectra and found to be higher than that of bulk CdS (512 nm \approx 2.42 eV) and ZnS (348 nm \approx 3.54 eV) which show a blue shift with respect to the bulk value. This blue shift can be attributed to quantum confinement effects in the crystal. Radii of the synthesized nanoparticles have been evaluated from the absorption spectrum by using Effective mass approximation (EMA) formula which corresponds well with the value obtained from XRD.

The room temperature PL spectra of PVA capped CdS:Mn nanoparticles doped with different concentrations of Mn^{2+} show two peaks at 533.6 nm and 609.6 nm respectively. The green emission peak is due to the excitation from S interstitial to conduction band and orange-red emission is due to the radiative recombination with a deeply trapped hole at surface state. In contrast, the PL spectra of PVA capped ZnS:Mn nanoparticles with different doping concentrations show a blue-green emission peaks at 430 nm and 501 nm for undoped ZnS. The blue emission at 430 nm is due to the transition of electrons from the shallow states near the conduction band to sulphur vacancy present near the valence band and green emission at 501 nm is assigned to elemental sulphur species on the surface of ZnS nanoparticles. The PL spectra for the different Mn^{2+} doped ZnS nanoparticles show an orange-red emission peak at 618 nm which is due to the radiative transition between 4T_1 (excited) to 6A_1 (ground) states within the $3d^5$ orbitals of Mn^{2+} . In this case, concentration quenching is observed at the Mn^{2+} doping concentration of 10% which is due to the formation of MnS and hence the luminescence density decreases.

The presence of PVA molecules on the surface of CdS:Mn and ZnS:Mn nanoparticles are observed in FTIR spectra. In the FTIR spectra for CdS nanoparticles, the sharp band at 1114 cm^{-1} is attributed to C-H bonding which is due to the presence of PVA. This may be due to the formation of co-ordinate bonding between PVA and Cd which indicates the presence of capping agent on CdS nanoparticles. Whereas the FTIR spectra for ZnS show the bands at 1561 cm^{-1} and 1423 cm^{-1} due to C-H stretching and bending bonds respectively which resulted in the co-ordinate bonding between PVA and Zn indicating capping on ZnS.

7.2. Avenues for Future Work:

The studies have been conducted only on six different doping concentrations of Mn^{2+} that is between 0% to 10%. Research can be done on a greater range of

concentrations especially above 10% to observe whether there is any change in the structural and optical properties.

It is reported in this thesis that the band gap of the materials increases with the decrease in particle size. The occurrence of blue shift is attributed to quantum confinement effect. Studies can be conducted to see the effect on the particle size and band gap by shortening the reaction time.

Nanocomposites can be formed by mixing the CdS and ZnS nanoparticles and observe the UV-visible absorption and emission spectra for technical applications such as LED, Solid state lasers and biological labelling.

By preparing pellets of the synthesized samples, research can be done to study the electrical and magnetic properties of CdS and ZnS nanoparticles.

The samples have been synthesized only at room temperature so work can also be conducted by annealing the samples from 50 °C up to 1000 °C.

Embedding CdS and ZnS nanoparticles in different matrices is another useful technique that can be carried out.

CdS and ZnS can be doped with rare earth elements and observe the luminescence properties and compared with that transition metal.