# CHAPTER-7

# Conclusions and Future Perspectives

## 7.1 Conclusions

This chapter is focused on conclusions of the research work carried out during my Ph.D thesis work. This thesis deals about the synthesis and investigations for properties like optical, structural and thermal of some II-VI type semiconductor nanomaterials. In the present course of work, nanomaterials with desirable quality of Cu (0.01M) doped $Cd_{1-x}Zn_xS$; Cu(0.01M) and Mn(0.01M) doped $Cd_{1-x}Zn_xS$; $Cd_{0.7}Zn_{0.3}S$:Cu,Mn (0.01,0.03,0.05) have been synthesized successfully by co-precipitation technique. Further, for temperature dependent investigations we have also synthesized some samples undoped $Cd_{0.7}Zn_{0.3}S$; $Cd_{0.7}Zn_{0.3}S$ at 350°C; $Cd_{0.7}Zn_{0.3}S$:Cu at 250°C; $Cd_{0.7}Zn_{0.3}S$:Cu at 350°C and $Cd_{0.7}Zn_{0.3}S$ :Cu,Mn at 350°C. This technique is very simple, cost effective and materials can be tailored up to molecular level by using this method. Moreover, these synthesized nanomaterials were also characterized by XRD, FTIR, AFM, SEM, UV-Visible, TEM, TGA-DTA and Photoluminescence methods. The overall conclusions of the thesis based on the results and their interpretations are presented below.

- ❖ Crystallite size of Cu doped $Cd_{1-x}Zn_xS$ ($0\leq x \leq 1$) nanomaterials was estimated by the Debye Scherrer's formula and its value found in the 2-12 nm range which is very small. XRD results show the crystalline nature with hexagonal crystal structure having (002) plane as the preferential orientations for all the samples. It has been concluded that lattice parameters and crystallite size changes with the change in concentration of Zn in alloy $Cd_{1-x}Zn_xS$ due to the different value of ionic-radii of $Cd^{2+}$ ion (0.97 Å) and $Zn^{2+}$ ion (0.74 Å). Further, analysis of W-H plots, indicates the presence of negative strain with the addition of Zn. The TEM results conclude the spherical shape of nanomaterials with almost uniform size distribution and agglomeration found with the increase in Zn concentration. The AFM results show almost spherical particles which also matched with the TEM results. FTIR spectra confirm the presence of COO- acetate group, water group O-H. The EDX spectrum is showing the presence of

Cd, Zn, S and Cu which confirms for composition of the prepared series and doping of Cu in the lattice of CdZnS. UV-Visible results for absorption spectra of all the samples show blue shifting in comparison to the bulk form of materials. A band gap tuning with Zn composition has been observed from 3.75 eV to 5.44 eV in Cu doped samples which again confirms the formation of CdZnS ternary alloy. Furthermore, PL results gives the broad and asymmetric emission spectra in orange-red region centered at 600 nm wavelengths which may be due to the recombination of $Cu^{2+}$ related defects states. From the results of UV-visible and PL we conclude that the emission transitions lying within the band gap. A very small value of heat energy found in exothermic and endothermic thermal properties indicates thermally stable nanomaterials. It has been concluded that formation of Cu doped $Cd_{1-x}Zn_xS$ semiconducting ternary alloy quantum dot are confirmed by results of XRD, TEM, EDX, UV-visible and PL. In the case of, Cu doped CdS (x=0) quantum dot nanomaterial has been confirmed with particle size 11.58 nm, 10 nm, 10.2 nm, and 1.33 nm by XRD, TEM, W-H and UV methods respectively. Hence all our results supported the formation of Cu doped $Cd_{1-x}Zn_xS$ alloy nanomaterials.

- With the addition of Cu,Mn in $Cd_{1-x}Zn_xS$ again show crystalline nature, hexagonal crystal structure and (002) plane is the preferential orientations. The change in color from dark yellow to pale yellow with the addition of Zn has been clearly observed. However with the addition of double dopants Cu,Mn the crystallite size decreases very much and quantum dots are formed. The formation of quantum dot has been verified by the broadening of XRD peaks. As the broadening increases the full width at half maxima (FWHM) increases and consequently the crystallite size decreases. Further, presence of Cd-S/Zn-S confirmed by the FTIR spectra at 676 $cm^{-1}$. The formation of quantum dot has also been confirmed by the TEM results. The particle size from XRD and TEM results are found in the 2-4 nm range. Here, compressive strain present in the samples due to smaller radii of $Cu^{2+}$ and $Mn^{2+}$ ions in comparison of the $Cd^{2+}$ ions. Observation of the results of TEM and AFM for $Cd_{0.1}Zn_{0.6}S$:Cu leads to the same conclusion that spherical shape of nanomaterials is confirmed. Root mean square (RMS) roughness of AFM results in case of co-doped samples was found very small in comparison to the only Cu doped samples. Effect of doping is also confirmed from the results of three dimensional AFM images. Hence, we concludes that the Cu,Mn doped $Cd_{1-x}Zn_xS$ quantum dots have smooth surface. An optimum value of band gap 3.83eV has been achieved at x=0.7 of Zn, after this, at x=0.9 there is decrement in the band gap value due to concentration quenching effect. This effect is also supported by the PL investigations by having low emission intensity in the case of $Cd_{0.7}Zn_{0.3}$:Cu,Mn. The PL spectra of co-doped $Cd_{1-x}Zn_xS$:Cu,Mn ($0 \leq x \leq 1$) show a broad green emission band at around 488 nm has been arised from the sulfur vacancy and the $t_2$ level of $Cu^{2+}$ which is embedded in the CdZnS matrix by substitute ion of the $Zn^{2+}$ ions. Further, an orange color emission also observed at 565 nm which may be due to recombination of trap states located within the band gap designated by $^4T_1$ and $^6A_1$ levels of $Mn^{2+}$ ions. Hence our PL results show the doping of both Cu,Mn ions in CdZnS.

- ❖ By the increase of dopant's concentration of Cu and Mn (0.01,0.03,0.05) in the $Cd_{0.7}Zn_{0.3}S$ nanomaterials the crystallite size decreases. The hexagonal structures with polycrystalline nature of the prepared samples are also confirmed. The EDX spectrum shows the presence of Cd, Zn, S and also Cu, Mn which confirms the composition of the prepared series and successful doping of Cu, Mn in the lattice of CdZnS. Quantum dots particle size range 4-12nm was determined by the TEM results. The SEM images of all the samples clearly indicate the formation of nanoclusters. The particles were aggregated to form clusters due to the absence of capping agent. It has been concluded from the Tauc plot that highest band gap energy at optimum concentration of Cu=0.03M was obtained and after that at Cu=0.05M the band gap energy decreases. This may be understood on the basis of concentration quenching effect. With the increase in Cu concentration more energy levels are created within the band gap and thus decrease in the band gap energy is observed. However in case of codoped samples with the concentration of Mn(0.01-0.05M) and Cu(0.01M) in $Cd_{0.7}Zn_{0.3}S$ sample, band gap continuously increases from 3.88 - 4.96 eV. Furthermore, with increase in Mn (0.05M) concentration in co-doped samples, sharp peak of PL spectra found with higher intensity in blue green region at 458 and 488 nm again attributed due to the sulfur vacancy and Zn defects states respectively. It has been concluded that emission was found blue shifted with the increase in Mn concentration. It may be concluded that single and narrow emission peaks were observed for co-doped samples $Cd_{0.7}Zn_{0.3}S$:Cu(0.01M),Mn(0.03M,0.05M) as compared to multiple peaks found in only Cu doped samples $Cd_{0.7}Zn_{0.3}S$:Cu(0.03M,0.05M). Hence PL results concludes that codoped samples with Cu(0.01M),Mn(0.03,0.05M) in $Cd_{0.7}Zn_{0.3}S$ nanomaterials are confirmed as highly luminescent materials as compared to single Cu doped.

- ❖ The X-ray diffraction pattern of as prepared, Cu doped and Cu,Mn doped $Cd_{0.7}$ $Zn_{0.3}S$ samples at 350°C show the polycrystalline nature and hexagonal structure. The broadening in Cu doped samples decreases as compared to undoped, but in Cu,Mn codoped sample at 350°C again broadening has increased and crystallite size decreases which may be due to smaller ionic radii of $Mn^{2+}$ ion (0.67 Å) than the $Cd^{2+}$ (0.97 Å) ion. Further, lattice parameters were refined by using check cell program. It has been concluded that with the increase in temperature the crystallite size increases and lattice strain and dislocation density are found to decrease because surface defects reduces with increase in temperature. TEM results indicate spherical shape of nanomaterials however agglomeration presents in all the samples. The absorption of FTIR spectra for OH group of water reduces with the increase of temperature and deepness of acetate group increases at 1533 $cm^{-1}$. FTIR spectra also show the presence of vibrational modes of sulphide ions in the nanocrystals. From the UV-visible results it is concluded that band gap decreases with doping of Cu,Mn in CdZnS at temperature 350°C. However, the blue shift in the absorption spectra has also been observed. Furthermore, our findings from the PL results indicate that PL emission increased and becomes sharp with the effect of temperature. The PL spectra of undoped $Cd_{0.7}Zn_{0.3}S$ have broad emission at 488 nm that may be attributed to the emission from the state of sulphur vacancy to the Zn defect states. Temperature dependent investigations on photoluminescence properties revealed that the codoped sample $Cd_{0.7}Zn_{0.3}S$:Cu(0.01M),Mn(0.01M) at 350°C, have smooth and symmetrical emission peak with enhanced intensity as compared to the Cu doped $Cd_{0.7}Zn_{0.3}S$:Cu(0.01M) at 350°C and undoped sample $Cd_{0.7}Zn_{0.3}S$.

- Our results conclude that the formation of quantum dots of Cu doped $Cd_{1-x}Zn_xS$ ternary semiconducting alloy is confirmed by XRD, EDX and UV-visible methods. From the results of TEM, XRD and FTIR Cu,Mn doped $Cd_{1-x}Zn_xS$ ternary semiconductor quantum dot nanomaterials are confirmed. However, in our of codoped samples T5(350°C); $Cd_{0.7}Zn_{0.3}S$:Cu(0.01M),Mn(0.01M) comparatively less strain is found than undoped samples T1 as deposited and T2 (350°C). We conclude that the blue shifting in absorption spectra and increment in the band gap energy are found in almost all the prepared samples that clearly indicates the formation of quantum dots nanomaterials. On the basis of PL results, it has been concluded that different emission peaks appeared at different wavelengths were originating due to the presence of surface and vacancy defects due to the presence of dopants Cu,Mn and Cd/Zn vacancy states. For concentration dependent investigations, luminescence intensity has inhanced for the codoped samples $Cd_{0.7}Zn_{0.3}S$:Cu(0.01M),Mn(0.03M,0.05M) as compared to the codoped sample $Cd_{0.7}Zn_{0.3}S$:Cu(0.01M),Mn(0.01M). In the case of temperature effects on codoped sample $Cd_{0.7}Zn_{0.3}S$:Cu(0.01M),Mn(0.01M) at 350°C, the PL emission peak found smooth and symmetrical with enhanced intensity as compared to the single Cu doped $Cd_{0.7}Zn_{0.3}S$:Cu(0.01M) at 350°C and undoped sample $Cd_{0.7}Zn_{0.3}S$. Hence, less defects and strain may be believed as a consequence of codoping effects with Cu,Mn and annealing at 350°C of $Cd_{0.7}Zn_{0.3}S$ sample. Overall in our thesis work, it is concluded that Cu, Mn co-doped $Cd_{1-x}Zn_xS$ ternary semiconducting alloy quantum dots are found with smaller crystallite size (2-4nm), high thermal stability, high surface smoothness, highly luminescent and more tunable emission in the blue-green region as compared to only Cu doped of same materials. Hence, these prepared codoped samples of wider band gap due to smaller size 2-4 nm quantum dots are having expected applications in the field of photovoltaic, optoelectronic and chemical sensor based devices.

## 7.2 Future Perspectives

A proper synthesis and characterization were required for future possibility in the device applications for these materials. In the light of the importance of obtained results for scientific improvement and technological development, the possibilities for future work are also suggested.

- There are many synthesis methods for the preparation of such types of nanomaterials. In future these nanomaterials may also be prepared by another methods (like sol-gel, solvothermal etc.) and also by varying the solvent medium, effect of pH value and use of proper capping agents (like PVP, Thioglycerol, Mercaptoethanol etc.) so that surface can be passivated and to investigate which particular synthesis method produces the best quality of results.
- In order to synthesize better quality of the quantum dot nanomaterials prepared under this thesis work, the atmosphere must be clean from the impurity atoms to avoid contamination. For this purpose the synthesis should be performed in inert gas or nitrogen gas environment.
- With other doping species, the band gap energy can be made more tunable and thereby the photoluminescence intensity can also be further more increased. So by using the doped ternary quantum dot nanomaterials possibility of different device fabrication may be enhanced by suitable dopants at a particular concentration and temperature.
- Instead of transition metal ions (Cu, Mn etc.), rare earth ions like La and Eu can also be doped in these binary and ternary semiconducting nanomaterial quantum dots, because some of rare earth ions like La may increase the fluorescence intensity furthermore.
- One can also investigate the other properties like electrical and magnetic of these prepared nanomaterials which may be more helpful for fabrication of electrical and magnetic devices. Further increase in the magnitude of photocurrent of Cu doped ternary CdZnS nanomaterials may be prepared for more suitable and efficient optoelectronic devices.
- One can also investigate the PL emission at other possible different exciting wavelengths of these quantum dots so that the emission in the entire visible spectrum can be tuned properly.
- In this thesis research work, we have prepared desirable quality quantum dots nanomaterials of Cu,Mn doped CdZnS successfully. By using these quantum dots there is possibility that high density information storage devices may be fabricated for different applications. For further research, we can also prepare

the quantum wires of these nanomaterials for usable data at suitable dopant's concentration, pH value and appropriate temperature which are applicable in lasers and light emitting diodes.

- Another II-VI semiconducting quantum dot and quantum wire nanomaterials like selenides (CdZnSe, ZnSe, CdSe) and tellurides (CdZnTe, CdTe, ZnTe) types can also be synthesized and characterized for the possibility of the fabrication of optoelectronic devices.