CHAPTER 5

CONCLUSION

One-dimensional nanostructures have slowly gained momentum as a dominate field of research within the nanoscience community. The focus of this work has been to gain an understanding of the underlying mechanisms controlling the morphology and one-dimensional growth. This work focused a systematic investigation of growth of one-dimensional nanostructures of ZnS having both the sphalerite and wurtzite crystal structure. We have employed a simple sol-gel via ultrasonication method for obtaining ZnS nanostructures using an organic capping agent, namely, mercaptoethanol. The study revealed that in addition to the process parameters like precursor concentration, pH, stirring etc., temperature and time played a significant role in the formation of ZnS nanostructures.

- Zinc sulfide nanostructures with different morphology, namely, cubes, rods and clusters were prepared by a simple soft chemical route via ultrasonication by varying the calcination temperature and time.

- The X-ray diffraction studies indicate that the average crystallite size was found to increase with increase in temperature and time.

- A significant change in morphology was noticed by altering the reaction parameters namely, temperature and time. This was evidenced by SEM and TEM images.
• A roughly cubical shape nanostructure was visualized for ZnS calcined at 300°C, while hexagonal rod like structures were observed for ZnS calcined at 800°C and were evidenced by both SEM and TEM images. SEM images indicated the formation of ZnS nanoclusters for samples calcined at 1000°C.

• The thermal analysis results indicate 48, 21 and 26% weight loss for nanocubes, rods and clusters, respectively.

• These results may play an important role in the evolution of ZnS nanostructures and may promote their integration into optoelectronic devices.

• Highly hexagonal-faceted ZnS nanorods have been synthesized through a simple sol-gel route via ultrasonication using mercaptoethanol as a capping agent.

• The as-obtained product was then calcined at 800°C for different time intervals to get the hexagonal shaped ZnS nanorods along with some nanograins.

• X-ray diffraction study suggests that the average crystallite size of ZnS nanorods increases from 19.2 to 33.6nm with increase in anneal time.

• SEM images exhibited the different stages for the ZnS nanorods formation.

• Both SEM, TEM images revealed the formation of nanorods while the HRTEM indicated the growth direction of ZnS nanorods along the c axis.
• A growth model was formulated for obtaining the one-dimensional nanorods.

• These nanograins along with rods rather than pure nanorods exhibited better luminescence property and may find application in optoelectronic devices, in solar cells and photonic sensors due to their green emission.

• The preferential orientation of these nanorods helps us to understand the mechanism of formation and to utilize them for the controlled junctions in electronic devices.

• ZnS nanostructures were also synthesized and calcined at different temperatures (500-1000°C) and time (1h).

• From X-ray diffraction patterns, it was found that the crystallite size of ZnS nanoparticles increases with increasing annealing temperature from 11.24-34.2 nm for the temperature range of 500-1000°C.

• The Scanning Electron Microscope images clearly show the formation of ZnS nanoclusters.

• The calcination temperature and time significantly influence the microstructure of nano ZnS.

• The activation energy for ZnS nanocrystallite growth during heat treatment was calculated to be 9.35 kJ/mol. These ZnS nanostructures are found to be promising as advanced functional materials for nanoscale devices.

• Followed by doping of Mn(II) and Ni(II) onto ZnS by sol-gel via ultrasonication, the samples were calcined at 300, 500 and
800°C. Their structural, morphological, photoluminescent and magnetic properties were studied.

- SEM images of both undoped and Mn(II) doped ZnS clearly showed the formation of nanocubes for samples treated at 300°C (1h) and nanorods for samples 800°C (5h), respectively. The nanoclusters were observed for undoped ZnS treated at 500°C (1h), while their corresponding doped counterparts indicated the formation of nanorods along with clusters.

- X-ray diffraction studies of both undoped and Mn(II) doped ZnS exhibited a cubical sphalerite structure for samples treated at 300°C (1h) and hexagonal wurtzite structure for samples treated at 500°C (1h) and 800°C (5h), respectively.

- The average diameter of the nanorods were found to vary between 30-50nm. Both TEM and HRTEM investigation shows that the as-obtained nanorods are highly crystalline.

- The undoped ZnS nanostructures exhibited an emission peak around 426nm.

- A strong orange luminescence centered at 579nm was observed for Mn(II) doped samples in addition to the weak emission peak around 426nm.

- The undoped ZnS show a typical diamagnetic behavior, while paramagnetic behavior was observed for the Mn(II) doped ZnS nanostructures.

- No ferromagnetic behavior was observed probably due to low dopant concentration and decreased defect sites.
• Thus, Mn(II) doped ZnS nanostructures with enhanced photoluminescent properties hold a good potential to be applied in future optoelectronic devices such as photoelectrochemical cells, light emitting diodes, and field effect transistors.

• X-ray diffraction data exhibited a cubic phase for both undoped and Ni(II) doped samples treated at 300°C. The SEM and TEM images also show roughly a cubical structure and are in agreement with the results obtained from the X-ray diffraction data analysis.

• TEM and HRTEM measurements have shown that the Ni(II) doped ZnS are crystalline structures, having controllable nickel concentration and are homogeneously doped with no evidence of secondary phases.

• For samples calcined at 500 and 800°C (both undoped and Ni(II) doped) the XRD data exhibited a predominant hexagonal phase. The SEM images also show the formation of nano clusters for undoped samples calcined at 500°C, while a rod-like structure was observed for Ni(II) doped ZnS nanostructures calcined at 500 and 800°C. However some amount of agglomerates was also noticed.

• PL measurements of individual Ni(II) doped ZnS nanocubes (300°C) and nanorods (800°C) show characteristic orange emission at 580 nm along with two weak emission at 425 and 530nm, respectively.

• The excitation wavelength was fixed at 325nm. The fluorescence intensity for Mn(II) and Ni(II) doped samples
treated at 300 and 800°C are found to be significantly enhanced in comparison with undoped ZnS.

- It is expected that the possible growth mechanism for the formation of ZnS nanocubes were based on Oswald ripening.

- The rod-like structures may be due to the inherent crystallographic structure of wurtzite ZnS nanostructures.

- Vibrating Sample Magnetometer (VSM) measurements confirm the diamagnetic behavior for undoped and paramagnetic behavior for all Ni(II) doped ZnS nanostructures, respectively.

- The synthesis of nano ZnS doped with magnetic metal ions opens up opportunities for fundamental studies of optical, photoluminescent and magnetic properties in transition metal doped systems and could lead to the development of nanoscale optoelectronic devices.

The goal of gaining more control and understanding over the growth of morphology tuned and one-dimensional nanostructures within this experimental setup has been achieved. By careful control over the reaction parameters, it is possible to reduce variability, increase yield, and gain insight into the more simple mechanism for controlled growth of both undoped and Mn(II) and Ni(II) doped ZnS nanomaterials.