CHAPTER 5

SUMMARY AND CONCLUSIONS

5.1 SUMMARY OF RESULTS

This Chapter consists of conclusive remarks made on the observations and the results derived there of, in the course of this study.

Possibilities for various future investigations are also pointed out in this Chapter 5. The main objectives of the present research work are to synthesis and characterize the II-VI semiconductor nanoparticles. In this work, nanoparticles of zinc sulphide, copper-doped zinc sulphide and silver-doped zinc sulphide have been synthesized and are characterized for their structural and impedance properties such as high temperature conductivity study has been carried out.

Details about the characterization and results obtained are summarized as follows

1. The samples such as ZnS, ZnS:Cu and ZnS:Ag were prepared by chemical co-precipitation method.

2. The structural characterization of all the samples has been carried out by XRD and HRTEM.

3. X-ray powder diffraction has been used to estimate the size of the crystallite and identify to the phase synthesized
4. It has been observed that all the nanoparticles prepared have crystallized into hexagonal structure in agreement with the JCPDS data.

5. SEM has been used to identify crystalline nature of the sample.

6. HRTEM patterns have been used to identify the structure and the average sizes of nanocrystallites calculated, are compared with XRD results.

7. Experimental value of interplanar distance is compared with theoretical value and they are good agreement with one another.

8. EDAX has been used to confirm the elements present in the sample.

9. Impedance Spectroscopy measurements have been carried out for three types of the nanocrystallites viz. ZnS, ZnS:Cu, and ZnS:Ag samples. Grain effect, Grain interior effects are analyzed by using impedance data.

10. Activation energies for low and high temperature regions are calculated for three types of samples by using Arrhenius plots.

11. Energy gap values are calculated for all the prepared samples from the impedance data.

12. The dielectric constant and its variation with respect to temperature and frequency for the three types of prepared samples are analyzed by using the impedance data.
5.2 CONCLUSIONS

In the present work, ZnS, Cu doped ZnS, Ag doped ZnS nanocrystallites were prepared by chemical precipitation method and have been found to have average crystallite sizes of 4 nm, 3 nm, and 8 nm, respectively. The XRD and HRTEM measurements have confirmed hexagonal structure for all the samples.

The ZnS:Cu nanocrystallites have been observed to have slightly decreased crystallite-size and it is attributed to the doping of copper (Cu), since the conditions of sample preparation are identical for both ZnS and ZnS:Cu.

Silver doped ZnS (ZnS:Ag) nanocrystallites have been found to have its average size increased considerably when compared to that of ZnS nanocrystallites. Depending upon the nature of dopant element, the volume fraction either increases or decreases. In the present case, it is found that silver doping has the effect of increasing the average particle size of ZnS, while copper doping has the effect of decreasing the average particle size of ZnS.

The effect of electrical conduction through grain interior and grain boundary regions at different temperatures were studied for ZnS, ZnS:Cu samples using the impedance spectroscopy method.

Using the impedance spectroscopy method, the effect of grain interior and electrode-electrode effect on their conductivity have been studied at various temperatures for ZnS:Ag sample. This effect appears for the property of the sample.

The presence of two distinct relaxation processes associated with both the grain interior and grain boundary regions of the nanocrystallites are identified for ZnS, ZnS:Cu samples.
For ZnS:Ag sample, one semicircular arc with a straight line and it implies that arc represents the presence of relaxation process of grain boundary and a straight line indicates that the electrode-electrode interface effect.

The impedance results have indicated that the conduction through the grain boundary regions exceeds the conduction across the regions of inter-granular contact for ZnS, ZnS:Cu samples. But for ZnS:Ag sample, the grain boundary disorders have decreased, thereby enhancing the grain-grain interaction as temperature increases.

At high temperatures, the impedance arcs describe that the conduction of grain boundary is very much greater than that of grain interior. In the high temperature region, the electrode-electrode effect is found to be larger than that of the grain interior region.

At still higher temperature, increase in activation energy is observed because of the increase in grain interface, thereby lowering the barrier height for the electrons to flow for all the nanocrystallite (ZnS, ZnS:Cu, and ZnS:Ag) samples.

The increase in conductivity with the increase in temperature implies that the defect density decreases for ZnS, ZnS:Cu, ZnS:Ag samples.

The phase transition indicated by the Arrhenius plots has been attributed to the transition from a defective phase to a more ordered crystalline phase. Hence very consistent values of activation energy for even high temperature range have been obtained for ZnS, ZnS:Cu, ZnS:Ag samples.
The dielectric constant and dielectric loss angle for the samples are found out as a function of temperature and frequency. The magnitudes of dielectric constant and dielectric loss have been compared for the ZnS, ZnS:Cu, ZnS:Ag samples and the results are reported.

The variation of dielectric constant and dielectric loss for ZnS:Cu, ZnS:Ag nanocrystallites, when compared to the values of pure ZnS nanocrystallites, is attributed to the effect of doping with noble metals in ZnS nanocrystallites.

Impedance spectroscopy method has yielded the energy gap values of 3.91 eV, 4.05 eV and 3.72 eV for the ZnS (~4 nm), ZnS:Cu (~3 nm) and ZnS:Ag (~8nm) nanocrystallites. These values are greater than the value (3.67 eV) of bulk ZnS sample and clearly conform to the quantum confinement effect of the nanoparticles.

5.3 SCOPE FOR FUTURE WORK

The present studies have brought out very well the trends of variation of size and electrical properties of ZnS when doped with metals. Hence, for a better understanding and exploring the possibilities of tailor-making the size and impedance properties for the desired applications of II-VI semiconductors, similar studies may be carried out by varying the concentration of doping, nature of dopant metals, etc. upon different host semiconductors. Following are the various activities of research work that can be carried out for the above purpose:

- The different rates of molar concentration of reactants (both host and dopant) can be used to prepare the nanocrystallites.
• In the present work, one type of capping agent (ethylene glycol) is used while preparing the samples. Various capping agents can be used in this regard and the results can be compared.

• Doping with other noble and/or rare earth metals can be carried out in ZnS and also in other II-VI semiconductors and the studies may be repeated.

• In the present work, electric and dielectric properties have been studied. However, other properties such as optical, thermal, mechanical properties, etc., may be analysed.