

A Comparative Study on the Properties Of ZnO And ZnS Nanoparticles

Panchavarnam D., Menaka S., Anitha A. and *Arulmozhi M.

Department of Physics, Jayaraj Annapackiam College for Women (Autonomous)
Periyakulam – 625 601, Theni District, Tamil Nadu, India

Abstract: ZnO and ZnS nanoparticles are synthesized by a simple precipitation method by varying the growth temperature. These nanoparticles are characterized by X-ray Diffraction (XRD), Ultraviolet-Visible Spectroscopy (UV-Vis), Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). In addition, the conductivity of the synthesized ZnO and ZnS nanoparticles are measured for different concentrations. The average particle size of the as-prepared ZnO and ZnS nanoparticles is determined by XRD in the range of 30 - 50 nm and 40 - 60 nm respectively with hexagonal form. The functional groups were confirmed by FTIR. SEM images confirm the nanocrystalline nature of the particles. The optical band gaps of ZnO and ZnS particles are calculated from the UV-Vis spectra in the range of 4.5- 4.6 eV and 5.2 - 5.4 eV respectively. The conductivity of the prepared samples increases with the growth temperature as well as the concentration. The results of the as-prepared ZnO and ZnS nanoparticles are compared with each other and with those reported in literature.

Keywords: XRD, UV-Vis, FTIR, SEM, Conductivity.

1. Introduction

Zinc oxide (ZnO) nanoparticles have much attention due to their novel optical and electronic properties for applications in various fields such as solar cells [1-3], gas sensors [4], optical devices such as LED, laser and thin film transistor and piezoelectric devices [5]. Zinc sulphide (ZnS)-based nanostructured materials are potentially important due to the large band gap. Because of the unique electronic properties, ZnS nanoparticles can be used in light-emitting diodes [6], cathode-ray tubes [7], photocatalysis [8], biosensors [9] and thin film electroluminescent displays [10]. ZnO and ZnS semiconductors have wide band gap of 3.37 eV and 3.8 eV respectively at room temperature and large exciton binding energy which leads to stable excitation even at room temperature. ZnO nanoparticles are prepared by several methods such as hydrothermal method, sol-gel method and simple precipitation method [11-13]. ZnS nanoparticles are synthesised by wet-chemical synthesis route, co-precipitation method and simple precipitation method [14-16].

In the present work, ZnO and ZnS nanoparticles are synthesized by cost effective simple precipitation method with different growth temperatures. The optical properties of the synthesized samples were investigated by Ultra Violet Visible Spectroscopy (UV-Vis) and Fourier Transform Infrared Spectrometry (FTIR). Structural properties were analysed by X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). The conductivity of the samples is measured for different concentrations.

2. Experimental Procedure

2.1 Preparation of ZnO nanoparticles

ZnO nanoparticles are synthesized by simple precipitation method. The aqueous solutions of Zinc sulphate and Sodium hydroxide are slowly added drop wise under vigorous stirring. The stirring was continued for 5 hours and precipitation is observed. The obtained precipitate is filtered and washed thoroughly with deionised water. Then the precipitate is dried in hot air oven at 100°C, 150°C and 200°C and ground to make fine powder using agate mortar.

2.2 Preparation of ZnS nanoparticles

ZnS nanoparticles are synthesized by mixing Zinc chloride and Sodium sulphide. 1:1 ratio of Sodium sulphide and Zinc chloride are separately dissolved in distilled water and stirred constantly for one hour at 100°C separately. After allowing them to cool to room temperature, Zinc chloride is added drop wise to Sodium sulphide with constant stirring. This is maintained at 100°C and stirred constantly for one hour, which resulted in formation of ZnS nanocolloid. The nanoparticles are collected by centrifugation at 2000 rpm for 15 minutes and extracted with distilled water. The precipitate is washed with distilled water and the sample is dried with different temperature such as 100°C, 150°C and 200°C. The fine ZnS nanopowder is obtained by grinding the powdered sample to its finer form.

All steps of synthesis are carried out in distilled water for its inherent advantage of being simple and environment friendly.

All the chemicals used in all the methods of synthesis are of analytical reagent grade.

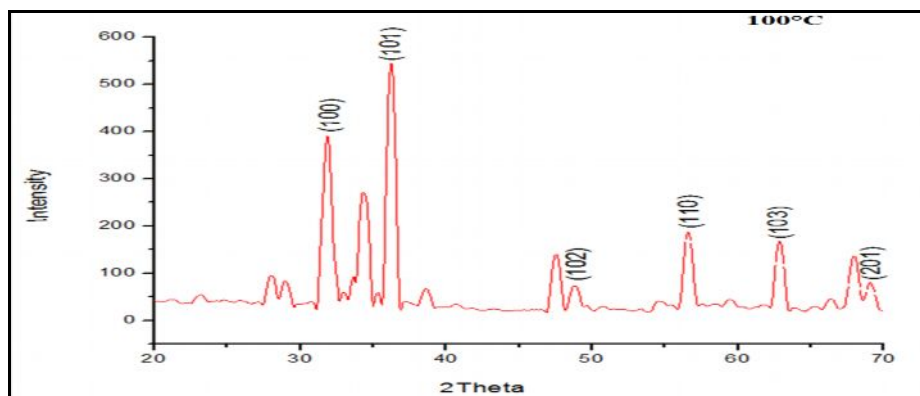
3. Results and Discussion

3.1 XRD studies

XRD patterns of the ZnO nanoparticles for various growth temperatures are shown in Fig. 1 for a 2θ range of 20°-70°. All diffraction peaks are well indexed with hexagonal structure of ZnO reported in JCPDS File Card No. 89-0510. No impurity peaks are observed which shows the high purity of ZnO. Fig. 2 displays the XRD patterns of ZnS nanoparticles which confirm the presence of pure hexagonal structure of ZnS from the JCPDS File Card No. 74-5018 for various growth temperatures. The mean grain size of the particles is calculated using the Debye-Scherrer equation,

$$D = 0.89\lambda/\beta\cos\theta \quad (1)$$

where λ is the wavelength of (Cu K_{α}) X-rays, β is the full width at half maximum (FWHM) and θ is the angle of half diffraction.



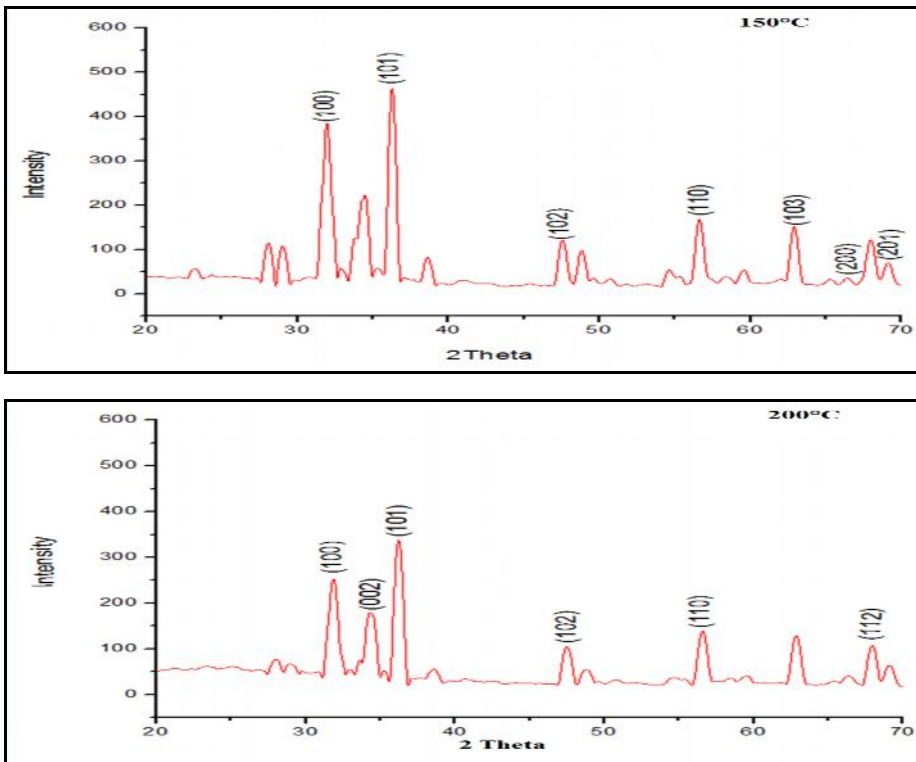
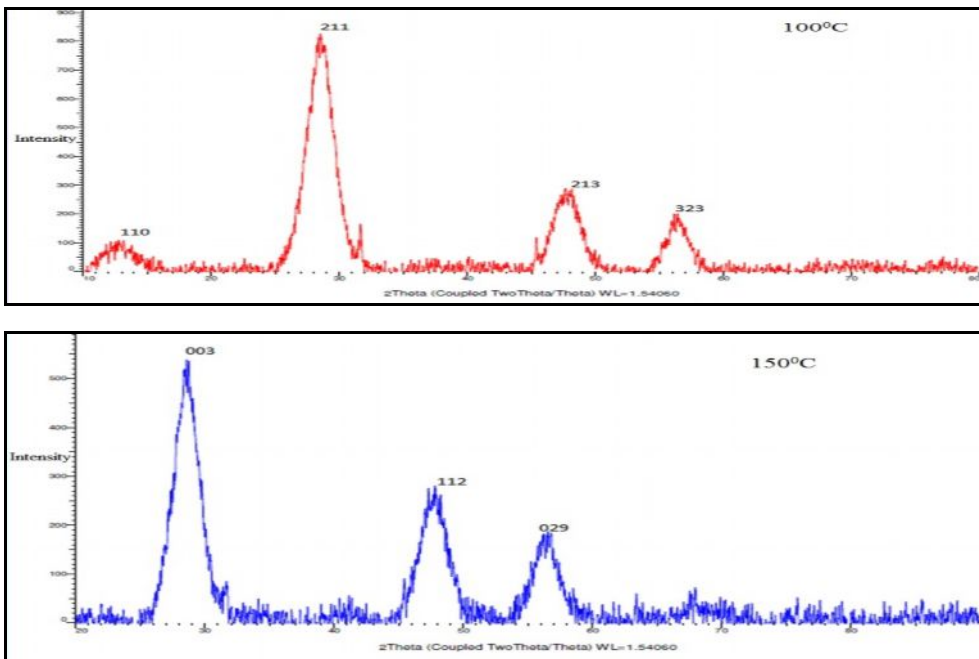


Fig. 1 XRD patterns of ZnO nanoparticles for various growth temperatures

The grain size of the ZnO nanoparticles are calculated in the range of 36 - 46 nm while ZnS nanoparticles are in the range of 49 - 56 nm. The grain size decreases when growth temperature increases for both ZnO and ZnS nanoparticles which is in contradiction to the results of Aneesh et al [11]. ZnO nanoparticles are smaller in size than the ZnS nanoparticles.



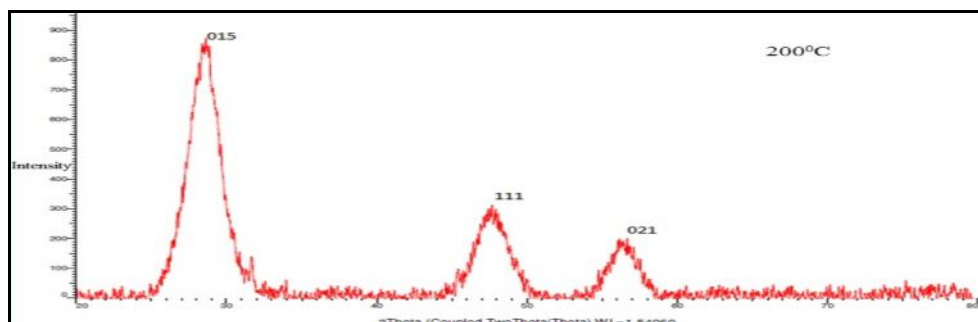


Fig. 2 XRD patterns of ZnS nanoparticles for various growth temperatures

3.2 UV-Visible absorption studies

Fig. 3 presents the UV-Visible absorption spectra of ZnS nanoparticles for various growth temperatures. The absorption peaks are observed at 344 nm, 343 nm and 342 nm for growth temperatures 100°C, 150°C and 200°C respectively. A systematic blue shift is observed in the absorption peak with the increase in the growth temperature which implies an increase in the band gap, i.e., 4.5 - 4.6 eV.

Fig. 4 exhibits the absorption spectra of ZnO nanoparticles and the absorption peaks are found at 272 nm, 274 nm and 269 nm respectively for growth temperatures 100°C, 150°C and 200°C, which are large blue shift from the bulk absorption at 315nm [15]. The optical energy gaps for the ZnO samples are calculated to be in the range 5.2 - 5.4 eV. Hence ZnO nanoparticles show larger blue shift than ZnS nanoparticles which agrees with XRD results.

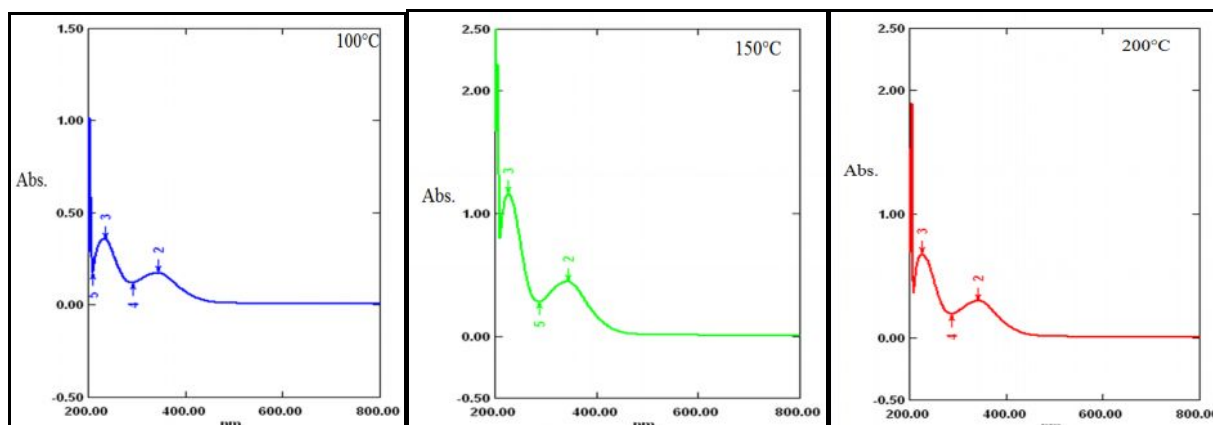


Fig. 3 UV-Visible absorption spectra of ZnS nanoparticles for various growth temperatures

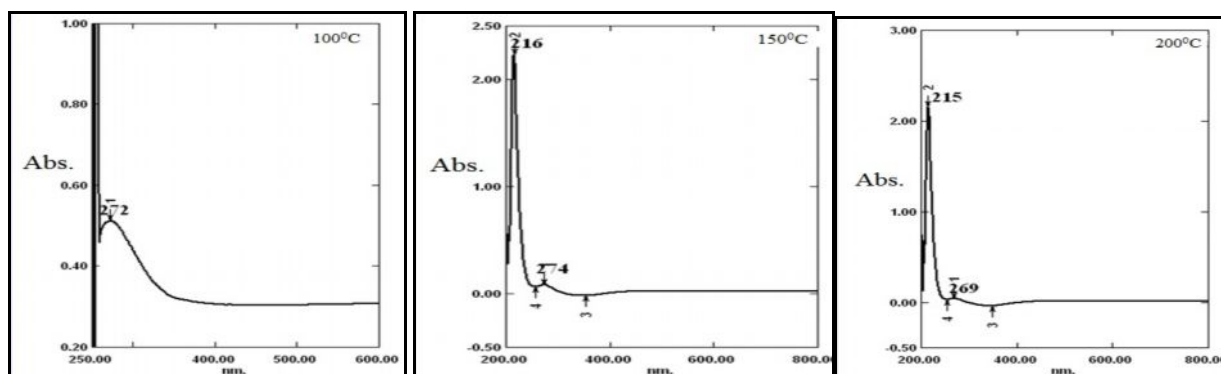


Fig. 4 UV-Visible absorption spectra of ZnO nanoparticles for various growth temperatures

3.3 FTIR studies

Fig. 5 provides the FT-IR spectra of ZnO nanoparticles for various growth temperatures. It is observed that the O-H stretching mode is represented by the absorption band at 3504.66 cm^{-1} , 3506.59 cm^{-1} and 3506.59 cm^{-1} for various growth temperatures 100°C , 150°C and 200°C respectively. Similarly C-O stretching mode is represented by 1122 cm^{-1} , 1118 cm^{-1} and 1120 cm^{-1} .

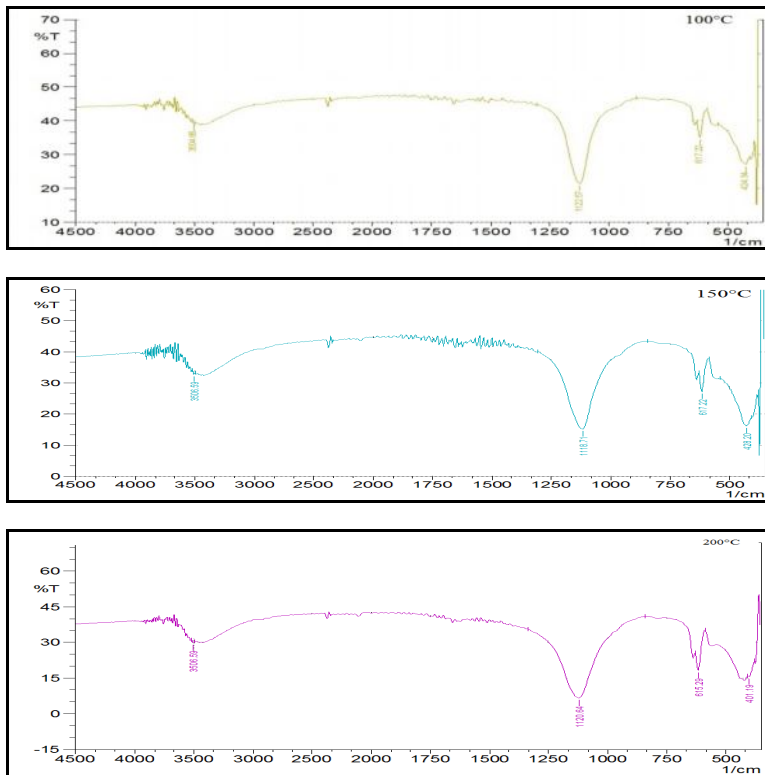
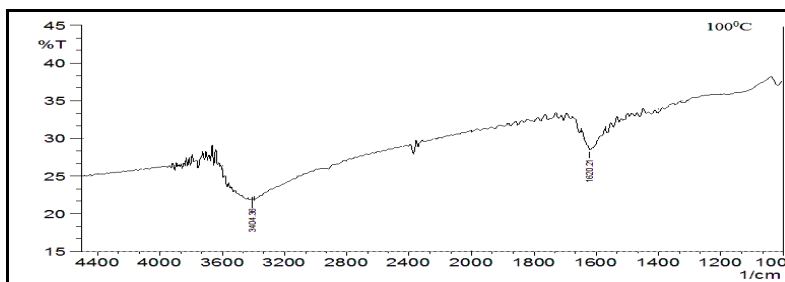


Fig. 5 FTIR Spectra of ZnO nanoparticles with various growth temperatures

The absorption bands at 617 cm^{-1} , 616 cm^{-1} and 615 cm^{-1} belong to C-Br stretching and those at 424 cm^{-1} , 428 cm^{-1} and 401 cm^{-1} for various growth temperatures 100°C , 150°C and 200°C respectively are related to Zn-O stretching.

Fig. 6 presents the FT-IR spectra of ZnS nanoparticles for various growth temperatures. It is observed that the O-H stretching mode is represented by the absorption band at 3404.36 cm^{-1} , 3408.22 cm^{-1} and 3396.64 cm^{-1} for various growth temperatures 100°C , 150°C and 200°C respectively. 1620.2 cm^{-1} , 1614.2 cm^{-1} and 1606.7 cm^{-1} absorption bands belong to O-H bending mode. Zn-S stretching is represented by absorption bands at 402 cm^{-1} , 403 cm^{-1} and 443 cm^{-1} .



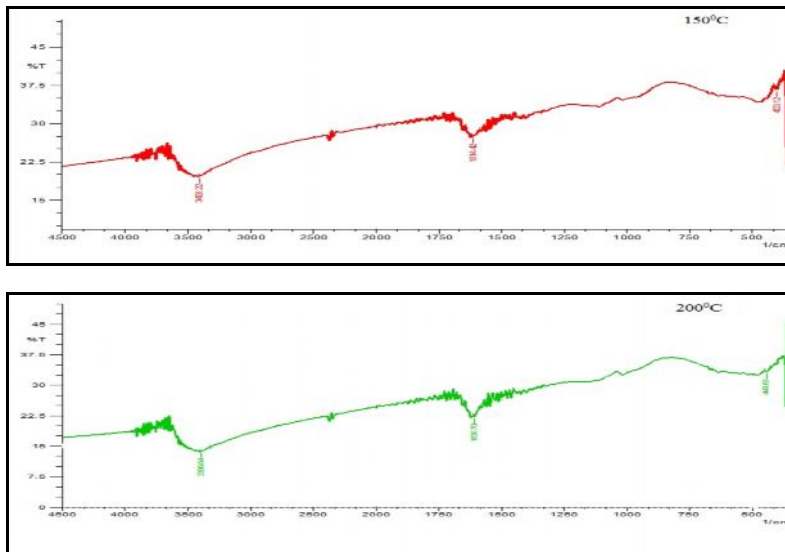


Fig. 6 FTIR Spectra of ZnS nanoparticles with various growth temperatures

3.4 SEM studies

Fig. 7 and 8 display the SEM images of ZnO and ZnS nanoparticles for various growth temperatures respectively. It can be seen from Fig. 7 that the morphology of the ZnO nanoparticles prepared at the growth temperatures 100°C and 200°C is spherical but for 150°C , it is found to be sheets. From Fig. 8, it is observed that the morphology of the ZnS nanoparticles is cluster structure for the growth temperatures 100°C and 150°C . For 200°C , the morphology of the ZnS nanoparticles is found to be the cluster of sheets.

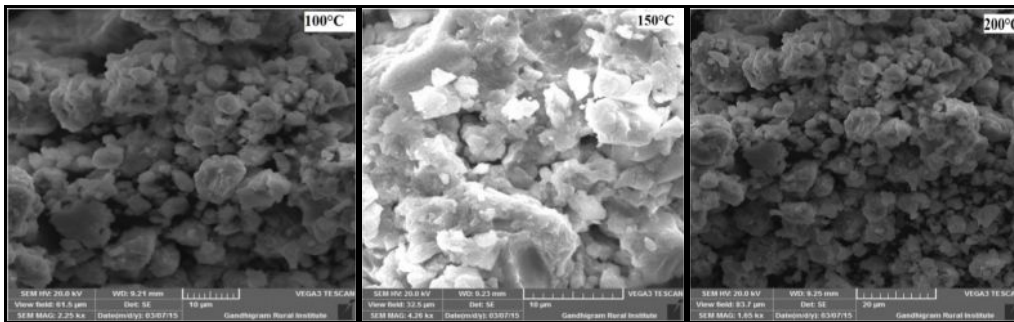


Fig. 7: SEM images of ZnO nanoparticles for various growth temperatures

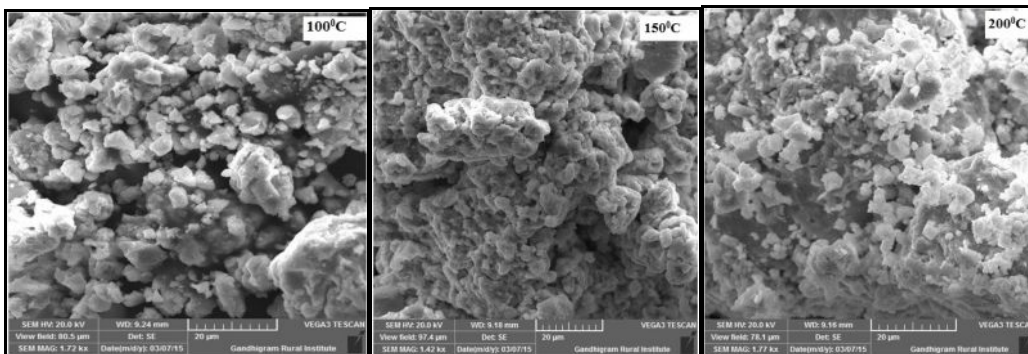


Fig. 8 SEM images of ZnS nanoparticles for various growth temperatures

3.5 Conductivity studies

ZnO and ZnS nanoparticles are dissolved in HCl at various concentrations and the conductivity is measured using a digital conductivity meter.

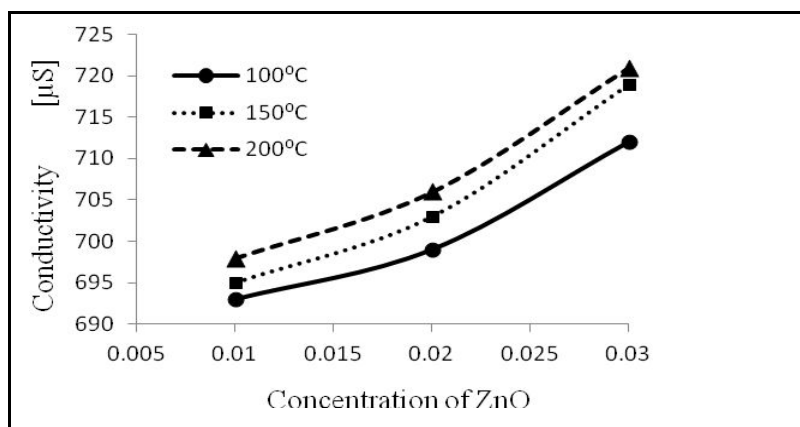


Fig. 9 Variation of conductivity of ZnO nanoparticles as a function of concentration for various growth temperatures

Fig. 9 and 10 show the variation of conductivity with the growth temperatures of ZnO and ZnS nanoparticles respectively. As expected, the conductivity increases with the growth temperature as well as concentration for both nanoparticles. Moreover, ZnO nanoparticles are found to be more conducting than ZnS nanoparticles.

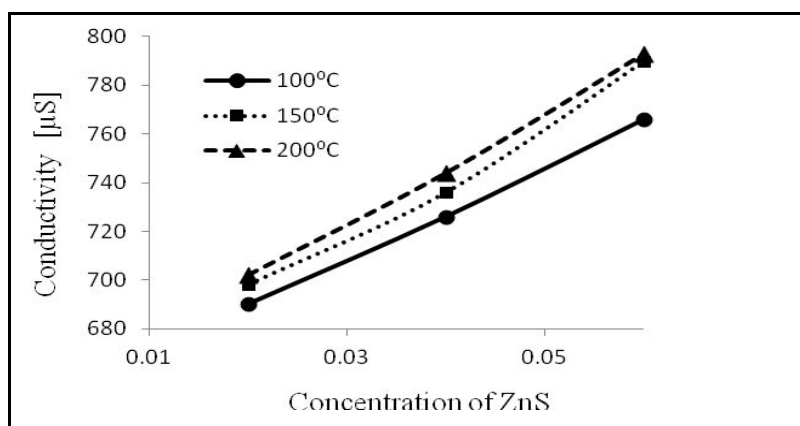


Fig. 10 Variation of conductivity of ZnS nanoparticles as a function of concentration for various growth temperatures

4. Conclusion

ZnO and ZnS nanoparticles are successfully synthesized by simple precipitation method with various growth temperatures. The XRD patterns clearly indicate that ZnO and ZnS nanoparticles prepared with various growth temperatures have hexagonal structure, but the size of the particles vary with growth temperature. The band gaps are calculated from the UV-Visible absorption spectra for each sample. The functional groups are analysed by FTIR spectra. SEM images show that the ZnO nanoparticles have the morphology of spherical for 100°C and 200°C, sheets for 150°C. The morphology of ZnS nanoparticles is cluster structure for the growth temperatures 100°C and 150°C, cluster of sheets for 200°C. The conductivity of both ZnO and ZnS nanoparticles increases with the growth temperatures as well as concentration. Comparing the characterization studies, it is found that ZnO nanoparticles are more application oriented (ie., more suitable for optoelectronic devices) than ZnS nanoparticles.

Acknowledgements

The authors thank the University Grants Commission (UGC), New Delhi, India for the financial support through Major Research Project (No. F. 42-836/2013 (SR) dated 22.03.2013) and the authorities of Jayaraj Annapackiam College for Women (Autonomous), Periyakulam, Theni District, Tamilnadu, India for the encouragements.

References

1. J. Han, F. Fan, C. Xu, S. Lin, M. Wei, X. Duan and Z. L. Wang, ZnO nanotube-based dye sensitized solar cell and its application in self-powered devices, *Nanotechnology*, 2010, 21, 405203.
2. S. Agrawal, R. Rane and S. Mukherjee, ZnO thinfilm deposition for TCO application in solar cell, 2013 doi: 10.1155/2013/718692
3. R. R. Thankalekshmi, S. Dixit and A. C. Rastogi, Doping sensitive optical scattering in zinc oxide nanostructured films for solar cells, *Adv. Mat. Lett.*, 2013, 4, 9.
4. X. L. Cheng, H. Zhao, L. H. Huo, S. Gao and J. G. Zhao, ZnO nanoparticulate thin film: preparation, characterization and gas-sensing properties, *Sens. Actuat. B Chem.*, 2004, 102, 248.
5. U. Ozgur, D. Hofstetter and H. Morko, *Proceedings of the IEEE*, ZnO devices and applications: A review of current status and future prospects, 2010, 98, 1255.
6. P. Thiagarajan, M. Kottaisamy and M. S. Ramachandra Rao, SrS:Ce/ZnS:Mn – A diband phosphor for near-UV and blue- LED converted white light emitting diodes, *J. Luminescence*, 2009, 129, 991.
7. M. Bredol and J. Merikhi, *J. Mater. Sci.*, ZnS precipitation: morphology control, 1998, 33, 471.
8. H. R. Pouretdal, A. Norozi, M. H. Keshavarz and A. Semnani, Nanoparticles of zinc sulfide doped with manganese, nickel and copper as nanophotocatalyst in the degradation of organic dyes, *J. Hazard Mater.*, 2009, 162, 674.
9. E. Mohagheghpour, M. Rabiee, F. Moztarzadeh, M. Tahriri, M. Jafarbeglou, D. Bizari and H. Eslami, Controllable synthesis, characterization and optical properties of ZnS:Mn nanoparticles as a novel biosensor, *Mater. Sci. Eng. C.*, 2009, 29, 1842.
10. K. Hirabayashi and H. Kozawaguchi, ZnS: Mn electroluminescent device prepared by metal-organic chemical vapor deposition, *Jpn. J. Appl. Phys.*, 1986, 25, 711.
11. P. M. Aneesh, K. A. Vanaja and M. K. Jayaraj, Synthesis of ZnO nanoparticles by hydrothermal method, *Proceedings of SPIE*, 2007, 6639, 66390J-1.
12. T. V. Kolekar, H. M. Yadav, S. S. Bandgar and P. Y. Deshmukh, Synthesis by sol-gel method and characterization of ZnO nanoparticles, *Indian streams of research journal*, 2011, 1, 1.
13. S. Sivakumar, P. Venkateswarlu, V. R. Rao and N. Rao, Synthesis, Characterization and optical properties of zinc oxide nanoparticles, *International Nano letters*, 2013, 3, 1.
14. A. I. Cadis, E. J. Popovici, E. Bica, I. Perhaita, L. Barbu Tudoran, E. Indrea and L. Silaghi Dumitresch, Synthesis of Manganese doped Zinc sulphide nanocrystalline powders by wet chemical synthesis route, *Digest Journal of Nanomaterials and Biostructures*, 2011, 6, 1479.
15. B. Bodo, R. Singha and S. C. Das, Structural and optical properties of chemically synthesized ZnS Nanostructures, *International Journal of Applied Physics and Mathematics*, 2012, 2, 287.
16. S. Sasi Florence and Rita John, Synthesis and structure studies of ZnS semiconducting nanoparticles, *Proceedings of ICMSRN*, 2008, 131.
