Journal of Basic and Applied Engineering Research
p-ISSN: 2350-0077; e-ISSN: 2350-0255; Volume 3, Issue 13; October-December, 2016, pp. 1210-1214

http://www.krishisanskriti.org/Publication.html

# Grain size and Luminance Variation of ZnS:Mn and ZnS:Ni Nano Materials

**Apurba Kumar Das**

*Arya Vidyapeeth Coollege, Guwahati-16*

**Abstract—***There is a wide application of undoped and doped ZnS nano-particles in optical sensors ,electroluminescence devices, digital displays etc. In low-dimensional semiconductors, like ZnS composite nano-structured thin films have valuable photoluminescence properties. ZnS nano-crystals were grown at different weight percentage using poly-vinyl alcohol by chemical route. The nano structures were studied with the help of X-ray diffraction(XRD) and Hi-resolution Transmission ElectronMicroscopy(HRTEM).*
*Scanning Electron Microscopy (SEM) was used to study the surface morphology. The particle size of ZnS, ZnS-Mn and ZnS-Ni were found to be 5 nm, 3 nm and 3.5 nm respectively. Peaks of Photo-luminescence (PL) emission and absorption spectra of undoped and doped ZnS nanoparticles confirmed the doping as well as the blue shift. Optical absorption were studied in UV-VIS Spectrophotometer and showed a strong absorbance with a tendency towards blue shift. The band gap energy varies in the range 3.76 eV to 4.72 eV corresponding to different doping percentage of ZnS-Mn and ZnS-Ni. The grain size decreases with doping*
*percentage which is one of the fundamental requirements in nanoparticles. Energy dispersive X-ray fluorescence (EDX) spectra showed presence of Zn, S, Mn & Ni. Selected area electron diffraction (SAED) showed a set of three well defined rings corresponding to planes 111, 220, 311 which matched well with the JCPDS card No. 05-0566.*

**Keywords***: XRD, TEM, HRTEM, SEM, EDX*

## 1. INTRODUCTION:

The physical and chemical properties of nano materials such as catalytic activity, optical absorbance, fluorescence, electrical and thermal conductivites etc are significantly different that from the corresponding bulk materials. The significant properties of nano particles are due extremely large surface to volume ratio compared to bulk materials. Low-dimensional semiconductors, like ZnS composite nano-structured have attracted much interest because of their valuable photoluminescence properties and therefore, synthesis and characterization of nano crystals grown with different chemicals have created interest among the researchers. Chemical growth method is a very simple, economical and efficient, method among the various researchers. In electroluminescence devices like optical sensor, digital displays, etc. doped ZnS nano materials are widely used. Photo luminescent properties of ZnS depends upon the intrinsic surface states of the particles, as well as nature of the chemicals technique employed in the fabrication ZnS nanoparticles[1]. The doped ZnS nanomaterials find the application in thin films such as light-emitting materials as well as on their optical properties. The optical light emission in blue – red spectral region is characterized by blue shift at smaller crystallite dimension [2]. The characterization of ZnS with doping agents Mn and Ni) were done with the help of instrument like X-ray Powder Diffractometer (XRD), High Resolution Transmission Electron Microscopes (HRTEM), Photo-luminescence spectrometer, UV visible spectrophotometer Scanning Electron Microscopes etc.

## 2. EXPERIMENTAL:

Polyvinyl Alcohol (PVA) as a matrix at different weight percentage of Mn and Ni as dopent. PVA and $ZnCl_2$ in deionised water were taken and stirred at 200 rpm in a magnetic stirrer at temperature $70^o$ C for 3 hours . The solution was kept overnight for complete dissolution and found to be transparent. A 2 weight % $Na_2S$ solution was added till the whole solution appears milky. The solution was kept the overnight inside a dark chamber. As soon as the nano-structure was formed, it embedded into the gap .The chemical reaction took place as follows

$ZnCl_2 + Na2S = ZnS + 2NaCl$

To make different % of ZnS : Mn solution, $MnCl_2.4H_2O$ was mixed by weight % with deionized water . Solution so obtained was mixed with a solution of PVA and $ZnCl_2$. Then the solution was stirred at 200 rpm in a magnetic stirrer at constant temperature $70^o$ C. 0.08 M weight % $Na_2S$ solution was added to the solution. Precipitation found was washed with deionized water and take for study.

To make different % of ZnS : Ni solution, $NiCl_2.6H_2O$ was mixed by weight % with deionized water . Solution so obtained was mixed with a another solution of PVA and $ZnCl_2$. Then the solution was stirred at 200 rpm in a magnetic stirred at constant temperature $70^o$ C. 0.08 M weight % $Na_2S$ solution was added to the solution. Precipitation found was washed with deionized water and taken for study.

## 3. MICROSTRUCTURE STUDIES

### XRD studies

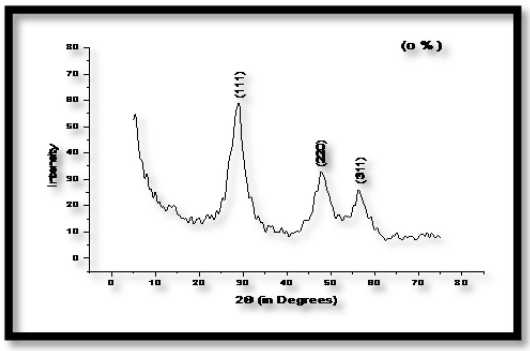



**Fig1(a). XRD of ZnS**

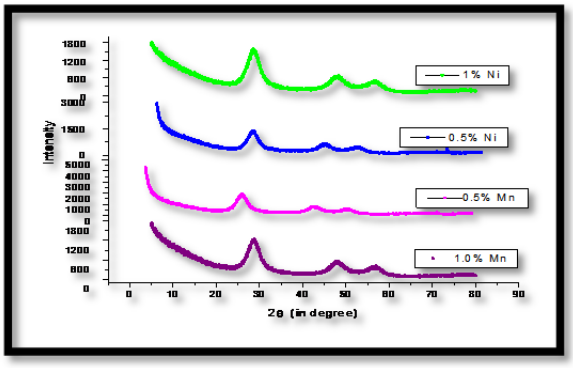



**Fig. 1(a). XRD of ZnS:Mn,and ZnS:Ni**

*Fig.1 represents the XRD of ZnS, ZnS-Mn at different weight percentage of Mn as observed from XRD.* The operating voltage and the current are 40kV and 40 mA respectively.The structural analysis of the nanoparticle was done with JCPDS-Card No-50-0566, (λ= 1.5405, Zinc blande, CuKα, system= cubic face centratded). The X ray diffractogram and 2Θ-value of ZnS and Zns:Mn were found to be well matched and confirm the Zinc cubic crystal structure. The broadening in the peaks might be due to nano size effect .Of course, the structure of ZnS remains virtually unchanged with of dopent percentages but the peaks get broadened. The broadening of the peaks is due to lesser lattice planes ( in comparision to bulk) in nanosize crystallite. This may be insufficient energy needed by an atom to move to a proper site in forming the crystallites [3,4].

$$D=\frac{0.91\lambda}{\beta_{\frac{1}{2}}\cos\theta}$$

The particle size was found to be 3.5 nm [5].

## 4. HRTEM AND ELECTRON DIFFRACTION STUDIES.

HRTEM image shows clear lattice fringes of the (001) plane indicating crystal growth along [001] direction. The particle sizes found from HRTEM image are 5 for ZnS nm and 4 nm for ZnS:Mn and 3.5 nm for ZnS:Ni respectively shown in fig.2(a,b, c). TEM images of undoped and doped Zns are shown in fig 3(a,b,c) .SAED(Selected area electron diffraction) was done with the help of HRTEM. Photo of SAED of undoped ZnS (fig.3 a,b.c) also showed a set of three well defined rings corresponding to the planes (111), (220) and (311) in case of undoped ZnS, which is also in well agreement with that of XRD data. The lattice plane distance is shown in fig 4(a,b).

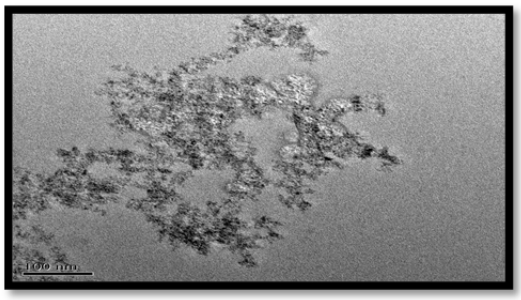



**Fig2(a). TEM of ZnS**

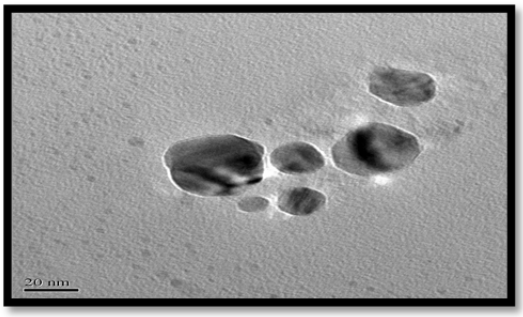



**Fig2(b). TEM of ZnS;Mn**

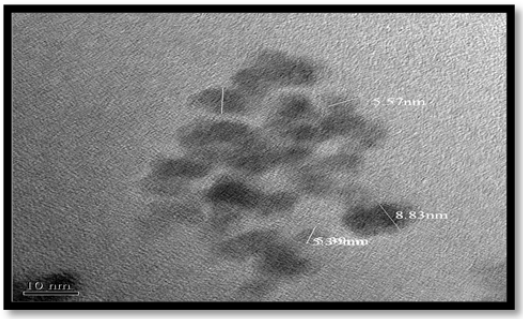



**Fig2(c). TEM of ZnS:Ni** **Fig2(c). TEMof ZnS:Ni**

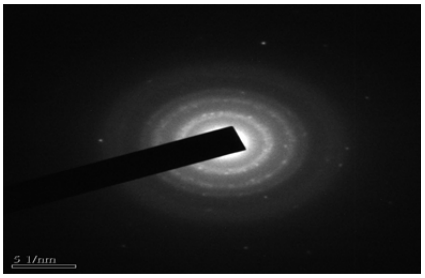


**Fig3(a). SEAD of ZnS**

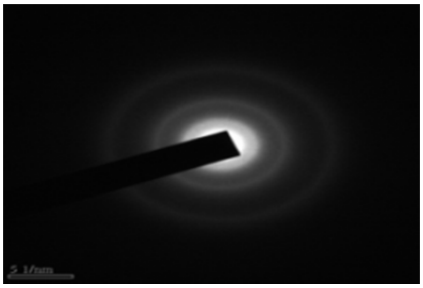


**Fig3(b). SEAD of ZnS:Mn**

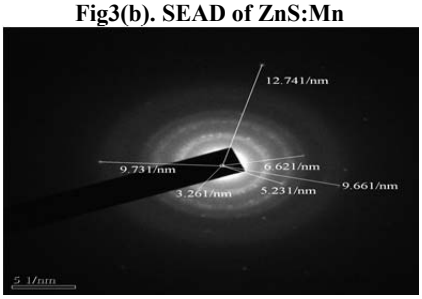



**Fig3(c). SEAD of ZnS:Ni**

## 5. SEM STUDIES

The surface morphology of the film prepared at 70°C with PVA was observed and found that all the particles formed spherical which was observed with the (JEOL, JSM-6360) SEM and the photographs are shown in fig5. Study showed surface of the film was smooth, uniform and without any crack. The particle size of ZnS:Mn , ZnS:Ni were found to be 4.5 and 6 nm respectively.

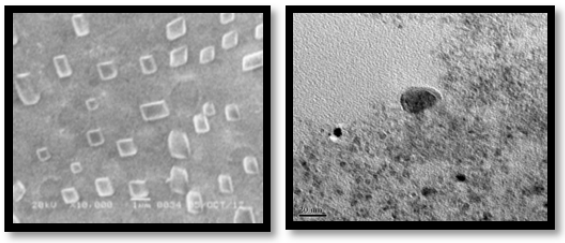


**Fig5(a) SEM of ZnS:Mn Fig5(b). SEM of ZnS:Ni**

## 6. PHOTO LUMINESCENCE STUDIES:

The photo luminescence was studied with F-2500 FL Spectrophotometer at room temperature and shown in Fig. 6. The excitation wavelength was 240 nm. Emission spectra showed a broad peak at 378 nm and another small broad peak at 451 nm for ZnS. Emission spectra of Mn showed a broad peak at 346 nm and another small broad peak at 468 nm while 375 nm and 433 nm for ZnZ-Ni and at 382 nm for ZnS-Ni. PL in this region is due to the presence of S vacancies in the lattice. PL spectra of ZnS:Mn thin film revealed yellow-orange emissions. Mn dependent yellow emission was found at 580 nm which was also a confirmation successful Mn doping. Starting with the blue emission (at 468 nm), intensity decreases towards the orange emission (at 580 nm)[7]. PL spectra of ZnS:Ni revealed yellow-orange emissions.

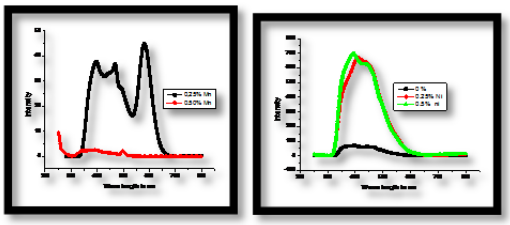


**Fig6(a)Pl of ZnS:Mn Fig6(b) Pl of ZnS:Ni**

### 7. Optical absorbance study

A Double Beam Automated ((Hitachi – U3210)Spectrophotometer was used to study the optical absorbance at room temperature and the measurement of optical absorbance was done in the range 200 – 800 nm and it is shown in fig 7. A strong absorption has been observed at 287 nm for ZnS. The peak of the absorption showed blue shift for both ZnS:Mn as well as ZnS:Ni with respect to bulk attributing quantum confinement effect in the nano- particles. Optical absorbance spectrum of ZnS:Mn and ZnS-Ni showed strong peak around 286 nm, 296 nm (ZnS:Mn) and 390 nm , 397 nm (ZnS:Ni) for 0.25% and 0.5% doping respectively. This spectra of ZnS, ZnS:Mn and ZnS:Ni nano crystal are distinguishable. This indicates that Mn and Ni doping has effect on the electronic absorption spectra of ZnS[6-8].

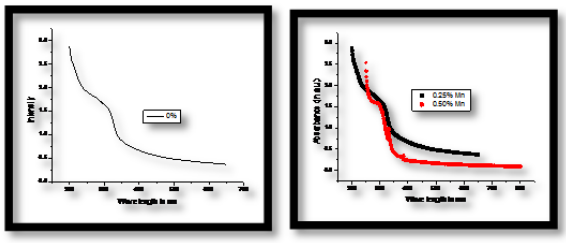


**Fig7(a) Absorbance ZnS Fig7(a) Absorbance ZnS:Mn**

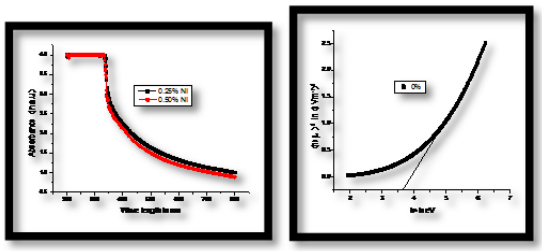
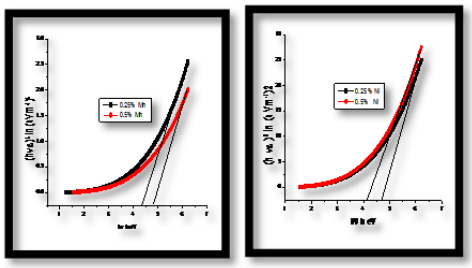


**Fig7(c) Absorbance ZnS:Ni (a)**



**(b) (c)**

**Fig. 7(a,b,c): Plots of $(h\nu\alpha)^2$ vs hν obtained from absorption spectra**

Transmittance (T) at different wave length (λ) is measured and then absorption coefficient (α) at corresponding wavelengths is calculated using Beer-Lambert's relation equation (1).

$$\alpha = \frac{1}{d}\ln\left(\frac{1}{T}\right) \quad \text{--------(1)}$$

d = path length

The relation between the incident photon energy ( hν ) and absorption coefficient ( α )is given by the following equation.(Tauc relation)

$$(\alpha h\nu)^{1/n} = B\,(h\nu - E_g) \quad \text{------ (2)}$$

B= Constant

$E_g$ = band gap of the material

For direct allowed transition n=$\frac{1}{2}$, for indirect transition n= 2 and for direct forbidden n=$\frac{3}{2}$. For calculating direct band gap value $(h\nu\alpha)^2$ Vs hν is plotted and is shown in fig.7(a, b, c). By extrapolating the straight portion of the graph on hν axis at α = 0, the optical band gap are calculated and found as 3.65 eV for ZnS, 3.66 eV, to 4.34 eV for ZnS:Mn and for ZnS:Ni the band gaps are 4.16 eV to 4.70 eV respectively for 0.25%, and 0.5% doping.The increase of band gap energies from 3.65 eV to 4.70 eV when the doping percentage increases from 0.25% to 0.50% indicate the blue shift of and ZnS:Mn and ZnS:Ni which is also an indication of quantum confinement effect due to decreasing size of nanostructure [9].

**Table:I: particle size of ZnS, ZnS:Mn, ZnS:Ni**

| Element | Doping percentage | Particle size in nm from XRD | Particle size in nm from TEM |
|---|---|---|---|
| ZnS:Mn | 0.25% | 3 | 4 |
| ZnS:Mn | 0.5% | | |
| ZnS:Ni | 0. 25% | 3.5 | 3.5 |
| ZnS:Ni | 0.5.% | | |

Table;I:Particle sizes

## 7. EDX STUDIES OF MN AND NI:

From the EDX result, the percentage of elements present is given in the table-III below. The compositional analysis of ZnS:Mn andZnS-Ni were carried out. The EDX spectra for Mn andNi doping at 0.25%, .50%, also corroborate the presence of Mn and Ni in ZnS.

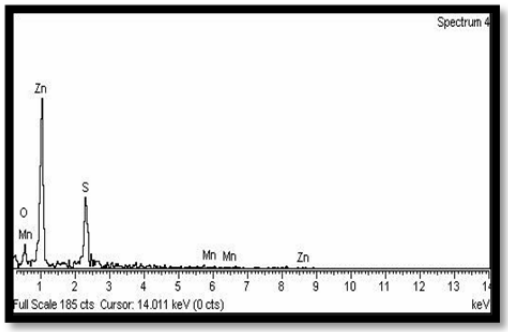



**Fig7(a)EDXof ZnS:Mn**

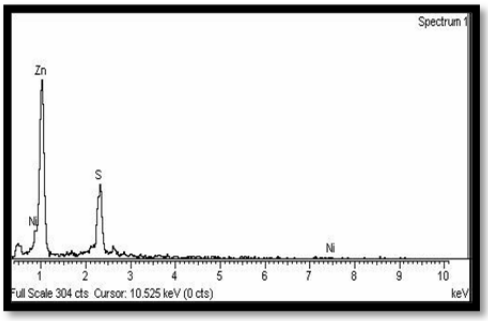



**Fig7(b) EDX of ZnS:Ni**

## 8. CONCLUSION

The structural and optical characterization of the films were done with the help of XRD, TEM, SEM, PL and UV-VIS spectrophotometer reveals formation of doped as well as un-doped nano particles. The emission bands at 377 nm, 449 nm (for 0%), the emission bands with respect to 375 nm & 451 nm for ZnS-Mn, 375 nm, 433 nm (for 0.25% Ni) and 382 nm for 0.5% Ni may be attributed due to impurities or defect state. The third emission band at 496 nm may be attributed in the 3d shell transition of $Mn^{+2}$. The peak position of the blue emission does not change with concentration, which indicates that the energy level of zinc vacancy relative to conduction band nearly remains constant. The particle size for both ZnS:Mn and ZnS:Ni are in almost equal size in the three reports(XRD, TEM,.

## 9. ACKNOWLEDGEMENT:

Authors are also like to offer their gratitude to SAIF, Guwahati, Department of Instrumentation & USIC, Gauhati University for providing XRD & XRF facility. The authors are very much thankful to Dr. P. K. Baruah, Department of Chemistry, Gauhati University for his help in taking UV-VIS and PL data. We are also thankful to SAIF, Shillong for providing TEM and SEM facility. The authors are also like to offer their heart felt gratitude and thanks to CIF and dept. of Nano- Science and Technology, IITG for providing HRTEM and XRD facility. The authors are also grateful to Prof. K. C. Sarma, Head, Dept. of Instrumentation & USIC, Gauhati University for constant guidance and help.

## REFERENCES

[1] Yang,P, Lu,M.,Xu, D., DYuan, Chang,J. G.Zhou,M.Pan, "Strong green luminescence of $Ni^{2+}$-doped ZnS nanocrystals" , Applied Physics A Materials, 74, 257-259, doi 10.1007/s003390100889

[2] Thi, T.M., Van, B.H. Ben, P.V. "Study of Microstructure and Optical Properties of PVA-Capped ZnS: Cu Nanocrystalline Thin Films"
Journal of Nonlinear Optical Physics & Materials, Vol. 19, No. 02, pp. 237-245

[3] Sanjeev Kumar,N.K.Verma, M.L.Singla, "Reflective Characteristics of Ni Doped ZnS nanoparticle-Pigment and their Coating", Chalcogenide Letters, Vol. 8, No.9 september 2011, p.561-569

[4] Singh,S.P.,. PeralesO.J.,-Perez,. Tomar, M.S,, and Mata, O.V., "Synthesis and charecterization of nanostructured Mn-doped thin films and nanoparticles", Phys.Stat.Sol.(c)1, No.4,811-814(2004) doi 10.1002/pssc.200304292

[5] Jayanthi, K.; Chawla, S.; Chander, H.; Haranath, D.,"Structural, Optical and Photoluminescence properties of ZnS:Cu nano particles thin film as a function of dopant concentration and quantum confinement effect" journal of Nonlinear Optical Physics and Materials.Vol.42,976,2007, doi 10.1002/crat.200710950

[6] MURUGADOSS,G, RAJAMANNAN,B., U. MADHUSUDHANA,U., "SYNTHESIS AND CHARACTERIZATION OF WATER-SOLUBLE
ZnS: Mn2+ NANOCRYSTALS**",** Chalcogenide Letters ,Vol. 6, No. 5, May 2009, p. 197 - 201

[7] Rema, B.S. Devi, R. Raveendran and A V Vaidyan,"Synthesis and characterization of Mn2+-doped ZnS Nanoparticles" . Pramana Indian Academy of of Sciences Vol. 68, No. 4| journal of April 2007physics pp. 679{687

[8] .Goudarzi,A,. Aval,G.M.,. Park, S.S.,. Choi,M.C., .Sahraei,R.,.HabibUllah, M.A.Avane A.,and . Ha,C.S., "Low-Temperature Growth of Nanocrystalline Mn-Doped ZnS Thin Films Prepared by Chemical Bath Deposition and Optical Properties" Chemistry of Materials, 2009, 21 (12), pp 2375–2385 doi 10.1021/cm803329w

[9]. Prabhu,R.R., Abdulkhadar,M., "Characterization of chemically synthesized CdS nanooparticles", Pramana. J. Phys, Vol.65 No 5. Nov., 2005.

[10] Qadri SB, Skelton EF, Hsu D, Dinsmore AD, Yang J, Gray HF, Ratna BR (1999) "Size-induced transition-temperature reduction in nanoparticles of ZnS". Phys Rev B 60:9191–9193

[11] Chun Lan, Kunquan Hong, Wenzhong Wang, Guanghou Wang "Synthesis of ZnS nanorods by annealing precursor ZnS nanoparticles in NaCl flux" Solid State Communications 125 (2003) 455–458