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# Impact of pH value on the Structural and Optical Studies of ZnS & ZnS-Ni Nano Materials

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***Abstract-*** The behavior of doped and undoped nano-particles find a great deal of application in opto-electronic and semi-conductor devices, so ZnS nano-crystals were grown into poly-vinyl alcohol matrix by chemical route at different wt percentage. Optical properties of both undoped and doped with ZnS nano-crystalline compounds were studied. The nano structure was characterized with the help of X-ray diffraction (XRD) and Hi- resolution Transmission Electron Microscopy (HRTEM). Surface morphology was studied with the help of Scanning Electron Microscopy (SEM). Average particle size of ZnS and ZnS-Ni were found to be obtained from XRD was about 2.28 nm. Peak of Photo-luminescence (PL) emission spectra was found at 515 nm and another peak at 495 nm corresponding to dopant 0.5 % and 1.0 % at different pH value. Energy dispersive X-ray fluorescence (EDX ) spectra showed presence of Zn, S, & Ni with 67.92, 27.50 & 4.58 weight% respectively. Optical absorption with different value of pH were studied in UV-VIS Spectrophotometer and showed a strong absorbance with a tendency towards blue shift. As the value of pH decreases more blue shift occurs the particle size decreases. As the surface states are important for optical properties, at 0.5% doping with pH=3, the particle size is 2 nm which is least leads to increase in surface to volume ratio and because of it the surface states of Ni in ZnS increases which can leads to reduce the excitonic emission. Selected area electron diffraction (SAED) showed a set of three well defined rings corresponding to planes 111, 220, 311 which tallied well with the JCPDS card No. 05-0566.

***Index Terms***- Nano-crystalline, XRD, EDX, SEM, TEM, HRTEM

## I. Introduction

The synthesis and characterization of nano crystals grown with different chemicals have generated lots of interest among the researchers. Low-dimensional semiconductors, like ZnS composite nano-structured thin films have attracted much interest because of their valuable photoluminescence properties. Chemical growth process is a very simple, economical and convenient method. In optical sensors, electroluminescence devices, digital displays, etc. doped ZnS nano materials are being used extensively. Photo luminescent properties and efficiency of ZnS depends on intrinsic surface states of the particles, and nature of the chemicals treatment employed in their fabrication. Research is also noticed on the application of these types of films in light-emitting materials as well as on their optical properties[1,2]. The optical light emission in blue – red spectral region is characterized by blue shift at smaller crystallite dimension. We are trying to characterize the properties of ZnS with different percentage of doping agent (Ni) at different pH value with the help of instrument like X-ray Powder Diffractometer (XRD), Scanning Electron Microscopes (SEM), High Resolution Transmission Electron Microscopes (HRTEM), Photo-luminescence spectrometer (PL), UV visible spectrophotometer (UV-VIS), etc.

## II. Experimental

Polyvinyl Alcohol (PVA) was used as a matrix in synthesizing ZnS nano-particles. Different weight percentage solutions of PVA and $ZnCl_2$ were taken in deionized water 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 percentage $Na_2S$ solution was added till the whole solution appears milky. The solution was kept over night inside a dark chamber. As soon as the nano-structure was formed, it embedded into the gap . The chemical reaction between $ZnCl_2$ and $Na_2S$, the product were ZnS, 2NaCl. To prepare different percentage of ZnS : Ni solution, $NiCl_2.6H_2O$ was mixed by weight percentage 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 percentage of $Na_2S$ solution was added to the solution. Precipitation found was washed with deionized water and taken for study.

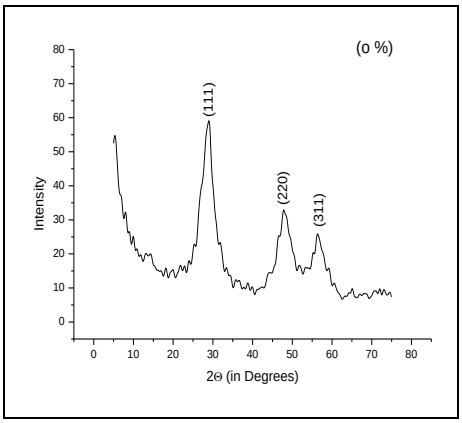


**Fig.1a:X-ray diffractogram of ZnS**

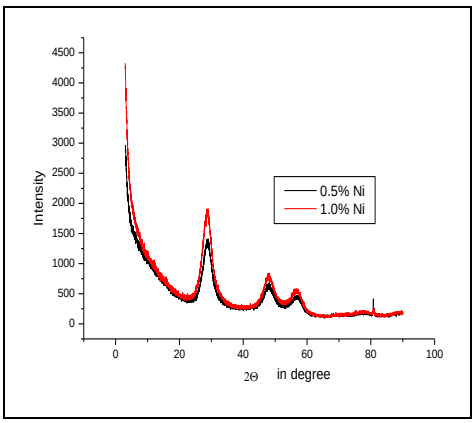


**Fig.1b:X-ray diffractogram of ZnS-Ni**

**XRD studies**.

The XRD studies were obtained from powder pattern scanned in Philips X'pert Pro Powder diffractometer using Cu-K radiation with the operating voltage 40 kV and current 20 mA. The intensity peaks at different percentage of of doping are almost same although the heights are different which indicate that Ni is corporate with size of the particle. The pattern observed was found to be within the nano range[3,4]. XRD patterns revealed the films to be polycrystalline [5]. Planes (111), (220) and (311) were found to be present which satisfied well with the JCPDS card No. 05-0566. The average particle size corresponding to the FWHM was calculated with the Scherrer formulae.

$$Dp = \frac{0.94\lambda}{\beta_{1/2}\cos\theta}$$

and found to be 2.28 nm[6,7].

**Photo luminescence studies:**

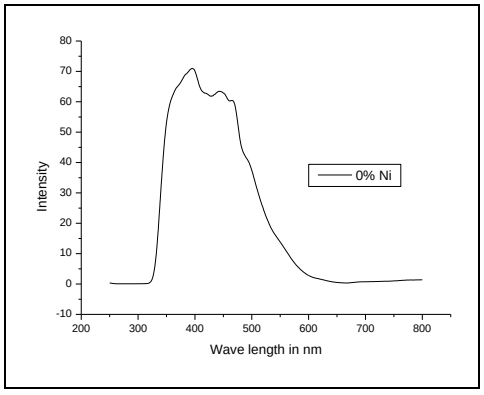


**Fig.2a: PL spectra of ZnS**

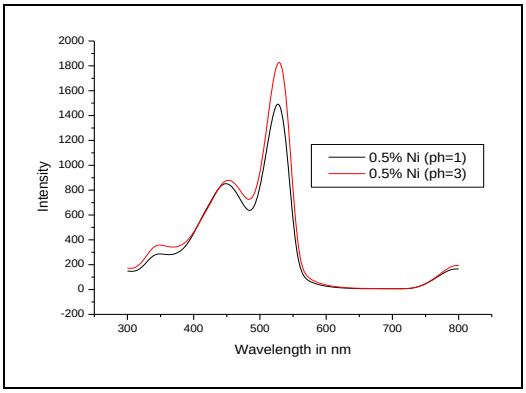


**Fig.2b: PL spectra of ZnS-Ni with ph=1,3**

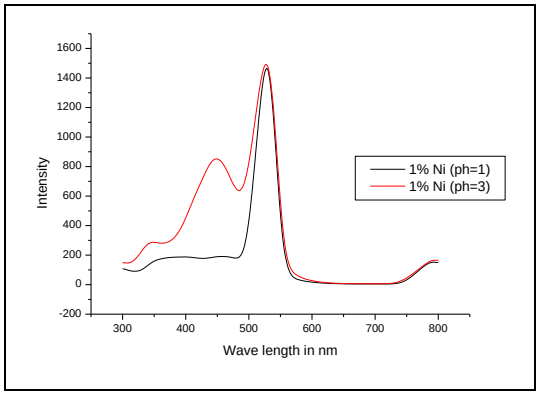


**Fig.2c: PL spectra of ZnS-Ni with pH=1,3**

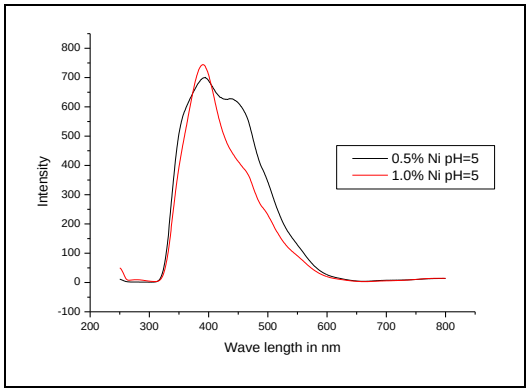


**Fig.2a: PL spectra of ZnS-Ni with pH=5**

The photo luminescence studies of nano crystalline undoped ZnS & doped ZnS-Ni were done at room temperature by using F-2500 FL Spectrophotometer and the Pl graphs are shown in fig 2 (a, b, c, d ). In all the measurement the excitation wavelength was 240 nm . For 0% doping the three Pl peaks wereat 398 nm, 440 nm. 469 nm. Photo-luminescence peak for 0.5% doping were observed at 515 nm, 525 nm, 556 nm both for pH value at 1 and 3 shown in Fig 2b while that for 1% doping the peaks were at 495 nm, 523 nm, 544 nm at pH value 1 and 3 shown in fig2c. When pH=5, the Pl peaks for 0.5% doping were at 391 nm, 448 nm while for 1% doping the peak is at 394 nm. The intensity decreases with increase of concentration ( from 0.5% to 1% ) for both values of pH 1 and 3 and this is because of non-irradiative recombination. Localized electronic states occurs because of incorporation of Ni ZnS and the band-gap that comes from the 3d shell of Ni in ZnS [8]. In case of 1% doping (pH=1), there is only one peak at 544 nm and for pH=5 there is one peak at 394 nm and this is because of the impact of pH on the sample.

**Optical absorbance study:**

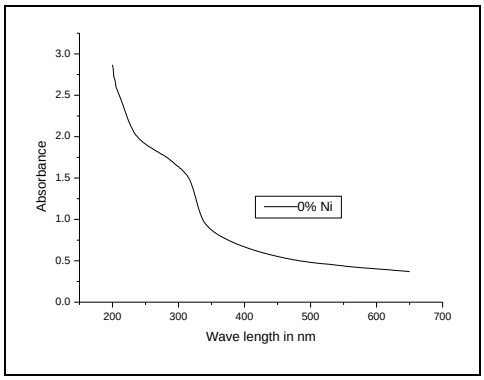


**Fig3a: Absorbance graph of ZnS**

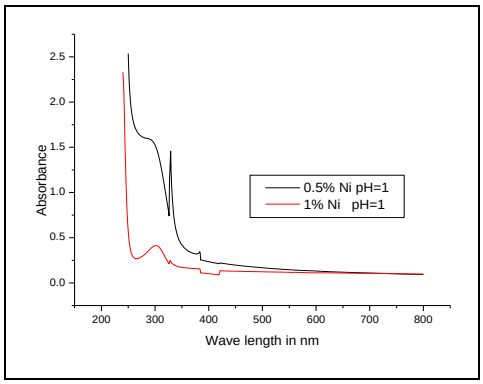


**Fig3b: Absorbance graph of ZnS-Ni, pH=1**

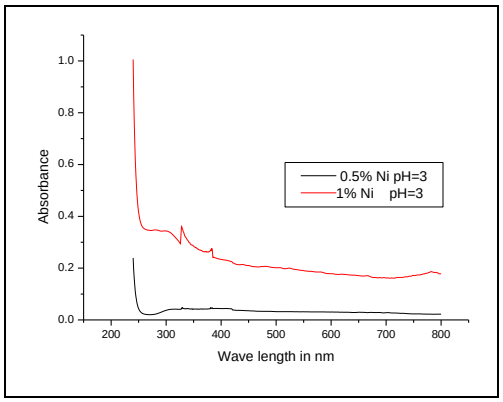


**Fig3c: Absorbance graph of ZnS-Ni, ph=3**

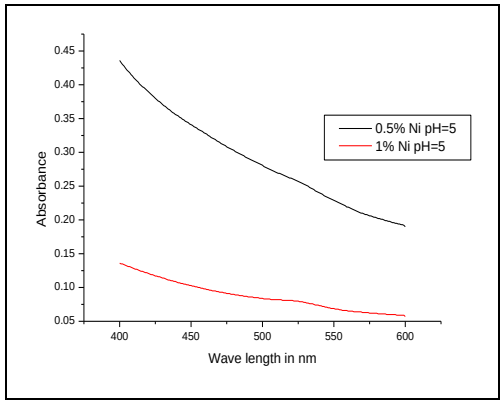


**Fig3d: Absorbance graph of ZnS-Ni, pH=5**

Optical absorption studies were carried out with UV-VIS in a Double Beam Automated spectrophotometer (Hitachi – U3210) and showed absorbance at wavelength 357 nm and 337 nm respectively when doping percentage are 0.5% and 1.0% with pH=1. For pH = 3, the absorbance of 0.5% and 1.0% doping are at 323 nm and 390 nm respectively. Again for pH = 5, the absorbance of 0.5% and 1.0% doping are respectively at 543 nm and 541 nm. For 0% doping the band gap energy in 3.49 eV. This spectra of undoped and Ni doped ZnS nano crystal are distinguishable. This indicates that Ni doping has effect on the electronic absorption spectra of ZnS[9,10]. The spectra showed a blue shift due to quantum confinement of the excitons present in ZnS-Ni for which more discrete energy spectrum of individual particles exist. As the value of pH decreases more blue shift occurs ( pH value from 5 to 1) the particle size decreases. As the surface states are important for optical properties, at 0.5% doping with pH=3, the particle size is 2 nm which is least leads to increase in surface to volume ratio and because of it the surface states of Ni in ZnS increases which can leads to reduce the excitonic emission[11,12]. The blue shift energy is maximum for pH=5, which is due to the fact that Ni is forming new energy levels in ZnS energy band.

| pH | Doping percentage | Band gap energy in eV | Blue shift energy in eV | Particle size in nm from TEM |
|---|---|---|---|---|
| 1 | 0.5% | 3.48 | 0.01 | 4.4 |
| 1 | 1.0% | 3.69 | 0.20 | 7.97 |
| 3 | 0.5% | 3.85 | 0.36 | 2.0 |
| 3 | 1.0% | 3.19 | 0.30 | 5.3 |
| 5 | 0.5% | 2.30 | 1.19 | 8.83 |
| 5 | 1% | 2.29 | 1.20 | 11.0 |

***Table: I: Variation of particle size with pH***

**SEM studies:**

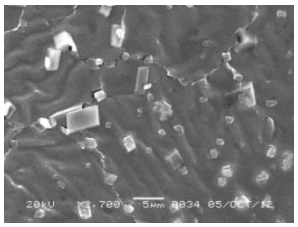

**Fig 4a: SEM photo of ZnS**

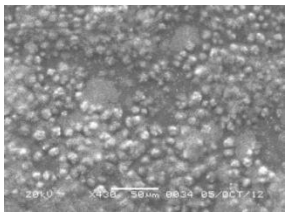

**Fig. 4b: SEM photo of ZnS-Ni**

Photographs of the nano-crystalline thin film were taken with (JEOL, JSM-6360) SEM and shown in Fig. 4. The surface morphology of the film prepared at 70$^{o}$C with PVA was observed and found that all the particles thus formed not exactly spherical. Study showed surface of the film was smooth, uniform and without any crack. Average particle size of ZnS and ZnS-Ni were found to be 5 and 21nm respectively. The SEM studies showed the well crystalline structure of ZnS nano particles.

**HRTEM:**

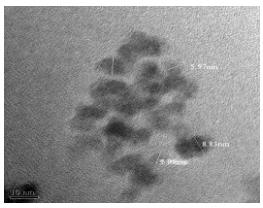

**Fig.5a: ZnS ,**

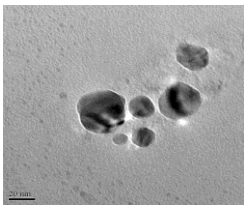

**Fig.5b: ZnS-Ni**

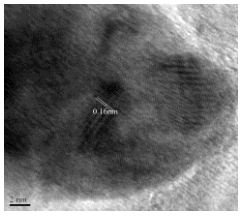

**Fig.5c: Lattice distance of ZnS-Ni**

HRTEM image showed in fig 5, give clear lattice fringes of the (001) plane indicating crystal growth along [001] direction. The particle size obtained from HRTEM image was 5 -11 nm. The lattice distances for the planes (111) and (311) were found to be 0-32 nm and 0.16 nm respectively obtained from TEM studies which well satisfied with those values 0.31098 nm and 0.1625 nm obtained from XRD data.

**Electron diffraction studies:**

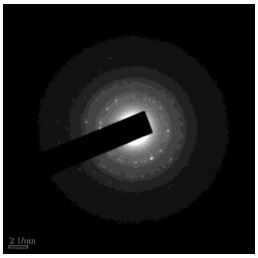

**Fig.6a: SAED image of ZnS**

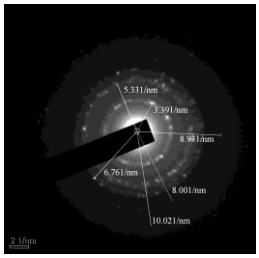


**Fig.6b: SAED image of ZnS-Ni**

Selected area electron diffraction (SAED) was done with the help of HRTEM. Photos of SAED of undoped ZnS [fig.6a and 6b] 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 good agreement with that of XRD data.

**EDX Studies:**

| Element | Weight% | Atomic% |
|---|---|---|
| SK | 27.50 | 43.44 |
| NiL | 4.58 | 3.95 |
| ZnL | 67.92 | 52.62 |
| Total | 100.00 | |

***Table: II Weight percentage of elements from EDX***

Table II shows the composition of ZnS-Ni particles with the help of Energy Dispersive X-ray Spectroscopy (EDX). Energy dispersive X-ray fluorescence (EDX ) spectra showed presence of Zn, S, & Ni with 67.92, 27.50 & 4.58 weight% respectively.

## III. Conclusion

ZnS nano crystalline materials ( un-doped and doped with Ni) had been synthesized by chemical route. The structural and optical characterization of the nano particles were done with the help of XRD, TEM, SEM, SAED, UV-VIS spectrophotometer. PL spectra revealed formation of doped as well as un-doped nano particles. EDX study reveals the presence of Zn, S and Ni in nano materials. As the value of pH decreases more blue shift occurs ( pH value from 5 to 1) and the particle size decreases. Since the surface states are very important for optical properties, at 0.5% doping with pH=3, the particle size is 2 nm which is least leads to increase in surface to volume ratio and because of it the surface states of Ni in ZnSincreases which can leads to reduce the excitonic emission.

## Novelty Statement

It is observed that as the value of pH decreases more blue shift occurs ( pH value from 5 to 1) and the particle size decreases. As the surface states are important for optical properties, at 0.5% doping with pH=3, the particle size is 2 nm which is least leads to increase in surface to volume ratio and because of it the surface states of Ni in ZnS increases which can leads to reduce the excitonic emission.

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