

An Analysis of Structural and Optical Properties Undoped ZnS and Doped (with Mn, Ni) ZnS Nano Particles

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ABSTRACT

The behavior of nano-particles finds a wide application in opto-electronic and semi-conductor devices. ZnS nano-crystals were grown into poly-vinyl alcohol matrix by chemical route at different weight percentage. Optical properties of both un-doped 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). The average particle sizes of ZnS, ZnS-Ni and ZnS-Mn were found to be 6.51, 7.3 and 12 nm respectively in TEM and that obtained from Debye-Scherrer formula is about 2.3 and 2.5 nm for undoped and doped ZnS respectively. Peak of Photo-luminescence (PL) emission spectra was obtained at 375 nm at room temperature and another peak at 433 nm for Ni. Again the peak of Photo-luminescence (PL) emission spectra was obtained at 334 nm at room temperature for Mn, Mn dependant emission was found at 580 nm. These data showed successful doping. PL studies also confirmed presence of dopant in the nano crystallites. Optical absorption studies were carried out with UV-VIS Spectrophotometer and showed a strong absorbance at wavelength 400 nm with a tendency towards blue shift. Selected area electron diffraction (SAED) shows a set of four well defined rings corresponding to diffraction from different planes of the nano crystallites. HRTEM image showed a well crystalline ZnS doped with Ni and Mn. Both Raman spectra and XRD studies confirmed the well crystalline states of ZnS.

Keywords: Nano-Particle; PVA; XRD; SEM; TEM; HRTEM; SAED

1. Introduction

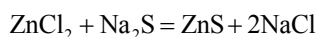
The physical and chemical properties of nano materials like optical absorbance, fluorescence, catalytic activity, electrical and thermal conductivity etc. are significantly different from the corresponding bulk materials. The special properties of nano particles are due quantum size confinement in nano structure and extremely large surface to volume ratio relative to bulk materials and therefore it is possible to keep high percentage of atoms or molecules in lower reactive boundaries.

The synthesis and characterization of nano crystals grown with different chemicals have created interest among the researchers. Low-dimensional semiconductors, like ZnS composite nano-structured have attracted much interest because of their valuable photoluminescence properties [1]. Chemical growth process is a very simple,

economical, efficient, and convenient method among the various researchers. In optical sensors, electroluminescence devices, digital displays, etc. doped ZnS nano materials are being used extensively. Photo luminescent properties and efficiency of ZnS depend 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 [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 doping agents (Ni and Mn) 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.

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Experimental The synthesis of ZnS nano-particles were done by using Polyvinyl Alcohol (PVA) as a matrix. Different weight% solutions of PVA and ZnCl₂ in deionized water were taken and stirred at 200 rpm in a magnetic stirrer at temperature 70°C for 3 hours. The solution was kept overnight for complete dissolution and found to be transparent. A 2 weight% Na₂S solution was added till the whole solution appears milky. The solution was kept overnight inside a dark chamber. As soon as the nano-structure formed, it embedded into the gap. The chemical reaction took place as follows



To make different % of ZnS:Ni solution, NiCl₂·6H₂O was mixed by weight% with deionized water. Solution so obtained was mixed with another solution of PVA and ZnCl₂. Then the solution was stirred at 200 rpm in a magnetic stirrer at constant temperature 70°C. 0.08 M weight% Na₂S solution was added to the solution. Precipitation found was washed with deionized water and taken for study.

To make different % of ZnS:Mn solution, MnCl₂·4H₂O was mixed by weight% with deionized water. Solution so obtained was mixed with another solution of PVA and ZnCl₂. Then the solution was stirred at 200 rpm in a magnetic stirrer at constant temperature 70°C. 0.08 M weight% Na₂S solution was added to the solution. Precipitation found was washed with deionized water and taken for study.

2. Microstructure Studies

2.1. XRD Studies

The XRD studies shown in **Figures 1(a)** and **(b)** were obtained from powder. Diffraction pattern was obtained from a Philips X'pert Pro Powder diffractometer using Cu K α radiation with the operating voltage 40 kV and current 20 mA. 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 present which tallied well with the JCPDS card No. 05-0566. The average particle size corresponding to the FWHM was calculated with the Scherrer formulae

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

and found to be 2.3 nm [6].

2.2. Electron Diffraction Studies

Selected area electron diffraction (SAED) was done with the help of HRTEM. Photo of SAED of undoped ZnS (**Figures 2(a)-(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 good agree-

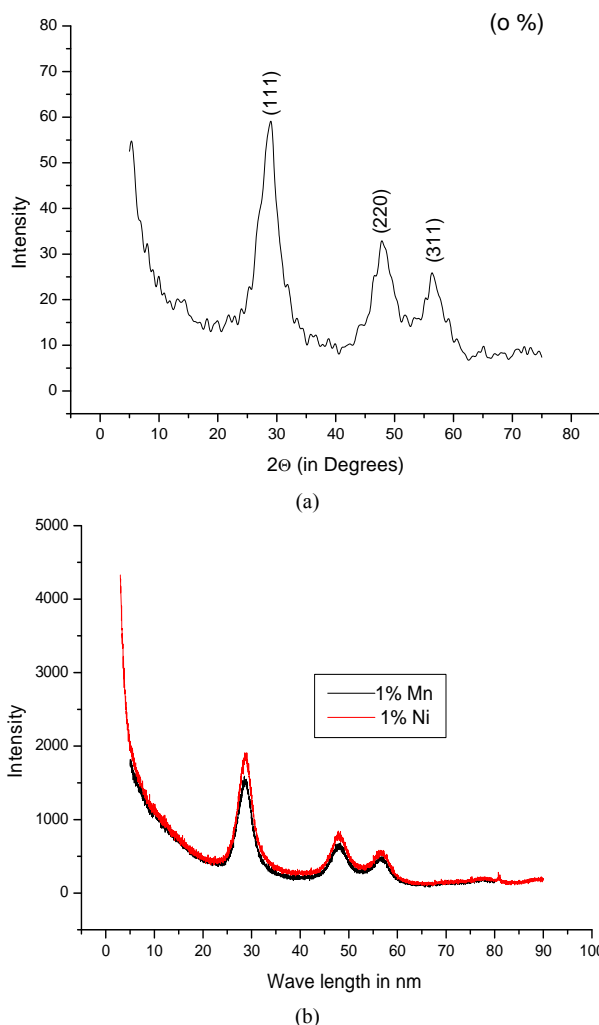


Figure 1. (a) XRD diffractogram of ZnS; (b) XRD diffractogram of ZnS-Mn.

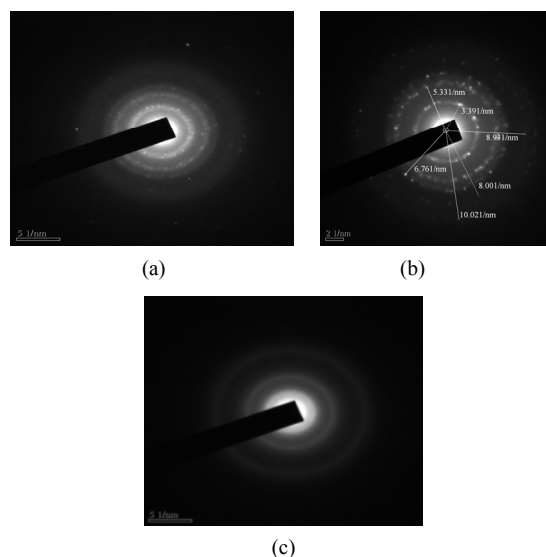


Figure 2. (a) SAED of ZnS; (b) SAED of ZnS-Ni; (c) SAED of ZnS-Mn.

ment with that of XRD data.

2.3. SEM Studies

Photographs of the nano-crystalline thin film were taken with (JEOL, JSM-6360) SEM and shown in **Figure 3**. The surface morphology of the film prepared at 70°C with PVA was observed and found that all the particles formed not exactly spherical. Study showed that the surface of the film was smooth, uniform and without any crack. The particle sizes of ZnS-Ni, ZnS-Mn were found to be 7 - 16 and 7 - 15 nm respectively.

2.4. Photo Luminescence Studies

The photo luminescence studies of nano crystalline doped & un-doped (**Figure 4**) were done at room temperature by using F-2500 FL Spectrophotometer. In all the measurement 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 while 375 nm and 433 nm for ZnZ-Ni (0.5%) and at 382 nm for ZnS-Ni. For Mn the emission spectra showed a broad peak at 346 nm and another small broad peak at 468 nm. 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.

2.5. Optical Absorbance Study

The optical absorbance (**Figure 5**) of ZnS was recorded at room temperature using a Double Beam Automated Spectrophotometer (Hitachi-U3210) where the measurement of optical absorbance was done in the range 200 - 800 nm. The wavelength showed strong absorption. The peak of the absorption showed at 287 nm for ZnS. The peak of the absorption showed blue shift with respect to bulk attributing quantum confinement effect on the nano-particles. Optical absorption studies were carried out with UV-VIS Spectrophotometer and showed a

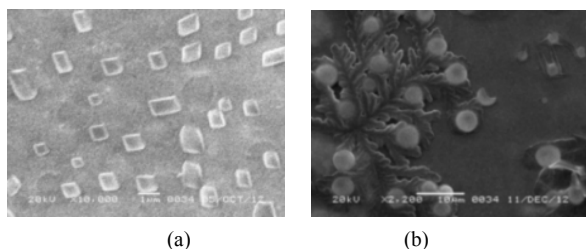


Figure 3. (a) SEM micrograph of ZnS-Ni; (b) SEM micrograph of ZnS-Mn.

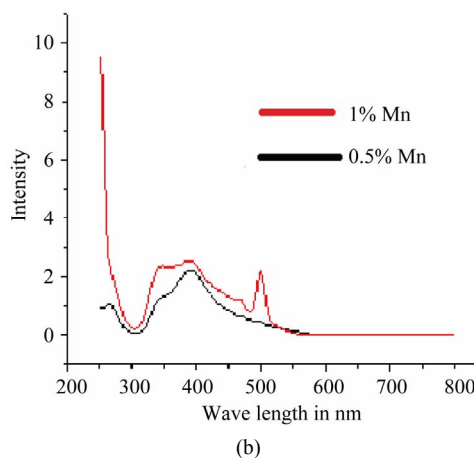
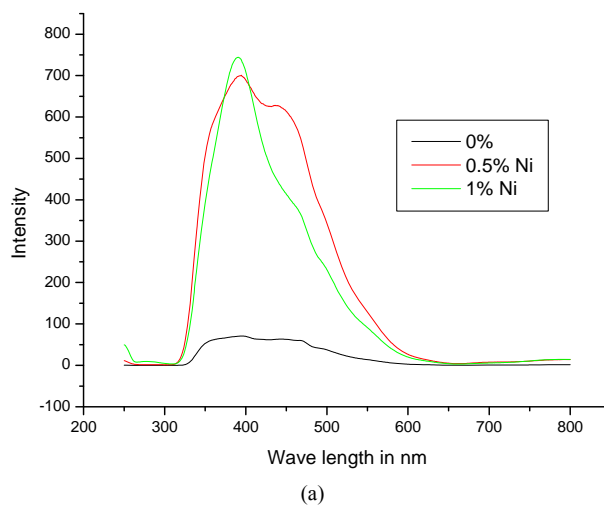


Figure 4. (a) PL spectra of Zn-S, ZnS-Ni; (b) PL spectra of Zn-S, ZnS-Mn.

strong absorbance at wavelength 400 nm with a tendency towards blue shift.

Optical absorbance spectrum of ZnS-Ni (0.5%, 1.0%) features a strong peak around 400 nm. 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 [8]. This may be possible for low doping level.

2.6. HRTEM

HRTEM image shows clear lattice fringes of the (001) plane indicating crystal growth along (001) direction. The particle size obtained from HRTEM image is 6 nm and 7.3 nm for ZnS-Ni and ZnS-Mn respectively.

2.7. Raman Studies

In **Figure 6** the sharp peak of Raman spectra indicated ZnS in well crystalline state. The peaks at 58 cm^{-1} and 335 cm^{-1} , 347 cm^{-1} are the characteristic Raman scattering of ZnS and indexed to LO phonon mode [9]. Another

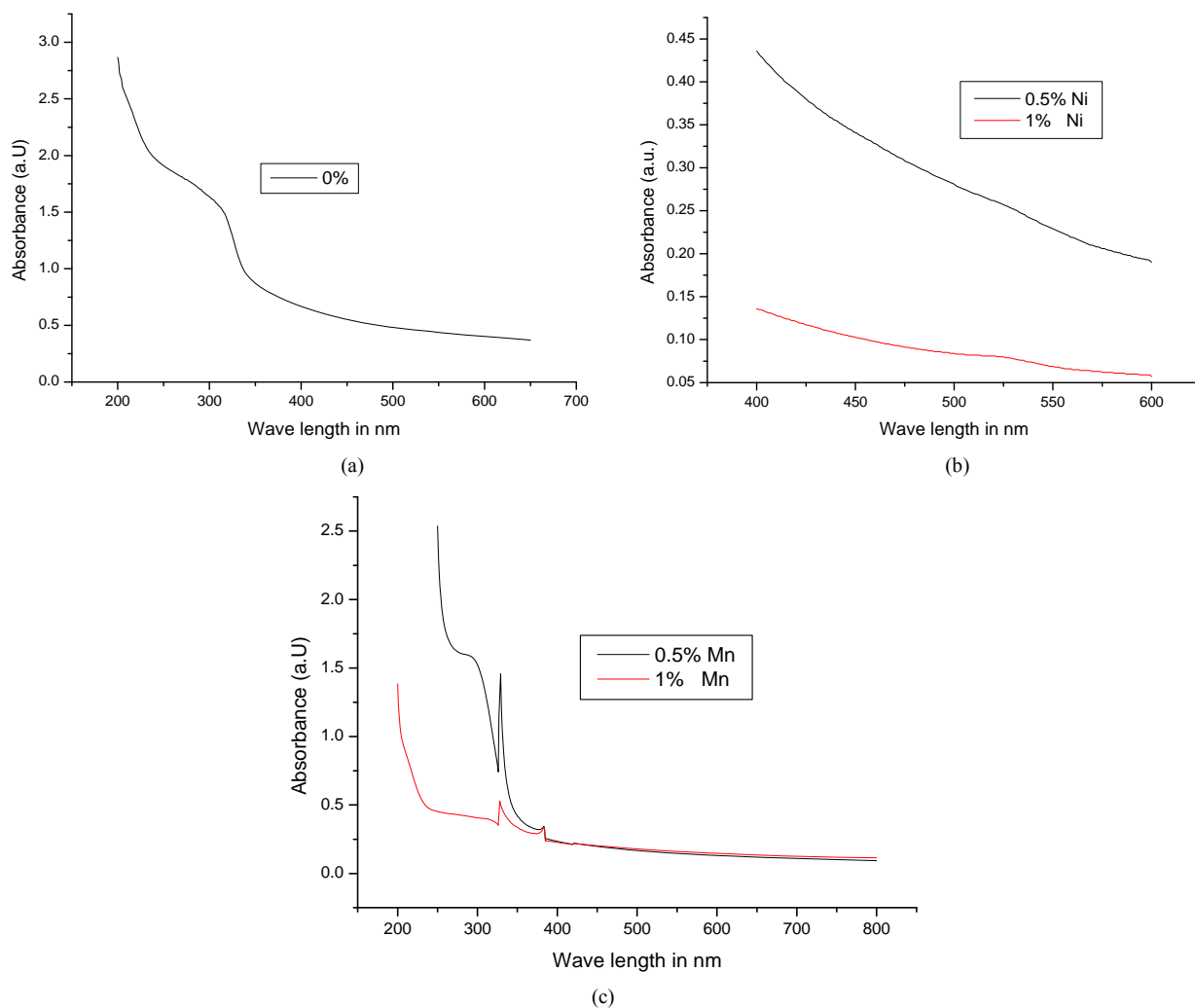
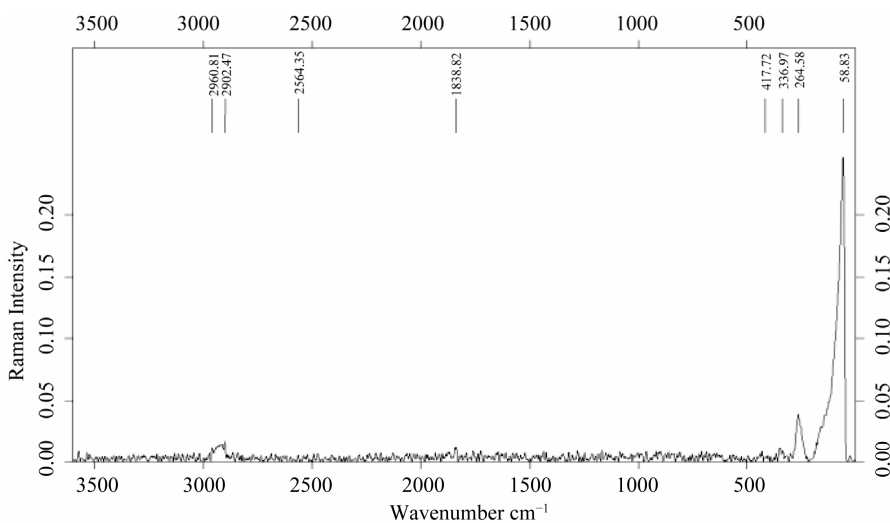


Figure 5. (a) Absorbance spectra of ZnS; (b) Absorbance spectra of ZnS-Ni; (c) Absorbance spectra of ZnS-Mn.



Sample Name: AKDIR

Figure 6. Raman spectra.

peak at 264 cm^{-1} corresponds to TO phonon mode [10] of ZnS.

3. Conclusion

ZnS nano crystalline films (un-doped and doped with Ni and Mn) have been synthesized by chemical route. The structural and optical characterization of the films done with the help of XRD, TEM, SEM, SAED, UV-VIS spectrophotometer and PL reveals formation of doped as well as un-doped nano particles. The emission bands at 377 nm, 449 nm (both for 0%), 375 nm, 433 nm (both for 0.5% Ni) and 382 nm for 1% Ni may be attributed to impurities or defect state. Similarly the emission bands with respect to 375 nm & 451 nm for ZnS-Mn may be attributed to defect states. The third emission band at 496 nm may be attributed in the 3d shell transition of Mn^{2+} . The sharp peak of Raman spectra indicated ZnS in well crystalline state which is in good agreement with that obtained from XRD result.

4. Novelty Statement

From Photo luminescence study it has been observed that in case of ZnS-Ni, with the increase of doping% (from 0.5 - 1.0), the intensity of doping related emission spectra is found to be increased. In case of ZnS-Mn, with the increase of doping% (from 0.5 - 1.0), the intensity found to be increased. It is also observed from the PL that with the increase of doping% (from 0.5 - 1.0) of both ZnS-Ni and ZnS-Mn, there is blue shift of doping related emission spectra due to quantum confinement effect. The bands with respect to 375 nm & 451 nm may be attributed to defect states. The sharp peaks of Raman spectra indicated ZnS nano particles were in well crystalline state.

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