# OPTICAL CHARACTERIZATION OF DOPED AND UNDOPED ZNS NANO PARTICLES

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## Abstract:

The study of nano crystalline semi-conductor thin films received much attention due to various application in opto-electronic and semi-conductor devices. Thin films of ZnS nano-crystals were grown into poly-vinyl alcohol matrix by chemical methods at different pH and volume ratio. A studies on the properties of un-doped and doped (with Mn) ZnS nano-crystalline films were done. 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). Particle size was found to be 30 - 40 nm. Optical absorption studies were carried out with UV-VIS Spectrophotometer and showed a strong absorbance at wavelength 297.2 nm with a tendency towards blue shift . Peak of Photo-luminescence (PL) emission spectra was obtained at 346 nm at room temperature. Due to ageing of ZnS thin film, the formation of ZnO crystals were observed. The role of oxygen on the ageing of the films and deficiency of sulphur were studied by X-ray Fluorescence (XRF) method.

**Keywords**: Nano-crystalline, Thin film, XRD, XRF, SEM, HRTEM

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**Introduction:**

Study on the properties and characteristics of synthesized nano crystals grown with different chemicals have generated great deal of interest in the minds of different researchers. Low-dimensional semiconductors, especially ZnS composite nano-structured thin films have attracted much interest because of their valuable photoluminescence properties [1,2]. ZnS is used as cathode[3] in the manufacture of hot electron, thin-film, cold-cathode . Chemical growth process is a very simple, efficient, economical and convenient method among the various researchers[4]. The optical properties of ZnS thin film is very suitable its use as filter, reflector and planar wave guide[5]. Photo luminescent properties and its efficiency of ZnS depends on intrinsic surface states of the particles, and nature of the chemicals treatment employed in their fabrication [6,7]. Research is also noticed in on the application of these types of films in light-emitting materials as well as on their optical properties[8]. The optical light emission in blue – red spectral region is characterized by blue shift at smaller crystallite dimension[9]. The study of different characteristics of ZnS Nano Crystalline thin film particularly associated with ageing is very rare. Therefore, we intend to explore this field with the help of instrumental means like X-ray Fluorescence Spectrometer (XRF), X-ray Powder Diffractometer (XRD), Scanning Electron Microscopes (SEM), Transmission Electron Microscopes (TEM), Photo-luminescence spectrometer (PL), UV visible spectrophotometer (UV-VIS), etc.

**EXPERIMENTAL:**

(A) ZnS nano-particles were synthesized by using Polyvinyl Alcohol (PVA) as a matrix. Different weight % solutions of PVA and $ZnCl_2$ of deionized water were taken. They were stirred at 200 rpm in a magnetic stirrer . The temperature was kept constant at $70^o$ C for 3 hours . The solution was kept overnight for complete dissolution and found to be transparent . Different pH of the solution were made by adding concentrated $HNO_3$. A 2 %w $Na_2S$ 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 took place as follows

$$ZnCl_2 + Na_2S = ZnS + 2NaCl$$

(B) To make 0.1 mole ZnS : Mn solution, $MnCl_2.4H_2O$ was mixed 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 stirrer. The temperature was kept constant at $70^o$ C for 3 hours . A 2 %w $Na_2S$ solution was added. Precipitation found was washed with deionized water and taken for study.

The solutions (A) and (B) were cast separately over glass substrates to produce thin films.

**Results and Discussion:**

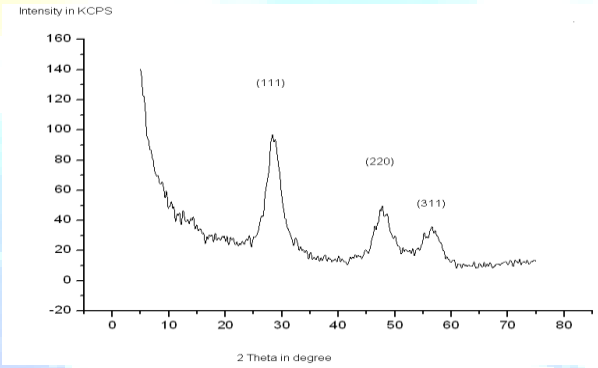



Fig. 1 (a) : X-ray diffractogram of ZnS

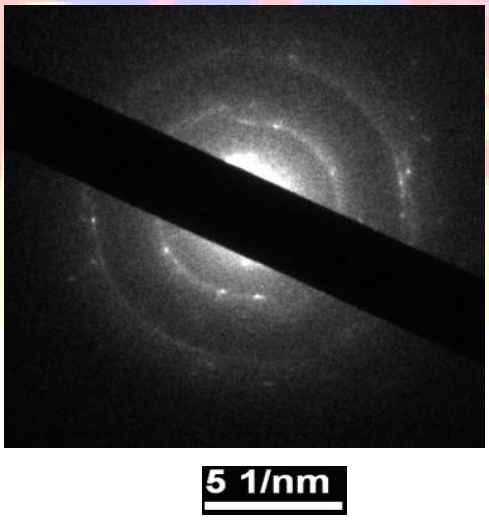



Fig. 2 (a). : Selected area electron diffraction photo of ZnS

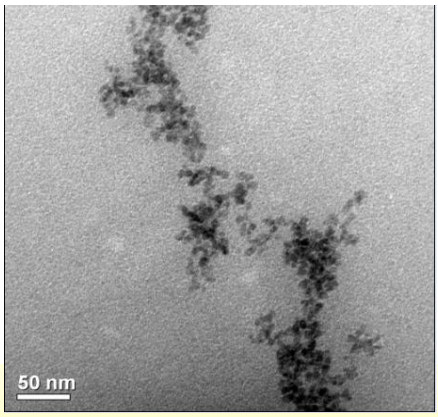



Fig. 2 (b) : HRTEM image of ZnS nano particles

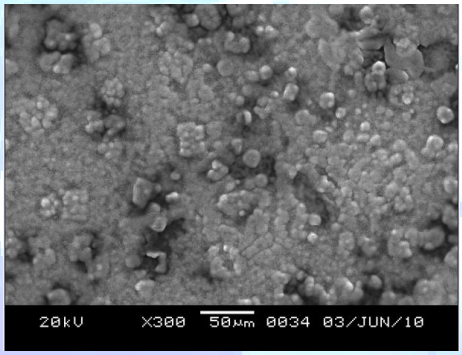
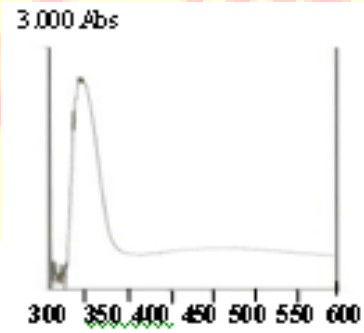



Fig. 3 : SEM micrograph of ZnS



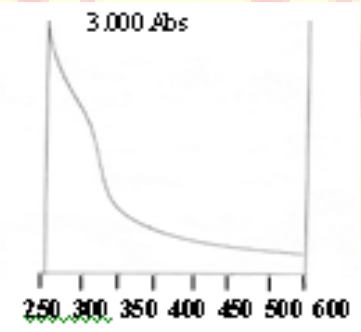




Fig. 4 (a) : Optical absorbance spectra of undoped ZnS

(b) Optical absorbance spectra on ZnS-Mn

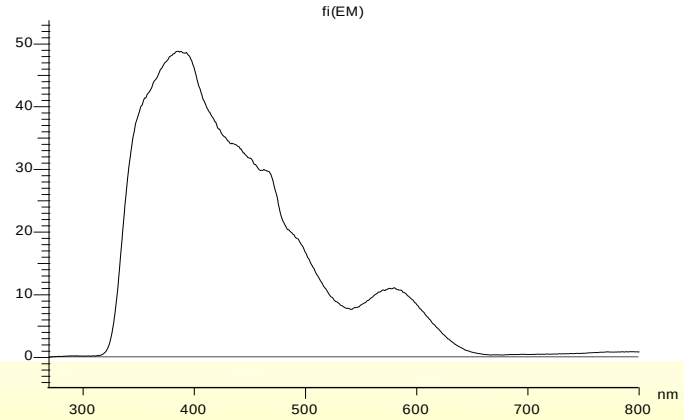



Fig.5 : PL spectra of ZnS doped with Mn

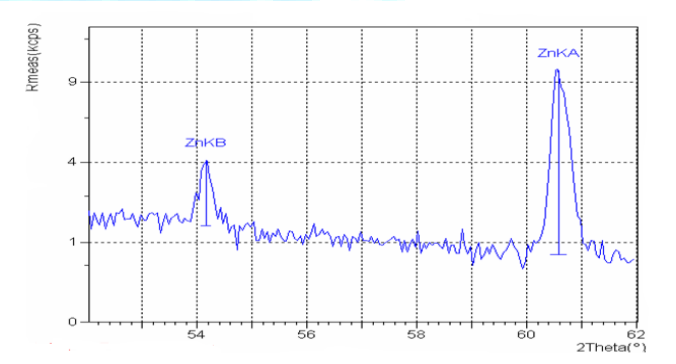



Fig. 6 (a) : XRF spectra of Zn of ZnS

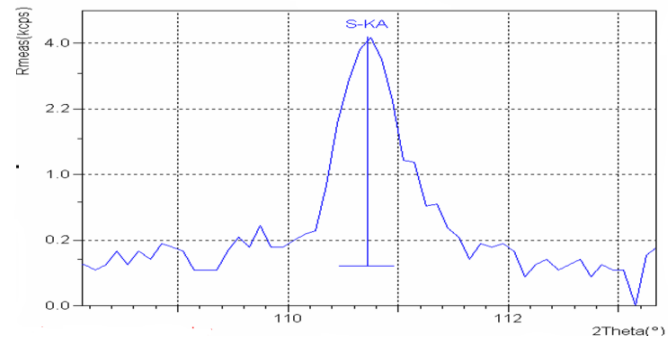



Fig. 6(b) : XRF spectra of S of ZnS

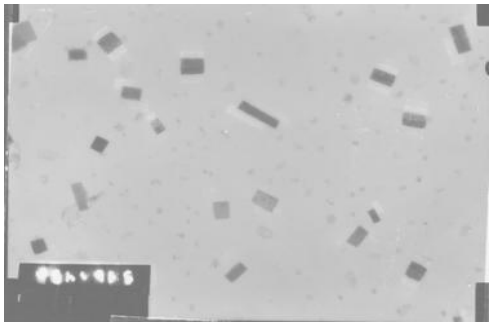


Fig. 7 : TEM image showing formation of ZnO due to ageing

**Microstructure studies**

XRD studies :

For XRD studies, film was obtained by casting the solution over a glass slide of 20mm x 15mm size. Diffractogram was obtained from a Philips X'pert Pro Powder diffractometer using Cu K□ radiation with the operating voltage 40 kV and current 20 mA. The pattern observed was found to be within the nano range (fig. 1). Planes (111), (220) and (311) were found to be present. The average particle size corresponding to the FWHM was calculated with the Scherrer formulae

$$Dp = \frac{0.94\ \square}{\square_{1/2}\ COS\ \square} \qquad (1)$$

and found to be 2.8 nm. Where, Dp is particle size of the crystallite, □ is wavelength of X-ray used, □ is the full width at half maxima (FWHM) and □ angle of X-ray diffraction.

Electron diffraction studies :

Selected area electron diffraction (SAED) was done with the help of HRTEM. Photo of SAED of ZnS [fig. 2 (a)] also showed a a set of three well defined rings corresponding to the planes (111), (220) and (311). The result so found was in a good agreement with that of XRD data. Bulk photo of the ZnS was shown fig 2(b).

SEM studies :

Photographs of the nano-crystalline thin film were taken with (JEOL, JSM-6360) SEM and shown in fig. 3. 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.

Optical absorbance study :

The optical absorbance of ZnS (fig. 4) was recorded at room temperature using a Double Beam Automated Spectrophotometer (Hitachi – U3210). The measurement of optical absorbance of the Zns and ZnS-Mn thin films in the range 250 – 600 nm wavelength showed the strong absorption at slightly different wavelength. The peak of the absorption showed blue shift with respect to bulk attributing quantum confinement effect in the nano- particles.

Photo luminescence studies :

The photo luminescence studies of nano crystalline doped (fig. 5) and un-doped (not shown) were by 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 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[10]. This was also supported by XRF studies. PL spectra of ZnS:Mn thin film revealed yellow-orange emissions[10]. 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)[11].

XRF studies :

The elemental analysis of ZnS thin film was done with the help of a X-ray Fluorescence Spectrometer (Axios). The clear peak of Zn and S found from XRF were shown in fig. 6 (a) & (b). The abundance of Zn is found to be much higher than S, it may be due to the presence of S vacancies in the lattice which also supported by PL study. With the scanning of fresh film of ZnS

it was found that there was no oxidation. But after a month with the ageing of the film oxidation took place and a nice peak of oxygen was found (not shown ).

**CONCLUSION:**

ZnS nano crystalline films ( un-doped and doped with Mn) of different pH 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. XRF study reveals the presence of Zn and S in the film and also indicates a interesting result about oxidation of the film which is found to take place due to ageing. It is also observed from the TEM study that with the elapse of time structure of ZnS transformed into ZnO (fig. 7). The emission bands with respect to 346 nm & 468 nm may be attributed to impurities or defect states[12]. The third emission band at 580 nm may be attributed due to transition took place in the 3d shell of Mn2+.

**ACKNOWLEDGEMENT:**

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. 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 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:**


- Hayashi S and Yamamoto K, J. Lumin. 70, 352, 1996
- Yoffe A D, Adv.Phys., 42 1993, 1993
- N Dalacu and A H Kitai, Appl. Phys. Letter., 58, 613, 1991
- Mane R S and Lokhhande C D , Thin Solid Films, 65, 1 , 2000
- Mach R and Muller G O, Physics.Status Solidi A69, 11, 1982
- Chen W, Wang Z, Lin Z and Lin L, J. Appl. Phys., 83, 3111, 1997
- Kumbhojar N, Nikesh V V, Kshirsagar A and Mahamuni S, J. Appl. Phys., 88, 6260, 2000
- Kannemoto M, Hosokawa H, Wada Y, Murakoshi, K, Yanagida S, Sakata T, Mori H, Ishikawa M and Kobayashi H, J. Chem. Soc. Faraday. Trans. 92, 2401, 1996
- Rossetti R, Ellison L, Gibson J L and Brus L E, J. Chem. Phys. 80(9), 4464, 1984
- Maity R and Chattopadhyay K K, Nanotechnology 15, 812 – 816, 2004
- Manzoor K, Aditya V, Vadera S R, Kumar N and Kutty T R N, J. Phys & Chem of Solids, 66(7), 1164-1170, 2010
- Goudarzi A, Aval G M, Park S S, Choi M C, Sahraei R, Ullah M H, Avane A and Ha C S, Chem Mater, 21, 2375-2385, 2009