OPTICAL STUDIES OF UNDOPED AND DOPED ZNS (WITH NI & AL) NANO-PARTICLES

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Abstract: *Extensive studies are done on semiconductor nano-particles because of their potential applications in opto-electronic devices. Semiconductor nano crystallites electronic devices have potential applications with the growth of science and technology. Optical properties of undoped and doped ZnS (with Ni and Al) are studied. ZnS and its doped nano crystals are grown into polyvinyl alcohol matrix synthesized by chemical route. Nanostructure is characterized with the help of X-ray diffraction (XRD) and Transmission Electron microscope (TEM). Surface morphology is studied with the help of Scanning Electron Microscope . Average particle size of ZnS, ZnS-Ni and ZnS-Al are found to be 7.5nm, 10nm and 11nm. 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 photoluminescence(PL) Emission spectra is found around 510 nm at room temperature for undoped ZnS . Ni dependent emission is found at 440nm and Al dependent emission is found around 510nm, which implies successful doping. X-ray Fluorescence studies show larger peak for Zn and S compared to dopant materials Ni and Al. PL studies also confirm presence of dopant in the nano-crystallites. SAED patterns show a set of three well-defined rings corresponding to diffraction from different planes of Nano crystallites of ZnS, ZnS-Ni and ZnS-Al.*

Key Words: *Nano Materials, XRD, XRF, SEM,TEM,HR-TEM, PL, UV-VIS.*

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1.INTRODUCTION :

ZnS is one of the important materials in the manufacture of various opto-electronic devices (e.g. Solar Photo-voltaic cell, Photo catalysis, lasers etc) ZnS has wide energy band gap of 3.68 ev for bulk cubic phase and 3.80 eV for bulk hexagonal phase [1] and also due to high optical transmittance in the visible region resulting blue shift[2]. Nano crystalline ZnS plays an important role as its properties differ considerably from the bulk counterparts [3]. Doped Nanocrystalls of Semiconductors can increase efficiency of its luminescent property. ZnS doped with Copper and Aluminum (Green phosphor) [4] used in cathode Ray Tubes(CRT).The origin of luminescence ZnS phosphor is due to electron-hole recombination of donor-acceptor pairs chemical growth process is a very simple, efficient, economical and convenient method among the various researchers. In Phosphors, optical sensors, electroluminescence devices, digital displays etc. doped ZnS nano materials are being used extensively. To control the size, morphology and crystalinity of ZnS nano-crystals, sudy of their physical properties is very much essential.

We are trying to characterize properties of ZnS, with different transitional elements(Al, Ni) with the help of instruments e.g. XRD, SEM, HR-TEM, TEM, PL, UV visible spectrophotometer etc.

2.EXPERIMENTAL:

(A) ZnS nano-particles were synthesized by using Polyvinyl Alcohol(PVA) as a matrix. Different wt% of PVA and $ZnCl_2$ solutions of deionised water were taken. They were stirred at 200 rpm in a magnetic stirrer for three hours. The temperature was kept constant at 70^0C 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 wt% 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 ZnS-Al solution, $AlCl_3$ was mixed with 50 ml of deionised water at room temperature. This solution of $AlCl_3$ was mixed with another solution of 5 wt% PVA and $ZnCl_2$**.** The mixed solution was stirred at 200rpm in a magnetic stirrer. During this process the temperature was kept constant at 70^0C for 3 hours. A 2 wt% Na_2S solution was added to the solution and pH of the solution was kept at 1.1. The colour of the mixed solution appeared to be milky.

(C) Again saturated solution of $NiCl_2$ was prepared by dissolving $NiCl_2$ in 50 ml of deionised water at room temperature. This solution was mixed with another solution of 5 wt% PVA and 4 wt% $ZnCl_2$. Then the solution was stirred at 200 rpm.The temperature was kept constant at 70^0C for 3 hours. 2 wt% Na_2S solution was added to the solution. pH of the solution was kept at 1.0. The colour of the mixed solution was appeared to be milky.

3.RESULTS AND DISCUSSION:

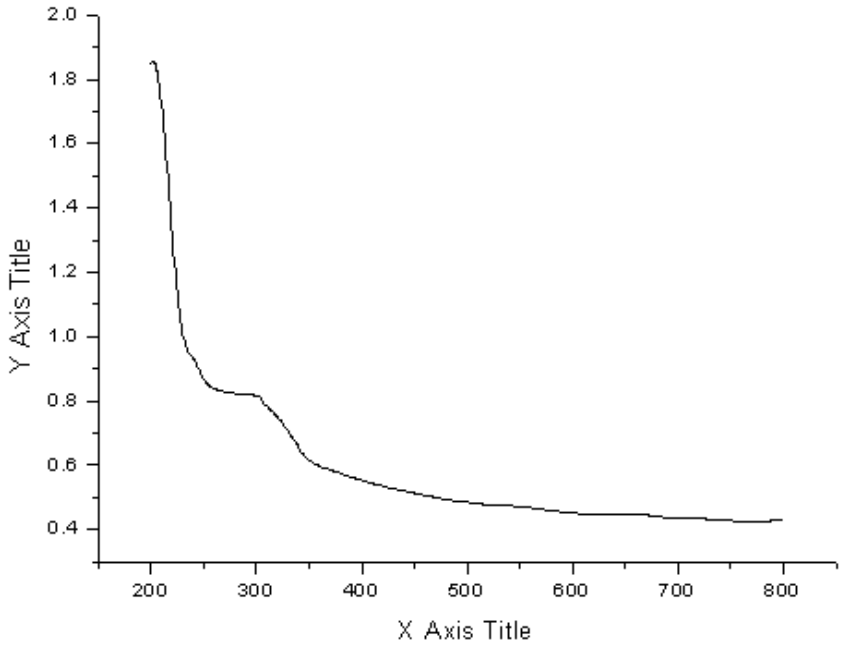

Fig. 1 (a)1 : UV-VIS spectra of ZnS

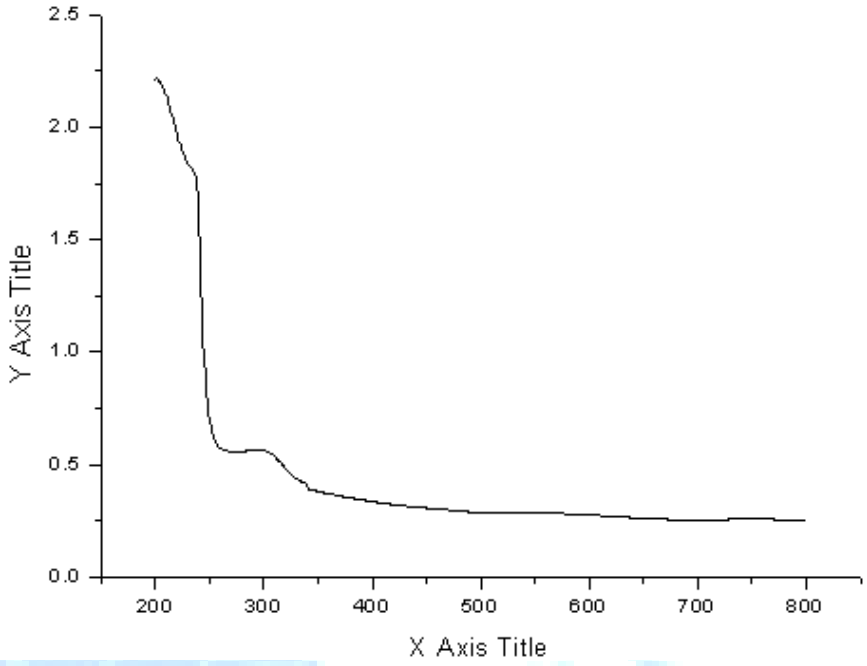

Fig. 1(b) : UV-VIS spectra of ZnS-Ni

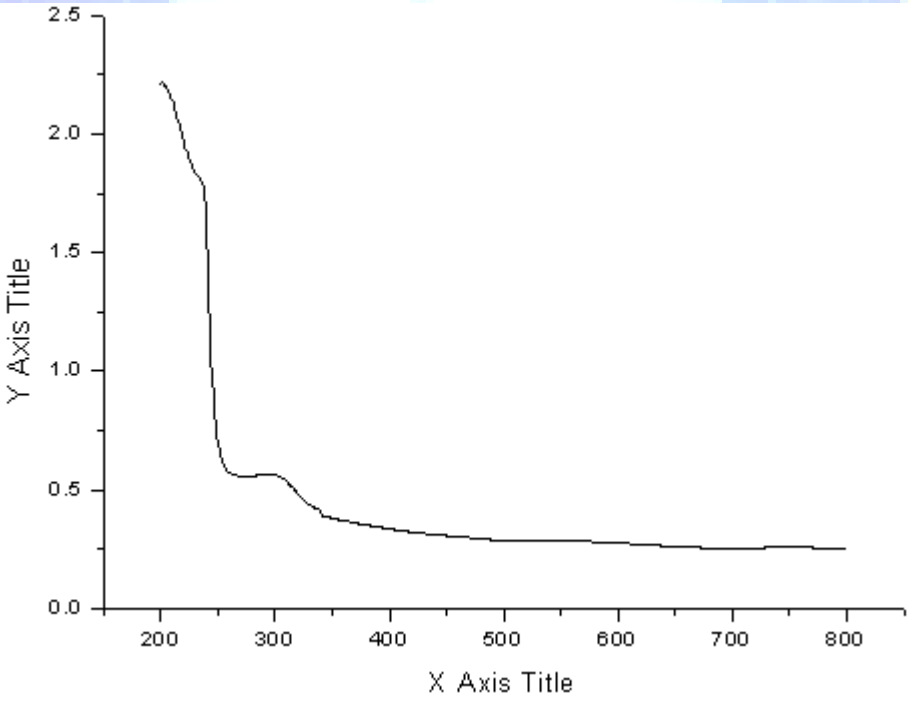

Fig:1(c): UV-VIS spectra of ZnS-Al

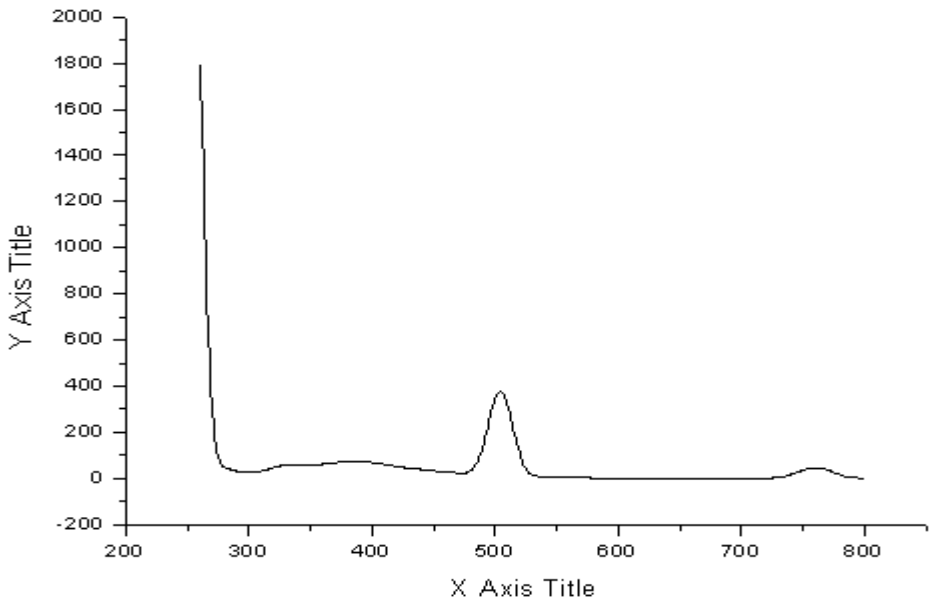

Fig 2(a) : PL spectra of ZnS

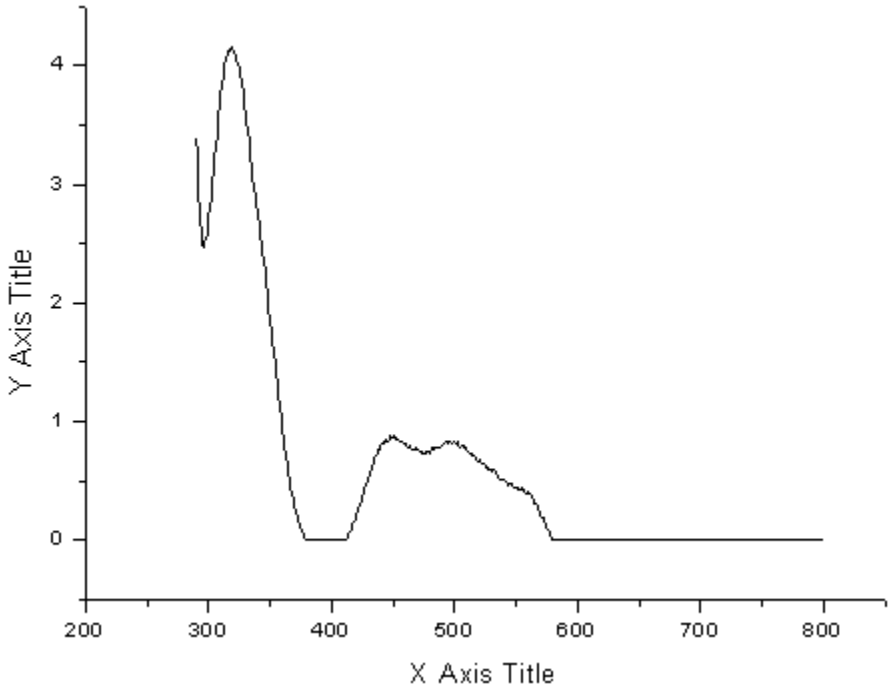

Fig 2(b): PL spectra of ZnS-Ni

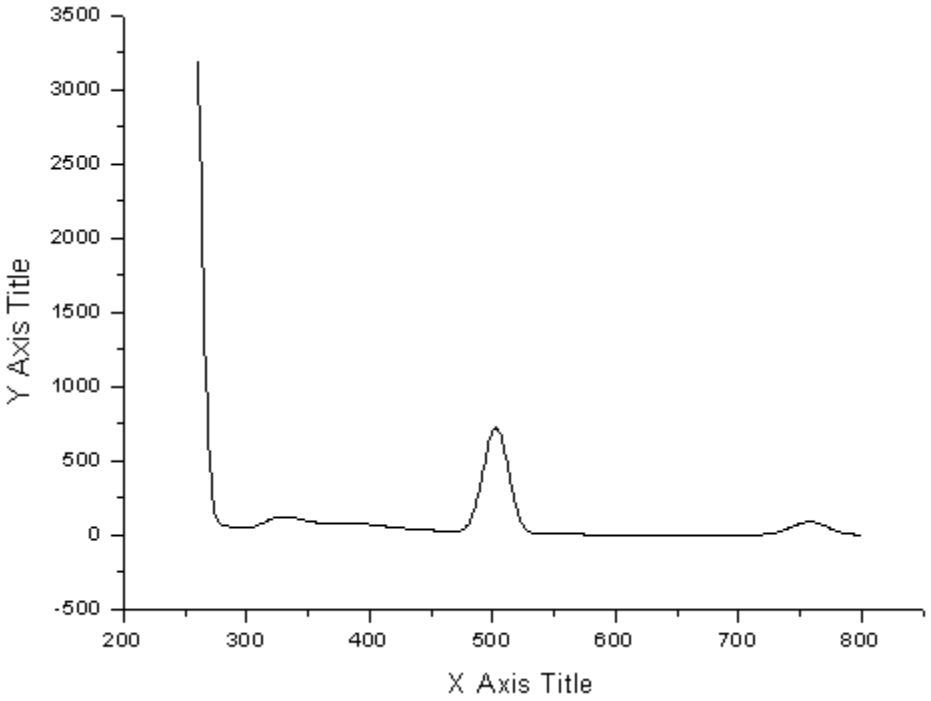

Fig. 2(c): PL spectra of ZnS-Al

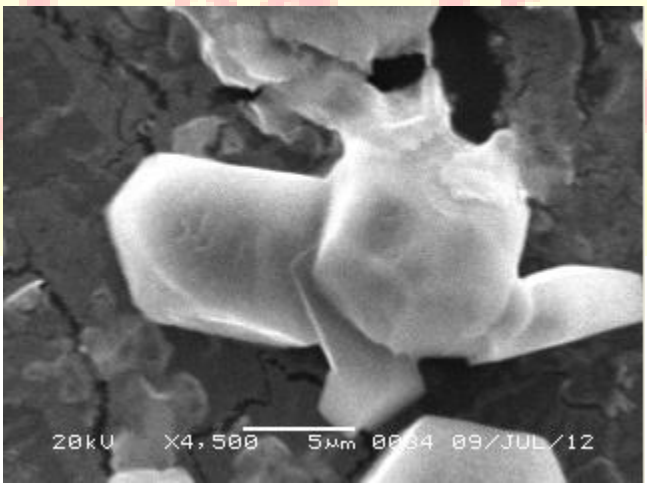

Fig.3(a): SEM photo of ZnS-Ni

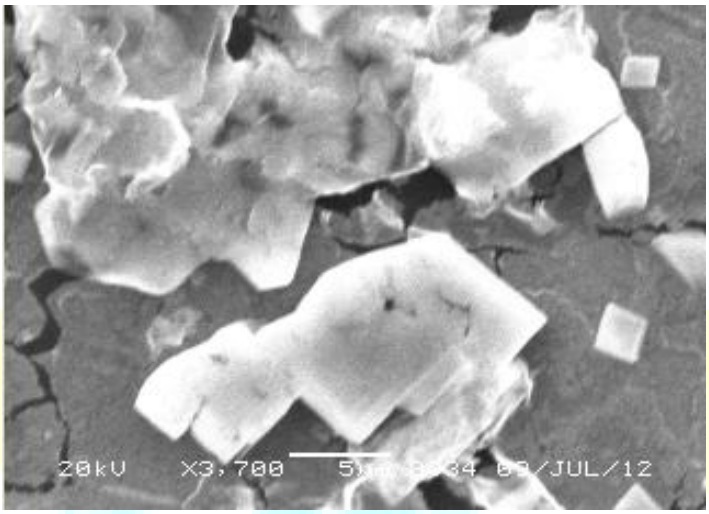

Fig. 3(b): SEM photo of ZnS-Ni

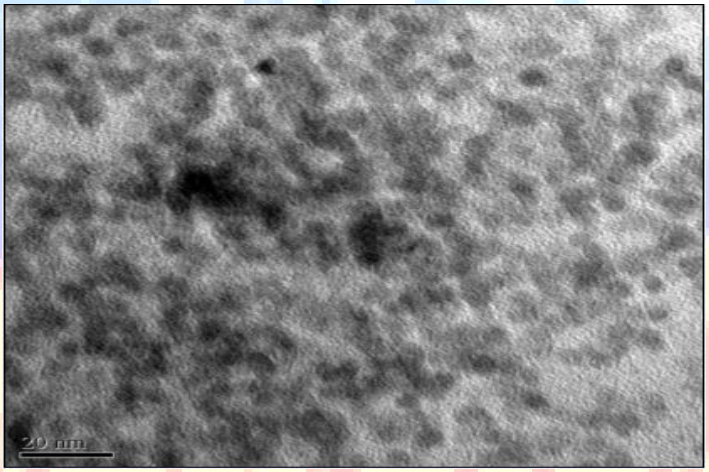

Fig. 4 : TEM photo of ZnS

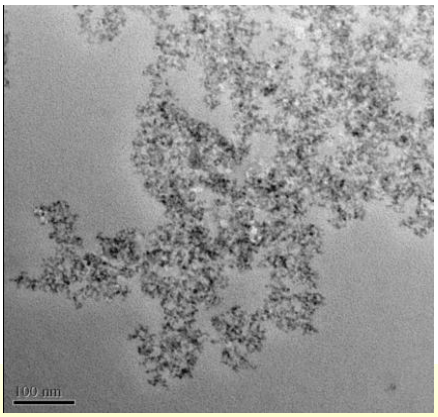

Fig. 5 : HRTEM photo of ZnS

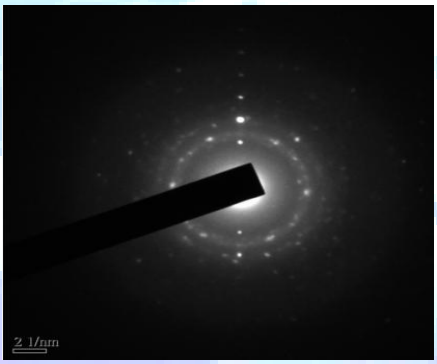

Fig. 6 (a) : SAED diffraction pattern of ZnS

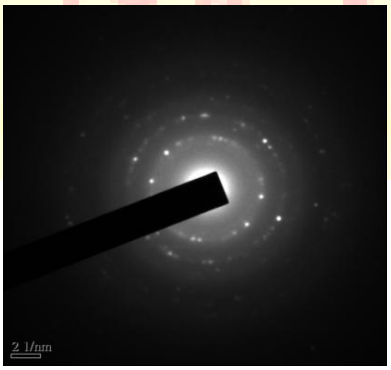

Fig. 6 (b) : SAED diffraction pattern of ZnS:Al

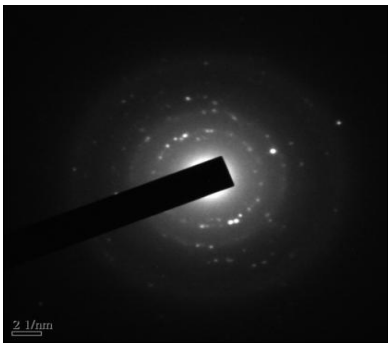

Fig. 6(c): SAED diffraction pattern of ZnS:Ni

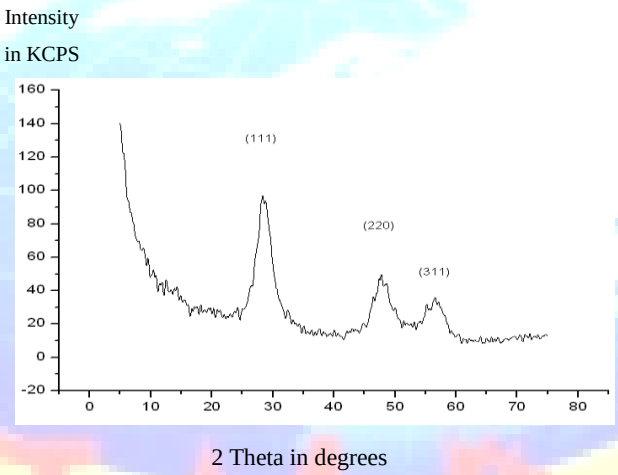

Fig. 7 : XRD spectra of ZnS

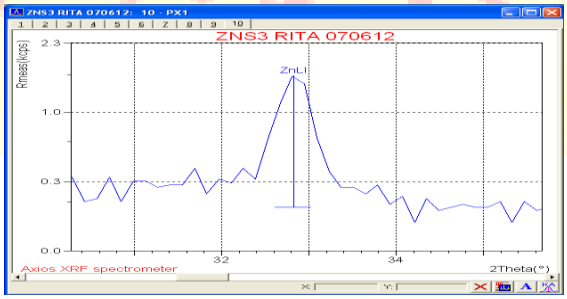

Fig. 8(a) : XRF spectra of Zn of ZnS

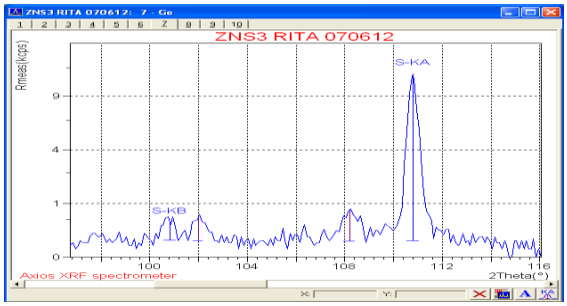

Fig. 8(b) : XRF spectra of S of ZnS

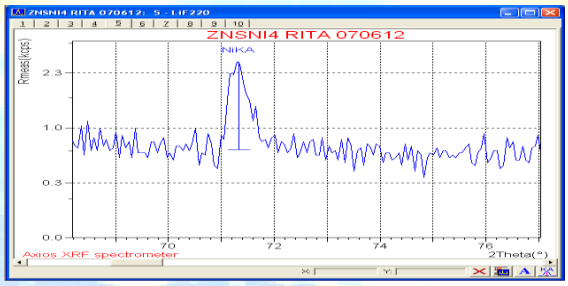

Fig. 8(c) : XRF spectra of Ni of doped ZnS

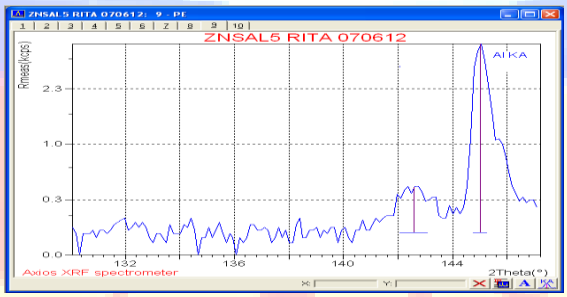

Fig. 8(d) : XRF spectra of Al of doped ZnS

3.1 Optical absorbance study

The optical absorbance of ZnS was recorded at room temperature using a Double Beam Automated Spectrophotometer (Hitachi – U3210) shown fig.1. The measurement of optical

absorbance of the films of different pH in the range 200 – 800 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. 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 . Optical absorbance spectrum of ZnS-Ni features a strong peak around 310 nm and ZnS-Al at 300 nm, with volume ratio being 5:4 and ph 1.0. The axes have their usual meaning.

3.2 Photo luminescence studies:

The photoluminescence studies of nano crystalline doped and un-doped & doped ZnS were done at room temperature by using F-2500FL Spectrophotometer (shown fig. 2). Peak of photoluminescence(PL) emission spectra is found around 510 nm at room temperature for undoped ZnS. Ni dependent emission is found at 440nm and Al dependent emission is found around 510nm, which implies successful doping.

3.3 SEM studies:

Photographs of the nano-crystalline thin film were taken with (JEOL-6360) SEM and shown in the fig. 3. The surface morphology of ZnS-Ni film prepared at 70^0C with PVA as matrix was observed. Formation of Hexagonal [fig. 3(a)] and cubic crystals [fig. 3(b)] were observed.

3.4 TEM studies:

For TEM studies film was deposited in the microscopic grids. Analysis was done with the help of TEM(JEOL-100 CX).TEM micrographs and corresponding electron diffraction pattern were shown in fig. 4. TEM photo of ZnS showed abundance of nearly spherical crystallites of mean particle size 8 nm.

3.5 HR-TEM:

HR-TEM image shows clear lattice fringes of the (001) plane indicating crystal growth [001] direction (fig. 5).

3.6 Electron diffraction studies :

Selected area electron diffraction (SAED) was done with the help of HRTEM. Photo of SAED of undoped & doped ZnS [(fig. 6 (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 good agreement with that of XRD data.

3.7 XRD studies:

For XRD studies films were obtained by casting the solution over a glass slide of 20mm×15mm size. Diffractogram was obtained from a Brukar (D8 ADVANCE) powder diffractometer using Cu Kα radiation with the operating voltage 40kV and current 40mA (fig 7). The XRD Diffractogram was found to be within the range [5,6]. From the XRD pattern the films are seemed to be Polycrystalline [7]. The average particle sizes corresponding to FWHM was calculated with the Scherer formulae (1) and were found to be 7 nm.

$$Dp = \frac{0.94\,\lambda}{\beta_{1/2}\,\cos\theta} \qquad (1)$$

Where,

Dp is the particle size of the crystallite.

λ is the wavelength of X-ray used

$\beta_{1/2}$ is the full width at half maxima(FWHM) and θ is the angle of X-ray diffraction.

3.8: XRF studies:

The elemental analysis of undoped ZnS thin films were scanned with the help of X-ray Fluorescence Spectrometer (Axios XRF) with operating voltage 50kV & 10 mA. The peaks of Zn, S, Ni, and Al were found from XRF were shown in fig. 8 (a), (b), (c) & (d).

4. Conclusion:

ZnS nano crystalline thin film of different pH and volume ratio have been synthesized by chemical route. The structural and optical characterization of the films done with the help of

TEM, SEM, UV-VIS spectrophotometer, XRD and PL studies reveal formation of nanoparticles within the range 8nm. XRF study reveals the presence of ZnS and doping agents Ni and Al in the film.

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