International Journal of Science and Research (IJSR)
ISSN (Online): 2319-7064
Impact Factor (2012): 3.358

Effect Of pH Variation on Size and Structure of Undoped and Doped ZnS (With AL & Ni) Nano Particles

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Abstract: ***Undoped and doped ZnS (with Al and Ni) nanoparticles have been successfully synthesized by chemical route at room temperature by using Polyvinyl Alcohol matrix. The nano particles have been characterized by using X-ray diffraction (XRD), UV-Visible and Photo-luminescence (PL) spectroscopy, Scanning Electron Microscopy (SEM), Transmission Electron Microscopy(TEM). The structural properties of the nanoparticles are determined by XRD, TEM and their Optical properties by UV-Visible and PL (photoluminescence) analysis. Surface morphology is studied with the help of Scanning Electron Microscope (SEM).Average particle size of Zns, Zns-Al & ZnS-Ni are found to be 2.48 nm at different pH value.Pl peaks for Zns, Zns-Al and ZnS-Ni nano particles at different values of PH show significant difference. Optical absorption spectra with different values of PH show a strong absorption with a tendency towards blue shift.SAED show a set of three well defined rings.***

Keywords: Nanoparticles, XRD, SEM, TEM, HRTEM, XRF

1. Introduction

The properties of Semiconductor nanoparticles strongly depend on its size, shape, composition, crystallinity and structure [1]. It is a string aim and a great challenge to precisely control these parameters of nanoparticles for the chemists. Recently Semiconductor nanoparticles have been extensively investigated and gained much interest due to their unique properties and applications in diverse areas of science and technology [2]. Because of their unique and size dependent properties arising from quantum confinement and surface effect nanocrystals of ZnS have been extensively studied. Chemical growth process is a very simple, economical and convenient method to create nanocrystals of the desired size. In optical sensors, electroluminescence devices, digital displays etc doped ZnS nanoparticles are being used extensively. ZnS nanoparticles stimulated great interest because of their unique optical [3] properties. Doping with optically active luminescent materials also play key roles in luminescence effiency and thus influencing their practical applications in LEDS, Lasers or as phosphors. Here we are trying to characterize the properties of undoped ZnS and ZnS doped with Al & Ni at different pH value.

2. Experimental

(A) ZnS nano-particles are synthesized by using Polyvinyl Alcohol (PVA) as a matrix. We have taken 5 wt% solutions of PVA and 2, 3 & 4 wt% solutions of $ZnCl_2$ in deionized water. They are stirred at 200 rpm in a magnetic stirrer at constant temperature of 70^0C for 3 hours. The solutions are kept overnight for complete dissolution and found to be transparent. A 2 wt% Na_2S solution was added till the solutions mentioned above appeared to be milky. The solutions were kept overnight inside a dark chamber. As soon as the nano-structure is formed, it embedded into the gap. The chemical reaction took place as follows-

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

In the preparation of undoped ZnS nano particles we have mixed $ZnCl_2$ and Na_2S in the volume ratio of 5:2 and pH of the solutions are kept at 1, 1.5,2 & 2.5 by adding conc. HNO_3

(B) To make ZnS-Al solution, 0.1 wt% $AlCl_3$ is mixed with demonized water at room temperature. This solution of $AlCl_3$ is mixed with another solutions of 5 wt% PVA and (2, 3 & 4) wt% $ZnCl_2$. The mixed solution is stirred at 200 rpm in a magnetic stirrer. During this process the temperature is kept constant at 70^0C for 3 hours. A 2 wt% Na_2S solution is added to the solution. The reactants are mixed in the volume ratios of 5:2 and pH of the solutions are kept at 1, 1.5, 2 and 2.5. The solutions appeared to be transparent.

(C) To make ZnS-Ni solution 0.1 wt% $NiCl_2.6H_2O$ is mixed with demonized water at room temperature. This solution is mixed with another solution of 5 wt% PVA and (2, 3 & 4) wt% $ZnCl_2$. The solutions are stirred at 200 rpm at a constant temperature of 70^0C for 3 hours. 2 wt% Na_2S solution was added to the solutions. The pHs of the solutions are kept at 1, 1.5, 2 and 2.5. The mixed solutions appeared to be transparent.

3. Results and Discussion

3.1 XRD studies

The XRD studies are obtained from Brukar (D8 ADVANCE) Powder Diffractometer using Cukα radiation with the operating voltage 40 kV and current 40 mA. The intensity peaks of undoped and (Edit) doped ZnS remain the same. Again it is observed that peaks are sharp at lower pH value [4]. The pattern observed is found to be within the nanorange [5]. XRD patterns reveal the particles to be polycrystalline [6]. Planes (111), (220) and (311) are found

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to be present. The average particle size of the samples at different pH is calculated by using sherer formulae [7]

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

Where Dp is the particle size.

λ is the wavelength of incident X- ray.

θ is the angle of diffraction peak.

$\beta_{1/2}$ is the full width at half maxima of the XRD peak.

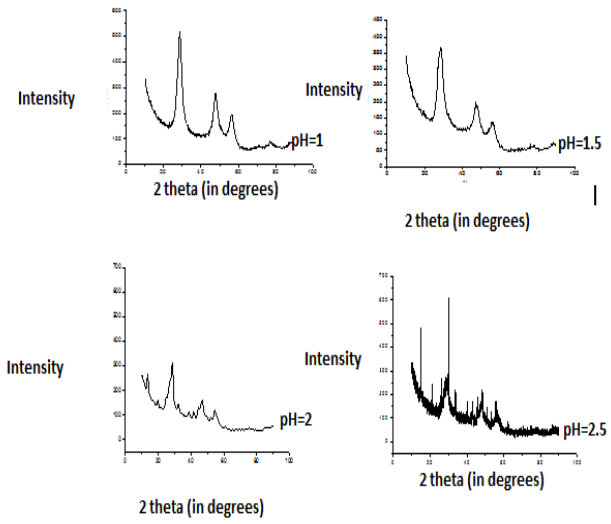


Figure 1: (a),(b),(c) & (d) XRD of ZnS at pH (1,1.5,2 & 2.5)

Table 1: Shows the crystallite size of the samples at different pH values.

pH	Crystallite size(nm) (From Sherer formulae)
1	2.0
1.5	2.1
2	2.2
2.5	3.6

Table 1. Variation of crystallite size with pH values. The calculated crystallite size is found to be 2.48 nm. From the calculation it is found that when pH increases the particle size increases [8].

3.2 Optical Properties

(a) Optical absorption studies

The optical absorption of ZnS is recorded at room temperature using a Double Beam automated Spectrophotometer (Hitachi-U3210). For undoped ZnS we get the absorbance peak for pH 1, 1.5,2 and 2.5 at 371nm, 255 nm, 313 nm and 317 nm respectively. For Al doped ZnS the peaks for the same pH value are at 262 nm, 312 nm, 315nm and 259 nm respectively. For Ni doping the peaks are at 260 nm, 262nm, 310nm and 312nm respectively. These positions reveal that Al and Ni doping have effect on the electronic spectra of ZnS [9]. Table 2 shows variation of band gap energy with doping and pH value.

Table 2: Variation of band gap energy with doping and pH value

Sample	pH	Band gap energy(eV)
Undoped ZnS	**1**	**3.34**
	1.5	**3.80**
	2	**3.96**
	2.5	**3.98**
Al doped ZnS	1	3.34
	1.5	3.94
	2	3.97
	2.5	4.7
Ni doped ZnS	1	4.66
	1.5	4.68
	2	4.73
	2.5	4.9

We have seen that with the increase of pH the band gap energy also increases[11].By plotting $(\alpha h\nu)^2$ vs $h\nu$ using Tauc relation as given below we get the optical band gap value.

$$\alpha h\nu = B (h\nu - E_g)^n$$

Where α is the absorption coefficient is a constant, ν photon energy, Eg band gap energy. n =1/2 foe direct band gap and n=2 for indirect band gap. An extrapolation of the linear region of the plot $(\alpha h\nu)^2$ vs $h\nu$ gives the value of the optical band gap as 3.75 for undoped ZnS, 3.85 for ZnS-Al and 4.25 eV for ZnS-Ni. We have seen that o_n doping E_g increases [10].

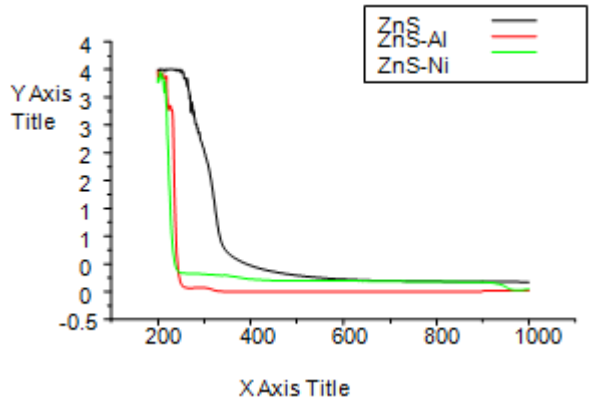
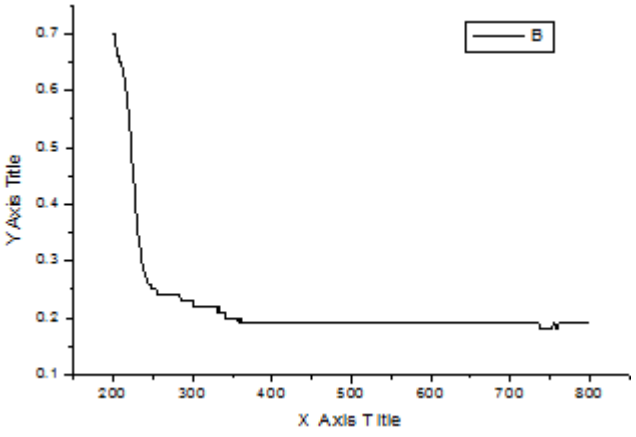


Figure 2(a): UV-VIS Spectra of ZnS, ZnS-Al &ZnS-Ni(pH=1)



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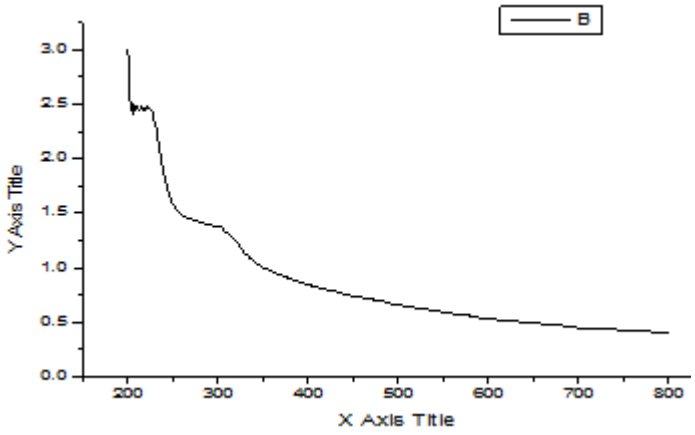


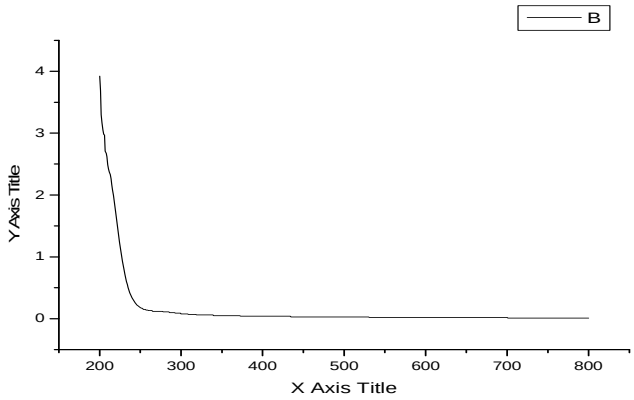


Figure: 2(d),(e) & (f)**ZnS-Al (pH= 1.5,2 &2.5)**

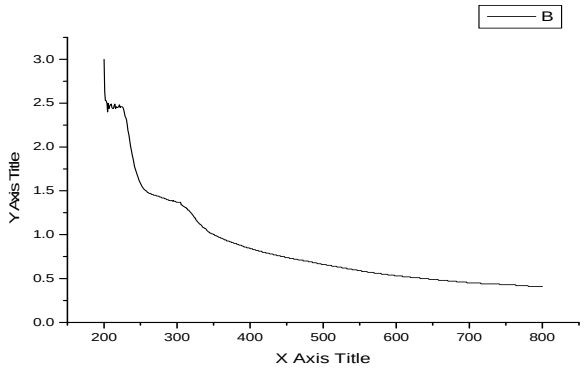
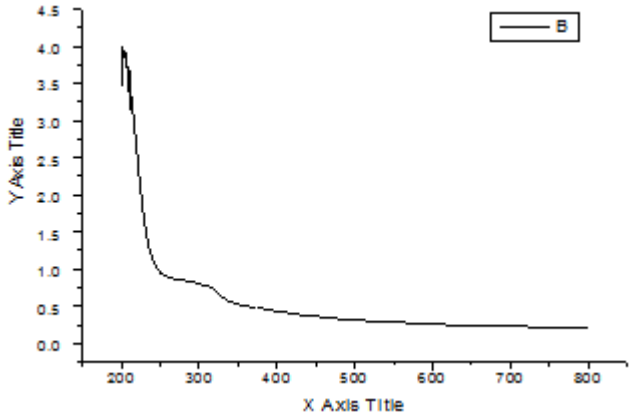
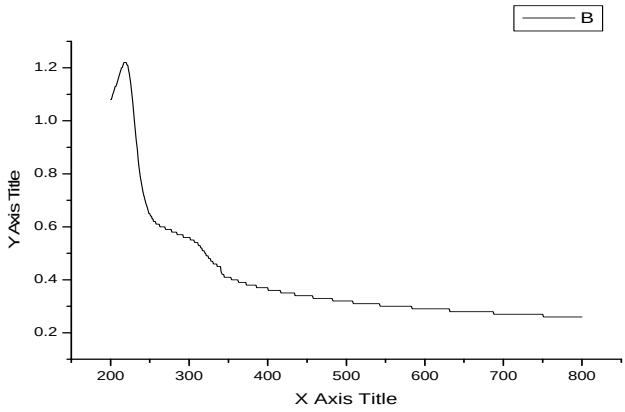
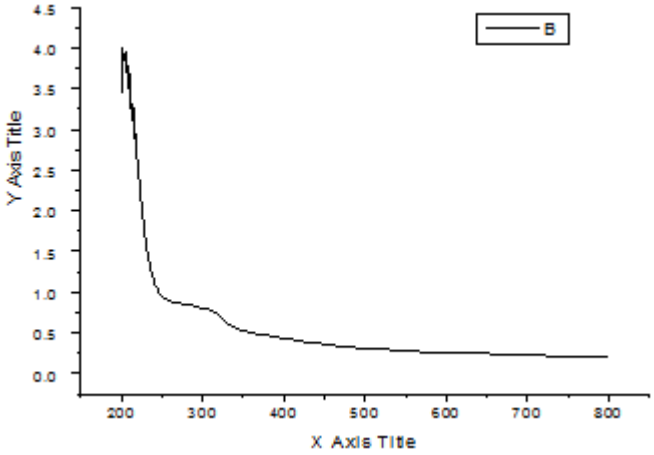


Figure 2: (b),(c) & (d) UV of ZnS (pH= 1.5,2 & 2.5)



(g)





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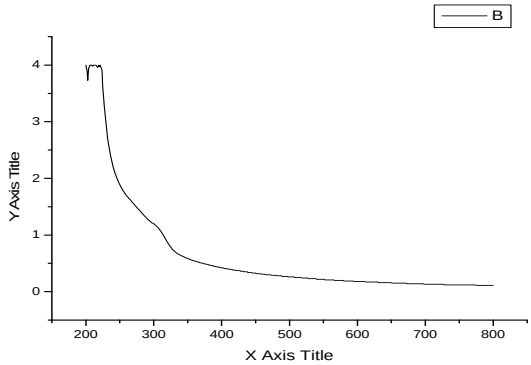

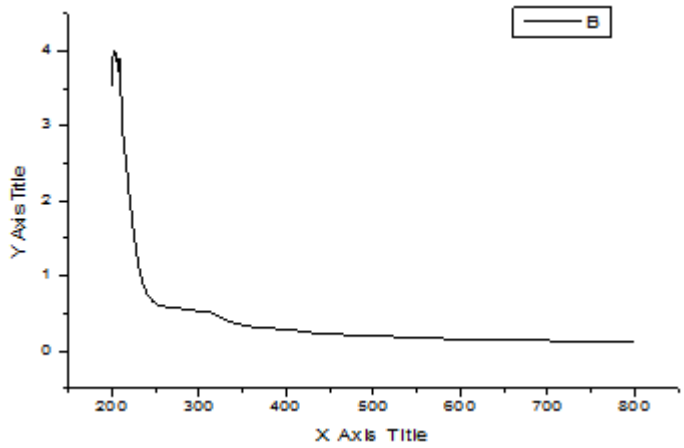

(i)

Figure 2: (g), (h) & (i) **ZnS-Ni (PH = 1.5, 2 &2.5)**

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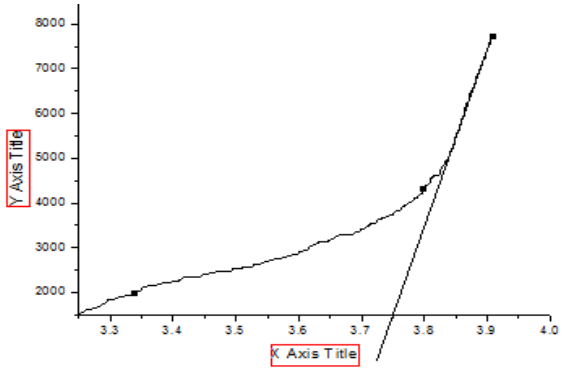


Figure 3: (a)Plot of $(\alpha h\nu)^2$ vs hν obtained from absorption data of undoped ZnS

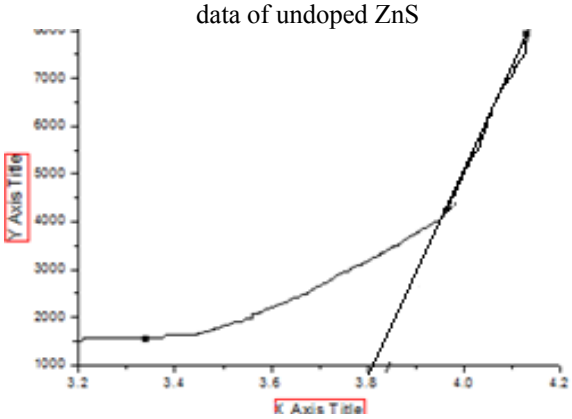


Figure 3: (b) Plot of $(\alpha h\nu)^2$ vs hν obtained from absorption data of ZnS-Al

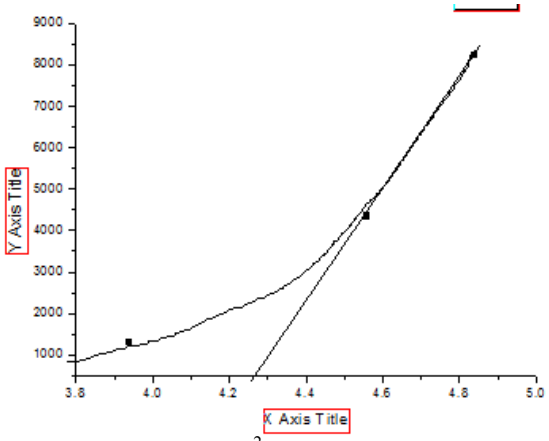
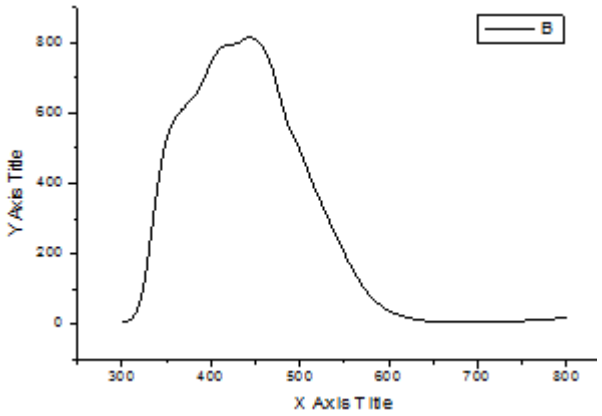


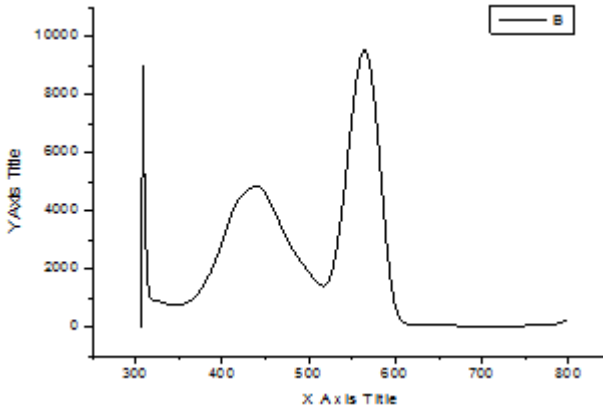
Figure 3: (c)Plot of $(\alpha h\nu)^2$ vs hν obtained from absorption data of ZnS-Ni

(b) Photoluminescence study

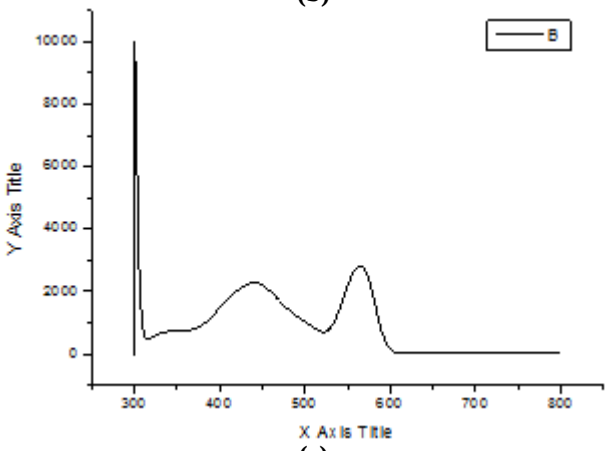
At room temperature, Photoluminescence (PL) spectra of ZnS, ZnS-Al and ZnS-Ni nanoparticles at an excitation wavelength of 260 nm are illustrated in Figure



(a)

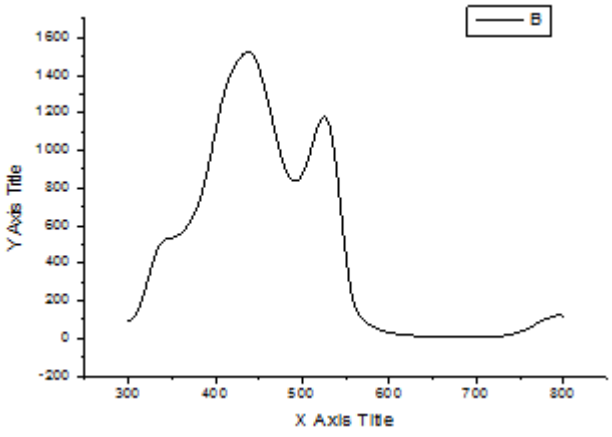


(b)



(c)

Figure 4: (a), (b) & (c) PL Spectra of ZnS, ZnS-Al &ZnS-Ni (pH=1)



(d)

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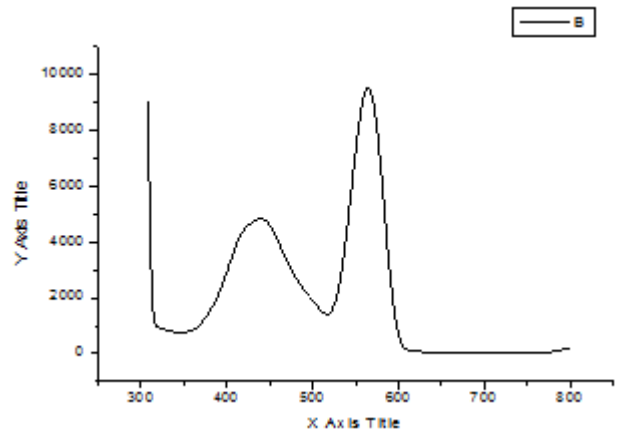
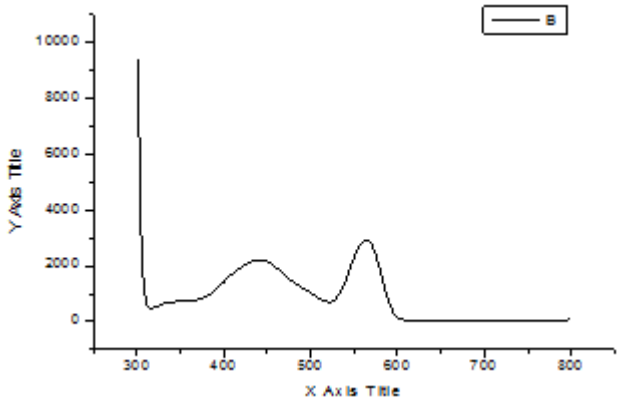
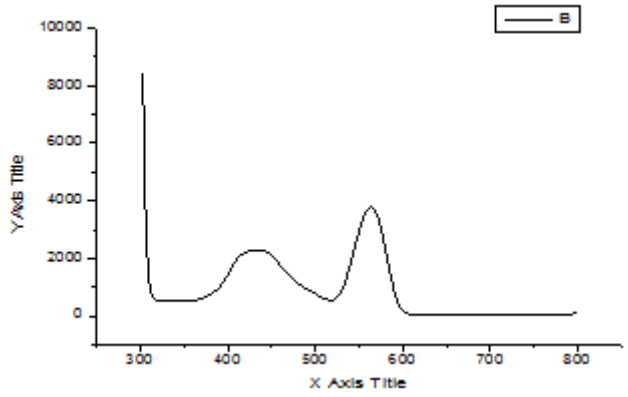


(e)

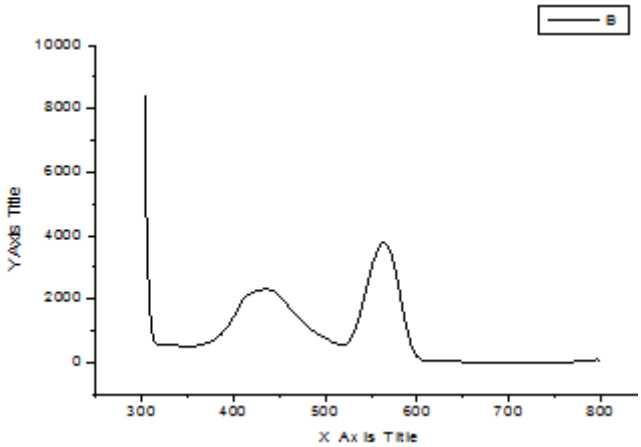


(f)

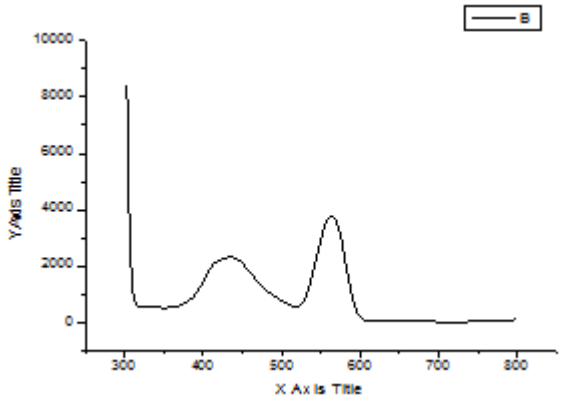
Figure 4: (d), (e) & (f) PL spectra of ZnS, ZnS-Al & ZnS-Ni (pH=1.5)



(g)

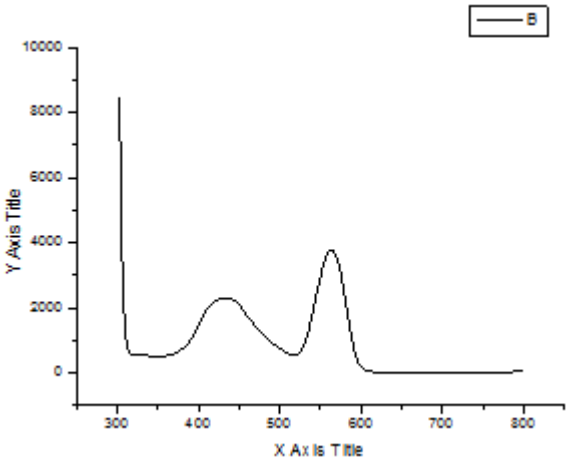


(h)

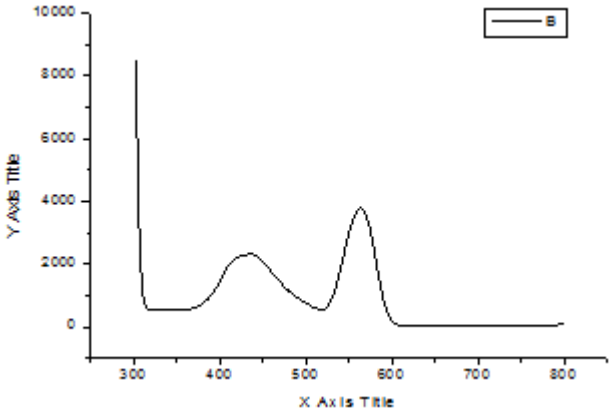


(i)

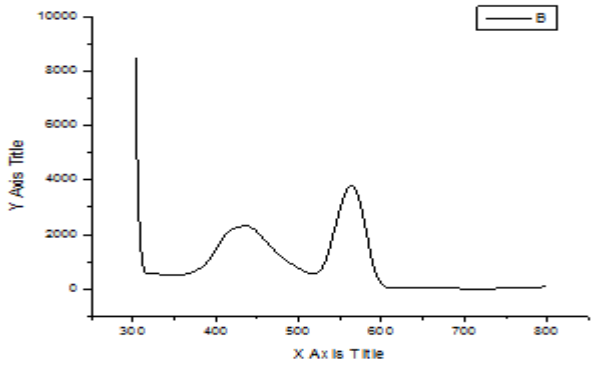
Figure 4: (g), (h) & (i) PL spectra of ZnS,ZnS-Al & ZnS-Ni(pH=2)



(j)



(K)



(L)

Figure 4: (j) (k) & (l) PL spectra of ZnS,ZnS-Al & ZnS-Ni (pH=2.5)

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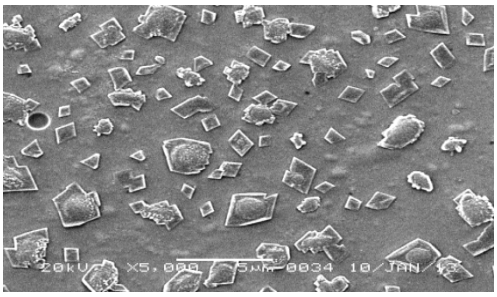
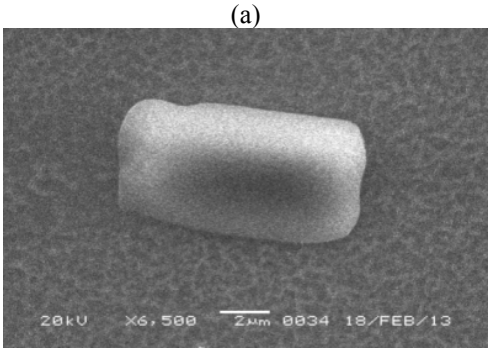
At pH=1, PL peaks for ZnS, ZnS-Al & ZnS-Ni are at 440 nm, 439 &568 nm and 438 & 562 nm respectively. At pH=1.5 peaks for ZnS are at 421 & 527 nm, for ZnS-Al peaks are at 437 &567 nm and for Zns-Ni peaks are at 422 & 528 nm . when the pH value is at 2 we get peaks for ZnS at 449 nm, for ZnS-Al at 433 &568 nm and for ZnS-Ni at 441 &562 nm.When the value of pH is increases to 2.5, the PL peaks for ZnS are at 443nm &526 nm, for ZnS-Al are at 421 &558 nm and for ZnS-Ni peaks are at 437 & 560nm. We have seen that with doping there is slight decrease in intensities. Increase in pH also has effect in the intensities of the PL peak.

3.3 SEM Studies

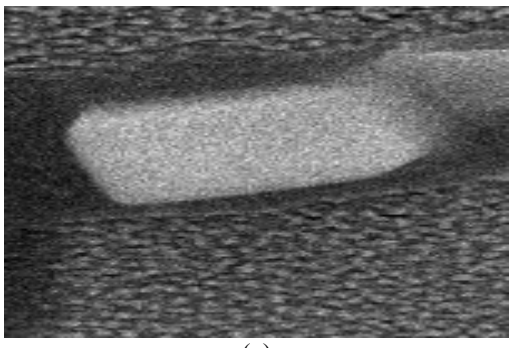
Photographs of the nano-crystalline ZnS, ZnS-Al & ZnS-Ni thin films are taken with JEOL-6360. SEM photograph are shown in fig4 (a), 4 (b) & 4 (c). The surface morphology of the film are observed. Formations of cubic and orthorhombic crystals have been observed. Study shows surface of the films are smooth and uniform.



(a)



(b)



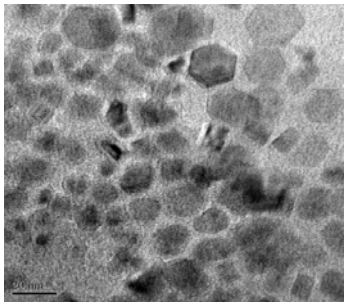
(c)

Figure: 5(b) & (c): SEM PHOTO OF ZnS-Al, & ZnS-Ni

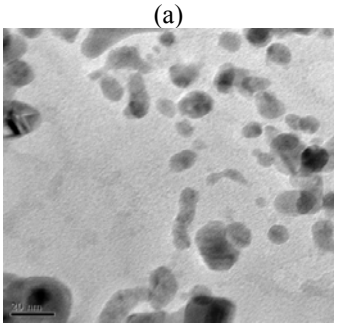
SEM analysis shows that there is uniformity of the undoped and doped ZnS nano particles. Doping has no effect on the morphology of the nano particles [11].

3.4 TEM Studies

For TEM studies solutions are deposited in the microscopic grids. With the help of TEM (JEOL-100CX), images are taken. TEM micrographs and corresponding electron diffraction patterns are *shown in fig* 5(a), 5(b) & 5(c).Table 3 shows variation of particle size with increase in pH.



(a)



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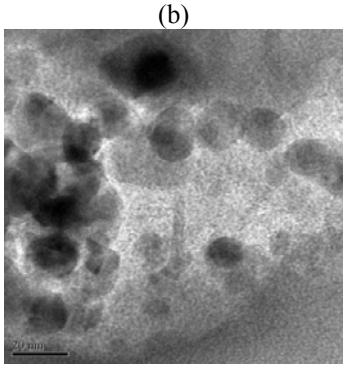

(c)

Figure: 6 (a),(b) (c): TEM image of ZnS, ZnS-Al & ZnS-Ni

Table 3: variation of particle size with increase in pH.

Samples	pH	Particle sizes from TEM
ZnS	1	10
	1.5	9.33
	2	8.33
	2.5	8
ZnS-Al	1	11.42
	1.5	8.57
	2	7.78
	2.5	6.67
ZnS-Ni	1	7.78
	1.5	7.55
	2	5
	2.5	3.33

Average particle sizes for ZnS, ZnS-Al & ZnS-Ni are found as 8.92nm, 8.61nm and 4.97 respectively

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3.5 HR-TEM

HR-TEM images show clear lattice fringes of the (001) plane indicating crystal growth along [001] direction

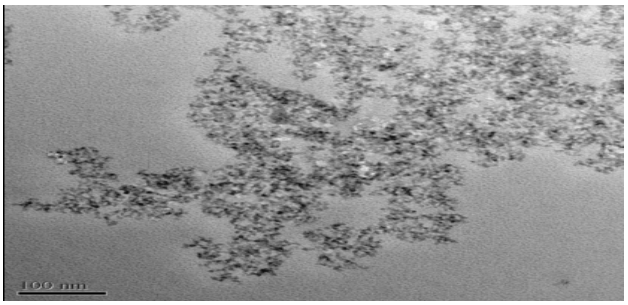


Figure 7: HR-TEM photo of ZnS

3.6 SAED Studies

Selected area electron diffraction studies are done with the help of HRTEM. Photos of SAED of undoped & doped ZnS show 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.

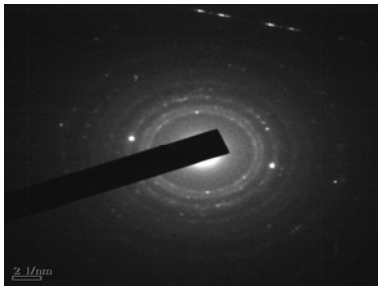
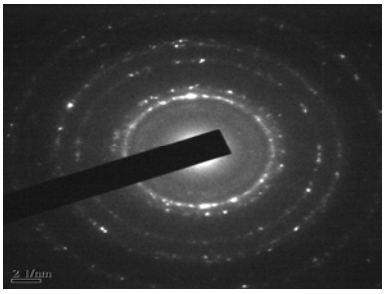


Figure: 8(a): SAED diffraction pattern of ZnS



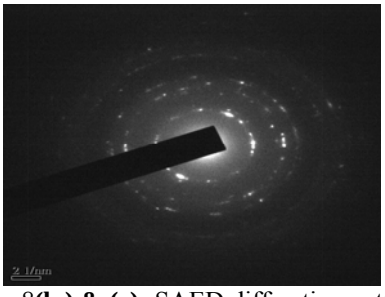


Figure: 8(b) & (c): SAED diffraction pattern of ZnS -Al & ZnS -Ni

3.7 EDX Studies

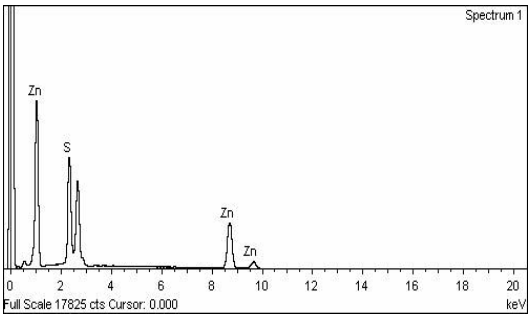


Figure 9(a): EDX spectra of ZnS

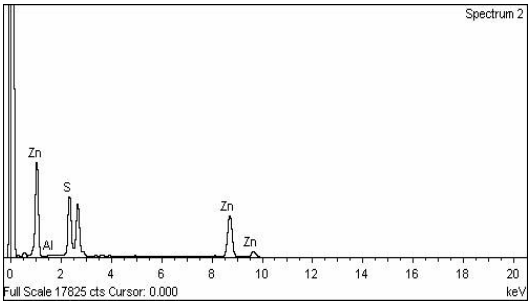


Figure 9(b): EDX spectra of ZnS-Al

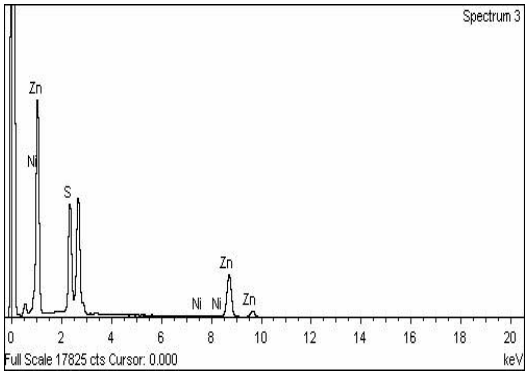


Figure 9(c): EDX spectra of ZnS-Ni

Table 4(a)		
Element	Weight%	Atomic%
S K	45.39	62.89
Zn K	54.61	37.11
Totals	100	

Table 4(b)		
Element	Weight%	Atomic%
Al K	0.26	0.46
S K	36.77	54.1
Zn K	62.96	45.44
Totals	100	

Table 4(c)		
Element	Weight%	Atomic%
S K	49.82	66.92
Ni K	0.23	0.17
Zn K	49.95	32.91
Totals	100	

Table 4(a), 4(b) & 4(c) show the composition of ZnS, ZnS-Al & ZnS-Ni particles with the help of Energy Dispersive X-ray Spectroscopy (EDX). Energy Dispersive X-ray

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fluorescence (EDX) spectra showed presence of Zn, S, Al & Ni and their wt%.

4. Conclusion

We have successfully synthesized the ZnS, ZnS: Al and ZnS:Ni nanoparticles by chemical route. The structure and optical characterization of the films were done with the help of XRD, TEM, SEM, SAED, UV-VIS spectrophotometer. PL, XRD, SEM and TEM studies reveal formation of nanoparticles. XRF study reveals the presence of Zn & S and doping agents Ni & Al in the films. UV spectra reveals that the absorption band was blue shifted from the bulk. Photoluminescence investigation reveals the high crystalline nature of the ZnS nano particles. The reduction of particle size with variation of pH in ZnS nano particles has been observed. The result indicates that particle sizes are symmetric in nature and are of spherical in shape.

5. Acknowledgement

The Authors are very much thankful to Department of Chemistry, G.U for providing UV-VIS and PL facility. We are 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, and Gauhati University for providing XRF facility. We are thankful to IASST, Guwahati for providing XRD facility. We are thankful to Dept of Physics Tezpur University For Providing EDX facility. The authors are also grateful to Prof. K.C. Sarma, Head, Dept. of Instrumentation & USIC, and Gauhati University for constant guidance and help.

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