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Synthesis and Optical Property Studies of Undoped and Doped Zns (with Al & Ni) Nano-Particles

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Abstract:
Undoped and doped Zinc Sulphide Nano particles with aluminium and nickel at different volume ratios using Polyvinyl alcohol matrix were synthesized by chemical route. These ZnS thin films posses a nanocrystalline structure, exhibit quantum size effects due to the small crystal size and produce a blue shift in the optical spectra. With the help of X-ray diffraction (XRD) and Transmission Electron Microscope (TEM) Nanostructure is characterized. With the help of Scanning Electron Microscope (SEM) surface morphology is studied. We have prepared volume ratios of 5:2, 5:3 & 5:4 of ZnS, ZnS-Al and ZnS-Ni keeping pH = 1. In the volume ratio 5:2 absorption peak of undoped ZnS is found at 360 nm. After doping with Al the peak is found at 340 nm and doping with Ni it is found to be shifted to 290 nm. From PL studies excitation peaks of ZnS, ZnS-Al and ZnS-Ni are found at 540 nm, 510 nm and 460 nm. From UV and PL studies the effect of doping is well noticed and they support one another. But when volume ratios are changed to 5:3 and 5:4, no remarkable changes are noticed (from UV and PL studies). From TEM studies, average particle sizes of ZnS, ZnS-Al and ZnS-Ni are found to be 10.5 nm, 9.9 nm and 10.01 nm, and from XRD studies it is found to be 6.9 nm. SAED patterns show a set of three well-defined rings corresponding to diffraction from different planes of Nano crystallites of ZnS, ZnS- Al and ZnS- Ni. . X-ray Fluorescence studies show larger peak for Zn and S compared to dopant materials Al and Ni.

Keywords*: Nano materials, XRD, XRF, SEM, TEM, PL, UV-VIS*

1. Introduction

In recent years research on Semiconductor nano particles [1, 2] stimulated great interest because of their unique optical [3] and electrical properties. Among the semiconductor nanoparticles, Zinc Sulphide as an important II-VI semiconductor has been researched extensively because of its potential applications such as Cathode-ray tubes (CRT), field emission display (FED), phosphors for a long time. It can also be used for luminescent devices and photodiodes [4]. Recently much effort has been devoted to the research of doped nanostructured materials. Nanomaterials of this kind exhibit unusual physical and chemical properties in the comparison with their bulk [5] materials, such as size-dependent variation of the band gap energy. Impurity ions doped into these nanostructures can influence the electronic structure and transition probabilities [6]. Doped ZnS semi-conductor materials have a wide range of applications in electro-luminescence devices, phosphors, light emitting displays and optical sensors. Chemical growth process is a very simple, efficient, economical and convenient method among the various researchers. To control the size, morphology and crystalinity of ZnS nano-crystals, study of their physical properties is very much essential. The aim of this paper is to report the result of investigations of X-ray diffraction, SEM, HR-TEM, UV-VIS absorption and photoluminescence (PL) studies of un-doped and Al, Ni doped ZnS nanoparticles.

2. Experimental

(A) ZnS nano-particles were synthesized by using Polyvinyl Alcohol (PVA) as a matrix. We had taken 5 wt% solutions of PVA and 2, 3 & 4 wt% solutions of $ZnCl_2$ in deionized water. They were stirred at 200 rpm in a magnetic stirrer at constant temperature of 70^0C for 3 hours. The solutions were kept overnight for complete dissolution and found to be transparent. By adding concentrated HNO_3, pH of the solution was lowered and kept constant at 1. A 2wt% 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 was formed, it embedded into the gap. The chemical reaction took place as follows-

$ZnCl_2 + Na_2S = ZnS + 2\ NaCl$

Keeping pH = 1, we had mixed PVA and each of the $ZnCl_2$ solutions prepared in the following volume ratios- 5:2, 5:3 and 5:4.
(B) To make ZnS-Al solution, 0.1 wt% $AlCl_3$ was mixed with demonized water at room temperature. This solution of $AlCl_3$ was mixed with another solutions of 5 wt% PVA and (2, 3 & 4) wt% $ZnCl_2$. The mixed solution was stirred at 200 rpm 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 lowered by adding concentrated HNO_3 and kept constant at 1. The solution appears to be transparent. Here also PVA and $ZnCl_2$ solutions were mixed in the following volume ratios 5:2, 5:3 and 5:4.
(C) To make ZnS-Ni solution 0.1 wt% $NiCl_2$ was mixed with demonized water at room temperature. This solution was mixed with another solution of 5 wt% PVA and 2, 3 & 4 wt% $ZnCl_2$. The solutions were stirred at 200 rpm at a constant temperature of 70^0C for 3 hours. 2 wt% Na_2S solution was added to the solutions. By adding concentrated HNO_3 the pH of the solution was lowered and kept at 1. The mixed solutions appeared to be transparent. For preparation of films the PVA solution and $ZnCl_2$ Solutions were mixed in the following volume ratios 5:2, 5:3 and 5:4.

3 Results and Discussion

3.1 Optical Absorption Studies
The optical absorption of ZnS was recorded at room temperature using a Double Beam automated Spectrophotometer (Hitachi-U3210). The measurements of optical absorption of the films at different volume ratios and at constant pH=1 in the range 200-1000 nm showed the strong absorption at slightly different wavelength. The peak of absorption showed blue shift with respect to bulk attributing quantum confinement effect in the nano-particles. Fig 1(a) shows UV-VIS spectra of Al & Ni doped ZnS and undoped ZnS Nanoparticles. The absorption peak at 360 nm in the curve of undoped sample is attributing to be absorption of ZnS nanoparticles. Optical absorption spectrum of ZnS-Al features a strong peak around 340 nm and ZnS-Ni at 290 nm, with volume ratio being 5:2 nm and pH=1. UV-VIS spectra of undoped ZnS and Al, Ni doped ZnS shows a peak with a blue shift. This indicated that Al, Ni doping has an effect on the electronic absorption spectra of ZnS.

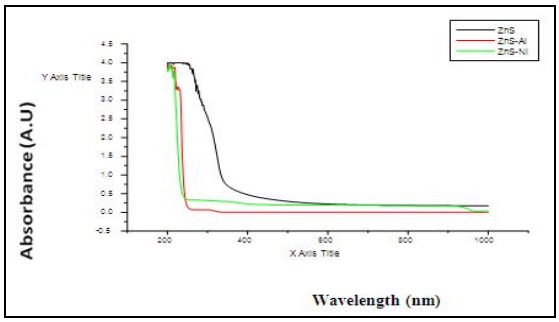
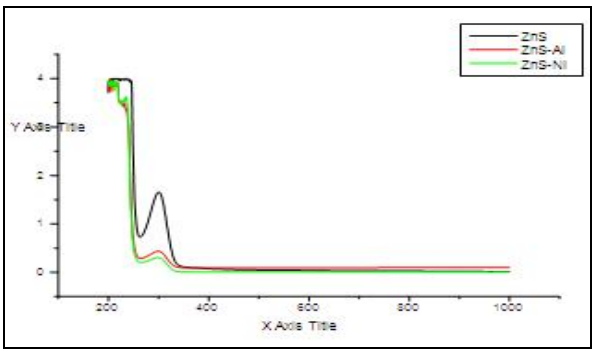


Figure 1(a): UV-VIS spectra of ZnS, ZnS-Al & ZnS-Ni (Volume ratio 5:2, pH=1.0)



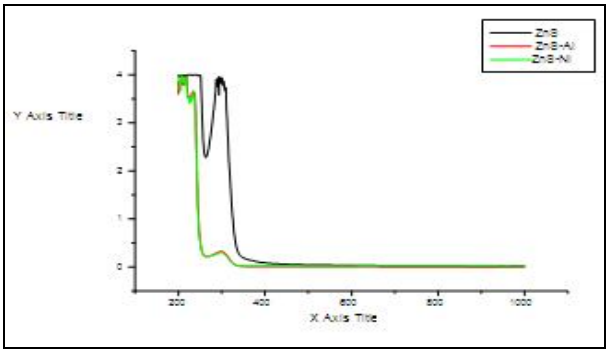


Figure 1(b): UV-VIS spectra of ZnS, ZnS-Al & ZnS-Ni (Volume ratio 5:3, pH=1.0)
Figure 1(c): UV-VIS spectra of ZnS, ZnS-Al & ZnS-Ni (Volume ratio 5:4, pH=1.0)

3.2. Photoluminescence Studies
The photoluminescence studies of ZnS, ZnS- Al and ZnS-Ni nanoparticles were done at room temperature by using F-2500FL spectrophotometer at an excitation wavelength of 270 nm. For undoped ZnS, the peak of PL emission spectra is found around 540 nm. Al dependent emission is at 510 nm and Ni dependent emission is found around 460 nm, which implies successful doping.

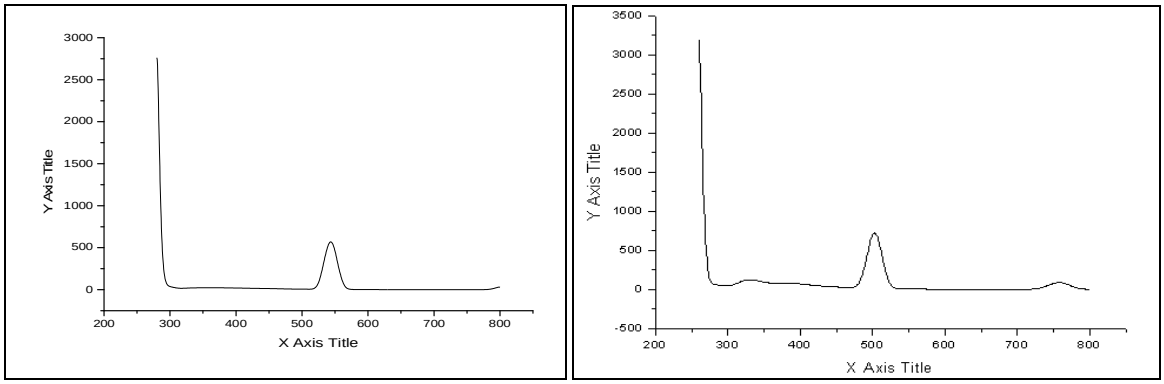


Figure 2(a): PL spectra of ZnS (Volume ratio 5:2, pH=1.0)
Figure 2(b): PL spectra of ZnS-Al (Volume ratio 5:2, pH=1.0)

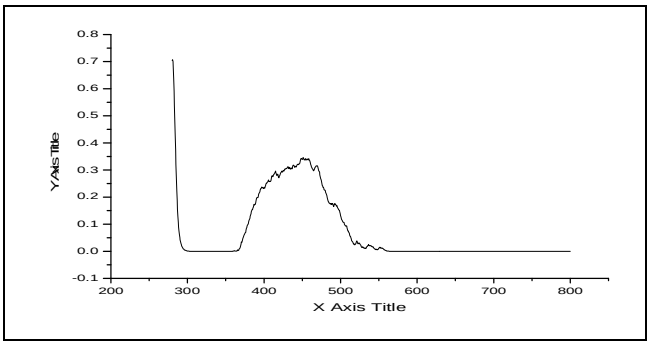


Figure 2(c): PL spectra of ZnS-Ni
Wave length (nm) (Volume ratio 5:2, pH=1.0)

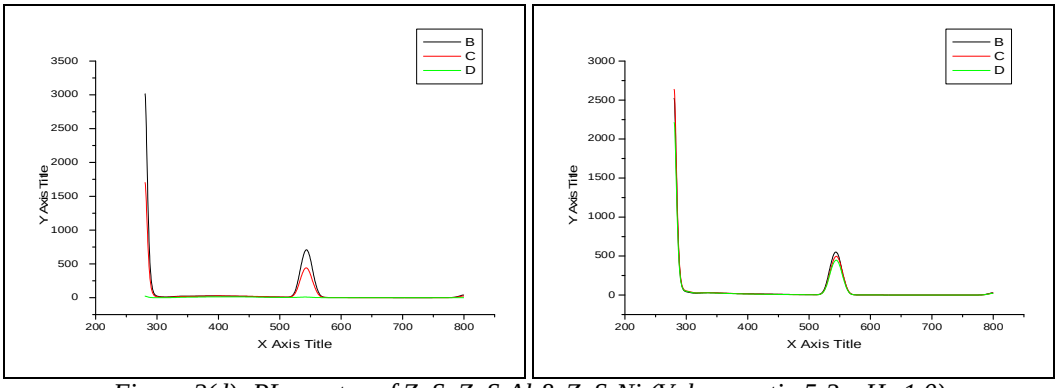


Figure 2(d): PL spectra of ZnS, ZnS-Al & ZnS-Ni (Volume ratio 5:3, pH=1.0)
Figure 2(e): PL spectra of ZnS, ZnS-Al & ZnS-Ni (Volume ratio 5:4, pH=1.0)

3.3. SEM Studies

Photographs of the nano-crystalline thin film were taken with JEOL-6360. SEM photograph are shown in fig3 (a), 3(b) & 3(c). The surface morphology of the film prepared at 70^0C with PVA was observed. Formations of cubic and orthorhombic crystals were observed. Study showed surface of the film was smooth and uniform.

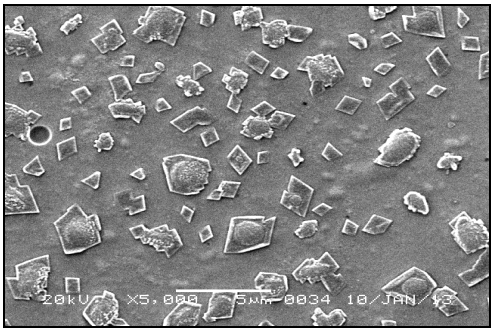


Figure 3(a): SEM PHOTO OF ZnS

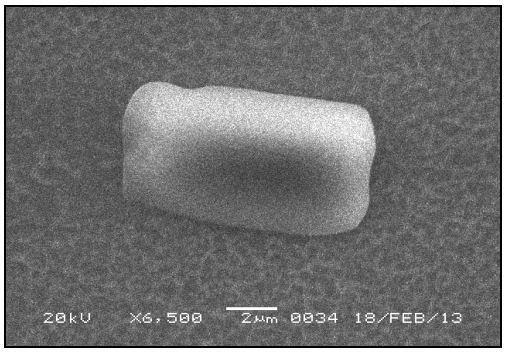


Figure 3(b): SEM PHOTO OF ZnS-Al

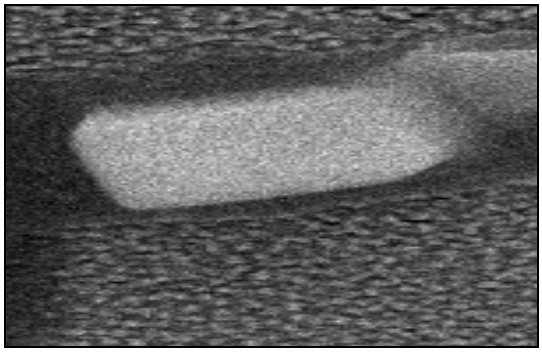


Figure 3(c): SEM PHOTO OF ZnS-Ni

3.4. TEM Studies

For TEM studies solutions were deposited in the microscopic grids. With the help of TEM (JEOL-100CX), images were taken. TEM micrographs and corresponding electron diffraction patterns were shown in fig 4(a), 4(b) &4(c). We get mean particle size of ZnS, ZnS-Al & ZnS-Ni as 10.14 nm.

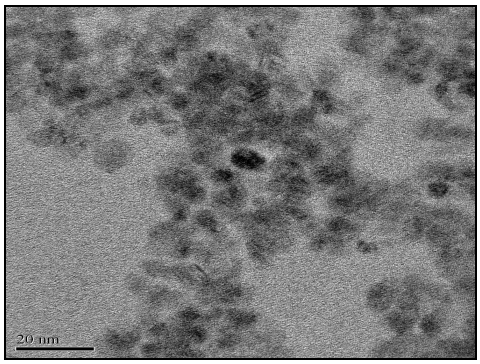


Fig 4(a): TEM PHOTO OF ZnS

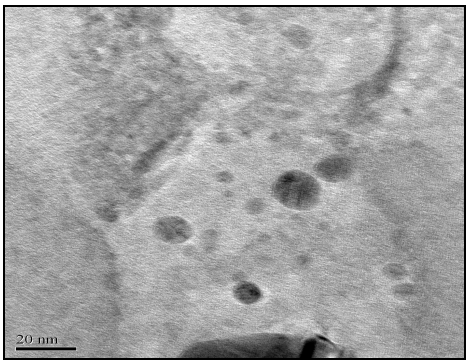


Fig 4(b): TEM PHOTO of ZnS-Al

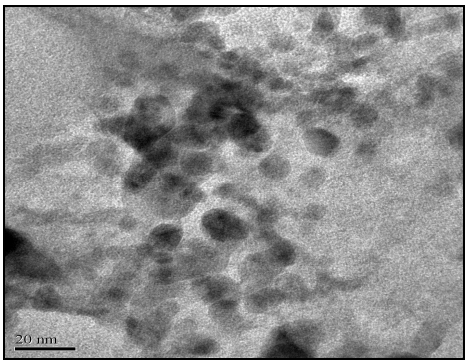


Fig 4(c): TEM PHOTO of ZnS-Ni

3.5 HR-TEM

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

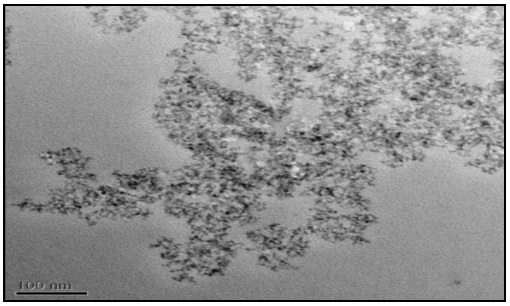


Figure 5: HR-TEM photo of ZnS

3.6. SAED Studies

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

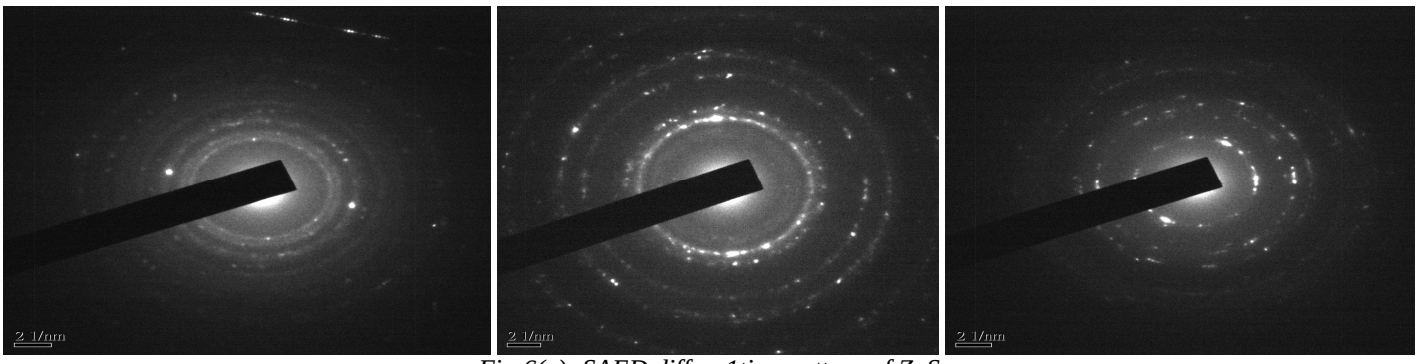


Fig 6(a): SAED diffrac1tion pattern of ZnS
Fig 6(b): SAED diffraction pattern of ZnS: Al
Fig 6(c): SAED diffraction pattern of ZnS: Ni

3.7. XRD studies

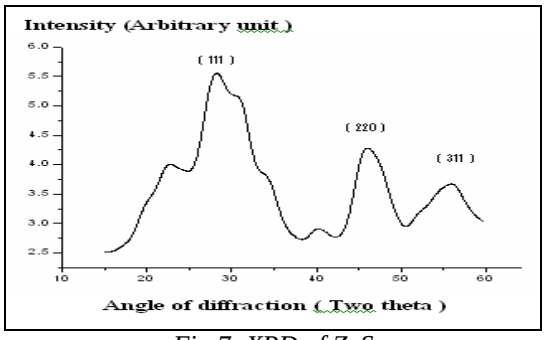


Fig 7: XRD of ZnS

For XRD studies, films were obtained by casting the solution over a glass slide of 20 mm × 15 mm size. Diffractogram was obtained from a Phillip's x'part Pro powder diffractometer using Cu Kα radiation with the operating voltage 40 kV and current 30 mA. The XRD diffractogram was found within the range [7, 8]. From the XRD pattern the films were seemed to be Polycrystalline [9]. The average particle sizes corresponding to FWHM was calculated with the Scherer formulae (1) and were found to be 6.9 nm [10].

$D_p = 0.94\lambda / \beta_{1/2} \cos\theta$ …….. (1)

Where,

- D_p is the particle size of the crystallite.
- λ is the wavelength of X-ray used.
- $\beta_{½}$ is the full width at half maxima (FWHM)
- θ is the angle of X-ray diffraction.

3.8. XRF Studies

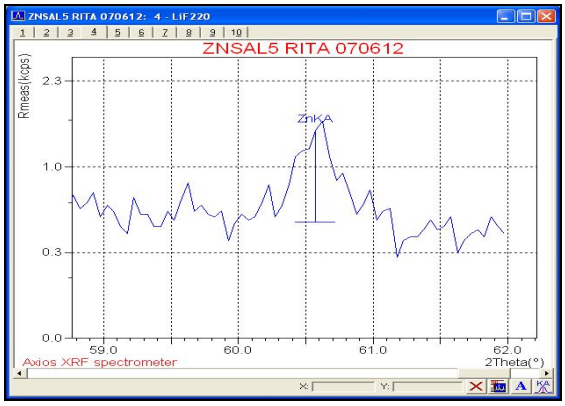


Fig 8(a): XRF spectra of Zn of ZnS

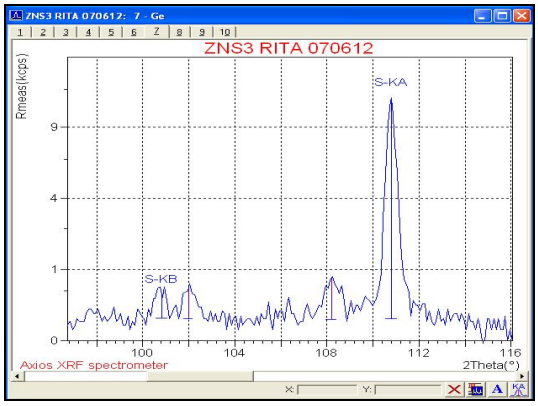


Fig 8(b): XRF spectra of S of ZnS

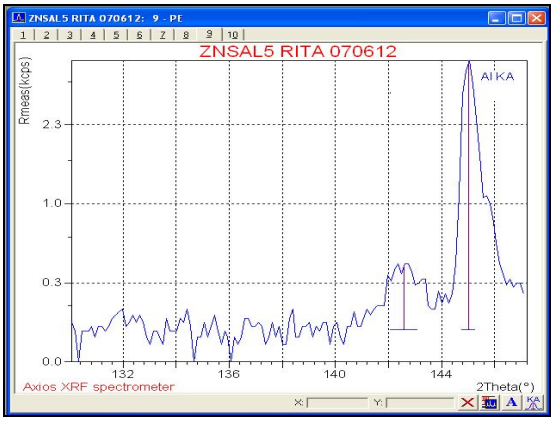


Fig 8(c): XRF spectra of Al of doped ZnS

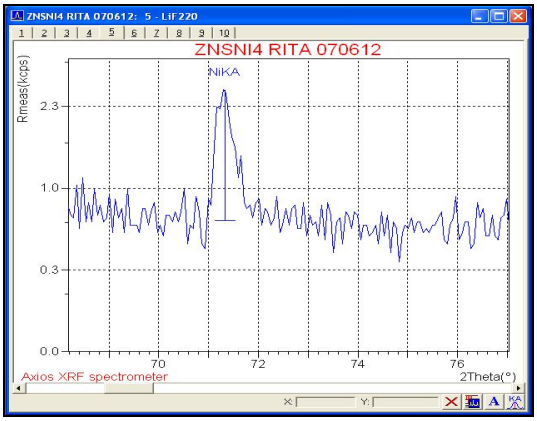


Fig 8(d): XRF spectra of Ni of doped ZnS

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

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 within the range of 10 nm. 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.

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6. References

1. Borah, J.P & Sarma, K.C. (2008). “Optical and optoelectronic Properties of ZnS Nanostructured
2. Thin Film”, ACTA, PHYSICA, 114, 713-719.
3. Brus L, 1991 “Luminescence of Direct and Indirect Gap Quantum Semiconductor crystallites”, Awppl, Phys. A53, 465.
4. Jayanthi, K., Chawala, S., Chander, H.,& Haranath., D. (2007).”Structural, Optical and Photo luminescent properties of ZnS:Cu nano particles thin film as a function of dopant concentration and quantum confinement effect”, crys. Res & Tech, 42,976.

5. Habubi N., Hashim M, & Yasiri - A.Al. (2010). “Structural and Characterization of irradiated ZnS thin films”, Baghdad Science Journal, Vol. 7 (4), 1421.
6. Chem YY., Duh JG., Chio B S, & Peng CG (2001).” Luminescent mechanisms of ZnS: Cu: Cl and ZnS: Cu: Al phosphors” Thin Solid Films, 392 50.
7. Peng, W., Cong, G., Qu,S, & Wang,Z. (2009).”Synthesis and Photoluminescence of ZnS:Cu nanoparticles,” Optical Materials, vol 29, no 2-3,p.p. 313-317.
8. Thi, T, M, Van., B.H, & Ben., P.V. (2010).”Study of Microstructure and Optical properties Of PVA caped ZnS: Cu nanocrystalline Thin film”, J.Nolin opt.phy & Mat (JNOPM, 19,237-245.
9. Krystab, T; KhomchenkO, V.S; Andraca-Adame, J.A; Khachatryan, V.B; Mazin, M.O; Rodionov, V.E; Mukhlio, M.F.2005 “ Phase transition in ZnS thin film Phosphor” J. cryst Growth 275, 1163-1167.
10. Goudarzi, A., Aval, G.M., Park, S.S., Choi, M.C., Sahraei, R., Ullah, M.H., Avane, A.,& Ha, C.S.,(2009).”Low-Temperature growth of Nano-crystalline Mn-doped ZnS Thin Films prepared by Chemical Bath deposition and optical properties”, Chem, Mater 21, 2375-2385.
11. Murugados., G, Rajamannan., B, Ramasamy., V, Viruthagiri., G.J.(2009).”Synthesis and Characterization of water soluble ZnS:Mn2+ nanoparticles” Chalgogenide Letters, Vol 6, no 5, pp 197-210