Impact of Nickel Doping on Structural and Optical Properties of Zinc Sulphide Nanoparticles

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Abstract: *This paper aims to report the impact of Nickel doping on the structural and optical properties of ZnS nano particles at room temperature .Undoped and Nickel (2% and,4%) doped ZnS nano particles were synthesized by Wet Chemical Synthesis method. The prepared samples are characterized by X-Ray Diffraction analysis (XRD), Scanning Electron Microscope (SEM), UV–Vis-NIR Spectrophotometer and Photo luminescence (PL). X- ray diffraction studies reveal hexagonal wurtzite and rhombohedral structure for the as prepared samples. SEM images clearly showed the formation of nanorods for samples prepared at room temperature. The average diameters of the nanorods were found to vary between 20-25nm.The PL spectra exhibit emission peaks in both UV and visible regions and these results are good agreement with the absorption spectra. The optical band gap of ZnS decreases with the increase of Ni concentration.*

Index Terms: Wet Chemical Synthesis, PL Spectra, Optical band gap, UV– Vis absorption

I. INTRODUCTION

Nanocrystalline materials have attracted much attention in recent years because properties in nanoforms differ significantly from those of their bulk counterparts. Many fundamental properties of materials (optical, electrical, mechanical, etc.) can be expressed as a function of their size, composition and structural order .The use of single source precursors for the synthesis of metal chalcogenide nanoparticles has proven to be efficient routes for the synthesis of high quality nanocrystals. Consequently, much effort has been made to control the size, morphology and crystallinity of nanocrystals with a view to tune their physical properties. The band structure, band gap changes due to decrease in particle size, the band gap increases with the edges of the band split into discrete energy levels. Zinc sulfide is a II–VI compound semiconductor with direct and wide band gap of 3.68 eV. It is an important material with an extensive range of applications such as optical coating, electro-optic modulator, photoconductors, optical sensors, phosphors, and other light emitting materials [1]. ZnS has been used widely as an important phosphor for photoluminescence (PL), electroluminescence (EL) and cathodoluminescence (CL) devices due to its better chemical stability. Nature and concentration of dopants play key roles in luminescence efficiency and the position of emission bands of semiconductor nanoparticles, Thus influencing their practical applications Therefore, it is very important to investigate how the dopant concentration of doped semiconductor nanoparticles affects optical properties form the perspective of basic science and application [2].Various research groups have reported the optical properties of various doped nanocrystals and the potential application of these luminescent materials.

Today, various transition metal ions and rare earth ions like as Cu^{2+}, Mn^{2+}, Pb^{2+}, Ni^{2+}, Cd^{2+}, Co^{2+}, Eu^{3+}, Sm^{3+},Tb^{3+}, etc., have been doped as impurities in Nanocrystalline ZnS host [3-10].Nickel is one of the transition metals which has ionic radius comparable to that of zinc ions. This makes Ni a suitable dopant for replacing zinc ions in ZnS lattice. Depending on dopant concentration, various morphologies like spherical, tetrapod's, sheet and long armed multipods are formed during synthesis Ni^{2+} doped ZnS nanoparticles were synthesized by Pathak et al. [11] at room temperature using chemical precipitation method without using any capping agents and their optical properties were investigated. Optical and electrical properties of pure and Ni doped ZnS were studied by Firdous [12] and it was observed that the optical and electrical band gap were red shifted compared to pure ZnS nanoparticles.

II. EXPERIMENTAL METHOD

A. Materials:, Undoped and Ni doped ZnS nano particles were obtained by using a novel, Wet Chemical Synthesis (WCS) with complete analytical reagen**t** grade chemicals such as Zinc Acetate Dehydrate $Zn(CH_3COO)_2{\cdot}2H2O)$,Sodium Sulfide ($Na_2S.H_2O$), Nickel Acetate Dehydrate ($Ni(CH_3COO)_{2.}4H_2O$) as source materials., Polyvinyl Pyrrolidone (PVP (C2H9NO)n) is used as a capping ligand to prevent agglomeration [13] Deionized water is used throughout the entire experimental process.

B. Synthesis: Samples of Undoped, 2% of Ni Doped & 4% of Ni Doped prepared with molar ratio of Zinc Acetate to Sodium Sulfide in 1:2 For the synthesis of Undoped Zinc Sulfide Nano particles, 0.3 mol of Zinc Acetate and 0.032gms of PVP were dissolved in 80 ml of de ionized water under continuous stirring followed with the dripping of 2 ml of Ammonia for an hour .Parallelly 0.6 mol of Sodium Sulfide is dissolved in 80 ml of de ionized water under stirrer. The Na_2S solution was then poured drop by drop in to the Zinc Acetate and PVP solution under continuous stirring. After the reaction was completed, a milky white precipitate was formed. The white mixture was centrifuged at 300 rpm for 30 minutes, dried at 120 ° C for about 1 hour in a hot air oven and crushed with the help of a mortar to get fine nano particles [14] Chemical precipitation of Ni doped ZnS Nano particles with 2% of Ni and 4% of Ni were carried out separately at room temperature using the reactants Zinc Acetate Dehydrate PVP, Sodium Sulfide and Nickel Acetate Dehydrate.

III. CHARACTERIZATION

The phase purity and crystal structure of as prepared Undoped and Ni doped ZnS Nano particles were carried out by analyzing the X-Ray Diffraction (XRD) patterns using monochromatic Cu- Kα radiation in 2θ range of 5º to 90 º with a Ka -XRD 786 running under the continuous scanning mode. A JEOL-Scanning Electron Microscopy (SEM) (Model JSM – 6390, Made in JAPAN) was used to record the micrograph for the samples of Undoped and Ni doped ZnS Nano particles. Optical absorption studies were carried out using a UV-Visible Spectrometer (JASCO V- 570, CANADA Make) in the range of 200 - 1200 nm .The elemental compositions of Undoped and Ni doped ZnS Nano particles were analyzed and the characteristic elements were identified by using EDAX .Photoluminescence (PL) spectra of the as prepared samples were recorded using Spectrofluorometer (HORIBA JOBIN-YVON-Fluorolg).

IV. RESULTS AND DISCUSSION

XRD Analysis:

From the XRD profile of the Undoped sample (1:2 molar ratio of Zn and sulfur source) it is revealed that the Undoped ZnS nano material has a Hexagonal structure and shows 3 distinct peaks well matched with the Joint Committee on Powder Diffraction Standard (JCPDS) Card No. 89-2182.The XRD patterns of Ni doped samples with 2% of Ni and 4% of Ni indicates that the samples are in Rhombohedral shapes and agreed with the JCPDS Card Nos 89-22176 and 89-2177 respectively. All the XRD profiles confirms the phase singularity of the synthesized Nanoparticles ,i.e no other peak is observed corresponding to their binary system, which confirms the formation of Nano particles[15-17] The average diameters of the nanorods were found to vary between 20nm and 25nm.

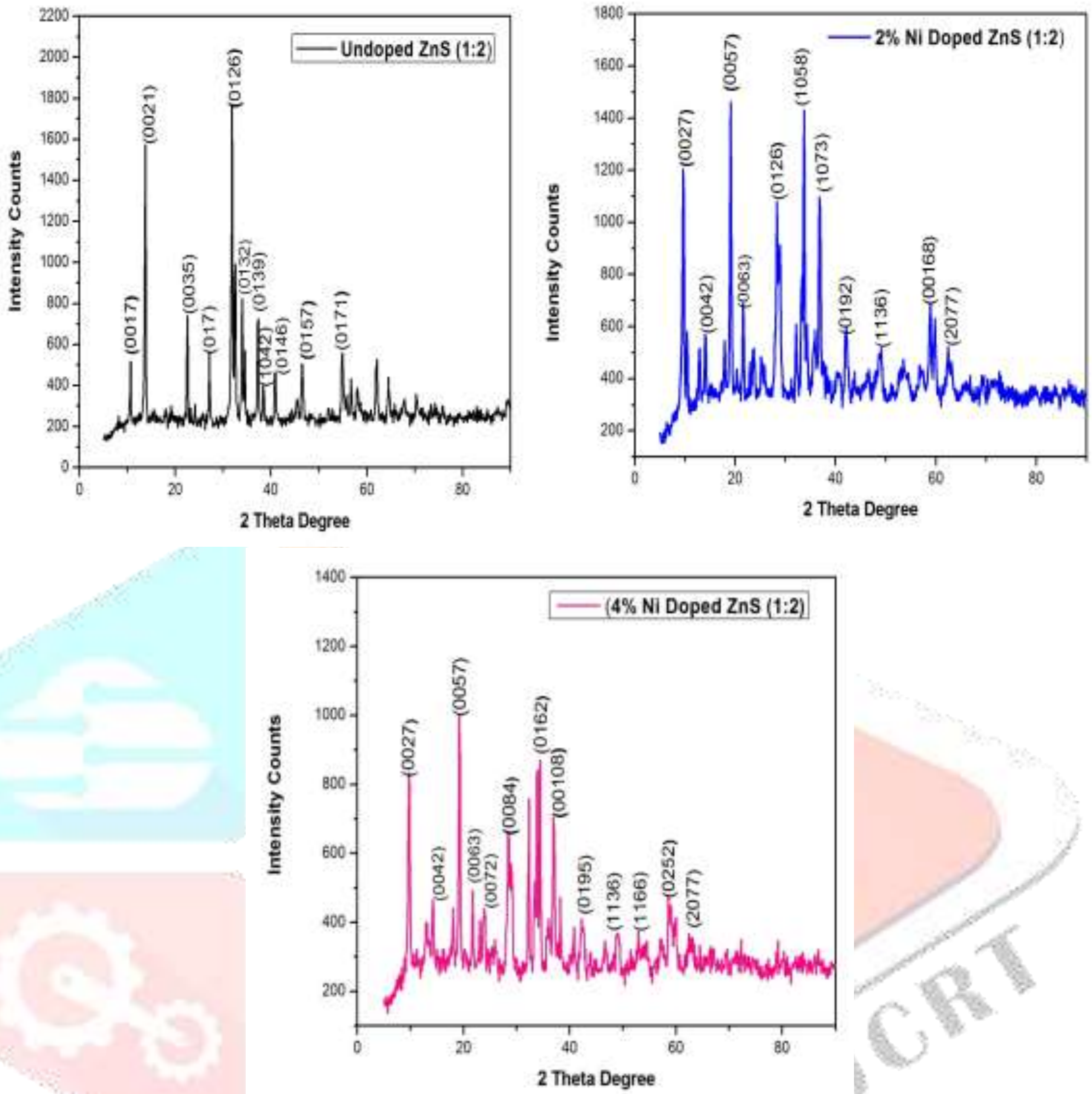


Figure 1 XRD pattern of Undoped, 2% Ni doped and 4% Ni doped Nanoparticles

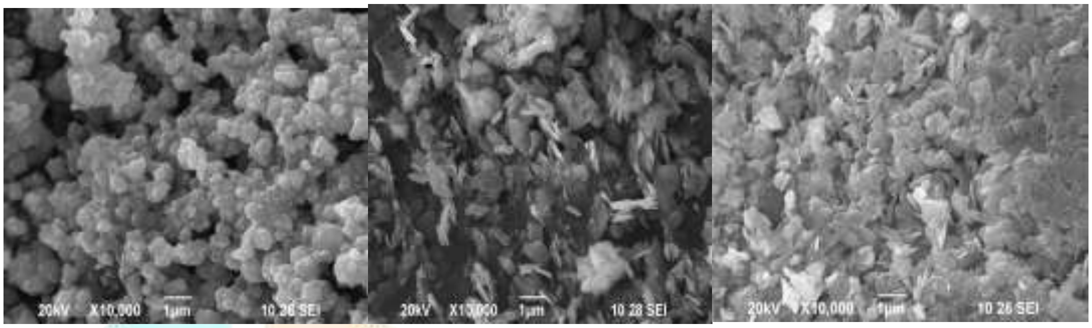
The structural parameters of the ZnS samples prepared with different dopant concentrations viz., 2%,4% % of Nickel were listed in the table.1. The grain sizes of the as prepared samples were determined using Scherer's semi-empirical formula and the values are shown in table.1

Table.1 The structural parameters of the ZnS samples prepared with different dopant concentrations

Nanoparticles	**2θ (º)**	**FWHM**	**Grain size (nm)**
Sample –I	31.86	0.32	23.2
Sample –II	33.51	0.31	24.5
Sample –III	34.36	0.32	22.9

SEM & EDAX Analysis:

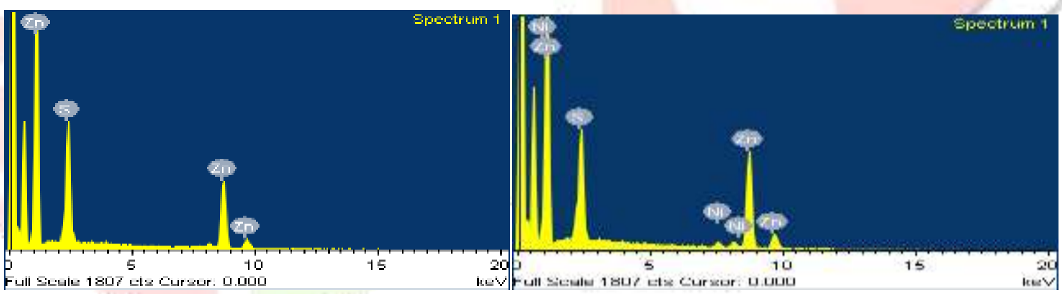
The Scanning Electron Microscope (SEM) was used to characterize the size, shape and morphologies of formed Nano particles. The SEM images of Undoped and Ni doped ZnS Nano particles shows that the as synthesized samples contain mainly the grains of ZnS Nanoparticles with regular shape. It was also observed that the microscopic images resemble like spherical ZnS Nanoparticles and the usage of PVP causes the stabilization of the small particles and the inhibition of agglomeration.



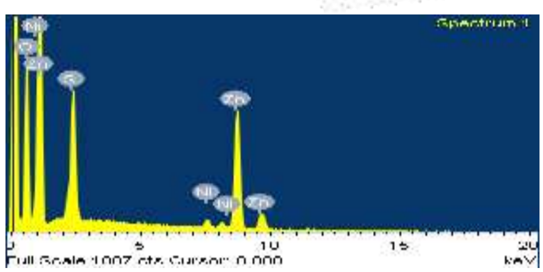
(a) (b) (c)

Figure 2 SEM images of (a) Undoped (b) 2% Nickel doped (c) 4% Nickel doped ZnS Nanoparticles

The EDAX spectra peaks corresponding to the elements Zn, Ni and S confirms the presence of the nanoparticles in the polymer matrix and it was proved that the chemical precipitation method is very effective as no loss of elements occurs during the synthesis[18-20]. From the EDAX studies, it was also observed that the Ni doped ZnS Nanoparticles are oxygen rich in nature.



(a) (b)

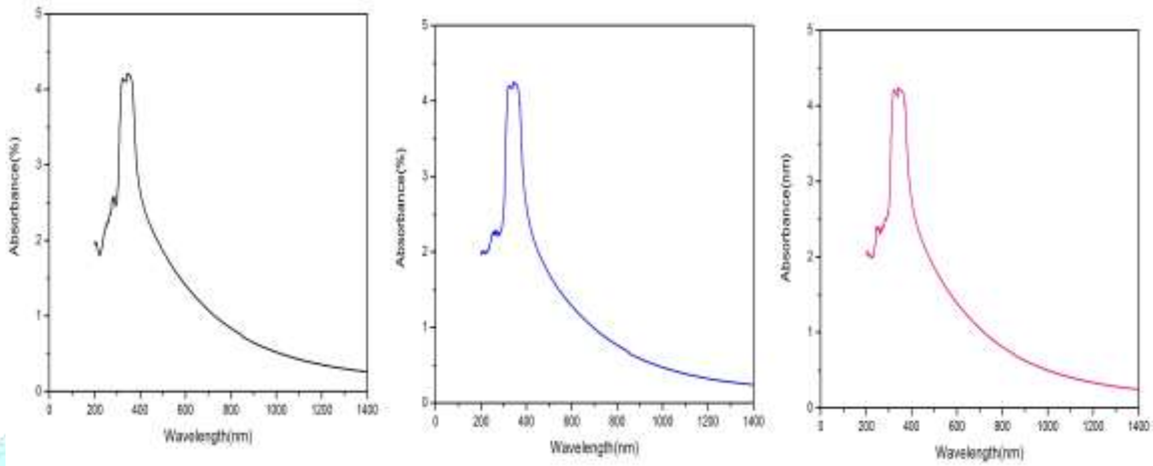


(c)

Figure 3 EDAX images of (a) Undoped (b) 2% Nickel doped (c) 4% Nickel doped ZnS Nanoparticles

UV-Vis absorbance:

Optical absorption studies were carried out with UV –VIS –NIR Spectrophotometer .It was cleared that the Ni doped ZnS nanoparticle has high absorbance than Undoped ZnS.The band gap values of samples ranges from 1.95 eV to 2.97eV. The obtained band gap value of Undoped ZnS is greater than the Ni doped ZnS and the bandgap of Ni doped sample shows a decrease with the increased Ni concentration. [21, 22].



(a) (b) (c)

Figure 4 UV-Vis absorption spectrum of (a) Undoped (b) 2% Nickel doped (c) 4% Nickel doped ZnS Nanoparticles prepared in 1:2 molar ratio

Photoluminescence Studies

The PL spectra of Undoped and Ni Doped ZnS nanoparticles were carried out at room temperature using Spectrophotometer. In all the measurements the excitation wavelength of was fixed as 350 nm. For the Undoped ZnS the peaks positioned at 395 nm (Violet) and at 500 nm(Green). Photoluminescence peak for the Ni doped (2%) sample is at 440 nm (Blue).

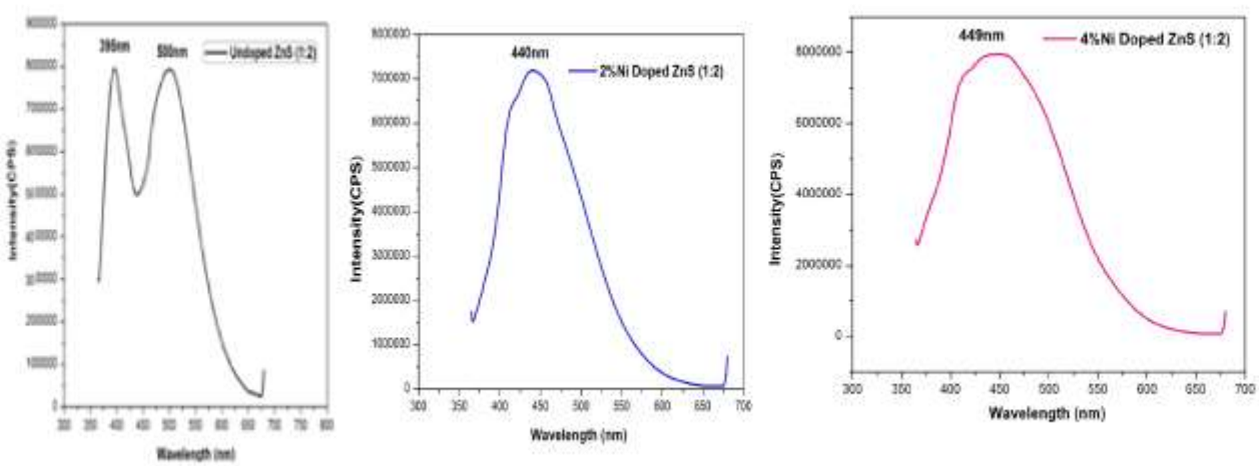


Figure 5 Photoluminescence spectra of (a) Undoped (b) 2% Nickel doped (c) 4% Nickel doped ZnS Nanoparticles

V. CONCLUSION

In the present work, Undoped and Ni doped nanoparticles were synthesized through Wet Chemical Co-Precipitation method using PVP as a capping ligand .The investigations of the impact of different percentage of doping on the structural, Morpological,Optical and photocatalytic properties were carried out using X-Ray Diffraction ,SEM, EDAX Spectra, Photo luminescence and UV-Vis spectroscopy . The average size of the Nano particle was calculated from the structural analysis. SEM images revealed that the ZnS nano particles possess spherical shape and not bulk with the use of PVP. The increased % of Nickel doped sample shows the higher absorbance in the UV studies. The Photoluminescence Studies of the Undoped and Ni doped samples were also reported.

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