

SYNTHESIS OF Ni²⁺ IONS DOPPED ZnS NANO PARTICLES BY CHEMICAL PRECIPITATION METHOD AND THEIR CHARACTERIZATION

R. ASHOKKUMAR, K. GEETHA*, P. PRABUKANTHAN

PG Research Department of Chemistry, Muthurangam Government Arts College, Vellore -632 002, Tamil Nadu, INDIA.

A simple wet-chemical co-precipitation method is optimized for the synthesis of different concentration Ni²⁺ ions doped ZnS nanocrystals. To obtain the 3% of Ni²⁺ ions doped ZnS nanoparticles were annealed at 100°C for 2, 3, and 4 hours, respectively. As prepared nanostructure of the particles and annealed samples have been analyzed by powder X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive analysis of X-rays (EDAX) and UV-Vis spectrometer techniques. XRD studies show the phase singularity of Ni²⁺ ions doped ZnS particles having cubic (zinc-blende) structure. XRD line broadening indicates that the average crystallite size of doped ZnS samples were approximately 4-5nm. The cubic phase of the ZnS nanoparticles has no change and does not affect the crystalline size with respect to doping different concentration of Ni²⁺ ions. The value of the band gap of Ni²⁺ doped ZnS was found to be lower than the pure ZnS.

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1. Introduction

In recent years properties of new nano sized materials have generated a great deal of interest because of the science involved in these studies and technological application on these materials research on semiconductor new particles stimulated great interest because of their unique optical and chemical properties. Among the semiconductor nanoparticles ZnS is an important semiconductor compound of the II - VI group with excellent physical properties and wide band - gap of 3.7 eV at room temperature and has attracted great attention. It has been extensively investigated due to its potential for device application such as window layers for solar cell, production of hydrogen, blue - light diodes, electro - luminescence displays and antireflection coating for infrared devices and other non-linear optical devices [1-3]. In recent year research on the novel optical and electrical properties of nanomaterials can be controlled as per their particle size and therefore attracted much interest for their fundamental and applied aspect. Because of the novel physical properties and potential application semiconductor nanoparticles have been studied extensively. The nano sized semiconductor crystallites have changed the properties such as increased energy band gap results from quantum confinement. The new sized semiconductor crystallites could change optical properties which are different from bulk materials [4-7]. Pure nano sized ZnS particles show emission at 420-450nm. In order to obtain different emission in the visible region ZnS nano particles can be doped with transition and rare earth metals such as Cu²⁺, Mn²⁺, Ni²⁺, Cd²⁺, Co²⁺, Eu²⁺, Sm²⁺, To²⁺, and Er²⁺. [8] The large varieties of metals are employed for synthesis new structure viz. Large absorption electrochemical lubrication, high temperature reaction and slow thermal method [9-10]. However Ni²⁺ doped ZnS nano Particles can be obtained in many ways (e.g) a spray -based method [11] Mechanochemical route [12], coating method [13] synthesis by gamma -irradiation of solution [14] and chemical reaction method [15-25]. The present reports, the highly efficient PL characteristic of Ni²⁺ doped ZnS nanoparticles, synthesized by chemical precipitation method. It is the most popular technique that is used in industrial

*Corresponding author: senthil_geetha@rediffmail.com

applications because of its chief raw material, easy handling and large scale production [26]. The monodisperse ZnS and ZnS: Ni²⁺ nanoparticles were prepared without using any surfactant and water is used as a solvent. The pure and Ni²⁺ ions doped ZnS compounds were characterized by different techniques like powder X-ray diffraction (XRD), UV-Vis spectra, scanning electron microscope (SEM) and energy dispersive analysis of X-rays (EDAX).

2. Experimental

ZnS with doped Ni²⁺ ions nanoparticles were synthesized through the chemical co-precipitation method without using any capping agent. All analytical reagent (AR) grade chemicals used in the present study were purchased from SD Fine Chemicals Ltd. India and they are used without further purification. The synthesis of pure and Ni doped ZnS were carried out at room temperature. All the chemicals such as zinc acetate Zn(CH₃COOH)₂·2H₂O, NiCl₂·2H₂O and sodium sulfide (Na₂S·XH₂O) are above 98% purity. The ZnS nanoparticles were synthesized by chemical co-precipitation method. The synthesis reaction was carried out in the aqueous medium. Solutions of 0.5M Zn(CH₃COOH)₂·2H₂O and 0.5M Na₂S were prepared individually in 50 ml de-ionized water. Zinc acetate solution is vigorously stirred using a magnetic stirrer upto 10 min at room temperature and then followed sodium sulfide solution was added drop by drop to the above solution. Immediately the white colour precipitate was appeared. The precipitate was collected from the solution by adding a known volume of acetone. Immediate flocculation of nanoparticles occurred, the particles were washed several times with de-ionized water and ethanol to remove unreacted chemical and all sodium particles. The wet precipitate was dried at 100°C in open atmosphere for one hour. The ZnS nanoparticles doped with different Ni²⁺ ions concentration were synthesized in water without using other complex agent. In a typical experiment, 0.5M of Zn(CH₃COOH)₂·2H₂O in 50 ml water and NiCl₂·2H₂O in 25 ml water with different concentration (1, 2, 3, 5, 7, 9 and 11%) were mixed drop by drop. The concentration of Ni²⁺ ions was adjusted by controlling the quantity of Nickel chloride in the above mixture. The mixture was stirred magnetically at room temperature until a homogeneous and colorless solution was obtained. Then sodium sulfide was added drop by drop to the above mixture. The ash coloured precipitate is separated from the reaction mixture by centrifugation for 5 min at 10,000 rpm and washed several times with de-ionized water and ethanol. The products were dried at 100°C in open atmosphere for one hour. The 3% Ni²⁺ ions doped ZnS nanoparticles were annealed at 100°C for 2, 3, and 4 hours, respectively.

The synthesized nanoparticles were characterized using various techniques. The techniques include powder X-ray diffraction (XRD), scanning electron microscopy (SEM). The elemental composition on the surfaces of nanoparticles was monitored by EDAX (energy dispersive X-ray analysis). The SEM were used to obtain the morphological information of nanoparticles. XRD was used to identify the crystalline phases of the nanoparticles size of the particles was measured using Debye-Scherrer's equation. The UV-Visible spectrophotometer was used to measure the absorbance value and band gap of the nanoparticles were calculated.

3. Result and discussion

The powder X-ray diffraction (XRD) patterns of the samples (pure ZnS and Ni²⁺ ions doped ZnS) were presented in Figure 1 (a). When dopant concentration is low (1%, 3% and 5%) level the XRD patterns of the precipitated samples are in good agreement with ZnS zinc blende crystal structure. The three diffraction peaks correspond to (111), (220) and (311) planes of the cubic crystalline ZnS with reflections positioned at $2\theta = 28.9^\circ$, 48.4° and 57.5° were observed respectively. [22-23] Typical wurtzite peaks (100), (101), (102) and (103) have not been observed. Due to the size effect, the XRD peaks broaden and their widths become larger as the particle become smaller.

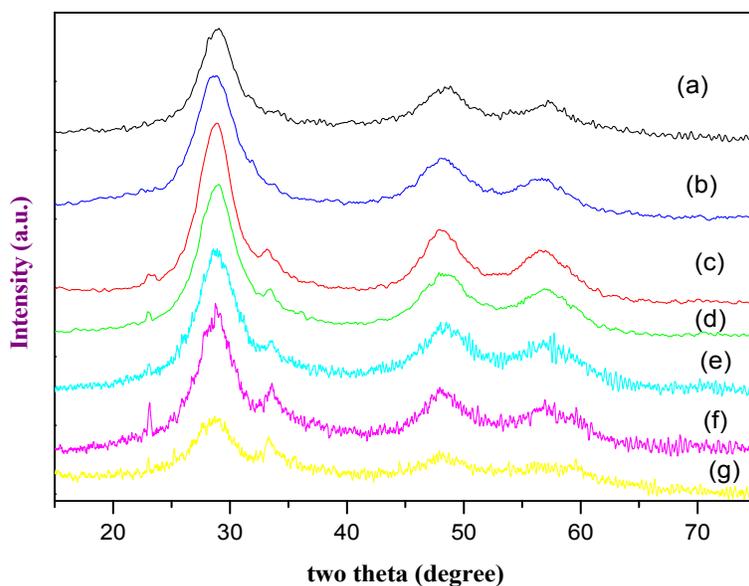


Fig 1(a) X-ray diffraction patterns of samples (pure ZnS and 1%, 3%, 5%, 7%, 9% and 11% Ni^{2+} ions doped ZnS compound (a- pure ZnS, b-g Ni doped ZnS))

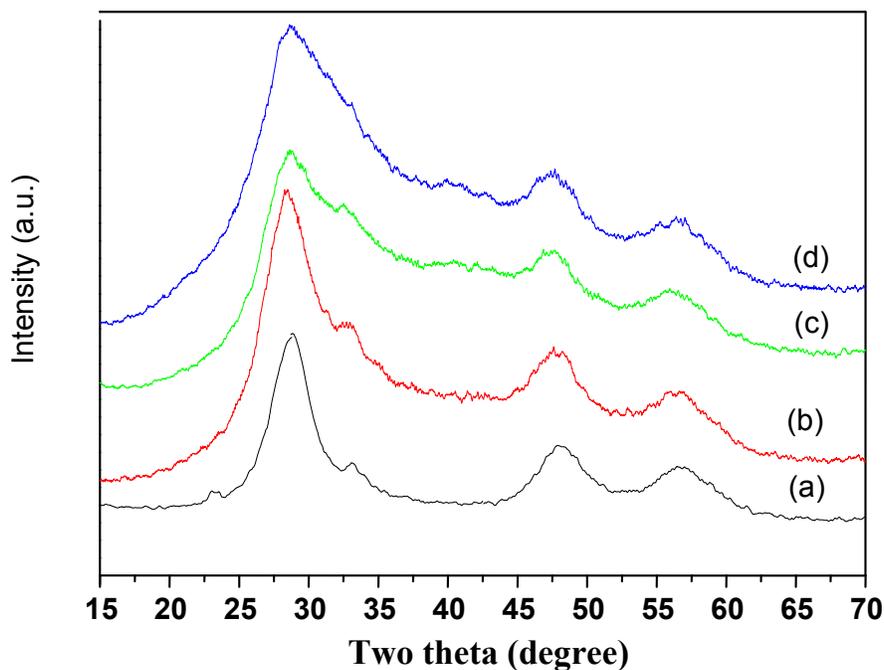


Fig. 1b(a-d) X-ray diffraction (XRD) pattern of 3% Ni^{2+} ions doped ZnS annealed 100°C annealed at different time interval (a) 1hr (b) 2 hrs (c) 3 hrs (d) 4 hrs.

The determination of phase composition, structure and particle size are very important for the discussions on the physical properties. We deduce there is no NiS or Ni in the precipitates for the following reason: the structure and XRD pattern of NiS and Ni is totally different from that of ZnS. XRD shows there is no detectable signal of Ni or NiS, when the corresponding co-precipitation ratio is at low co-precipitation ratio of $\text{Zn}_{1-x}\text{Ni}_x\text{S}$ samples otherwise the concentration of Ni^{2+} is quite low. These nanocrystals have lesser lattice planes compared to bulk, which

contributes of the broadening of the peaks in the diffraction pattern. This broadening of the peak could also arise due to the micro-straining of the crystal structure arising from defects like dislocation and twinning etc. These defects are believed to be associated with the chemically synthesized nanocrystals as they grow spontaneously during chemical reaction. As a result the chemical ligands get negligible time to diffuse to an energetically favorable site. It could also arise due to lack of sufficient energy needed by an atom to move to a proper site in forming the crystallite.

In the case of the mole percent of 9% and 11% Ni²⁺ ions doped ZnS samples the XRD planes of (220) and (311) could not be found. After 3 mole percent Ni²⁺ ions doped ZnS samples, the XRD peaks becomes broader (wide) with the increase of the Ni²⁺ ions dopant which is mostly due to the alloy fluctuation, amorphous state and more lattice stress & string in samples.

The 3 mole percent Ni²⁺ ions doped ZnS samples were annealed in open atmosphere at 100°C for different time interval (1,2, 3, and 4 hrs). The annealing effects in the XRD pattern of the Ni²⁺ ions doped ZnS samples are given in Figure 1(b). After annealing 3 mole percent Ni²⁺ ions doped ZnS different time interval samples, the three diffraction peaks correspond to (111), (220) and (311) planes does not change upto 5 hrs annealing at 100°C. And also in open atmosphere annealing process of the cubic crystalline ZnS with reflections positioned at $2\theta = 28.9^\circ$, 48.4° and 57.5° were observed respectively. No other peak of impurity phase such as Ni, NiS, ZnO and NiO was detected for such annealing for different time interval. It should be pointed that the XRD pattern of the sample did not show any diffraction peaks, which reveals here the crystalline NiS, NiO and ZnO phase could not be formed.

The crystallite size was estimated from the full width at half maximum (FWHM) of the major XRD peak using the Debye Scherrer equation[24-25]

$$D = 0.9 \lambda / \beta \cos\theta$$

with D being the crystallite size, λ the X-ray wavelength, β the full peak width at half-maximum (FWHM), and θ representing the Bragg angle. The average size (grain Size) of the undoped and Ni²⁺ doped ZnS samples as calculated by using the Debye Scherrer formula from the most intense peak are summarized in Table 1.

Table.1 Crystallite size as calculated by using the Debye- Scherrer's Formula from XRD

Samples	Peak position (111) plane	FWHM (degree)	Crystallite sizes (nm)
Pure ZnS	28.85	2.7677	4.398
1% Ni ²⁺ ions doped ZnS	28.79	3.2117	4.827
2% Ni ²⁺ ions doped ZnS	28.91	2.9936	4.806
3% Ni ²⁺ ions doped ZnS	29.91	3.2558	4.807
5% Ni ²⁺ ions doped ZnS	28.94	3.9925	4.802
7% Ni ²⁺ ions doped ZnS	26.05	2.8105	5.334
9% Ni ²⁺ ions doped ZnS	28.64	3.0031	4.852
11% Ni ²⁺ ions doped ZnS	28.48	2.5966	4.879
3% Ni ²⁺ ions doped ZnS – annealed for 2 hrs	29.77	4.5987	4.668
3% Ni ²⁺ ions doped ZnS – annealed for 3 hrs	29.82	4.4640	4.660
3% Ni ²⁺ ions doped ZnS – annealed for 4 hrs	29.74	4.8455	4.670

Figure 2(a-e) shows the scanning electron microscope (SEM) images of Ni²⁺ ions doped ZnS samples. SEM allows imaging of individual crystallites and the development of a statistical

description of the size and shape of the particles in a sample. As observed in the experiments, nanoparticles were stable for minutes, but after a few minutes, those particles were aggregated and their size become larger, because of their large surface area to volume ration and also the attractive force between the nanoparticles will increase and the particles will agglomerate.

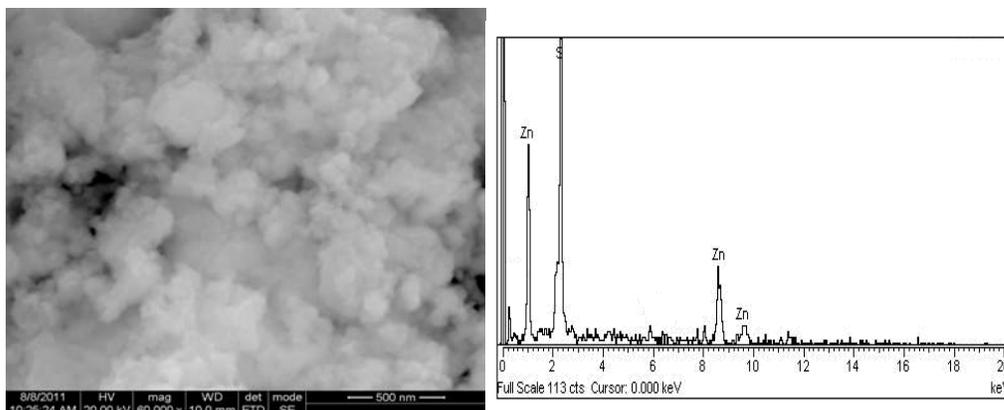


Fig. 2(a) SEM image of pure ZnS Compound The EDAX Spectrum of pure ZnS Compound

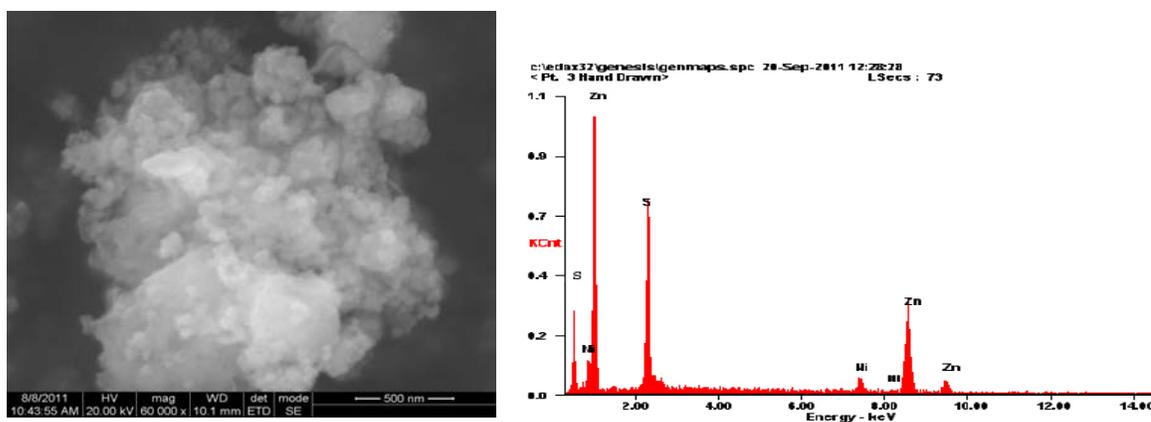


Fig. 2(b) SEM image of 3% Ni^{2+} ions doped ZnS Compound, the EDAX Spectrum of 3% Ni^{2+} ions doped ZnS Compound

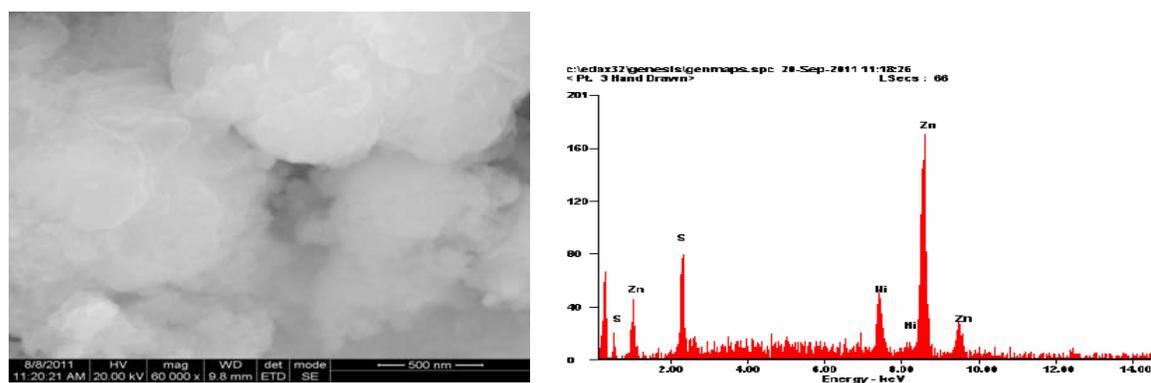


Fig. 2(c) The SEM image of the 5% Ni^{2+} ions doped ZnS compound
The EDAX Spectrum of 5% Ni^{2+} ions doped ZnS compound

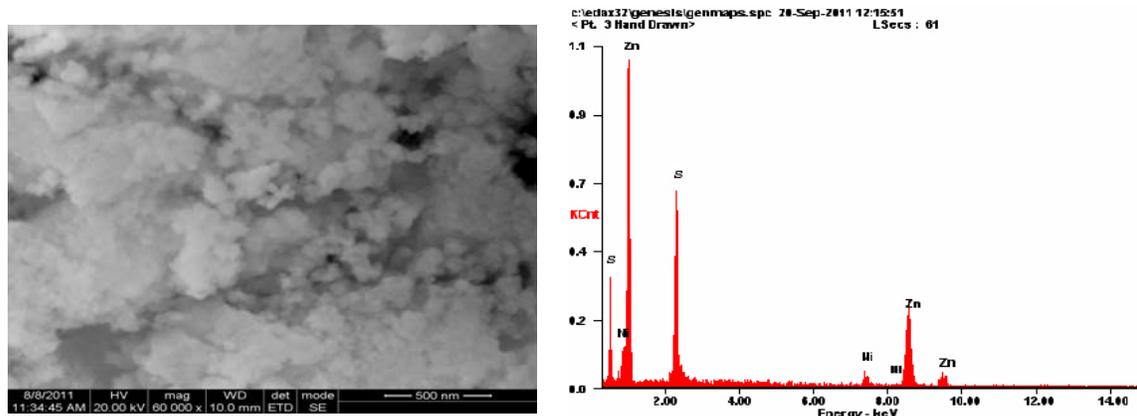


Fig. 2d The SEM image of the 3% Ni²⁺ ions doped ZnS compound (Annealed for 2 hrs)
The EDAX spectrum of the 3% Ni²⁺ ions doped ZnS compound (Annealed for 2 hrs)

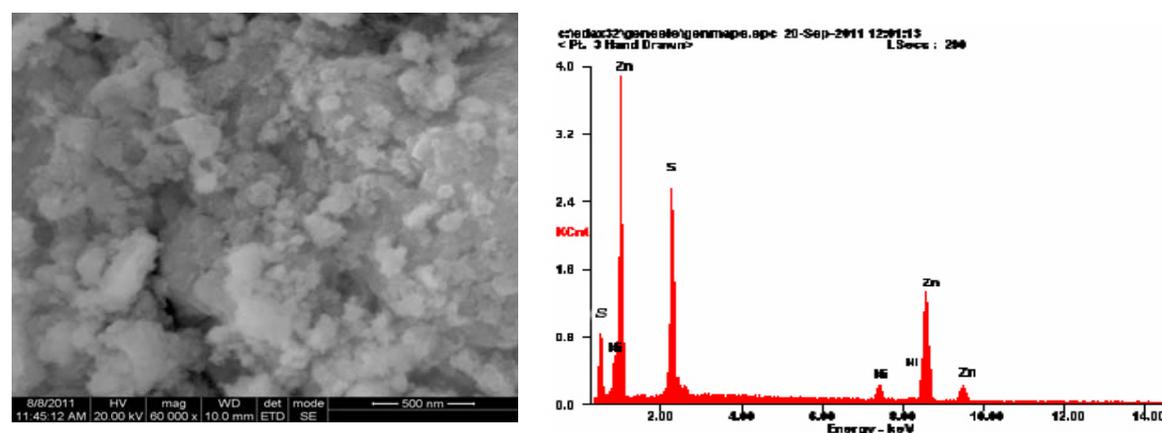


Fig. 2e The SEM image of the 3% Ni²⁺ ions doped ZnS compound (Annealed for 3 hrs),
The EDAX spectrum of the 3% Ni²⁺ ions doped ZnS compound (Annealed for 3 hrs)

The chemical composition of synthesis of pure ZnS and ZnS:Ni nanoparticles was characterized by energy dispersive analysis of X-rays (EDAX). The results of corresponding elements in atomic percentage are given in the Table 2. SEM inset images shows the EDAX spectra of pure ZnS and ZnS: Ni nanoparticles. The EDAX spectra confirmed the composition of ZnS and ZnS:Ni samples. This reveals that the Ni²⁺ ions are incorporated in the Zn²⁺ lattice sites. These results indicate that homogeneous phase of this compound, which are stable at 100°C.

Table 2 Compositions of pure ZnS and Ni²⁺ ions doped ZnS compound from EDAX

Sample	Compositions (Atomic % of element)
Pure ZnS	Zn = 69.91; S = 30.00
3% Ni ³⁺ ions doped ZnS	Zn = 37.11; S = 59.61; Ni = 3.2
5% Ni ³⁺ ions doped ZnS	Zn = 70.86; S = 19.27; Ni = 9.87
3% Ni ³⁺ ions doped ZnS – annealed for 2 hours	Zn = 35.58 S = 61.38; Ni = 3.04
3% Ni ³⁺ ions doped ZnS – annealed for 3 hours	Zn = 37.11; S = 55.75; Ni = 3.27

The absorption spectra of the pure ZnS and Ni²⁺ ions doped ZnS samples are given in Fig.3. The absorption edge for ZnS is very sharp and is determined by the nature of the electronic

transition between the valence band and conduction band. The absorption edges of suspension nanoparticles were much broader. The value of the band gap of Ni^{2+} doped ZnS was found to lower than the pure ZnS. This blue shift of the band gap takes place because of the quantum confinement effect and also could be attributed to the combined effect of optical transition to the excitonic state. The absorption spectra of Ni^{2+} doped samples are different from that of undoped samples. Due to the effect of doped ions on the band gap structure of the host materials, the absorption shoulder peak and absorption edge of the samples vary with change in the impurity mole ratios of Ni^{2+} ions. The shift of the absorption peaks (band gap) indicates a very mono-dispersed nanoparticle distribution. It has been found that the transitions from defect levels to the conduction band can be associated with the presence of Zn and Ni vacancies. The band gap in pure ZnS sample and Ni^{2+} ions doped ZnS nanoparticles are given in Table 3.

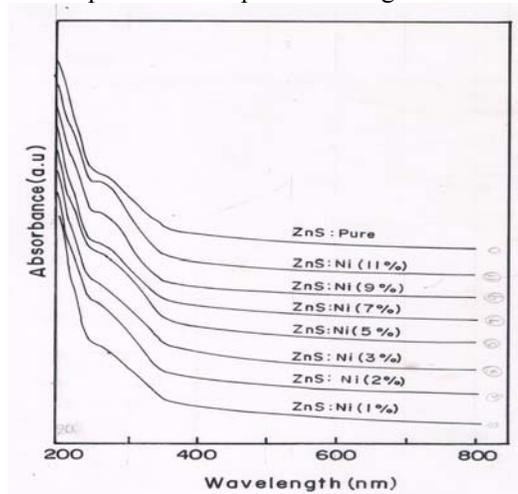


Fig. 3 UV_Visible spectra of pure ZnS and Ni^{2+} ions doped ZnS Compound.

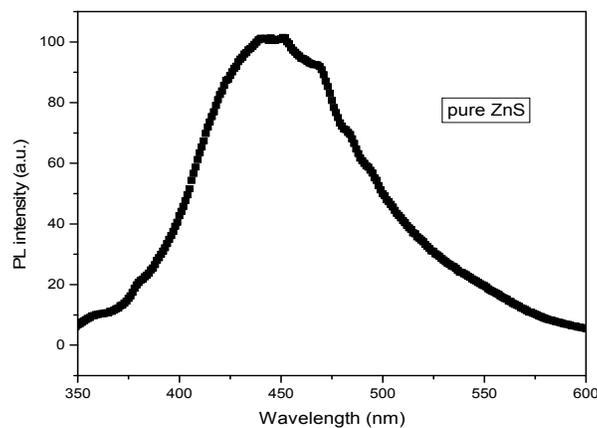


Fig. 4 (a) Photoluminescence spectra of pure ZnS compound

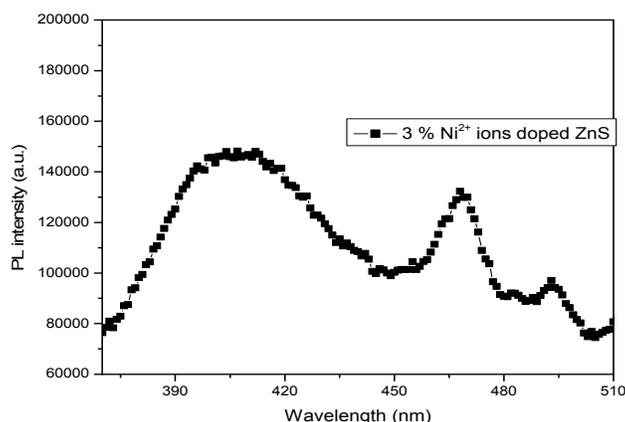


Fig 5(b) Photoluminescence spectra of 3% Ni^{2+} ions doped ZnS compound.

Table 3 Band gap of pure and Ni^{2+} ions doped ZnS compounds calculated from optical absorption spectrum

	Wavelength(nm)	Energy(ev)
Pure ZnS	320 nm	3.88
1%Ni doped ZnS	340nm	3.65
2% Ni doped ZnS	350nm	3.55
3% Ni doped ZnS	360 nm	3.45
5% Ni doped ZnS	370 nm	3.35
7% Ni doped ZnS	380 nm	3.27
9% Ni doped ZnS	390 nm	3.18
11% Ni doped ZnS	395 nm	3.14

The Photoluminescence study of ZnS and ZnS:Ni nanoparticles are given fig.4(a) and (b) measured at room temperature using F-2500 FL spectrophotometer. It is observed that PL emission band from undoped ZnS nanoparticles are broader and Ni^{2+} ions doped ZnS sample shows emission at visible region emission band with multiple peaks maxima indicate the involvement of different luminescence centre in the radiative. In the PL process, an electron from the valance band is excited across to some defect states. PL spectrum of ZnS and Ni^{2+} doped ZnS nanoparticles are shown in Fig. 4(a) and (b). It is observed that PL emission band from undoped ZnS nanoparticles found at 450nm and Ni^{2+} doped nanoparticles shows with multiple peaks in blue region. Peaks are found at 410;420 and 500 nm.

4. Conclusion

The pure ZnS and Ni^{2+} ions doped ZnS nanoparticles were successfully synthesized by co-precipitation method without using any capping agent from homogenous solution of zinc, nickel salt compounds with S^{2-} as precipitating anion formed. This method being simpler and with low cost chemical components is suitable for industrial large scale product and without any high cost instrument. Pure ZnS and Ni^{2+} ions doped ZnS nanoparticles synthesized by a co-precipitation method were investigated by XRD, SEM, EDAX and optical absorption studies. The XRD result show that nickel doped ZnS nanoparticles exhibit a zinc blende (cubic) structure with uniform size

distribution of approximately 4-5 nm calculated from XRD using Debye Scherrer's equation. Optimum concentration of doping Ni²⁺ ions was determined as 3% from the XRD study. The cubic phase of the ZnS nanoparticles has no change and does not affect the crystalline size with respect to doping the concentration of Ni²⁺ ions and annealing for different time intervals. 3% doped Ni²⁺ ions in ZnS compound were annealed at for different time intervals no secondary phase likes NiS, NiO, ZnO obtained. Increasing doping concentration and annealing at 100°C for different time intervals does not affect crystalline size of ZnS:Ni. Cluster formation was observed in SEM, because of agglomeration. The optical band-gap energies of Ni doped ZnS nanoparticles decreased as the concentration of Ni²⁺ ions increased. Photoluminescence (PL) measured at room temperature from the prepared nanoparticles are reported. It is found that the undoped sample exhibits PL emission peaks at 450 nm whereas Ni²⁺ doped ZnS sample exhibits PL emission covering the whole visible region with multiple peaks at 410;420 and 500 nm.

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