Synthesis of Co^{2+} ions doped ZnS nanoparticles by chemical precipitation method and their characterization

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Abstract: A simple wet chemical co-precipitation method was optimized for the synthesis of pure and different concentration of Co^{2+} ions doped ZnS nanocrystals. To obtained the 3 mole % of Co^{2+} ions doped ZnS nanoparticles were annealed at 100^{0}C for 1, 2, 3, 4 and 5 hours respectively. As prepared nanostructure Co^{2+} ions doped ZnS and annealed samples have been analyzed by powder X-ray differaction (XRD), scanning electron microscope (SEM), energy dispersive analysis of X-rays (EDAX) and UV-Vis spectrometer techniques. XRD studies show the phase singularity of Co^{2+} ions doped ZnS particles with cubic (zinc blend) structure. XRD pattern line broadening indicates that the pure and doped sample having nano size crystals with approximately 4-6 nm sizes. Co^{2+} does not affect the Zinc blend phase and crystalline size. The value of the band gap of Co^{2+} doped ZnS was found to lower than the pure ZnS.

Keywords: chemical precipitation, compound semiconductor, XRD, EDAX, PL.

Introduction:

During the past two decades the "small-particle research has become quite popular in various fields of chemistry and Physics. The "Small-Particles" now researcher call nanostructure materials, are of major significant, the technology of their production and use is rapidly in to a powerful industry. Nano sized semiconductor crystallites could change optical properties which are different from bulk materials [1-8]. This is called quantum confinement that is observed as a blue_ shift in absorption spectra with a decrease of particle size [9]. As the size is reduced to approach the excitation Bohr radius, there are some drastic changes in the electronic structure and physical properties, For example a shift to higher energy the development of discrete features in the spectra and concentration of the oscillator strength into just a few transitions [10] the electronic state is the limiting three-dimensional confinement which leads to molecular orbit (strong confinement) surface effects, and geometrical confinement of phonons. Therefore, it has stimulated great interest in both basic and applied research.

ZnS is a kind of wide band gap II – VI compound semiconductor materials (Eg = 3.6eV). It is commercially used as a phosphor and thin-file electro luminescence devices [11-14]. Recently cobalt has been found to be a prospective doping material in ZnS nano crystallite. Young e t al. [15] reported that Co^{3+} and Co^{2+} doped ZnS nanoparticles emit visible light. Also Zns nanoparticles after co-doping with Co^{2+} and Cu^{2+} showed enhancement the photo luminescence emission [16,17] doped materials show different types of luminescent property which are strongly depend on the type of dopant ions. These doping impurities play an

important role in changing the electronic structure and transition probabilities of the host material. In doped ZnS nano crystals, impurity ion occupies the Zn lattice site and behaves as a trap site for electron and holes. The electrons are excited from the ZnS valance band to conduction band by absorbing the energy equal to greater than their band gap energy.

In this paper, we synthesis Co^{2+} ions doped ZnS nanoparticles by chemical precipitate method at room temperature without any capping agent. The size of the prepared ZnS: Co samples have characterized by X-ray diffraction [XRD] and scanning electron microscope [SEM]. Meicro grip analysis with EDAX spectra confirmed presence of Co^{2+} ions in lattices of ZnS compound. The optical properties of absorption and emission were record.

2. Experimental:

All (AR) grade chemicals used in the present study were purchased from SD Fine Chemicals Ltd, India. ZnS with doped Co^{2+} ions nanoparticles were synthesized through the chemical co-precipitation method without using any capping agent and they are used without further purification. The synthesis of pure and Co^{2+} ions doped ZnS nanoparticles was carried out at room temperature. All the chemicals such as zinc acetate Zn $(CH_3COO)_2$. $2H_2O$,. $Co(CH_3COO)_2$ and sodium sulfide $(Na_2S.XH_2O)$ are above 98% purity. The synthesis reaction was carried out in the aqueous medium. Solutions of 0.5M Zn $(CH_3COO)_2.2H_2O$ and 0.5M Na_2S were prepared individually in 50 ml de-ionized water. Zinc acetate solution is vigorously stirred using a magnetic stirrer upto 10 minutes at room temperature and than sodium sulfide solution was added drop by drop to the above solution. Immediately the white color 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 100ºC in open atmosphere for one hour. The ZnS nanoparticles doped with different Co^{2+} ions concentration were synthesized in without complex agent. In a typical experiment, 0.5M of $Zn(CH_3COO)_2.2H_2O$ in 50 ml water and $Co(CH_3COO)_2$ in 25 ml water with different more concentration (1, 3, 5, 7, 9 and 11%) were mixed drop by drop. The concentration of Co^{2+} ions was adjusted by controlling the quantity of Cobalt acetate in the above mixture. The mixture was stirred magnetically at room temperature unit a homogeneous and colorless solution was obtained. Then sodium sulfide was added drop by drop to the above mixture. The ash colored precipitate is separate 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 100ºC in open atmosphere for one hour. The 3% Co^{2+} ions doped ZnS nanoparticles was annealed at 100ºC for 2, 3,4 and 5 hours respectively.

The synthesized nanoparticles were characterized using various techniques takes XRD were used to identify the crystalline phases of the nanoparticles size of the particles was measured using Debye-Scherrer's equation. Scanning electron microscopy (SEM), and the UV-Visible spectra, elemental composition on the surfaces of nanoparticles was monitored by EDAX (energy disperse X-ray analysis). The SEM was used to obtain the morphological information of nanoparticles. 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 diffractometry [XRD] patterns of the samples (pure ZnS and Co^{2+} 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 are correspond to (111), (220) and (311) planes of the cubic crystalline ZnS with reflections positioned at $2\theta =$ 28.9°, 48.4° and 57.5° were observed respectively. 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 [18].

The determination of phase composition, structure and particle size are very important for the discussions on the physical properties. We deduce there is no CoS or Co in the precipitates for the following reason: the structure and XRD pattern of CoS and Co is totally different from that of ZnS. XRD shows there is

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no detectable signal of Co or CoS, when the corresponding co-precipitation ratio is at low $Zn_{1-x}Co_xS$ samples otherwise the concentration of Co^{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 7%, 9% and 11% Co^{2+} ions doped ZnS samples the XRD planes of (220) and (311) could not be found. After 3 mole percent Co^{2+} ions doped ZnS samples, the XRD peaks becomes broader (wide) with the increase of the Co^{2+} ions dopent which is mostly due to the alloy fluctuation, amorphous state and more lattice stress & string in samples.
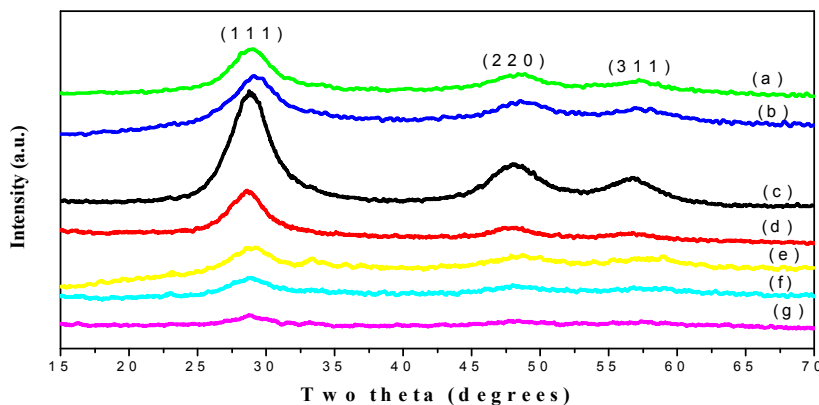

Fig1 (a) X-ray diffraction (XRD) pattern of samples (a) ZnS pure (b) 1% Co^{2+} ions doped ZnS (c) 3% Co^{2+} ions doped ZnS(d) 5% Co^{2+} ions doped ZnS (e) 7% Co^{2+} ions doped ZnS (f) 9% Co^{2+} ions doped ZnS (g) 11% Co^{2+} ions doped ZnS
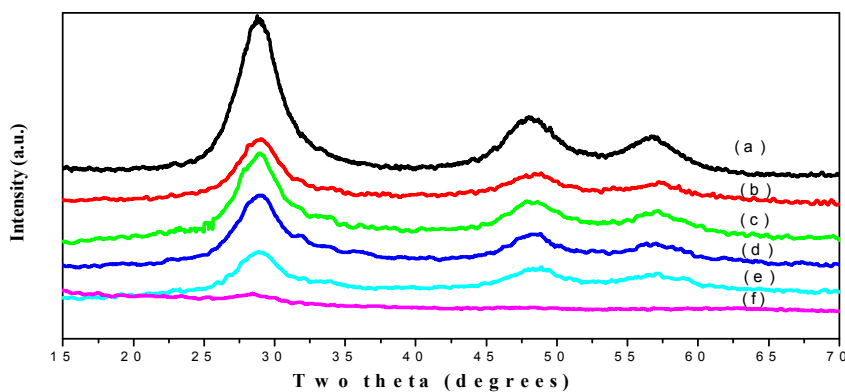

Fig1(b) X-ray diffraction (XRD) pattern of 3% Co^{2+} ions doped ZnS at 100ºC annealed at different time interval (a) 1hr (b) 2 hrs (c) 3 hrs (d) 4 hrs (e) 5 hrs (f) 6 hrs

The 3 mole percent Co^{2+} ions doped ZnS samples were annealed in open atmosphere at 100°C for different time interval (2, 3, 4, 5 and 6 hrs). The annealing effects in the XRD pattern of the Co^{2+} ions doped ZnS samples are given in Figure 1(b). After annealing 3 mole percent Co^{2+} 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 $2\theta = 28.9°$, 48.4° and 57.5° were observed respectively. No other peak of impurity

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phase such as Co, CoS, ZnO and CoO 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 CoS, CoS and ZnO phase could not be found.

The crystallite size was estimated from the full width at half maximum (FWHM) of the major XRD peak using the Debye Scherrer equation [19]

D= 0.9 λ / β cosθ

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 Co^{2+} doped ZnS samples as calculated by using the Debye Scherrer formula from the most intense peak are summarized in Table1.

Table 1: Crystallite size as calculated by using the Debye-Scherrer's formula from XRD spectrum

Samples	Peak position (111) plane	FWHM (degree)	Crystallite sizes (nm)
Pure ZnS	28.85	2.7677	5.27
1% Co doped ZnS	28.59	2.6524	5.07
3% Co doped ZnS	28.94	2.8392	4.84
5% Co doped ZnS	29.84	2.6310	5.45
7% Co doped ZnS	28.91	2.5212	5.68
9% Co doped ZnS	28.85	2.1531	6.68
11% Co doped ZnS	28.86	2.3429	6.61
3% Co doped ZnS – annealed for 2hrs	28.89	2.3429	6.61
3% Co doped ZnS – annealed for 3hrs	28.95	2.7697	5.17
3% Co doped ZnS – annealed for 4hrs	28.93	2.6106	5.48
3% Co doped ZnS – annealed for 5hrs	28.21	4.7873	5.12
3% Co doped ZnS – annealed for 6hrs	28.22	-	-

Figure 2(a-e) shows the scanning electron microscope (SEM) images of Co^{2+} 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 attractive force between the nanoparticles will increase and the particles will agglomerate.
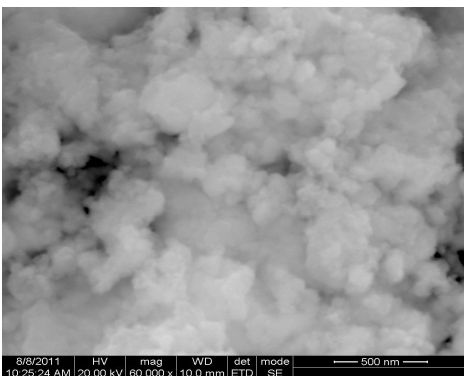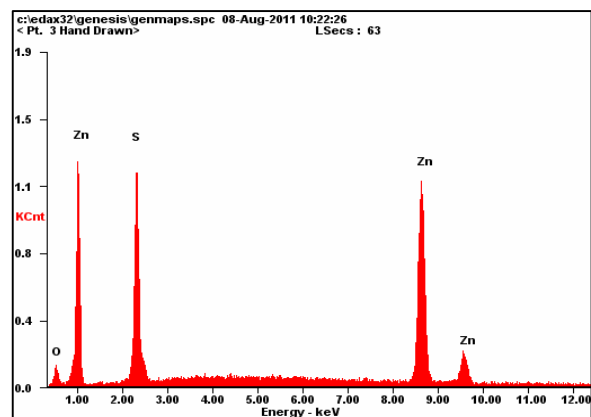

Fig. 2(a) SEM image of the pure ZnS compound   **EDAX spectrum of pure ZnS Compound**

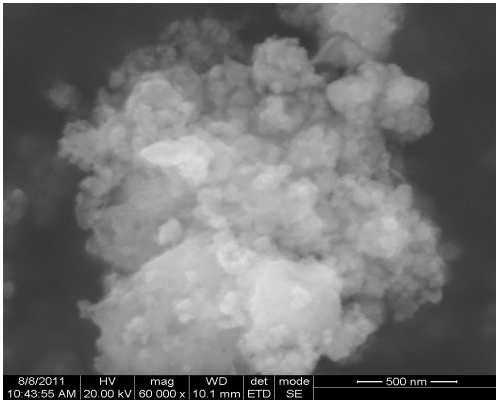**P.Prabukanthan** *et al* /Int.J. ChemTech Res. 2015,8(8),pp 286-294.
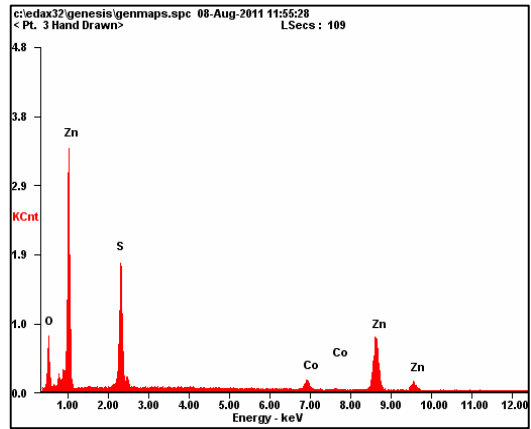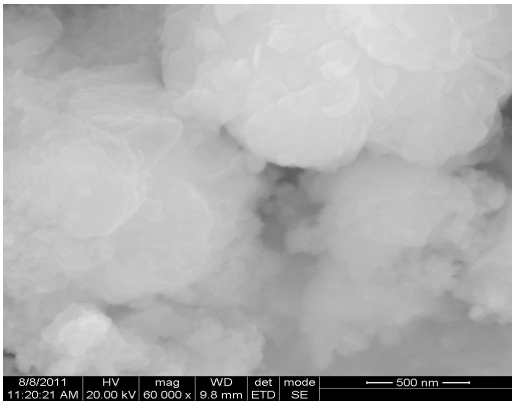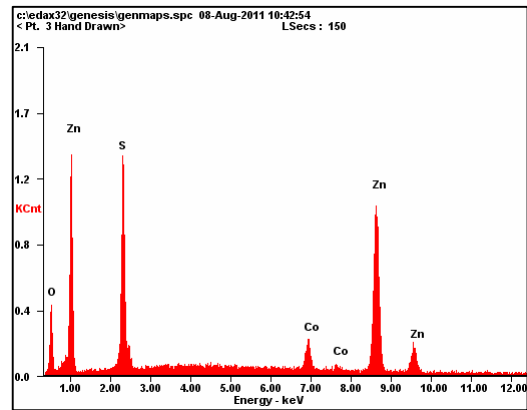
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Fig (b) The SEM image of the 3% Co^{2+} ions doped ZnS compound

EDAX Spectrum of 3% Co^{2+} ions doped ZnS compound

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

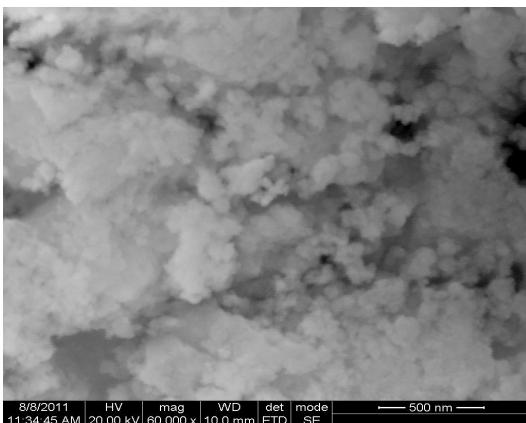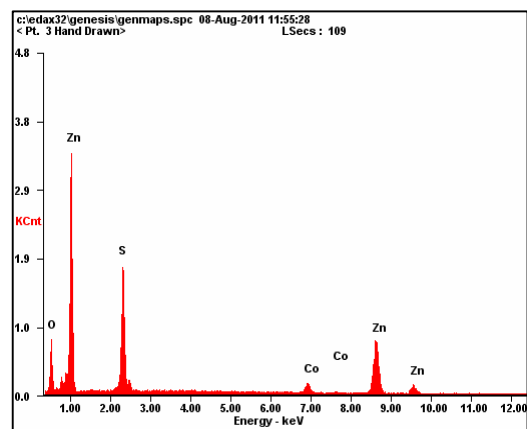**EDAX image of the 5% Co^{2+} ions doped ZnS**

Fig.(d) The SEM image of the 3% Co^{2+} ions doped ZnS Compound (Annealed for 2 hrs)

EDAX image of the 3% Co^{2+} ions dopeZnS Compound (Annealed for 2 hrs)

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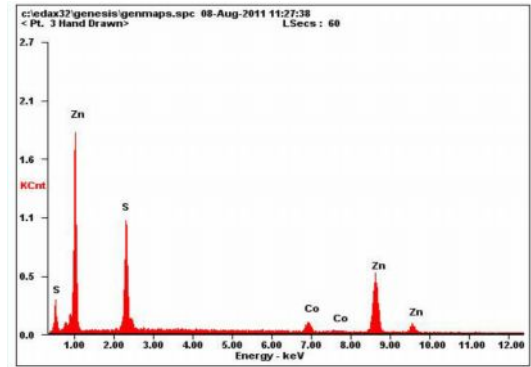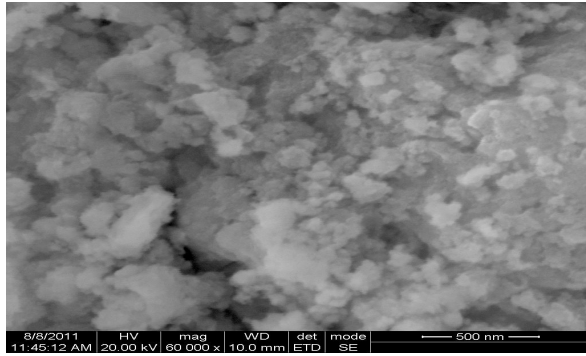
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Fig (e) The SEM image of the 3% Co^{2+} ions doped ZnS compound (Annealed for 3 hrs)

EDAX image of the 3% Co^{2+} ions doped ZnS Compound (Annealed for 3 hrs)

The chemical composition of synthesis of pure ZnS and ZnS:Co nanoparticles was characterized by energy dispersive analysis of X- rays (EDAX). The results of corresponding element in atomic percentage are given in the table 2. SEM inset images shows the EDAX spectra of pure ZnS and ZnS:Co nanoparticles. The EDAX spectra Zn^{2+} confirmed the composition of ZnS and ZnS:Co samples. This reveals that Co^{2+} ions are incorporated in the Zn^{2+} lattice sites. These results indicate that homogeneous phase of this compound, which are stable at 100^{0}C

Table 2 Composition of pure ZnS and cobalt doped ZnS compound from EDAX spectrum.

Samples	Composition (Atomic % of element)
Pure ZnS	Zn = 69.91 ; S = 30.00
3% Co^{2+} ions doped ZnS	Zn = 53.97; S = 41.34 ; Co = 4.59
5% Co^{2+} ions doped ZnS	Zn = 30.30; S = 66.83 ; Co = 4.78
3% Co^{2+} ions doped ZnS – annealed for 2 hrs	Zn = 44.95; S = 51.07 ; Co = 3.97
3% Co^{2+} ions doped ZnS – annealed for 3 hrs	Zn = 38.05; S = 68.43.07 ; Co = 3.52

The absorption spectra of the samples are given in Figure 3(a) and (b). 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 edge for a suspension of nanoparticles in much broader. This blue shift of the band gap takes place because of the quantum confinement effect. The absorption spectrum of Co^{2+} doped sample is 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 ratio of Co^{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 Co vacancies. The band gap in pure ZnS sample and Ni^{2+}ions doped ZnS nanoparticles are given in Table 3.
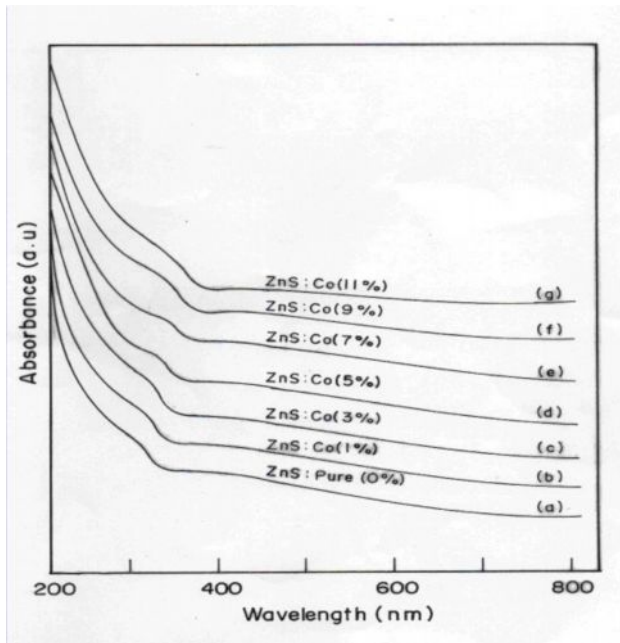
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Fig. 3(a) The UV – Visible spectrum of (1%, 3%, 5%, 7% and 11%) Co^{2+} ions doped ZnS compound

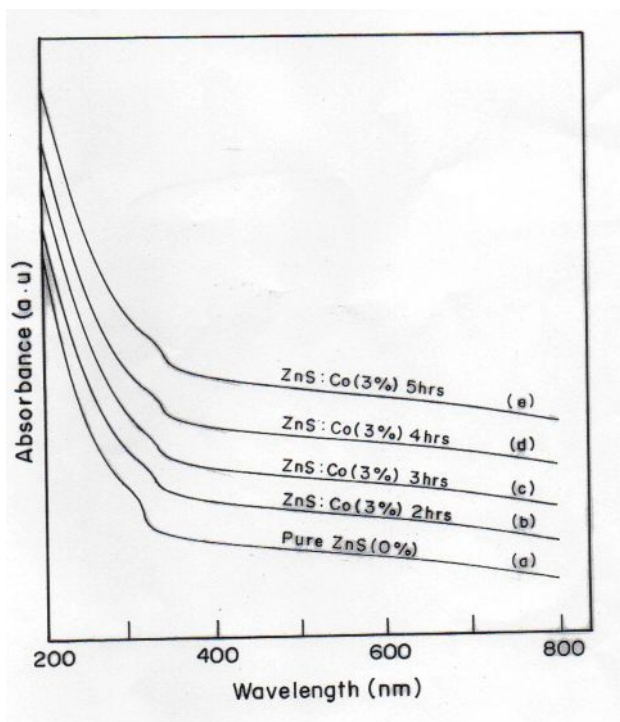**Fig. (b) The UV – Visible spectrum of Pure ZnS and 3% Co^{2+} ions doped ZnS compound (Annealed for 2Hrs, 3Hrs 4Hrs& 5Hrs)**

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Table 3 Band gap of pure and Co²⁺ions doped ZnS samples from optical absorption spectrum

Percentage of Co doped with ZnS	Wavelength(nm)	Energy(eV)
Pure ZnS	345 nm	3.59
1%Co doped ZnS	350 nm	3.54
3%Co doped ZnS	355 nm	3.49
5%Co doped ZnS	360 nm	3.44
7%Co doped ZnS	365 nm	3.39
9%Co doped ZnS	370 nm	3.35
11%Co doped ZnS	375 nm	3.30
Pure ZnS	330 nm	3.75
3% Co doped ZnS – annealed for 2hrs	407 nm	3.70
3% Co doped ZnS – annealed for 3hrs	464 nm	3.64
3% Co doped ZnS – annealed for 4hrs	498 nm	3.59
3% Co doped ZnS – annealed for 5hrs	323 nm	3.54

The 3 mole percent Co²⁺ ions doped ZnS samples were annealed in open atmosphere at 100°C. For different time interval (1,2,3,4,5 and 6 hrs). The annealing effects in the absorption spectra of the pure ZnS is 330 and the absorption peak of different concentration of Annealed Co²⁺ doped ZnS nanoparticles has little in the peak position.

Photoluminescence [PL] study of ZnS and ZnS: Co nanoparticles are measured at room temperature using F-2500 FL spectrophotometer. It is observed that PL emission band from undoped ZnS nano particles are broader and Co2+ 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 Co²⁺ doped ZnS nanoparticles are given Fig. 4(a) and (b). It is observed that PL emission band from undoped ZnS nanoparticles found at 450nm and Co²⁺ doped nanoparticles shows with multiple peaks in blue region. Peakes are found at 405, 468 and 495 nm.
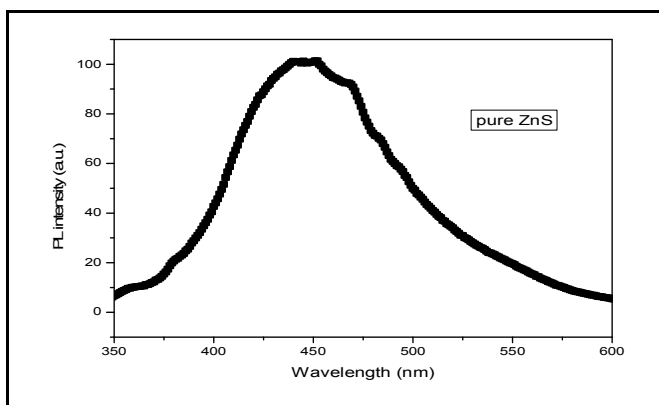
Fig. 4(a) Photolumiscence spectrum of pure ZnS
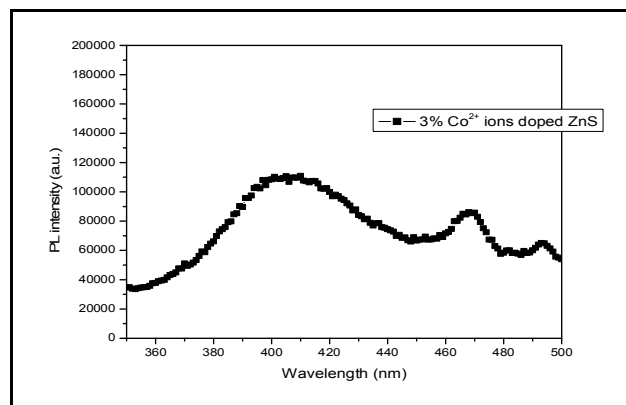
Fig. (b) Photolumiscence spectrum of 3% Co²⁺ doped ZnS.

4. Conclusion

The pure ZnS and Co²⁺ ions doped ZnS nanoparticles were successfully synthesized by co-precipitation method without using any capping agent from homogenous solution of zinc ,cobalt salt compounds with S²⁻ 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 Co²⁺ ions doped ZnS nanoparticles Synthesized by a Co-precipitation method were investigated by XRD, SEM EDAX and optical

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absorption studies. The XRD result show that cobalt doped ZnS nanoparticles exhibit a zinc blende (cubic) structure with uniform size distribution of approximately 4-6 nm calculated from XRD using Debye Scherer's equation. Optimum concentration of doping Co^{2+} ions was determined as 3% from the XRD study. The cubic phase of ZnS nanoparticles has no change and does not affect the crystalline size with respect doping the concentration of Co^{2+} ions and annealing for different time intervals no secondary phase likes CoS, CoO. ZnO obtained. Increasing doping concentration and annealing at $100^{0}C$ for differnt time intervals does not affect crystalline size of ZNS: Co Cluster formation was observed in SEM, because of agglomeration, large surface area to volume ratio. The optical band-gap energies of Co doped ZnS nanoparticles decreased as the concentration of Co^{2+} ions increased. Photoluminescence (PL) measured at room temperature from prepared nanoparticles are reported. It is found that the undoped sample exhibits PL emission peaks at 450nm whereas Co^{2+} doped ZNS sample exhibits Pl emission covering the whole visible region with multiple peaks at 405, 468 and 495 nm.

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