Optical characterization of CTAB assisted Ni doped ZnS nanoparticles

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Abstract. Ni doped zinc sulphide nanoparticles at different concentration of CTAB have been prepared via solvothermal route. The structural characterization of the ZnS:Ni nanoparticles has been made using XRD technique and it reveals cubic zinc blende structure of ZnS. The crystallite size calculated from the XRD pattern is in close agreement to that estimated from the TEM image. The UV-Vis study of ZnS:Ni nanoparticles indicates the red shift in the absorption peak as compared to bulk ZnS. The emission spectra ZnS:Ni sample at 5 mmol CTAB concentration has been fitted into three Gaussian peaks.

1. Introduction:
The nano-crystalline form of Zinc sulphide, a II-VI semiconductor, is commercially important because it demonstrates outstanding structural, optical and opto-electronic properties compared to bulk ZnS [1-3]. It is being used as catalysts and phosphors [4] as well as also being used in electro- luminescence devices, solar cells, flat panel displays, light emitting diodes, laser diodes, optical sensors and biological labelling [5-11]. The doping of d-block elements similar to Mn$^{2+}$, Co$^{3+}$, Cu$^{2+}$ and Ni$^{2+}$ ions modify the electronic structure as well as transition probabilities due to change in optical properties of ZnS [12-16]. Therefore, the doping method is being used as a valuable tool for altering the absorption and photoluminescence properties of ZnS nanostructures for technological applications. The physical and chemical properties of Ni doped ZnS nanostructures have been investigated by several workers. Poornaprakash et. al. [17] studied the structural, optical along with other properties of Fe, Co and Ni doped ZnS nanostructure and reported that these divalent ions easily substitute the Zn$^{2+}$ ions due to their electron structures and less ionic radii. The luminescence properties of Ni, Cu doped ZnS nanoparticles have been studied by Murugadoss [14] and an increase in energy gap along with improvement in PL intensity with the increase of Ni$^{2+}$ concentration has been observed. Kumar et al. [18] synthesized the ZnS:Ni nanoparticles via chemical precipitation method and reported a blue shift in absorption edge as well as the decrease in PL intensity. Ni doped ZnS nanopowders have been prepared by Zhou et al. [19] using hydrothermal method and observed a significant decrease in PL intensity due to incorporation of Ni$^{2+}$ ions in ZnS. The photo-catalytic degradation efficiency of Mn$^{2+}$, Co$^{2+}$ and Ni$^{2+}$ incorporated ZnS nanoparticles has been studied by Rajabi et. al. [20] and Kaur et. al. [21], and a reduction in degradation efficiency has been reported. Wu et. al. [22] prepared Ni doped ZnS nanorods via hydrothermal method in presence of ethylenediamine and reported a blue shift in absorption band along with the improved intensity in emission bands. It has been also reported that the hexagonal wurtzite phase does not change with substitution of Ni$^{2+}$ on Zn$^{2+}$ sites. A decrease in energy
gap along with the enhancement in PL intensity up to a certain concentration of Ni has been observed by Othman et al. [23] in Ni doped ZnS nanocrystals prepared via sonochemical route. Numerous techniques have applied to synthesized the ZnS:Ni nanoparticles such as sol-gel, chemical precipitation, wet chemical method etc. Among these techniques, solvothermal route is simple, inexpensive and able to control the morphology. The above concerned literatures resemble that the described optical properties are uncertain. Therefore, more investigations on the optical properties of Ni doped ZnS nanoparticles are essential. In the present study, Ni doped ZnS nanoparticles have been synthesized via solvothermal route at different CTAB concentration.

2. Materials and Methods
Analytical grade raw materials Zinc acetate [Zn (CH₃COO)₂.2H₂O], nickel acetate [Ni (CH₃COO)₂.4H₂O, sodium sulphide (Na₂S) and CTAB are used to prepare the Ni doped ZnS nanoparticles. The aqueous solutions of zinc acetate and sodium sulphide were stirred separately for 90 minutes at 60°C and mixed together. After that the required aqueous solution of nickel acetate was stirred for 1h at 60°C and mixed with prepared solution of zinc acetate and sodium sulphide. Thus, prepared solution was again stirred for 1h at 70°C and cooled to room temperature and divided into four parts. In each solution, the required amount of CTAB was added and transferred into stainless steel Teflon lined autoclave for 24 h kept at 70°C. The solutions obtained from autoclave were filtered and the precipitates were cleaned several times with ethanol and doubly distilled water. The obtained precipitates of Ni doped ZnS were dried and used for further characterization.

3. Result
3.1 Structural and morphological study:
The structural characterization of Ni doped ZnS nanoparticles has been studied using Cu-Kα line of Rigaku miniflex X-ray diffractometer and the observed pattern is represented in Fig 1. The observed peaks correspond to (111), (220) and (311) of ZnS demonstrating the cubic zinc-blende structure with lattice constant 5.406 Å and is in close agreement to that reported by earlier workers. In addition, diffraction pattern also exhibits that the intensity and the broadening of the observed peaks increases up to 5mmol of CTAB and then decreases which may be due to agglomeration of nanoparticles and doping of Ni²⁺ ions.

![Figure 1. XRD pattern of Ni doped ZnS nanoparticles at different CTAB concentrations.](image-url)
The average crystallite size of Ni doped ZnS nanoparticle has been calculated using Scherrer's formula and it is found to be about 4.7 nm. No additional peaks have been observed in the diffraction pattern which indicated that there is no impurity in the synthesized nanoparticles. The surface morphology of synthesized sample has been studied using SEM micrograph at 5 mmol concentration of CTAB and represented in figure 2(a). The observed fringes in the TEM image of Ni doped ZnS nanoparticles, shown in figure 2 (b), indicate the good crystallinity in the synthesized sample.

3.2 UV-Vis Study:
The room temperature absorption spectra of Ni doped ZnS nanoparticles has been recorded using lambda 35 spectrophotometer (Perkin Elmer) in the wavelength range of 200-800 nm and depicted in figure 3. A blue shift in the absorption edge of Ni doped ZnS nanoparticles has been observed as compared to bulk ZnS which is due to the reduction in size at nanoscale. The absorption spectra also reveal that the absorption edge is red shifted with increasing concentration of CTAB and which may be due to the agglomeration of the particles. In addition, an absorption peak near at 212 nm has been also observed in each synthesized sample and the further studied is going on. The band gap calculated from the tauc plot is found to be varied from 4.9 eV to 4.1 eV with the increase of CTAB concentration.

![Figure 3. Absorption spectra of Ni doped ZnS nanoparticles at different CTAB concentrations.](image-url)
3.3 Photoluminescence Study:
The nondestructive photoluminescence technique is applied to describe the impurity as well as defect energy states in semiconductor can be used even the impurity level is very minute [22]. The emission spectrum of Ni doped ZnS nanoparticles at 5 mmol CTAB concentration has been recorded in the wavelength range 450-700 nm using PerkinElmer Luminescent Spectrometer (LS-55) with excitation source of 370 nm. The three Gaussian fitted emission bands centered at 492, 555 and 624 nm of observed PL spectrum are shown in figure 4. Emission peak centered at 492 nm assigned as blue emission and is due to electron-hole recombination between sulphur vacancy and sulphur interstitial while the green emission peak centered at 555 nm can be assigned to trapped electron-hole recombination between sulphur vacancy and deeper zinc vacancy [23]. A slight shift of 4 nm has been observed in the orange emission peak centered at 624 nm as reported by Wu et. al. [22] and is attribute to the electron-hole recombination between interstitial zinc states and zinc vacancy.

![Figure 4. PL emission spectra of Ni doped ZnS nanoparticles at 5 mmol CTAB concentration.](image)

4. Conclusion:
Ni doped zinc sulphide nanoparticles at different CTAB concentration have been synthesized via solvothermal technique. The XRD technique confirms the formation of nanoparticles having crystallite size 4.7 nm. The absorption study of the synthesized samples has been made using UV-Vis spectroscopic technique and it has been observed that the absorption edge is blue shifted in all samples as compared bulk ZnS. In addition, the absorption edge of Ni doped ZnS nanoparticles is red shifted up to 5 mmol CTAB concentration and then blue shifted. The observed broad and asymmetric PL spectra of synthesized sample at 5 mmol CTAB has been fitted into three Gaussian peaks lying in blue, green and orange regions are analysed.

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