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CHARACTERIZATION AND OPTICAL PROPERTIES OF Ni^{2+} DOPED ZnS NANOPARTICLES

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In this work we synthesized undoped ZnS and ZnS:Ni nanoparticles by a simple chemical method, namely the chemical precipitation method. The structure and optical properties of the prepared samples were characterized using X-ray diffraction (XRD), Field Emission Scanning Electron Microscope (FESEM), UV–Vis-NIR Spectrophotometer and Fluorescence spectroscopy. XRD patterns showed that the ZnS and ZnS:Ni nanoparticles have zinc blende structure with the crystallite sizes of about 6-10 nm range. The value of optical band gap has been found to be in range 4.88- 3.93 eV. Room temperature photoluminescence (PL) spectrum of the undoped sample exhibits emission in the blue region with multiple peaks under UV excitation. Ni^{2+} doped ZnS samples visible light emissions under the same UV excitation wavelength of 310 nm.

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1. Introduction

In recent years, semiconductor nanoparticles have attracted great deal of attention because of their novel optical properties and potential applications. Nanocrystralline semiconductors behave differently from bulk semiconductors. 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. Luminescent properties of ZnS can be controlled using various dopants such as Fe^{2+}, Mn^{2+}, Ag^{2+} and Cu^{2+} etc. They not only give luminescence in various regions but also improve the properties of ZnS. A large variety of methods are employed for synthesizing during last few decades such as chemical method [2-3], mechano-chemical method [4-5], hydrothermal process [6], sol-gel method [7], electro-spinning technique [8] ,ultrasonic radiation method [9], colloidal chemical treatment method [10], reverse micelle method [11] and solvothermal method etc.[12].

This paper reports the characterization and optical properties of the undoped and Ni^{2+} doped ZnS samples at room temperature without using any capping agent. The value of optical band gap has been found to be in range 4.88-3.93 eV. PL emission band from undoped ZnS nanoparticles are highly asymmetric and broaden with multiple peaks in blue region. Peaks are found at 425, 448 and 486 nm. Ni^{2+} doped ZnS nanoparticles shows PL emission at 425, 445 and 485 nm in visible region under excitation wavelength of 310 nm.

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2. Experimental

All the chemicals used are of AR grade (Merck), without further purification. We prepare 10 ml each of zinc nitrate and sodium sulfide in distilled water. Zinc nitrate solution is first stirred using a magnetic stirrer up to 30 min, and then the solution of sodium sulfide is mixed with above solution drop wise and stirrer up to 1h. The precipitate is separated by centrifugation (Remi, PR 24) for 4 min at 5,000 rpm and is washed with methanol several times to remove all sodium particles. The precipitate is then heat treated at 200^0C for 2h for further measurements. ZnS with 2% Ni doped was prepared at room temperature by mixing calculated amounts of zinc nitrate solution, nickel nitrate in distilled water stirred using a magnetic stirrer up to 30 min and followed by drop wise addition of 10 ml. solution of sodium sulfide. The mixture was vigorously stirred using a magnetic stirrer up to 1h. The precipitate was separated from the reaction mixture by centrifugation for 4 min at 5,000 rpm and was washed with methanol several times to remove all sodium particles. The wet precipitate was then heat treated at 200^0C for 2h for further measurements.

3. Characterization techniques

3.1. X-ray diffraction

The samples were characterized by X-ray diffraction (XRD) using a D8 BRUKER AXS diffractometer with Cu Kα, operating at 40 kV and 30 mA. The crystallite size of the prepared ZnS and ZnS:Ni nanoparticles were determined by X-ray line broadening and calculated using the Scherrer equation:

$$D = \frac{0.9\lambda}{\beta\cos\theta} \tag{1}$$

where $\beta = (\beta^2_M - \beta^2_I)^{1/2}$, β_M is the full width at half maximum (FWHM), β_I is the correction factor for instrument broadening, θ is the angle of the peak maximum, and λ is the Cu K_α wavelength (= 0.15406 nm).

3.2. Field Emission Scanning Electron Microscope

Field Emission electron micrographs were obtained using a QUANTA FEI-200 with a field emission gun. Images were taken by fixing the sample powder on the aluminum stub by using a double sided adhesive carbon tape. The surface of these samples is coated with a very thin layer of gold (Au) by glow discharge sputtering before FESEM examination. Energy-dispersive analysis of X-Rays (EDAX) coupled with FESEM was used for the semi-quantitative investigation of the microstructure of the samples.

3.3. UV-Vis-NIR Spectrophotometer

The optical absorption spectra have been observed by UV-Visible –NIR spectrophotometer (Varian, Cary 5000) for measuring the absorption characteristics, the nanopowders were first dispersed in methanol and then taken on a quartz cuvette of path length 10 mm.

3.4. Fluorescence Spectrophotometer

The PL spectrum of the ZnS has been measured at room temperature using Hitachi F-2500 FL Spectrophotometer. For measuring the PL intensity, the nanopowders were first dispersed in methanol and then taken on a four side polished quartz cuvette of path length 10 mm.

4. Results and discussion

4.1. X-Ray Diffraction Studies

XRD pattern of the prepared ZnS and ZnS:Ni samples were obtained and these are shown in Fig.1. Fig.1 shows the three diffraction peak at 2θ values 28.6^0, 47.7^0 and 56.4^0 . The peaks are appearing due to reflection from the (111), (220) and (311) planes of the cubic phase of the ZnS. The obtained peak positions correspond to zinc blended type patterns for all the samples. The

XRD pattern of the nanocrystal is well matched with the Standard cubic ZnS . The crystallite size of the ZnS nanoparticle as calculated by using Eq. (1) from the most intense peak is in range of 6-10 nm. The broadening of the XRD pattern of the prepared undoped and ZnS:Ni sample takes place due to the nanocrystalline nature of the sample.

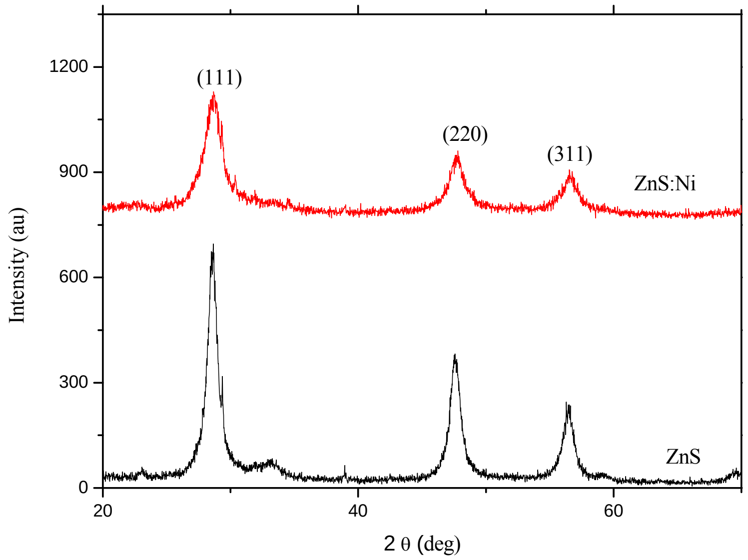

Fig.1. X-ray diffraction (XRD) pattern of ZnS and ZnS:Ni samples.

4.2. FESEM analyses

Figure 2 shows FESEM images of ZnS:Ni nanoparticles and corresponding EDAX spectrum, which confirmed the composition of ZnS:Ni samples. Strong peaks of Zn and S are found in the EDAX spectrum and also detectable amounts of Ni indicate that impurity has doped into ZnS nanocrystallites. The actual size of the nanoparticles cannot be determined from the FESEM images as it is limited by the resolution of the used FESEM instrument.

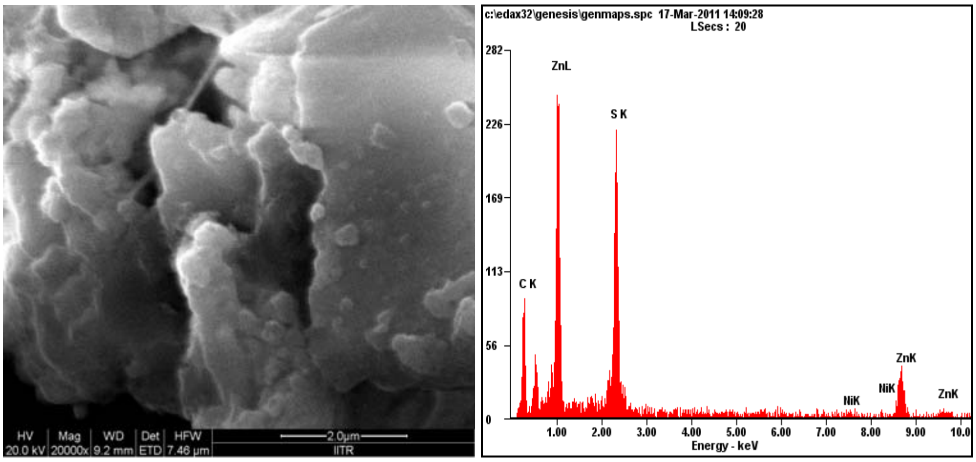

Fig.2. FESEM micrograph of 2% Ni doped ZnS and corresponding EDAX spectrum.

4.3. Optical absorption and band gap

The optical absorption spectra have been observed by using UV-Visible-NIR (Varian, Cary 5000) spectrophotometer and the results are shown in Fig.3. The characteristic absorption peaks due to undoped and Ni^{2+}doped ZnS nanoparticles appear in the wavelength range 250–340 nm. These peak positions reflect the band gap of nanoparticles and the synthesis ZnS nanoparticles have no absorption in the visible region (800 - 400 nm). The fundamental absorption, which corresponds to electron excitation from the valance band to conduction band, can be used to determine the value of the optical band gap of the synthesized ZnS nanoparticles.

The relation between the incident photon energy ($h\nu$) and the absorption coefficient (α) is given by the following relation

$$(\alpha h\nu)^{\frac{1}{n}} = A(h\nu - E_g) \tag{2}$$

Where A is constant and E_g is the band gap energy of the material and the exponent n depends on the type of transition. For direct allowed transition $n = 1/2$, for indirect allowed transition $n = 2$, for direct forbidden $n = 3/2$ and for indirect forbidden $n = 3$.

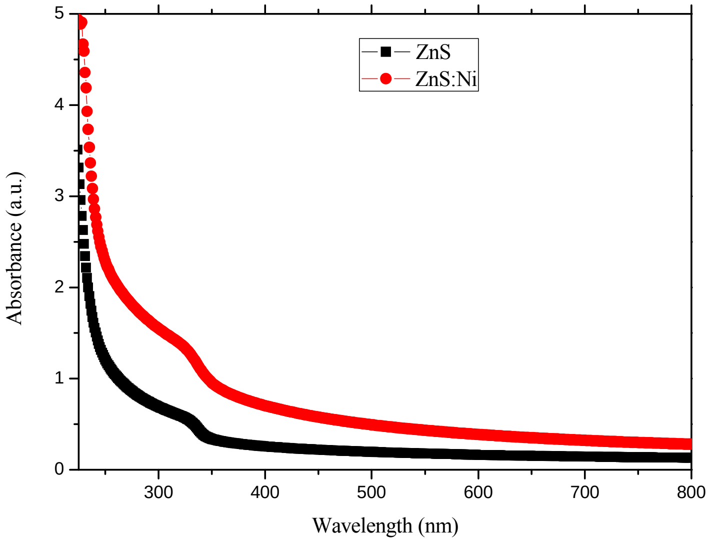

Fig.3. UV–Vis-NIR absorption characteristics of the ZnS and ZnS:Ni nanoparticles.

Direct band gap of the samples are calculated by plotting $(\alpha h\nu)^2$ verses $h\nu$ and then extrapolating the straight portion of the curve on $h\nu$ axis at $\alpha = 0$ as shown in Fig.4. The value of optical band gaps are 4.88eV and 3.93 eV respectively for undoped ZnS and Ni^{2+} doped ZnS.

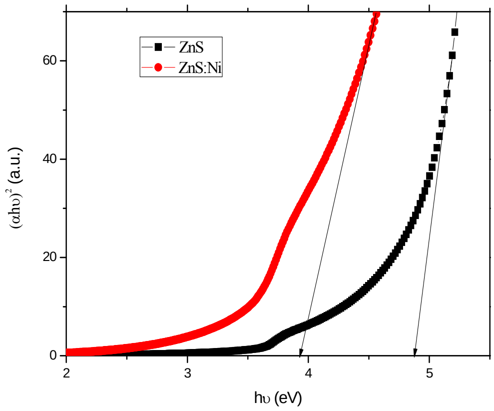

Fig.4. Calculation of optical band gap from UV-Vis-NIR absorption spectra.

The obtained values of the band gap of ZnS and Ni doped ZnS nanoparticles are higher than that of the bulk value of ZnS (3.68 eV). For undoped ZnS nanoparticles, we obtain a band gap of 4.88 eV. The bulk band gap value of ZnS is 3.68 eV. This implies that the band gap increases by 1.2 eV in the nanoparticles samples. On doping of 2% Ni in the ZnS nanoparticles, we obtain a band gap of 3.93 eV, the band gap is changed by 0.25 eV.

4.4. Photoluminescence study of ZnS and ZnS:Ni nanoparticles

Photoluminescence (PL) of ZnS and ZnS:Ni samples are measured at room temperature using F-2500FL Spectrophotometer. It is observed that PL emission band from undoped ZnS nanoparticles are broaden with multiple peaks and Ni^{2+} doped ZnS sample shows emission at visible region, emission band with multiple peak maxima indicate the involvement of different luminescence centers in the radiative process. In the PL process, an electron from the valence band is excited across the band gap and photo excited electron subsequently decays by a normal recombination process to some defect states. In Ni doped crystals an electron may be captured by the Ni^{2+} ions in the $^4T_1$ level, from which it makes a radiative transition to the ground state $^6A_1$ level. PL spectrum of ZnS and Ni^{2+} doped ZnS nanoparticles are shown in Fig.5, It is observed that PL emission band from undoped ZnS nanoparticles are broaden with multiple peaks in blue region. Peaks are found at 426, 444 and 485 nm. Ni^{2+} doped ZnS nanoparticles shows PL emission at 426, 448 and 486 nm in visible region with excitation wavelength of 310 nm.

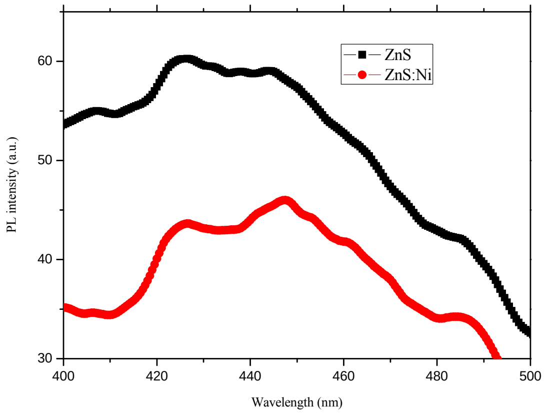

Fig.5. PL emission from the ZnS and ZnS:Ni nanoparticles.

5. Conclusion

Ni^{2+}doped ZnS nanoparticles are synthesized at room temperature using the chemical precipitation method without using any capping agent. This method is simpler and with low cost chemical compounds, it is suitable for industrial large scale production. The sizes of as prepared nanoparticles are found to be in 6-10 nm range. The band gap energy of the samples is found in the range 4.88-3.93. It is found that the undoped sample exhibits PL emission in the blue region with multiple peaks under UV excitation whereas Ni^{2+} doped ZnS sample exhibits PL emission in visible region.

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