Preparation and Characterization of ZnS Nanoparticles by Simple Chemical Route

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Abstract- *Zinc Sulphide (ZnS) nanoparticles have been synthesized by simple, cost effective chemical co-precipitation method. The structural characterizations of as synthesized nanoparticles are determined by X-ray diffraction (XRD) which showed hexagonal structures with calculated crystallite size 16.26 nm. Scanning electron microscopy (SEM) analysis shows the morphology as synthesized nanoparticles. The optical studies have been carried out by using UV-Vis spectrophotometer to determine the band gap of ZnS nanoparticles and they showed a blue shift with respect to the bulk. Fourier Transform Infrared Spectra (FTIR) was recorded in an FTIR spectrometer to verify the presence of the functional groups.*

Keywords-Nanoparticle, XRD, chemical co-precipitation, UV-Vis Spectrophotometer, photoluminescence, FTIR.

I. INTRODUCTION

In recent year's nano-sized semiconducting materials have been generating an extensive interest owing to their structure, chemical and physical properties, which are different from those of the bulk materials [1-2]. Among II-VI semiconductors, ZnS, with unique optical properties and a direct band gap of 3.68 eV at room temperature, is one of the important materials with wide range of applications such as light emitting devices, laser devices, cathode ray tubes, nonlinear optical devices and antireflecting coatings [3–6]. In order to tune surface states, energy levels, electrical, optical and magnetic properties of semiconductor material, doping with proper element is widely used [7]. ZnS nanoparticles can be obtained in many ways, such as spray-based method [8], mechanochemical route [9], ultrasonic radiation of solution [10], Gama irradiation method [11], chemical precipitation method [12], organic metallic method [13], polymerization [14], reverse Michelle method [15] and sol-gel method [16]. We preferred chemical method for the preparation of ZnS nanoparticles to get the cluster formation. This method is simple, low cost and availability of the equipments.In the present work is to synthesize ZnS nanoparticles using chemical method and investigate the properties such as size, structure, band gap, transmittance and luminescence.

II. MATERIALS AND METHODS

(i). Experimental Details:

The chemicals used in this work are zinc sulphate [$ZnSO_4$], sodium sulphide flakes [Na_2S] and deionised water as dispersing solvent.

ZnS nanoparticles were prepared by chemical method using zinc sulphate and sodium sulfide in aqueous medium without using any other reagent. In this, 0.2 M zinc sulphate was taken in 100 ml conical flask and it was dissolved in 50 ml distilled water, then 0.1 M sodium sulfide was dissolved in 50 ml distilled water separately. The prepared solutions were stirred 1hr and half an hour respectively. Using burette, the sodium sulfide solution was added drop wise. The mixture was vigorously stirred for 3 hrs. A white precipitate was obtained which was separated by centrifugation. The precipitate was washed several times with water and ethanol. The wet precipitate was then dried. After sufficient drying, the precipitate was grinded in an agate mortar to achieve fine powder for further analysis.

(ii). Characterization Techniques:

The structure and phase of the as synthesized nanoparticles were determined by X-ray diffraction (XRD) using P-Analytical X-ray diffractometer using Cu-Kα (λ=1.540 Å) radiation. Diffraction patterns had been recorded over the 2θ range of 20^o to 80^o at the scan rate of 2^o per minute. The surface morphology and elemental analysis of the synthesized samples were studied by FEI Quanta 250 Scanning electron microscope (SEM). The optical absorbance spectra for the synthesized samples were recorded using UV-vis spectrophotometer (Perkin-Elmer Lamda 35) in the wavelength range of 190 nm - 1100 nm. The room temperature photoluminescence spectra of the synthesized sample were measured to study the luminescence properties of the nanoparticles using Perkin Elmer LS 45 with an excited light wavelength of 340 nm. FTIR was recorded using Spectrum RX I spectrophotometer to verify the presence of functional groups.

III. RESULTS AND DISCUSSION

(i) Micro-structural analysis:

The crystalline structure of the synthesized sample was recorded with the X-ray diffraction using Cu-Kα radiation (λ=1.540 Å). The intensity data were collected over a 2θ range of 20° - 80°. The XRD pattern of as the synthesized ZnS nanoparticles are shown in figure 1. The patterns indicate that the prepared ZnS nanoparticles were consistent with a hexagonal structure of ZnS which are in close agreement with the standard JCPDS card number 89 – 2201. From the XRD patterns, the broadening of the diffraction peaks of the nanoparticles is obvious which reflects the characteristic of nano sized materials. The most prominent peak observed in the figure corresponds to the lattice plane of (0 1 8). Three other peaks corresponding to the lattice plane (0 1 4), (1 0 3) and (2 0 8) were observed with varying intensities.

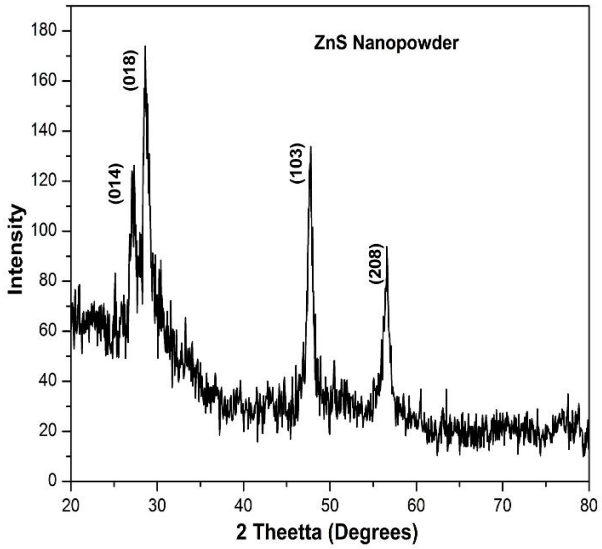

Figure 1: XRD pattern of ZnS nanopowder

The crystallite size of the prepared sample is calculated from the Debye-Scherrer's formula. Let λ be the wavelength of X-rays used and β and θ are full width at half maximum and Bragg's angles corresponding to the maximum intensity peak. The Debye-Scherrer's (DS) formula [17] is given as,

$$\mathbf{D} = \frac{k\lambda}{\beta Cos\theta}$$

According to uniform deformation model, we consider the prepared material is isotopic in nature and the strain is assumed to be uniform in all crystallographic direction. The Williamson-Hall equation according to UDM is given by [18]

$$\beta_{hkl} \cos\theta_{hkl} = \frac{K\lambda}{D} + 4\varepsilon \sin\theta_{hkl}$$

Dislocations an imperfection in crystal associated with the misregistry of lattice existing in different parts of the crystal. Dislocation density (δ) was evaluated using the relation [17]

$$\delta = \frac{1}{D^2}$$

The strain (ε) is calculated from the following relation

$$\varepsilon = \frac{\beta \cos\theta}{4}$$

The X-ray diffraction peak of films corresponding texture coefficient (T_C) is estimated using an expression [18]

$$T_c(h_i k_i l_i) = \frac{I(h_i k_i l_i)}{I_0(h_i k_i l_i)} \left[\frac{1}{n} \Sigma \frac{I(h_i k_i l_i)}{I_0(h_i k_i l_i)} \right]^{-1}$$

where I_0 represents the standard intensity, I is the observed intensity of $(h_i k_i l_i)$ plane and n is the reflection number.

Micro-structural properties	CdS Nanoparticles
Crystallite Size using Debye- Sherer's formula (nm)	16.26
Crystallite Size using Williamson-Hall equation (nm)	20.91
Dislocation Density (δ) X 10^{15} / m^2	3.379
Strain (ε) X 10^{-3}	7.613
Texture coefficient	1.24

Table 1: Micro- structural parameters of ZnS nanoparticles

(ii) Morphological analysis:

Figure 2 shows the SEM micrographs of the synthesized ZnS samples. The micrographs show that the particles had a rough morphology and spongy surface. Due to these reasons, it is difficult to determine the particle size of the synthesized samples [19]. In some places, various sizes of the particles (small and large size) are observed, i.e. nano sized particles seem to be randomly distributed.

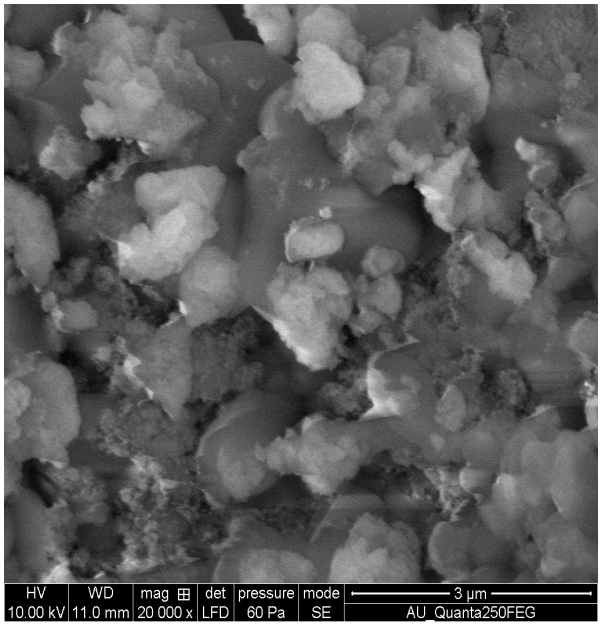

Figure 2: SEM images of ZnS nanopowder

(iii) FT-IR analysis:

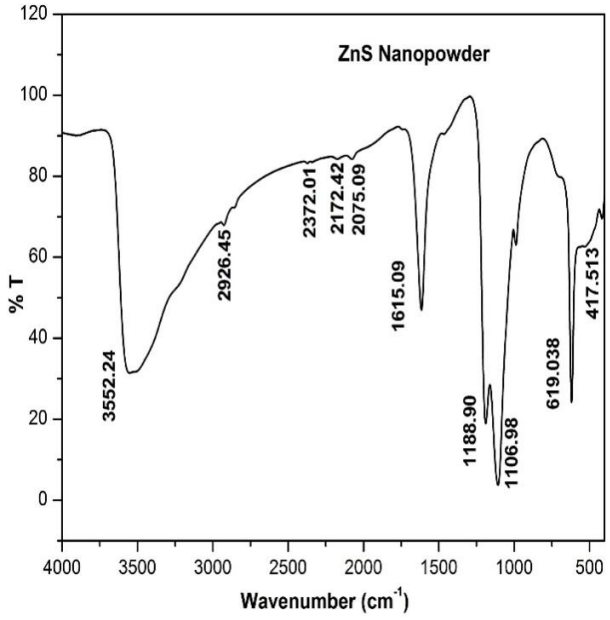

Figure 3: FTIR of ZnS nanopowder

FT-IR spectra of the prepared ZnS nanoparticles are given in Figure 3. The broadband around 3000−3600 cm^{-1} is due to the OH stretching frequency (existence of water absorbed on the surface of nanocrystals). The bands at 1430 and 1555 cm^{-1} can be assigned to C=O symmetric and asymmetric stretching modes arising from the absorption of atmospheric CO_2 on the surface of the nanocrystals [20-21]. The characteristic ZnS vibration peaks can be noticed at 1110 and 672 cm^{-1} [22].

3.4. Optical analysis

Figure.4 shows the optical transmittance of ZnS nanoparticles. It had a transmittance 55% in the visible region. Figure 5 shows the variation of $(\alpha h\nu)^2$ with the photon energy for Synthesized ZnS sample. The absorption coefficient (α) and incident photon energy (hν) can be related as

$$\alpha = \frac{A(h\nu - E_g)^m}{h\nu} \qquad (7)$$

where A is a constant and E_g is the band gap of the material. From the Tauc's plot, the band gap is found to be 3.76 eV for ZnS nanoparticles. These values can be compared with band gap values of 3.38 - 3.54 eV at room temperature for bulk ZnS [23].

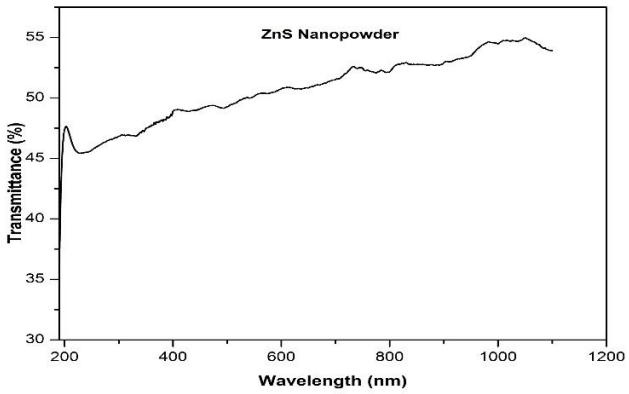

Figure. 4: Optical transmission spectra of ZnS nanopowder

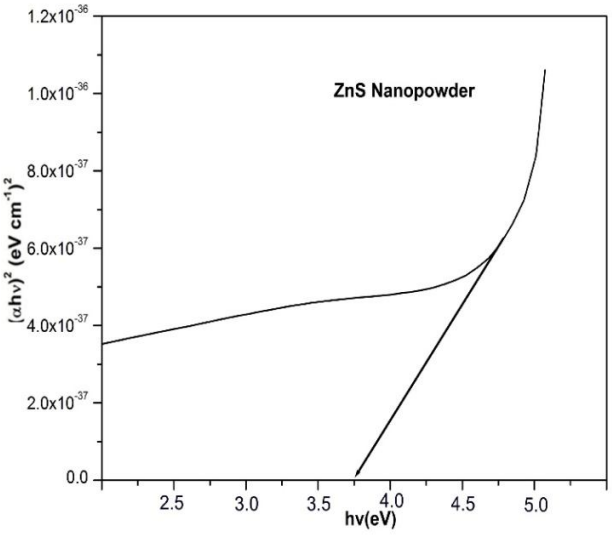

Figure.5: Tauc's plot of ZnS nanopowder

Photo Luminescence Analysis:

The recombination of surface states brings about the photoluminescence (PL) of the materials [24]. Room temperature photoluminescence spectra of ZnS samples are

given in Figure 3. The emission spectrum of the photoluminescence peak position at 664.31 nm has observed [25].

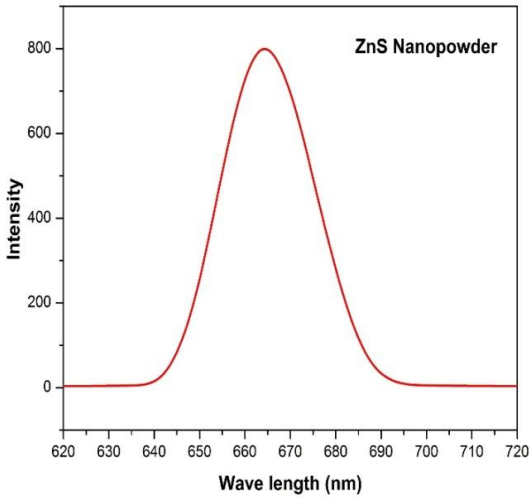

Figure.6: PL spectra of ZnS nanopowder

IV. CONCLUSION

ZnS nanoparticles are successfully synthesized by cost effective co-precipitation method. The X-ray diffraction pattern indicates the very good hexagonal structure of ZnS nanocrystals. The microstructural parameters were estimated. The crystallite size of the sample was calculated using Scherer's equation and found to be 16.26 nm. From the SEM results ZnS nanoparticles have a rough morphology and spongy surface. Functional groups were identified from the FT-IR spectra. The calculated direct band gap of energy was 3.76 eV for prepared samples. The PL spectrum consists of 664.31 nm emission bands.

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