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Structural and Optical Properties of ZnS Semiconductor Nanoparticles Synthesized by Chemical Co-Precipitation Method Methacrylic Acid as the Capping Agent

Ravindra C. Alange

Department of Physics, Shri. Madhavrao Patil Mahavidyalaya, Murum, Osmanabad, M.S., 413605, India
Email Id: *ravikiran.alange[at]gmail.com*

Abstract: ***Zinc Sulfide (ZnS) nanoparticles were successfully synthesized by chemical co-precipitation method using Zinc nitrate and sodium sulfide as a precursor material. Methacrylic acid was used as capping agent. The highly stable colloidal ZnS nanoparticles have been prepared at room temperature. The sample were characterized by X-ray diffraction (XRD), UV visible absorption spectroscopy, band gap measured by UV-Visible absorbance spectrum. In the XRD pattern of samples, there is no change in the cubic zincblende structure. The crystallite size of as prepared nanoparticles is found to be in the 7 nm range. The value of optical band gap has been found to be in the range 3.58 eV.***

Keywords: XRD, ZnS nanoparticles, UV visible Spectroscopy

1. Introduction

The semiconductor nano-material play an important role in the fields of photocatalytic [1] hyperthermia [2] as well as biomedical [3] LED applications [4]. The nano materials have excellent structural, electrical, magnetic properties than that of bulk material [5]. Among the semiconductor nono-material becomes promising candidate in the various applications because of its enhanced structural, optical and magnetic properties. Recent year, the investigation has been concentrated on the preparation and characterization of II–VI semiconductor nanoparticles for applications in optoelectronics and spintronic devices because of their size- and colour dependent properties [6, 7]. Among the group II-VI semiconductors, ZnS, with unique optical properties and a wide energy direct band gap at room temperature, is one of the important materials with wide range of applications [8]. In particular, doped-ZnS have been investigated extensively, because ZnS a good host material is an important versatile and luminescent material with a wide band gap. The band structure of the semiconductor changes with decreasing particle size. ZnS particles have two kinds of structures: zinc blende structure (cubic crystal) and wurtzite structure (hexahedron). ZnS applied in luminescent materials generally has zinc blende structure [8]. The optical properties of ZnS doped with different transition metal ions and the potential applications of these luminescent materials have been reported by different research group [9-13]. Different metal ions doped with ZnS have been studied by many researchers because of their extensive optical properties. Generally, ZnS doped with transition metal ion provide new opportunities for research and different applications.

Now days, different synthesis techniques are being used to prepare pure ZnS and doped with transition metal ions semiconductors nanoparticles [11, 14-18]. For the synthesis of ZnS nanoparticles chemical co precipitation method was used. In this work, we report the structural and optical studies of ZnS semiconductor nanoparticles prepared by chemical precipitation method. The techniques such as X-ray diffraction (XRD), and UV–Vis absorption spectroscopy was used to study its properties. In view of the potential applications and importance of ZnS semiconductors nanoparticles in optoelectronic devices applications.

In the present work, synthesis of ZnS nanoparticles by chemical co-precipitation method. Synthesized ZnS nanoparticles were characterized by standard characterization techniques to study the structural and optical absorption properties.

2. Experimental

For the synthesis of ZnS nanoparticles in this study, zinc Nitrate (Zn $(NO_3)_2 \cdot 6H_2O$), sodium sulfide nonahydrate (Na2S·9H2O) and methacrylic acid ($C_4H_6O_2$) were used, which were purchased from Sigma-Aldrich double distilled water was used as a solvent. Methacrylic acid was used as a capping agent. Double distilled water was used throughout the experiment. All of the chemicals used were of AR grade without further purification. In the present work, ZnS nanoparticles have been prepared by chemical co precipitation method at room temperature. For synthesis, zinc nitrate (0.5 M) and sodium sulfide (0.5 M) were dissolved in minimum amount of distilled water separately and stirred continuously separate for 30 min. While stirring zinc nitrate, freshly prepared sodium sulfide (0.5 M) solution was mixed drop by drop in (0.5 M) solution of zinc nitrate. In addition, methacrylic acid with concentration 0.1 M was added in zinc nitrate and sodium sulfide solution as the capping agent in order to control the growth of the nanoparticles during the reaction. The resulting solution was stirred once again continuously for 30 min. In the final step, white precipitate of the ZnS nanoparticles is formed slowly in the solution. The obtained precipitate was then filtered

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using centrifuged machine 3000 r.p.m. for 15 min and then washed with ethanol to remove impurity present in it. The obtained precipitate was dried at room temperature and crushed to fine powder with the help of mortar and pestle and used for structural and optical characterization.

3. Characterization

For the synthesis of ZnS nanoparticles chemical coprecipitation method was used. The crystallinity and the phase purity of the ZnS nanoparticles were examined by X-Ray powder diffraction (XRD) at room temperature on a Rigaku (Miniflex-II) X-ray diffractometer using monochromatic Cu-kα radiation with λ = 1.5405 Å operated at 30 kV and 15 mA with 2θ ranging from 10 to 80 degree at the speed of 5 deg / min. with sampling width 0.020 degree. Optical absorption was studied using Perkin Elmer UV-Visible spectrophotometer with wavelength range 200 nm to 800 nm.

4. Results and Discussions

4.1 X-ray diffraction Study

Fig.1 shows the X-ray diffraction pattern of ZnS nanoparticles. The XRD pattern shows the prominent peaks (2θ values) 28.52º, 47.91º and 56.56º were indexed (111), (220) and (311) planes respectively. The X-ray diffractogram and 2θ values of ZnS were found to be in fairly good agreement, thus confirming the cubic zinc blende crystal structure [19]The lattice parameter was determined by using Cohen's method and found to be 5.441 Å, which is good agreement with that of existing literature value 5.439 Å [20].Moreover, the broadening of the diffraction peak was observed due to a small size of the crystalline in the order of nanometer.

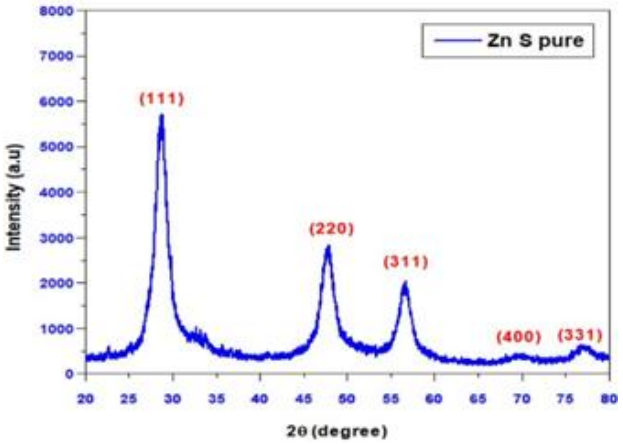

Figure 1: X-ray diffraction pattern of ZnS nanoparticles

The synthesized ZnS nanoparticle crystalline size was calculated using Debye-Scherrer formula [21], $d=0.89\lambda/\beta\cos\theta$, where D is the crystalline size, β is the full width at half maximum (FWHM), K is the constant factor (0.89), λ is the wavelength of X-rays (λ=1.5406 Å) and θ is the diffraction angle. The average crystalline size of the sample was found to be 7 nm which is derived from the FWHM of more intense peak corresponding to 111 planes located at 28.52° using Scherrer's formula.

4.2 Optical Absorption Study

The size of the nanoparticles plays an important role in changing the optical properties of semiconductor nanoparticles [22, 23]. Thus, size evolution of semiconducting nanoparticles becomes very essential to explore the properties of the materials. UV-visible absorption spectroscopy is widely being used technique to examine the optical properties of nanosized particles [24]. The optical absorption spectrum of synthesized ZnS nanoparticles sample is shown in Fig.2.

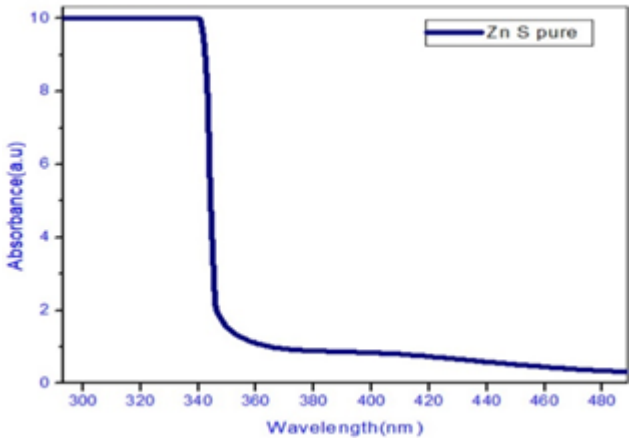

Figure 2: UV-vis absorption spectrum of ZnS nanoparticle

The relation between the incident photon energy (hυ) and the absorption coefficient (α) is given by the following relation:
$(\alpha h\nu)^{1/n} = A(h\nu - Eg)$, where C is constant and Eg is the band gap of material and the exponent m depends on the type of transition. For direct allowed transition m = 1/2, for indirect allowed transition m = 2, for direct forbidden m = 3/2 and for indirect forbidden m = 3.

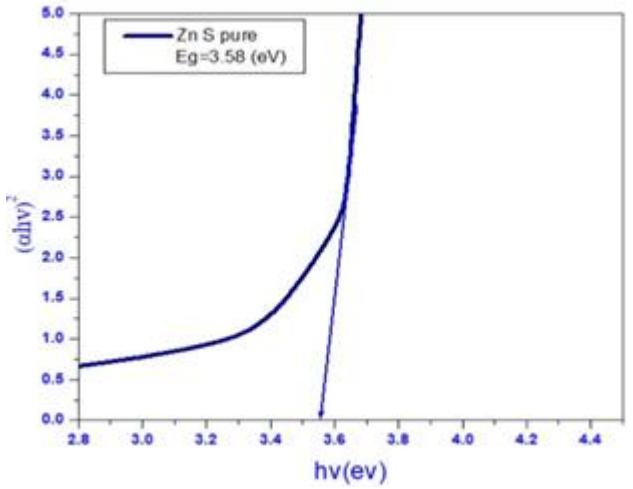

Figure 3: Extrapolation curve for band gap determination of ZnS nanoparticles

Direct band gap of the samples is calculated by plotting $(\alpha h\upsilon)^2$ vs. hυ and then extrapolating the straight portion of the curve on hm axis at a = 0, shown in Fig. 3. The optical band gaps of the ZnS nanoparticles are found to be 3.58 eV. The obtained values of the band gap of ZnS nanoparticles are higher than that of the bulk value of ZnS [25]. This blue shift of the band gap takes place because of the quantum

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confinement effect. The absorption spectrum of ZnS nanoparticle shifts towards the lower wavelength side, which can be explained as being due to the quantum size effect. Due to the quantum confinement effect of semiconductor nanoparticles in their electronic structure, which originates from the electron– hole confinement in a small volume, the increasing band gap energy occurred [26].

4. Conclusion

ZnS semiconductor nanoparticles synthesized by chemical co precipitation method by using of methacrylic acid as capping agent. The structural properties determined by X-ray diffraction study, lattice parameter determined by Cohen's method and parameter is found is 5.441 Å. The crystallite size of the prepared nanoparticles is found to be 7 nm. The optical properties are determined from UV- visible spectroscopy measurement in the range of 220 nm to 800 nm and calculated optical band gap is found in between 3.58 eV

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