

Research Paper

Structural and Optical Properties of High-Purity Cubic Phase ZnS Nanoparticles Prepared by Thermal Decomposition Route for Optoelectronic Applications

K VIJAI ANAND^{1,2}, R MOHAN², R MOHAN KUMAR², M KARL CHINNU³ and R JAYAVEL^{3,*}

¹*Department of Physics, Sathyabama University, Rajiv Gandhi Road, Chennai 600 119, India*

²*Department of Physics, Presidency College, Chennai 600 005, India*

³*Centre for Nanoscience and Technology, Anna University, Chennai 600 025, India*

(Received 27 June 2012; Accepted 12 February 2013)

Zinc sulfide (ZnS) is one of the important II-VI compound semiconductors used for a variety of applications such as optical coatings, photoconductors and electro-optic modulators owing to its wide band gap energy. In the present study, high-purity cubic phase ZnS nanoparticles were synthesized by the thermal decomposition of zinc acetate dihydrate and thiourea in air at 300°C for 6 h. The structural and optical properties of the prepared ZnS nanoparticles were characterized using X-ray diffraction (XRD), Transmission electron microscope (TEM), Fourier transform infrared spectroscopy (FTIR), Ultra Violet-visible (UV-vis) absorption spectra and Fluorescence (PL) spectroscopy. X-ray diffraction studies reveal that the prepared ZnS nanoparticles exhibit cubic zinc-blende structure with an average particle size of 3 nm. The UV-Vis absorption spectra of the ZnS nanoparticles have an absorption maximum around 326 nm, which is fairly blue shifted compared to bulk ZnS (345 nm) due to strong quantum confinement effect. From the photoluminescence (PL) spectra, a weak UV peak at around 355 nm and a broad and relatively strong peak of blue-green in the range of 400-560 nm were observed. The optical properties show that the prepared ZnS nanoparticles as a better candidate for various optoelectronic applications.

Key Words: ZnS Nanoparticles; Thermal Decomposition; Structural Properties; Optical Properties; Quantum Confinement; Optoelectronic Applications

Introduction

The physical and chemical properties of materials mainly deviate from the bulk with the reduction of size to nanometer scale. Among the different class of materials, semiconductor nanostructures have been extensively studied due to their potential applications and novel properties [1]. Zinc sulfide (ZnS), a wide band gap II-VI compound semiconductor, is a very promising material for its wide applications in electroluminescence, sensors, solar cells and lasers. In optoelectronics, it is used as a light emitting diode, reflector, dielectric filter and window material [2]. In

view of its technological importance, preparation of ZnS remains a main focus of interest for researchers to adopt new synthetic routes in order to get phase pure material via an economically and technically viable method. Primary synthesis routes like spray pyrolysis [3], surfactant assisted soft chemistry method [4], microwave irradiation technique [5], γ -irradiation technique [6] and hydrothermal method [7-9] were applied to prepare ZnS nanostructured materials. However, these methods involve a strictly controlled synthesis environment, complicated procedures and expensive equipments. In addition, high temperature synthesis processes consume more energy. A non-

*Author for Correspondence: E-mail: rjvel@yahoo.com

hydrolytic single-molecular precursor approach has been reported to prepare ZnS nanocrystals by means of thermal decomposition of zinc (II) cupferron complex (ZnCuP_2) in alkylamines using suitable reaction atmosphere [10-11]. In the present study, high-purity cubic phase ZnS nanoparticles have been prepared by a one-step non-hydrolytic route via thermal decomposition of zinc acetate dihydrate and thiourea in air atmosphere at 300°C for 6 h. The structural and optical properties of the prepared ZnS samples have been studied.

Experimental and Characterization

Zinc acetate dihydrate ($(\text{CH}_3\text{COO})_2\text{Zn}\cdot 2\text{H}_2\text{O}$) and thiourea (H_2NCSNH_2) are all analytical grade reagents which were used without further purification. For the synthesis of ZnS nanoparticles, 2.5 mmole of zinc acetate dihydrate and thiourea were taken in a crucible and placed in a box furnace. The crucible was heated to 300°C in air and held for 6 h, to synthesize high-purity cubic phase ZnS nanoparticles. The XRD patterns were recorded with Siemens D-5005 X-ray powder diffractometer, using CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$). Transmission electron microscope (TEM) images were obtained using JEOL 3010 TEM apparatus. Thermogravimetry analysis (TGA) was done with Perkin Elmer thermoanalyzer under air atmosphere at a heating rate of $10^\circ\text{C min}^{-1}$, to study the thermal decomposition phenomena of the zinc acetate dihydrate and thiourea mixtures. FTIR spectra were recorded using Perkin Elmer RX1 Model FTIR spectrophotometer by KBr pellet method in the range between 4000 to 600 cm^{-1} . Optical absorption studies were performed using Perkin Elmer UV-Visible spectrophotometer. Emission spectra were recorded at room temperature using Perkin Elmer LS 5B Fluorescence spectrophotometer over a range of 325 to 600 nm .

Results and Discussion

Fig. 1 shows the X-ray diffraction pattern of ZnS nanoparticles, which exhibit the high-purity single phase sphalerite (cubic) crystal structure. The three diffraction (111), (220) and (311) planes correspond to cubic crystalline ZnS (JCPDS Card No. 05-0566) [12]. The broadening of the diffraction peaks indicates

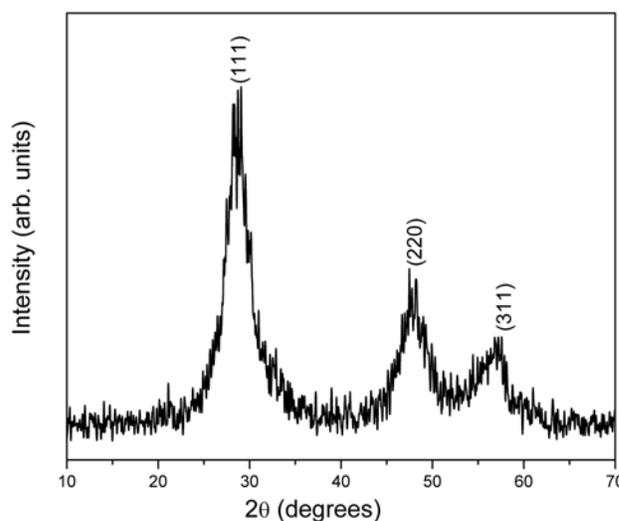


Fig. 1: XRD pattern of ZnS nanoparticles

the nanocrystalline nature of the material. The average grain size of the prepared ZnS samples is determined to be around 3 nm from the full width at half-maximum (FWHM) of the most intense peak using the Scherrer's formula [13].

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where λ is the wavelength of the X-ray radiation (for CuK_α radiation, $\lambda = 1.5418 \text{ \AA}$), β is the FWHM in radians of the XRD peak and θ is the angle of diffraction.

From the TEM images of ZnS nanoparticles (Fig. 2a), it is clear that the resulting particles possess spherical morphology with a mean particles size of around 3 nm. This is in good agreement with the particle size obtained from the XRD analysis. The structure of ZnS nanoparticles was revealed by the selected area electron diffraction (SAED) pattern (Fig. 2b). The SAED pattern shows a set of broad rings instead of spots due to the random orientation of the crystallites, corresponding to diffraction from different planes of the nanocrystallites [14]. The SAED pattern exhibits principally three rings corresponding to (111), (220) and (311) planes respectively, which is in agreement with the cubic phase of ZnS [15].

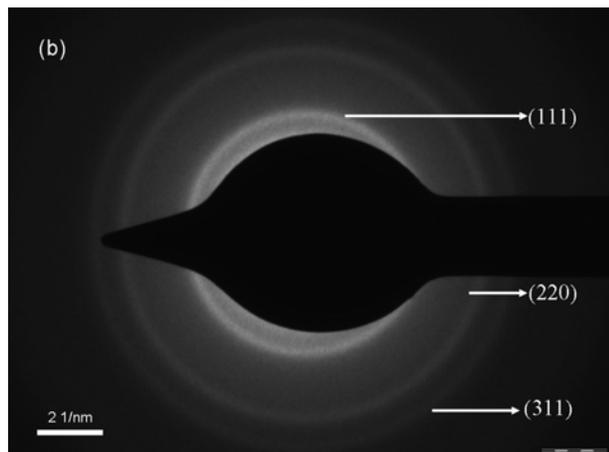
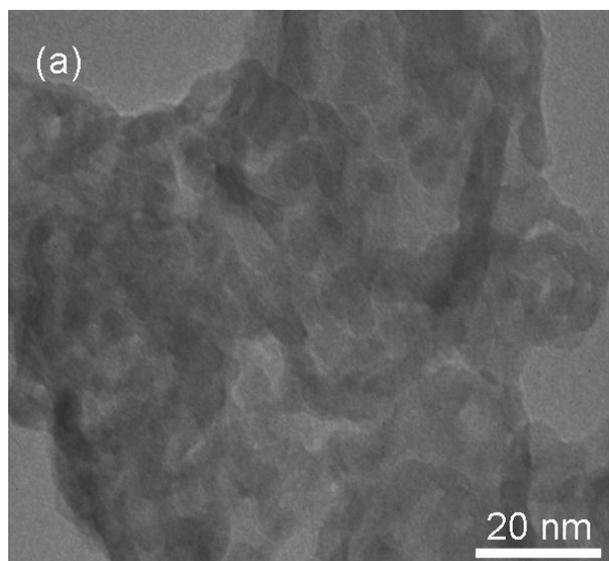


Fig. 2: (a) TEM images and (b) SAED pattern of ZnS nanoparticles

The results of TGA of a mixture compound of zinc acetate dihydrate and thiourea are illustrated in Fig. 3. The initial weight loss up to 125 °C was due to loss of water.

A major weight loss that started close to 150°C was due to decomposition of free thiourea [16]. It was followed by a small weight loss starting at about 250°C due to decomposition of zinc acetate. The zinc acetate decomposition extended up to 310°C [17]. The fourth weight loss occurring at about 500°C was due to decomposition of zinc sulfide [18]. Hence, a mixture composed of zinc acetate dihydrate and thiourea, when heated up to 300°C could yield ZnS.

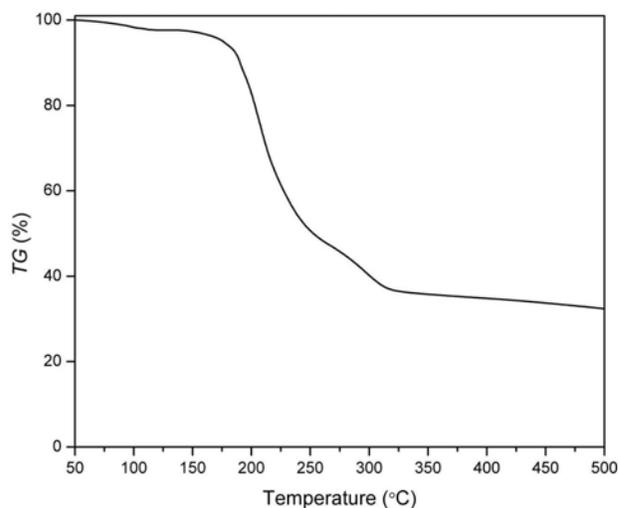


Fig. 3: TGA curve of zinc acetate dihydrate and thiourea mixtures

It supported the synthesis of ZnS nanoparticles by thermal decomposition of zinc acetate dihydrate and thiourea mixtures at 300°C followed in this study.

The FTIR spectrum of ZnS nanoparticles is shown in Fig. 4. The peaks at 2930 and 2866 cm^{-1} is due to alkyl CH_2 vibrations. The peak at 1714 cm^{-1} was due to $\text{C}=\text{O}$ stretching vibration. The peaks at 1367 and 1509 cm^{-1} were due to CH_3 bending modes. The peak at 1228 cm^{-1} was due to $-\text{COO}-$ vibration. Hence, this spectrum illustrates the presence of acetate groups on ZnS nanoparticles. The peak at 985 cm^{-1} can be attributed due to the presence of resonance interaction between vibrational modes of sulfide ions in the crystal [19]. The peak appearing at

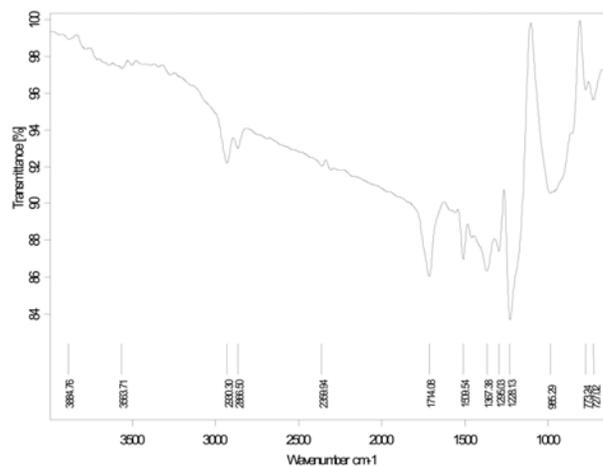


Fig. 4: FTIR transmission spectrum of ZnS nanoparticles

680 cm^{-1} was assigned to Zn-S stretching vibration [20].

The optical absorption spectrum of ZnS nanoparticles is shown in Fig. 5. In the optical absorption spectra, a pronounced excitonic structure is observed as expected for a highly crystalline material [10]. The excitation absorption peak of ZnS nanoparticles was observed at around 326 nm, which is fairly blue-shifted with respect to the bulk ZnS (345 nm) [1]. The blue shift in the absorption spectra is attributed to the quantum confinement of charge carriers in the nanoparticles, which is in good agreement with the theoretical reports [21]. The estimated optical energy band gap value of ZnS nanoparticles is found to be around 3.81 eV (Fig. 6). Thus the optical energy band gap of the resulting nanoparticles shows marked increment as compared with that of the bulk ZnS (3.6 eV).

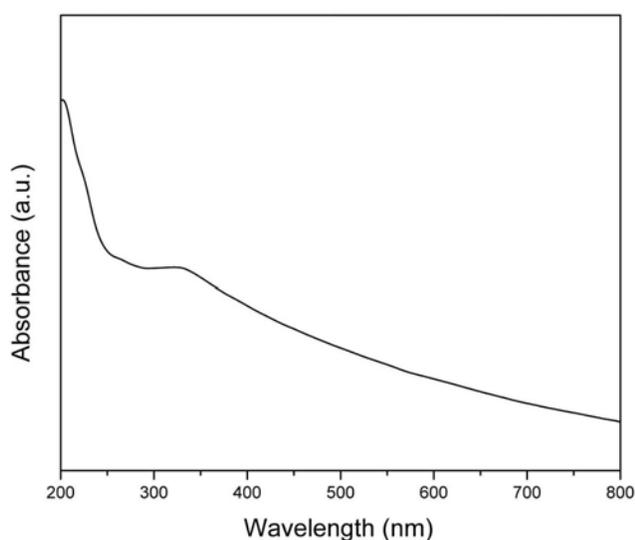


Fig. 5: Absorption spectrum of ZnS nanoparticles

The PL spectrum of the prepared ZnS sample was recorded at room temperature with an excitation wavelength (λ_{exc}) of 310 nm and is shown in Fig. 7. Broadening of the emission peak could be attributed to both size distribution and increase in the surface states owing to the increase in surface to volume ratio for nanoparticles. From the PL spectra, a weak UV peak at around 355 nm and a broad and relatively strong peak of blue-green emission in the range of

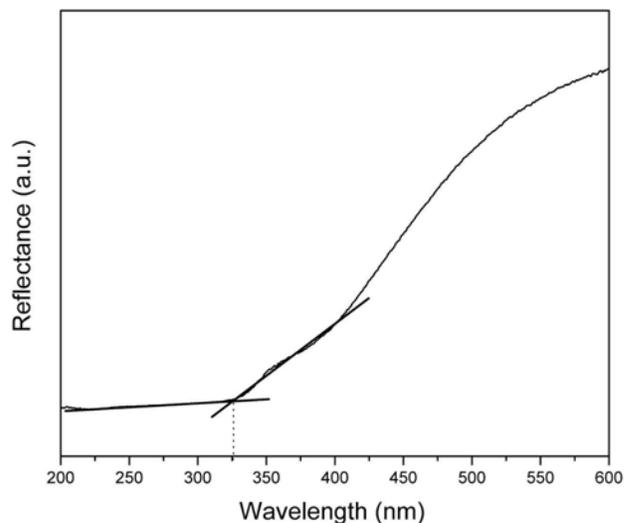


Fig. 6: Optical band gap energy determination of ZnS nanoparticles

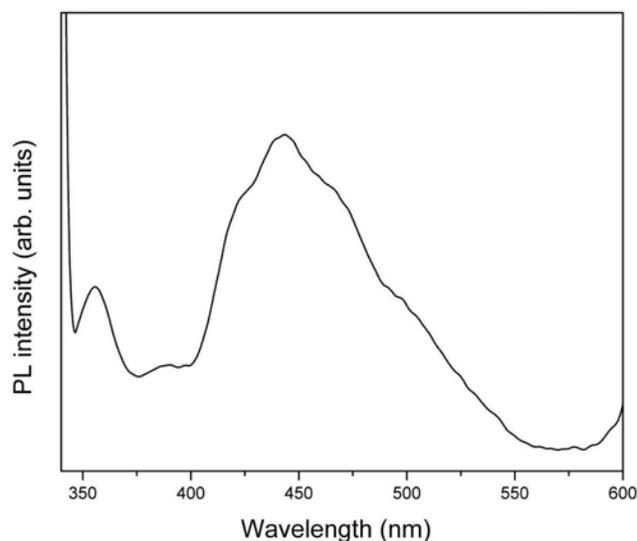


Fig. 7: Photoluminescence spectrum of ZnS nanoparticle

400-560 nm were observed. The UV emission is mainly attributed due to interstitial sulfur [22]. The blue emission could be attributed to the sulfur vacancy and interstitial lattice defects in the ZnS nanostructure [23]. The green emission may be due to some self-activated defect centers related to Zn-vacancies [24].

Conclusion

High-purity ZnS nanoparticles has been prepared via thermal decomposition of zinc acetate dihydrate and thiourea in air atmosphere at 300°C for 6 h. The crystal

structure and grain size of the nanoparticles were determined using XRD through Scherrer's formula. The UV-Vis absorption studies revealed that the prepared ZnS nanoparticles exhibit strong quantum confinement effect as the optical energy band gap increased significantly compared to the bulk ZnS. From the PL spectra, a weak UV peak at around 355 nm and a broad and relatively strong peak of blue-green in the range of 400-560 nm were observed. The optical properties show that the prepared ZnS

nanoparticles as a better candidate for various optoelectronic applications.

Acknowledgements

The authors are thankful to Dr. M Kandaswamy, Department of Inorganic Chemistry, University of Madras, Chennai for providing the UV-Vis absorption and fluorescence emission facility. TEM facilities provided by SAIF, Indian Institute of Technology, Mumbai are gratefully acknowledged.

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