Chalcogenide Letters Vol. 10, No. 9, September 2013, p. 319 - 323

# STRUCTURAL AND OPTICAL PROPERTIES OF ZnS NANOPARTICLES SYNTHESIZED BY MICROWAVE IRRADIATION METHOD

K. P. TIWARY[a *], SHIV KUMAR CHOUBEY[b], K. SHARMA[c]
[a]*Department of Applied Physics, Birla Institute of Technology, Patna Campus, India*
[b]*Department of ECE, Birla Institute of Technology, Patna Campus, India*
[c]*Department of Applied Chemistry, Birla Institute of Technology, Patna Campus, India*

ZnS nanoparticles were synthesized by Microwave assisted irradiation method. The obtained ZnS nanoparticles were characterized by XRD, SEM and UV-Vis spectroscopy. XRD characterization of the samples were taken which verify the crystalline form of the samples and also the average size of the nanocrystallites were measured by Debye-Scherrer formula as per the XRD spectrum, which was found to be around 6 nm. The surface morphology of the ZnS nanocrystallites was taken by Scanning Electron Microscopy. The UV-Visible absorption spectra of the nanocrystallites were taken and the optical bandgap of the ZnS nanocrystals were found to be 3.76 eV.

(Received July 29, 2013; Accepted September 2, 2013)

Keywords: Microwave, XRD, bandgap, nanoparticles

## 1. Introduction

II-VI compound semiconductors such as ZnS, CdS, CdSe, etc., are promising materials for technological application, mostly due to their large band gap. In recent years there has been increased interest in the scientific and technological aspects of the nanosized semiconductors. Nanoparticles of semiconductors are used as light emitting diode, phosphors in lighting, displays, solar cell, X-ray sensors and scintillators, photocatalyst and electrochemical cell [1-4]. In all of these applications the exciting energy in the II-VI host is efficiently transferred to an activator, generating a characteristic visible colour. ZnS is one of the most applied semiconductors in optical devices due to its high refraction index and high transmission within the visible range [5].

Several methods have been used for the preparation of various sulfides, such as gas phase reaction with sulfur vapor, solid-state reaction, sol–gel process, spray-prolysis methods, photolysis and sonochemical preparation [6-10]. For synthesis of nanoparticles of ZnS various methods are being used such as solvothermal method [11], hydrothermal method [12], gamma-irradiation [13] and microwave irradiation [14]. Among these methods, microwave irradiation is one of the novel methods and is being considered as new emerging area of research. In the present study microwave irradiation method is used for the synthesis of ZnS nanoparticles. This technique was chosen in this work due to its simplicity and potentiality for being adapted to industrial synthesis of nanoparticles, as it requires very short reaction time and capable of producing small particle size of high purity. Hence, the objective of this work is to synthesize nanoparticles of ZnS in aqueous dispersion using microwaves.

Water has a very high dipole moment and that is why it is one of the best solvent for microwave assisted reaction [15]. During the formation of the nanoparticles under microwave irradiation, solvents can have an important influence on the size and morphology of the final products. In different solvents, the collision rate between reactant molecules, the heating rate, and

*Corresponding asuthor: kptiwary@rediffmail.com

the temperature of the reaction are different [16]. Microwave heating results from the interaction of the electromagnetic wave with the irradiated medium which produce a force on charged particles and cause them to rotate or further polarized. The rotation of the dipoles in an alternating field causes friction, which produces heat up to $10^0$C/s [17-19].

**Experimental techniques:**

All the chemicals used in the synthesis of ZnS nanoparticles were taken of AR grade and also were used without further purication. Freshly prepared aqueous solutions were used for the synthesis of nanoparticles. In this experiment 0.5 M Zinc acetate was taken and the Molar concentration of thioacetamide was taken a little more. A solution of Zinc acetate ($Zn(CH_3COOH)_2.2H_2O$) and a solution of thioacetamide ($CH_3CSNH_2$) were prepared and stoichiometrically combined. With further addition of distilled water the solution was further diluted. The Volume of the solution was made to 400 ml and it was kept on magnetic stirrer for an hour with 840 rpm to make the solution homogeneous. Then the beaker containing solution was put in to microwave oven (LG make) with a power of 900W. The sample was microwaved for a period of 12 minutes with a duty cycle of 25%.

$Zn(Ac)_2$ + Thioacetamide $\longrightarrow$ ZnS $\downarrow$

Microwave irradiation time = 20 sec ($t_1$), Rest period = 60 sec ($t_2$) then duty cycle

$$D = \frac{t_1}{t_{1+}\, t_2} = 25\%$$

The white precipitates thus obtained were washed several times with distilled water and dried at $60^0$C for 6 hours in an oven. The nanoparticles as prepared were characterized by X-ray diffractometer (XRD). The XRD patterns of the powdered samples were recorded by Rigaku X-ray diffractometer with a CuK$\alpha$ radiation ($\lambda = 1.5418$ Å) in a range of $2\theta$ from $20^0$ to $70^0$. The UV-Vis absorption spectrum of the nanoparticles of ZnS was taken by the spectrometer Rayleigh UV-2601 and also the optical band gap of the material was obtained. The optical studies were carried out in the wavelength range of 200 – 1200 nm. The Scanning Electron Microscope technique is a common way to observe the morphology of the samples. SEM Micrograph of the nanoparticles of ZnS was taken to observe the surface morphology.

## 2. Result and discussion

The XRD pattern of the as- synthesized ZnS by microwave irradiation is shown in fig.1 which indicates that it has cubic phase as cross referenced to JCPDS 65- 9585. The X-ray diffraction of the samples were recorded by an X-ray diffractometer with a Cu$K_\alpha$ radiation ($\lambda = 1.5418$ Å ) in a range of $2\theta$ from $10^0$ to $80^0$. The three peaks are only produced at 2θ equal to 28.6, 47.4 and 56.5 respectively which further corresponds to the crystal planes (111), (220) and (311) respectively [20]. The broadening of the diffraction peak in the xrd pattern indicates the formation of the nanocrystallinity. Using Debye- Scherrer formula, the crystalline size of the sample was calculated from full width at half maxima of Xrd pattern shown in Fig.1. The average nanocrystallite size is calculated by the formula,

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

Where $\lambda$ is the wavelength of the incident ray, $\theta$ is the Bragg's angle and $\beta$ is the full width at half maxima. The average size of the nanoparticles was calculated to be 6 nm. The Scanning Electron Microscope (SEM) micrograph of the as synthesized sample was taken which is shown in Fig.2.

The solution of Zinc acetate and thioacetamide were stoichiometrically combined and with further addition of distilled water it was diluted and stirred and then the solution was put into microwave oven. At high power of microwave, the sample temperature increases faster, leading to

decomposition of thioacetamide, promoting a greater amount of nuclei which further gives greater concentration of particles in the dispersion.

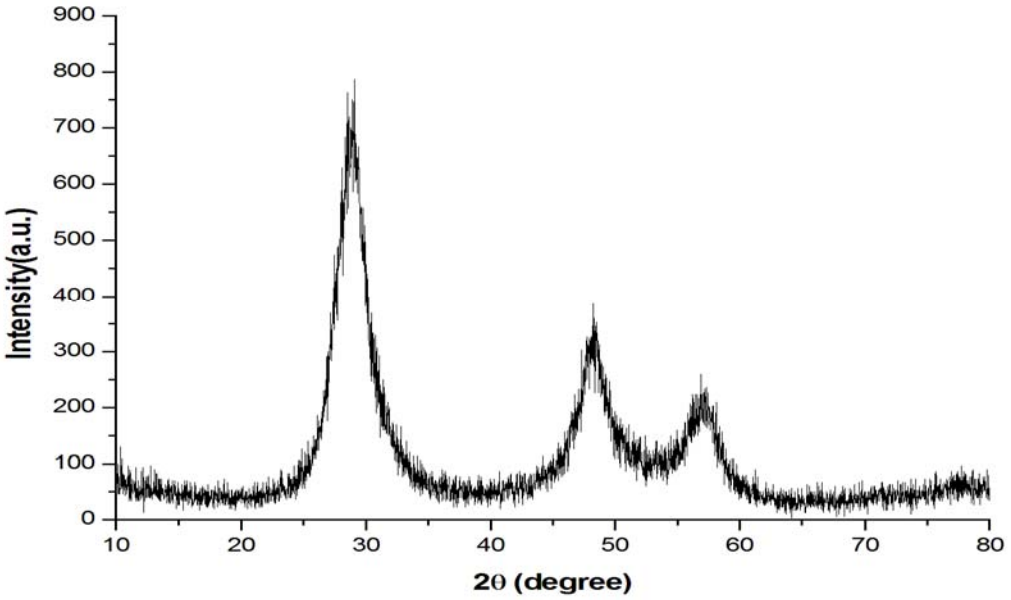


*Fig. 1. XRD pattern of the ZnS nanocrytals synthesized by microwave irradiation*

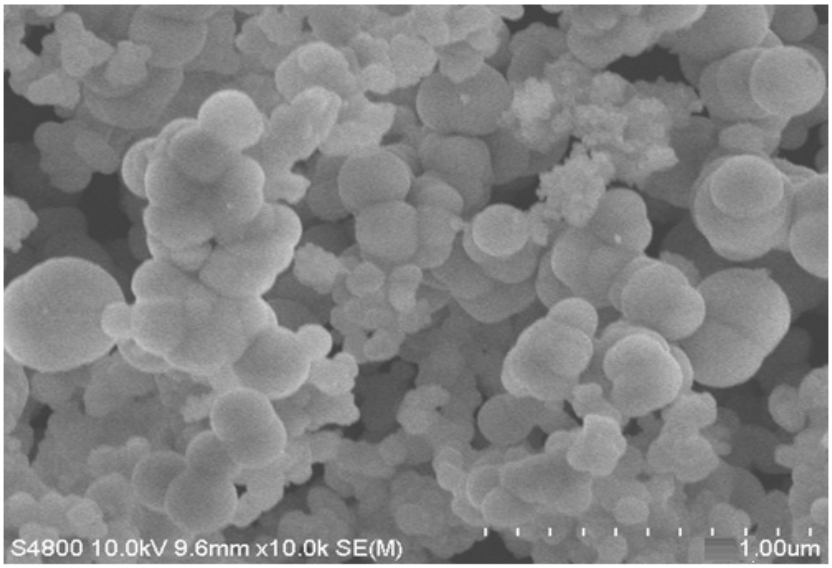


*Fig.2. SEM Micrograph of as synthesized ZnS nanoparticles.*

The UV-visible absorption spectrum of the ZnS nanoparticles is shown in Fig.3. The characteristic absorption peaks are appeared in the wavelength range 200 - 400 nm and the peak position reflects the band gap of the nanoparticles. UV spectra revealed that the absorption band was blue shifted from the bulk. The energy band gap of the ZnS nanoparticles was evaluated by plotting a graph between $(\alpha h\nu)^2$ versus $h\nu$ and by extrapolating the linear region of the curve to the energy axis [21].

$$\alpha h\nu \propto A\left(h\nu - E_g\right)^{1/2}$$

Where α is the absorption coefficient, $h\nu$ is the photon energy, $Eg$ is the direct band gap energy, and $A$ is a constant. Fig. 5 shows the graph between $(\alpha h\nu)^2$ versus $h\nu$, where the intercept of the graph on X- axis gives the value of band gap which is equal to 3.76 eV.

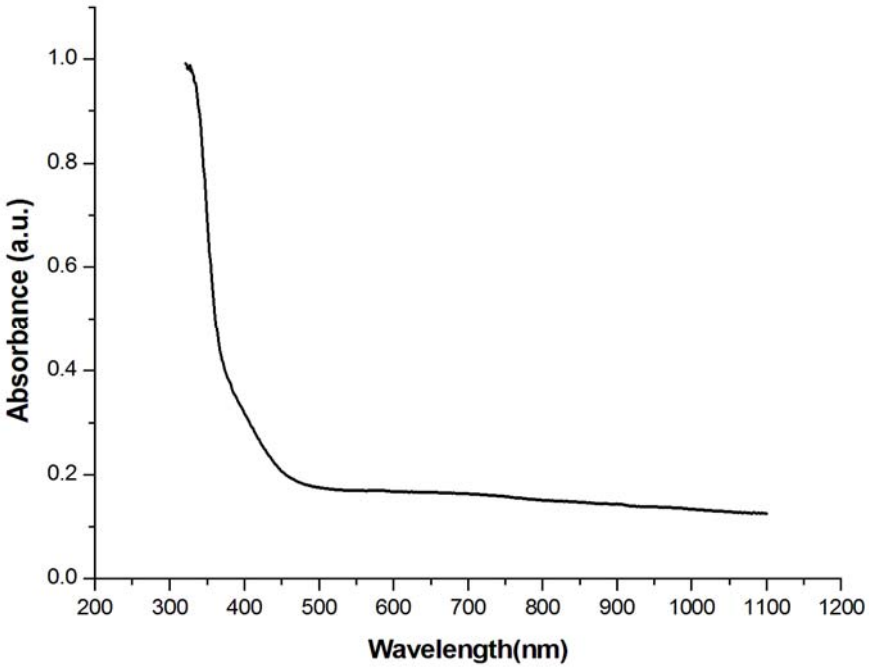


*Fig. 3. Optical absorption spectra of as-prepared ZnS nanoparticles*

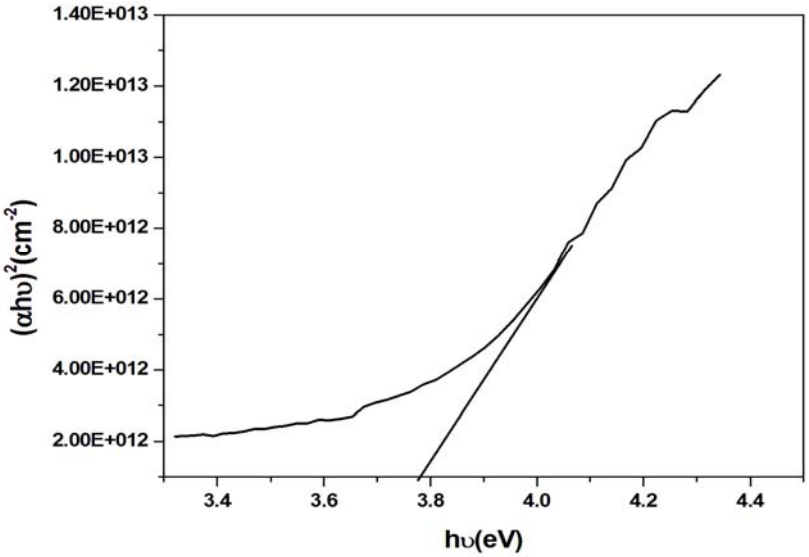


*Fig.4. Optical bandgap of ZnS nanoparticles.*

## 3. Conclusion

ZnS nanoparticles were synthesized by microwave irradiation method using Zinc acetate ($Zn(CH_3COOH)_2.2H_2O$) and a solution of thioacetamide ($CH_3CSNH_2$) and the average size of the nanoparticles were found to be around 6 nm which was calculated by Debye- Scherer formula. SEM image is used to study the morphology of the synthesized nanoparticles. The SEM micrograph of the sample also confirmed the nano size of the crystallites. The UV-Visible absorption spectra of the samples were recorded and the optical band gap was found to be 3.76 eV. UV spectra revealed that the absorption band was blue shifted from the bulk. In this study the focus was given on the structural and optical properties of the microwave assisted synthesis of ZnS nanoparticles. It has been observed that the reaction rate is faster in case of microwave assisted

synthesis. It was also concluded that the optical band gap of the microwave assisted synthesized ZnS was found to be increased as compared to that of the bulk ZnS.

**Acknowledgements**

The authors express the sincere thanks to Prof. (Dr) S. L. Gupta, Director Birla Institute of Technology, Patna for providing necessary facilities and lab equipments in synthesizing the nanoparticles.

## References

[1] B. O. Dabbousi, M. G. Bawendi, O. Onitsuka, M. F. Rubner, Appl. Phys. Lett, **66**, 1316 (1995).
[2] C-S Hwang, Cho IH , Bull, Korean Chem Soc. **26**, 1776 (2005).
[3] C. K. Grazel, M. Gratzel, J. Am. Chem. Soc. **101**,7741 (1979).
[4] A. Hagfeldt, M. Gratzel, Chem. Rev. **95,** 49 (1995).
[5] M. Abboudi, A. Mosset, J. Solid State Chem. **109**, 70 (1994).
[6] C. Kaito, Y. Saito, K. Fujita, Jpn. J. Appl. Phys. **26**, 1973 (1987).
[7] V. Stanic, T.H. Etsell, A.C. Pierre, Mater. Lett. **31**, 35 (1997).
[8] K. Okuyama, I.W. Lenggoro, N. Tagami, J. Mater. Sci. **32**, 1229 (1997).
[9] C. H. Fischer, A. Henglein, J. Phys. Chem. **93**, 5578 (1989).
[10] J. Z. Sostaric, R.A. Caruso Hobson, P. Mulvaney, F. Grieser, J. Chem. Soc., Faraday trans. **93**, 1791 (1997).
[11] L. Wang, L. Chen, T. Luo, and Y. Qian, Mater. Lett. **60**, 3627 (2006).
[12] L. Zhang, D. Qin, G. Yang, and Q. Zhang, Chalcogenide Letter. **9**, 93 (2012).
[13] H. Zhou, et al., Chem. Mater. **19**, 2144 (2007).
[14] J.Q. Sun, et al., Solid. State. Commun. **147**, 501 (2008).
[15] M.H. Entezari, N. Ghows, Ultrason. Sonochem. **18**, 127 (2010).
[16] Nayereh Soltani, et al., Chalcogenide Letters. **9**, 265 (2012).
[17] Z. Poormohammadi-Ahandani, A. Habibi-Yangjeh, Physica. E. **43**, 216 (2010).
[18] K. Bougrin, A. Loupy, M. Soufiaoui, J. Photoch. Photobio. C. **6**, 139 (2005).
[19] H. Qian, L. Li, J. Ren, Mater. Res. Bull. **40**, 1726 (2005).
[20] Pengfei Hu, et al., Advances in Materials Physics and Chemistry. **3**, 10(2013).
[21] S. Baset, H. Akbri, H. Zeynali and M. Shafie, Dig. J. Nanomater. Bios. **6**, 709 (2011).