

Synthesis and characterization of Cu doped ZnS nanoparticles by wet chemical method

Cite as: [AIP Conference Proceedings 2082, 030009 \(2019\); https://doi.org/10.1063/1.5093827](https://doi.org/10.1063/1.5093827)
Published Online: 22 March 2019

K. R. Bindu, and E. I. Anila



View Online



Export Citation

ARTICLES YOU MAY BE INTERESTED IN

[A novel UV-emitting poly \(vinylidene fluoride-hexafluoropropylene\)-CQD composite material for optoelectronic applications](#)

AIP Conference Proceedings 2082, 030001 (2019); <https://doi.org/10.1063/1.5093819>

[Synthesis and characterization of iron cerium tungstate nanoparticles and their dielectric studies](#)

AIP Conference Proceedings 2082, 030005 (2019); <https://doi.org/10.1063/1.5093823>

[Ultrafast nonlinear optical response in tungsten sulfide \(WS₂\) nanospheres](#)

AIP Conference Proceedings 2082, 030003 (2019); <https://doi.org/10.1063/1.5093821>

AIP | Conference Proceedings

Get **30% off** all
print proceedings!

Enter Promotion Code **PDF30** at checkout



Synthesis and Characterization of Cu Doped ZnS Nanoparticles by Wet Chemical Method

K R Bindu^{1,2} and E I Anila^{1a}

¹Optoelectronic and Nanomaterials' Research Laboratory, Department of Physics, Union Christian College, Aluva, Kerala, India, 683102.

²Department of Physics, Sree Sankara Vidyapeetom College, Valayanchirangara, Perumbavoor, Kerala, India, 683556.

^aCorresponding author: anilaei@gmail.com

Abstract. The synthesis of undoped ZnS and Cu doped ZnS have been carried out by wet chemical method at room temperature. The as-prepared ZnS and ZnS:Cu nanoparticles are characterized using X-ray diffraction, UV-Vis spectrophotometer and photoluminescence spectroscopy. The size of the synthesized nanoparticles is found to be in 2.5 nm range. The band-gap is found to be higher indicating blue shift compared with that of the bulk ZnS which is attributed to quantum size effect. Room temperature photoluminescence spectrum of the undoped sample exhibits a blue emission peaked at 430 nm whereas Cu doped sample exhibits the blue emission of ZnS and a green emission peaked at 520 nm under the same UV excitation.

INTRODUCTION

Semiconductor nanoparticles have attracted great deal of attention in the past few decades due to their novel unique properties and potential applications. The structural and optoelectronic properties of semiconductor nanoparticles differ from those of their corresponding bulk form due to quantum confinement effects. Among the II-VI semiconductors, ZnS is an important semiconductor compound with excellent physical properties and wide bandgap energy of 3.65 eV. Among the doped ZnS nanoparticles Mn and Cu doped ZnS nanoparticles are prominent phosphor materials for display and lightning. For the application of ZnS:Cu nanoparticles as phosphor materials, extensive research work is going on to tune their emissions by varying doping concentration in ZnS, by passivating the nanoparticles surface with different organic capping agents. The capping agents used for surface passivation in the synthesized nanoparticles may introduce unintended luminescent centers. Thus, the energy transfer mechanism for photoluminescence (PL) emission process becomes more complex. Hence, it is advantageous to obtain efficient PL emission from uncapped ZnS:Cu quantum dots.

In view of this, we have prepared ZnS:Cu nanoparticles through simple wet chemical method in aqueous medium without any capping agent and investigated structural and optical properties .

EXPERIMENTAL

ZnS and ZnS:Cu nanoparticles have been prepared by wet chemical method using zinc acetate [$\text{Zn}(\text{CH}_3\text{COO})_2$], copper nitrate [$\text{Cu}(\text{NO}_3)_2$] and sodium sulphide [Na_2S]. De-ionized water was used as the reaction medium in all the synthesis steps. In a typical synthesis, 25 ml of 1M $\text{Zn}(\text{CH}_3\text{COO})_2$ and 25 ml of 0.001M $\text{Cu}(\text{NO}_3)_2$ were mixed with continuous stirring. Subsequently, 1M Na_2S (25 ml) solution was added drop wise to the above mixture under continuous stirring for 20 min. at room temperature. The resulting white colloidal suspension was filtered, and the filtrate was washed with de-ionized water and dried by keeping in an oven at 70 °C for 1 day.

X-ray diffraction (XRD) patterns of the powder samples were collected with Bruker AXS D8 Advance X-ray diffractometer with Cu (1.5405 Å) as X-ray source. Diffuse reflectance measurements were performed using Varian Cary 5000 UV–Vis-NIR spectrophotometer. Photoluminescence (PL) spectra were obtained over the wavelength range 300–800 nm with Horiba Fluoromax 4C research spectrofluorometer with a xenon lamp as an excitation source.

RESULTS AND DISCUSSION

XRD pattern [Fig.1] of the samples exhibit three peaks, which are the characteristic peaks of the cubic ZnS as per JCPDS file No. 65-0309. The XRD peaks are fairly broad suggesting the nanostructure and the three peaks correspond to (111), (220) and (311) planes.

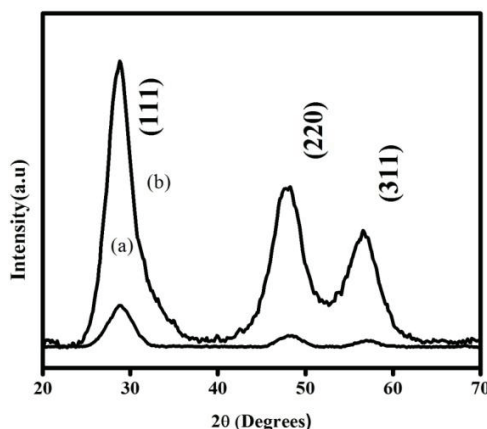


FIGURE 1. XRD pattern of (a) ZnS (b) ZnS:Cu nanoparticles

The grain size was calculated using Debye–Scherrer formula

$$D = 0.9\lambda/\beta \text{ Cos } \theta \quad (1)$$

where β is the full width at half maximum (FWHM), θ is the Bragg angle and λ is the wavelength (0.15405 nm) of the X-ray used. The average grain size D is found to be 2.37 and 2.54 nm for ZnS:and ZnS:Cu, respectively.

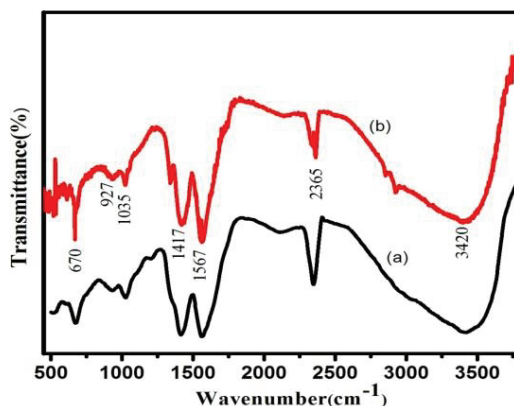


FIGURE 2. FTIR spectra of (a) ZnS and (b) ZnS:Cu nanoparticles

Fourier transform infrared (FTIR) spectra [Fig.2] of the samples were recorded in the wave number range 400-4000 cm^{-1} . The FTIR absorption peaks are the same for both the samples. The vibrational frequencies of the various bonds present in the materials can be assigned by observing the peak positions in the spectrum (Table.1).

TABLE 1. IR peaks and their assignments

Wave number (cm^{-1})	Assignment
1035	Zn-S vibration ^{1,2}
670	Zn-OH bending mode ^{3,4}
3420	O-H stretching mode ⁵
1567	O-H bending mode ⁴
1417	Carboxylic group ⁷
2345	C-H vibration ^{8,9}
912	Out-of-plane band due to O-H stretching ¹⁰

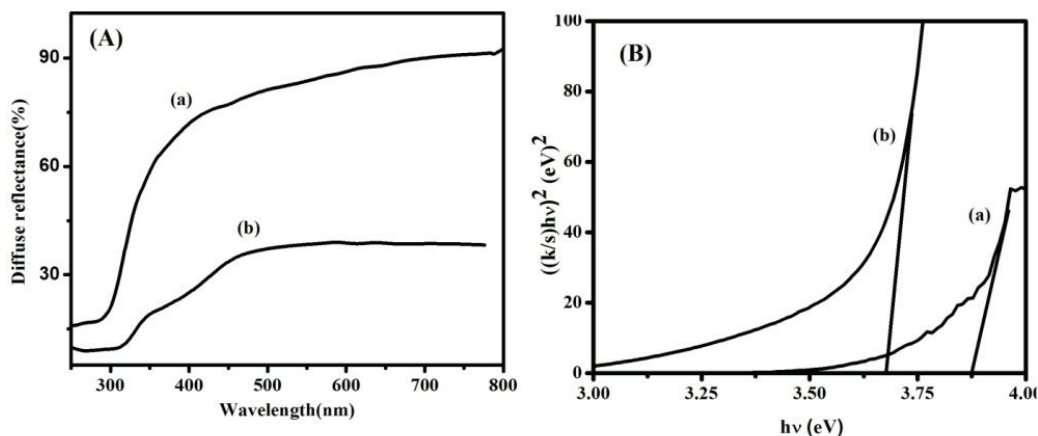


FIGURE 3. (A) Diffused reflectance spectra and (B) Plot of $((k/s)hv)^2$ versus $h\nu$ of (a) ZnS and (b) ZnS:Cu nanoparticles

The optical properties of the samples were determined from the diffuse reflectance measurements [Fig.3 (A)] in the range of 280-800 nm. The absorbance was calculated from the diffuse reflectance values by using the Kubelka–Munk function. ^{11, 12} The band gaps are 3.87 eV and 3.7 eV for the ZnS and ZnS:Cu samples which are estimated from the plot [Fig.3(B)] of $\{(k/s) hv\}^2$ vs. $h\nu$ where k and s denote absorption and scattering coefficients..

Room temperature PL emission spectra of undoped and doped ZnS nanoparticles are shown in Fig.4. The PL emission spectrum of undoped ZnS consist of blue emission around 430 nm which could be ascribed to the sulphur vacancy. ¹³ The PL spectra of the doped sample consists of a broad emission band in the range 450-550 nm. Due to the broad and unsymmetric nature of PL spectra, it is deconvoluted and found that it consists of two emissions, one blue emission of host ZnS around 430 nm and other green emission around 526 nm. The green emission with peak around 526 nm arises from the recombination of the shallow donor level related to sulphur vacancy and the t_2 level of Cu^{2+} , very close to the values reported by Xu et al. ¹⁴

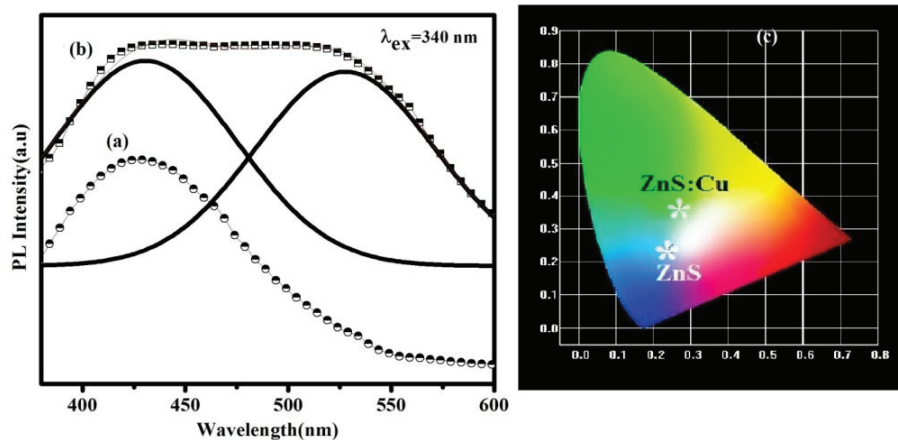


FIGURE 4. PL spectra of (a) ZnS (b) ZnS:Cu nanoparticles and (c) CIE diagram

To evaluate the performance of Cu doped ZnS on luminescence emission, CIE coordinates were calculated. We obtained CIE coordinates, $x=0.24$ and $y=0.24$ for ZnS and $x=0.27$ and $y=0.36$ for ZnS:Cu. The overall emission colour is green for ZnS:Cu whereas bluish white for ZnS.

CONCLUSION

Green emitting ZnS:Cu nanoparticles were successfully prepared by the wet chemical method without the aid of any capping agent. The XRD studies show the phase singularity of pure and Cu doped ZnS particles having zincblende structure. The results of PL studies showed that ZnS:Cu nanophosphor is a green phosphor and can be used for display applications.

ACKNOWLEDGEMENTS

One of the authors, Bindu K. R. is grateful to University Grants Commission for providing Teacher Fellowship. The authors acknowledge STIC, CUSAT, Kochi for the XRD and Department of Chemistry, Union Christian College Aluva for the FTIR measurements.

REFERENCES

1. R. L. Mishra, A. K. Sharma and Prakash Gas, *Biostruct.* **4**, 511–518 (2009).
2. B. S. Rema Devi, R. Raveendran, and A. V. Vaidyan, *Pramana Journal of Physics*, **68**, 679–687 (2007).
3. Y. Tong, Z. Jiang, C. Wang, Z.Y. Xin, S. Hong and Liu, *Mater. Lett.* **62**, 3385–3387 (2008).
4. F. Wegmuller, *J. Colloid Interface Sci.* **116**, 312 (1987).
5. J. W. Kauffman, R. H. Hauge and J. L. Margrave, *J. Phys. Chem.* **89**, 3541(1985).
6. F. Wegmuller, *J. Colloid Interface Sci.* **116**, 312 (1987).
7. S. D. Han et al. *Mater. Chem. Phys.*, **112**, 1083–1087 (2008).
8. B. Mokili, Y. Charreire, R. Cortes and D. Lincot, *Thin Solid Films*, **288**, 21–28 (1996).
9. X. Zhang, H. Song, L. Yu, T. Wang, X. Ren, X. Kong, Y. Xie and X. Wang, *J. Luminescence*. **118**, 251–256 (2006).
10. Chung Hsin Lu, Baibaswata Bhattacharjee and Shih Yen Chen, *J. Alloy Compd.* **475**, 116–121 (2009).
11. P. Kubelka, *J. Opt. Soc. Am.* **38**, 448 (1948).
12. P. Kubelka and F. Munk, *Ein Beitrag Zur Optik Der Farbanstriche. Zeitschrift für Technische Physik*, **12**, 593-601 (1931).
13. M. Ji Won, I. N. Ivanov, P. C. Joshi, B. L. Armstrong, W. Wang, H. Jung, A. J. Rondinone, G. E. Jellison, H. M. Meyer III, G. G. Jang, R. A. Meisner, C. E. Duty and T. J. Phelps, *Acta Biomater.* **10**, 4474–4483 (2014).
14. S. J. Xu, S. J. Chua, B. Liu, L. M. Gan, C. H. Chew and G. Q. Xu, *Appl. Phys. Lett.* **73**, 478 (1998).