International Journal of Luminescence and applications
Vol5 (4) December, 2015, pages 368-373

Effect of Thiourea and SHMP capping agents on structural and Photoluminescence studies of ZnS nanoparticles.

Meenakshi H.[1] Chandrasekharreddy K[2]

1.Assistant professor,Dept of Physics, G F G C, Chickballapur-562101, Karnataka.

2.Associative professor,Dept of Physics, S S B N UG and PG college, Anatapur-515001.(A P).

Corresponding author mail.id: meena.duggu@gmail.com

ABSTRACT:

In the present work, uncapped and capped ZnS nanoparticles were synthesized by chemical co-precipitation method using Thiourea and sodiumhexametaphosphate(SHMP) as capping agents at room temperature. The structural properties of ZnS nanoparticles were analysed using X-ray diffraction (XRD), Transmission electron microscopy(TEM), Scanning electron microscopy (SEM, while the optical properties were studied using UV-VISIBLE absorption and Photoluminescence.. The prepared samples had cubic zinc blende structure with particle size in the range 1.82 nm to 3.6 nm. TEM analysis revealed the formation of ZnS nanoparticles with nearly uniform spherical shape. The UV-VISIBLE absorption spectra showed a large blue shift . The emission peak was found to shift towards shorter wavelength side with reduction in particle size. In capped samples, enhanced luminescence intensities were observed. Among the capped samples, thiourea capped ZnS nanoparticles showed more luminescence intensity compared to that of SHMP capped samples.

Key words: II-VI group semiconductors, Co-precipitation method, Structural, Photoluminescence properties.

1. Introduction

Nanocrystalline semiconductor particles have more importance because of their novel properties, such as large surface to volume ratio and three dimensional confinement of electrons. Because of these two reasons many properties of nanomaterials are drastically different from the normal bulk properties [1]. In nanomaterials the decrease of particle size results in high surface to volume ratio. The enhanced surface area has increased the surface states, which in turn changed the activities of electrons and holes affecting the chemical reactions. The transition from bulk to nanoparticles have been mainly due to the display of quantum mechanical properties. Quantum mechanical effect at nano scale affect the optical, electrical and magnetic behaviour of nanomaterials. When the size of the nanoparticle becomes smaller than or comparable to the radius of the orbit of the electron hole pair (Bohr exciton radius) there are two situations, called the weak confinement and the strong confinement regimes. In the weak confinement regime, the particle radius is larger than the radius of the electron-hole pair, but the range of motion of the exciton is limited, which causes a blue shift in the absorption spectrum. When the radius of the particle is smaller than the orbital radius of electron-hole pair the motion of electron hole become independent and the exciton does not exist. The hole and electron have their own set of energy levels. Here also there is a blue shift. This confinement effect induces discrete electronic states in the valence and conduction band of the quantum dots compared to the continuous state of energy in the bulk material [1,2]. Among various classes of nanoparticles, II-VI class inorganic semiconductor nanomaterials like ZnS,CdS,ZnSe,ZnTe and CdSe are considered as important materials due to their applications in optoelectronic devices. ZnS is an important semiconductor material with a band gap of 3.68 eV and cubic zinc blende structure at room temperature. It has received considerable attention for its many technological applications in flat panel displays , phosphors, luminescent devices, cathode ray tube [3],LEDs [4], photovoltaic cell [5],sensors [6], solar cell [7], photocatalyst [8] etc. The Bohr exciton radius for ZnS is 2.5nm.

Addition of organic compounds to inorganic semiconductors will show different morphology, size confinement, and luminescent behaviour. In the present work, an attempt has been made to synthesize and characterize Thiourea and Sodium hexametaphosphopate(SHMP) capped ZnS nanoparticles by chemical co precipitation method in order to explore various interesting properties.

2. Experimental procedure

In the present study, ZnS quantum dots without and with capping agents were synthesized through chemical co-precipitation method as follows. All the chemicals were of AR grade and were used without further purification for the preparation of nanoparticles. The chemicals used were zinc acetate($Zn(CH_3COO)_2.6H_2O$), sodium sulphide ($Na_2S.XH_2O$) and capping agents Thiourea (CH_4N_2S) and Sodium hexa metaphosphopate($Na_6P_6O_{18}$)

ZnS WITHOUT CAPPING AGENT: 0.2M zinc acetate solution was prepared by dissolving 6.5847grams in 150ml (75ml of distilled water+75ml of methanol). 0.2M Na_2S solution was prepared by dissolving 3.1216 grams in 200ml (100ml distilled water+100ml methanol). To the solution of zinc acetate, sodium sulphide solution was added dropwise under continuous stirring using magnetic stirrer for 3-4 hours. The white precipitate was collected after centrifugation and washed 3 to 4 times using distilled water and ethanol to remove impurities.

ZnS WITH CAPPING AGENTS: 0.1M solution of Thiourea and 0.1M solution of SHMP were mixed separately with the 0.2M Zinc acetate solution in two different beakers for 30 minutes using magnetic stirrer. Then 0.2M Na_2S solution was added dropwise to each beaker under continuous stirring for 3 to 4 hours until the precipitates are formed. After centrifugation, precipitates were collected and washed 3 to 4 times using distilled water and ethanol to remove impurities.

The precipitates were dried using 60 watt bulb for 3 hours and crushed into fine power using mortar.

3. Instrumentation

The sizes of all the samples were determined using PXRD Panalytical X'PERT Pro MPD diffractometer with CuKα radiation (0.154nm). XRD data was collected over the range 20°-80° at room temperature. The particle size was calculated using Scherrer formula. Structural properties of samples were studied by SEM and TEM (Philips CM 200, Operating voltage 20-200 kV, Resolution-0.24nm) analysis. Optical properties of samples were studied using UV-VISIBLE Spectrometer from 200 nm to 600 nm and Photoluminescence properties were studied using WITEC α-300 Raman PL Setup from 250 nm to 800 nm.

4. Results and Discussion

4.1: XRD Studies

In the XRD pattern, there were three diffraction peaks corresponds to (111), (220) and (311) planes of the cubic ZnS. The peaks were broadened due to size effect, and this implies the formation of nanoparticles. The average crystalline size was calculated using Debye-Scherrer formula [9].

$$D=k\lambda/\beta\cos\theta \qquad \ldots.(1)$$

where K is geometrical factor=0.9, λ is wavelength of Cu-Kα radition=0.154nm, β is full width at half maximum(FWHM) in radians and θ is the diffraction angle. Particle sizes calculated using equation (1) for ZnS (uncapped) , Thiourea capped and SHMP capped particles were 3.6nm, 2.77nm and 1.82nm respectively.

Table 1: Band gap and size of ZnS (uncapped and capped) nanoparticles.

Sample	Absorption peak λ in nm	Band gap in eV from absorption spectrum	Band gap in eV from Brus eq	Crystal size in nm from UV	XRD	TEM
1.ZnS	206.5	6.015	4.530	2.17	3.606	3.678
2.(ZnS+ Thiourea)	205	6.060	5.101	2.148	2.77	2.670
3.(ZnS+ SHMP)	203	6.110	6.099	2.12	1.82	1.865

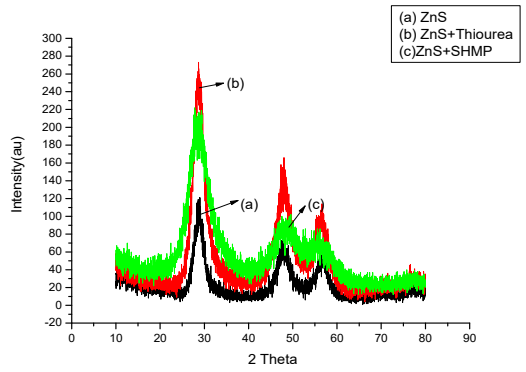


Fig 1.XRD Pattern of ZnS(uncapped and capped) nanoparticles.

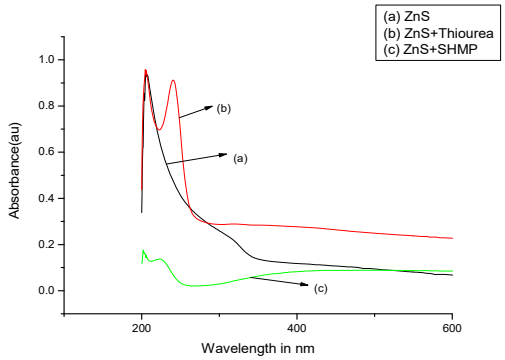


Fig2. UV-visible Absorption spectrum of ZnS(uncapped and capped)nanoparticles.

Three broad peaks in XRD pattern correspond to (1 1 1), (2 2 0) and (3 1 1) planes of the cubic zinc-blende phase of ZnS respectively.

4.2: Optical absorption studies

The absorption spectra of ZnS nanoparticles is shown in fig 2.The absorption peak is observed in the range 203 nm to 207 nm. The band gap was calculated using the formula.

$$E_g = h\vartheta = hc/\lambda \quad \ldots \quad (2)$$

where h, c, λ, E_g are the Plank's constant ,the speed of light in vacuum, the optical absorption wavelength and the band gap of nanoparticle respectively.

Brus has proposed a theoretical model relating to the effective band gap of material with the particle size. Using the average crystallite size obtained from X-ray diffraction spectrum, the band gap for each particle was calculated and the results are shown in Table 1. By applying the confinement effects, the optical size of nanocrystallites was calculated using Brus' equation [10].

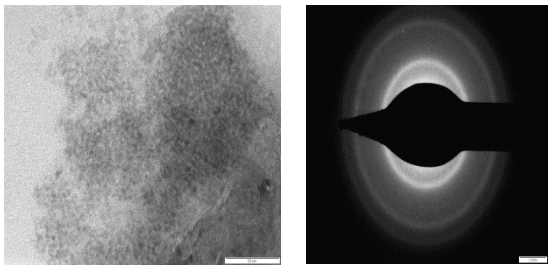
$$E_{g(nano)} = E_{g(bulk)} + h^2/8r^2(1/m_e + 1/m_h) - 1.8e^2/4\pi\varepsilon_o\varepsilon_r r \quad \ldots\ldots(3)$$

where $E_{g(bulk)}$ in ev is the band gap energy of bulk, m_e and m_h are electron and hole effective masses and r is the radius of particle in nm. ε_o is the permittivity of free space and ε_r is the permittivity of the sample, $m_e = 0.34m_o$ and $m_h = 0.23m_o$; m_o=free electron rest mass. The last term in equation (3) is the coulombic term and is generally neglected. By substituting the band gap

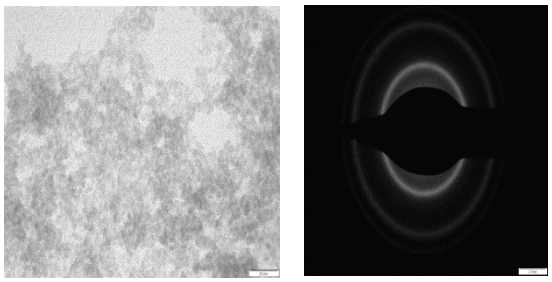
energy values of synthesized samples in equation (3), size of nanoparticleswere calculated and are reported in Table 1.

From these results, we can conclude that as the particles size is reduced, there is a clear blue shift of band gap for all the samples with respect to bulk ZnS; band gap of bulk ZnS with cubic structure Is 3.68 eV. This is due to the modification of valence band and conduction bands by quantum confinement effects [11]. Strong confinement is observed, when the particle size is smaller than the Bohr radius (approximately 2.5 nm); as a result of this strong confinement, absorption peaks which appear in the absorption spectra due to sub-band transitions, so that in this case band gap can be found from the maximum of this absorption peak. From the results, it is seen that band gap calculated from Brus equaion was less than the band gap calculated from absorption peak for each particle. This shows that the Brus equation is not quantitatively correct for very small particles. In absorption spectra of Thiourea and SHMP capped ZnS nanoparticles, two exciton peaks were observed indicating the formation of different morphology.

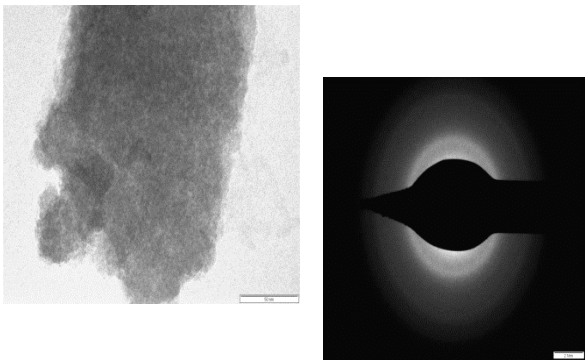
4.3: Transmission electron microscopic(TEM) studies



(a)



(b)

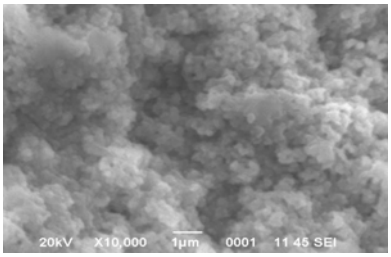


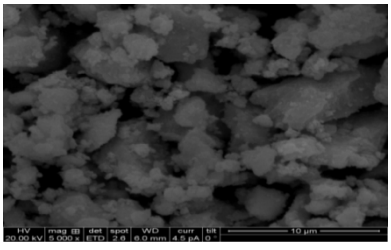
(c)

Fig 3: TEM and SAED Pattern of (a)ZnS(uncapped) (b) ZnS(Thiourea capped) and (c) ZnS(SHMP capped) nanoparticles.

The TEM and SAED images of ZnS (uncapped), Thiourea capped ZnS and SHMP capped ZnS nanoparticles are shown in fig 3a, 3b, and 3c respectively. The size and morphology of nanoparticles were determined by TEM images. From each image it is seen that particles are monodispersed, almost spherical in shape and the sizes calculated were well matched with XRD results. The selected area electron diffraction (SAED) patterns exhibit concentric circles, revealing that, ZnS samples are nanocrystalline being made up of small particles. The rings correspond to (111), (220), and (311) planes of the cubic zinc blende phase [12].

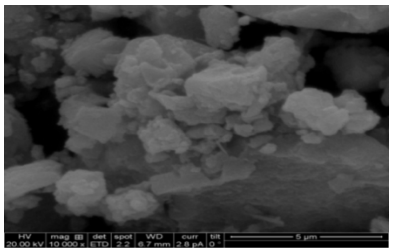
4.4 Scanning electron microscopic(SEM) studies





(a)

(b)



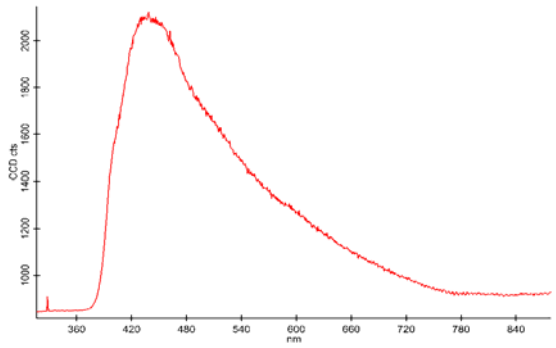
(c)

Fig 4: SEM images of (a) ZnS (uncapped) (b)ZnS(Thiourea capped) (c) ZnS (SHMP capped) nanoparticles.

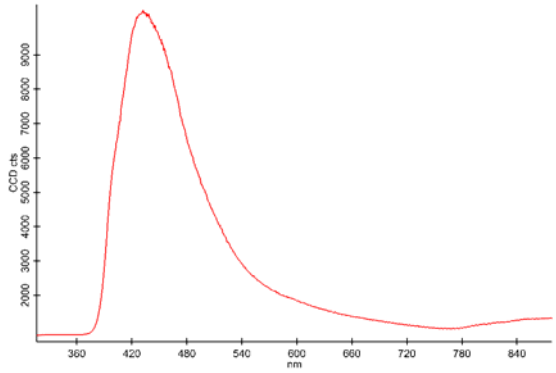
From the above SEM images of samples with different magnifications the formation of nanoclusters is clear [9,13].

4.5: Photoluminescence Studies

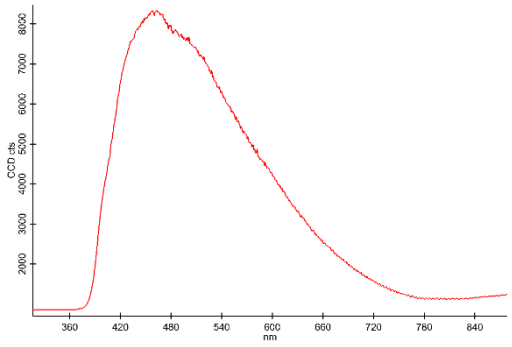
Room temperature photoluminescence spectra of ZnS (uncapped and capped) nanoparticles recorded using an excitation wavelength of 355 nm are shown in Fig 5a, 5b, 5c respectively. The uncapped ZnS nanoparticles showed broad emission peak at 439 nm originated from the host ZnS. This blue emission can be ascribed to a self activated centre presumably formed between a Zn vacancy and a shallow donor associated with a Sulphur vacancy [14]. Thiourea and SHMP capped particles showed the peaks at 433 nm and at 462 nm respectively. The emission intensity of capped ZnS nanoparticles are comparatively higher than the uncapped ZnS nanoparticles. This is expected because in the absence of capping agent, uncontrolled nucleation and growth of particles occurred, resulting in the formation of defect states. But in capped nanoparticles, enhanced luminescence was observed due to surface modification by capping agents with the effect of minimizing surface defects and also due to transfer of energy from chemisorbed capped molecules to interstitial sites and vacancy centres. The enhancement of luminescence intensity with decrease of particle size, was ascribed to quantum size effect. But in case of SHMP, capped ZnS nanoparticles the photoluminescence peak is red shifted as compared to that in uncapped ZnS nanoparticles, also the intensity is less than that of Thiourea capped ZnS nanoparticles. This shows that addition of SHMP quenches the photoluminescence properties of ZnS nanoparticles [9,12&15].



(a)



(b)



(c)

Fig 5: Photoluminescence spectra of (a) ZnS (uncapped) (b) ZnS(Thiourea capped) (c)ZnS(SHMP capped) nanoparticles.

5.Conclusion:

Uncapped and capped ZnS nanoparticles were successfully synthesized by co-precipitation method using Thiourea and SHMP as capping agents. The synthesized samples were studied by different characterisation techniques, XRD, SEM, TEM, UV-VISIBLE Absorption and Photoluminescence studies. XRD and SAED patterns confirm the cubic crystalline structure of ZnS. The morphology of the particles has been identified from the SEM and TEM analysis and revealed a spherical shape. As observed by XRD and TEM analysis, the size of particles is in the range 1.82 to 3.6nm.The UV-VISIBLE absorption spectrum peak for all the three samples exhibited blue shift from the bulk. Photoluminescence intensity was higher for capped particles compared to uncapped particles, PL peak for Thiourea capped ZnS nanoparticles was blue shifted, while for SHMP Capped ZnS nanoparticles PL peak was red shifted. This showed that SHMP act like a quenching agent for photoluminescence of ZnS nanoparticles.

Acknowledgement:

One of the authors Meenakshi H would like to express gratitude to spectroscopy department IISc Bangalore for providing XRD,UV-visible, SEM, and PL studies, also to IIT BOMBAY for providing TEM facility.

References:

1. Charles P.Poole,Jr.,Frank J.Owens,Introduction to nanotechnology,Wiley india (New Delhi), 2012, P 196,197.

2.Marusamy A, Agilan S, Muthukumarasamy, C. Senthilkmaran K, Saravanakumar M, *Chalcogenide letters*, Vol 10(may2013).

3.Sakshi Sahare. Meera Ramrakhiani, *International journal luminescence and its applications*, Vol 4(II)(2014).

4.Khalid T. Al-Rasoul, Nada K. Abbas, Zainb J. Shanan,*International Journal of electrochemical science*(2013).

5.Hadibah Ramli, Sharul Kamal Abdul Rahim, Tharek Abd Rahim, Muhammed Muhaimin Aminud, *Chalcogenide letters* (June 2013).

6.Kuldeep V, Joshi, Bhoomica K, Uma H.K, Manish Kumar B, Patel and Shobhana, *Royal society of chemistry*(2013).

7. Haque F, Rahman K S, Iscam M A,Rashi M J,. Alam M M, lothman Z A, Sopian Amin N,*Chalcogenide letters*(April 2014).

8.Khalid T. Al-Rasoul, Issam M. Ibrahim, Iftirkhar M Ali, Raad M.Al-Haddad, *IJSTR*,(May 2014).

9.Muralikrishna D, Vijayalakshmi R P,Venugopal R,Reddy B K, *Chlcogenide letters*, Vol 7 (may 2010) P 357-365.

10.Ephrem.O. Chukwuocha.Michaei.c. Onyeaju.Taylor.S.T. Harry, *World Journal of condensed matter physics* (2012).

11.Radhar, J*ournal of nanostructure in chemistry* (2013).

12.Mohan R,Sankarrajan S, and Santham P, *IJRSR* Vol.4.issue 4 (April 2013),P 405-409

13.Ashish Tiwari, Khan S A, and Khe R R S, . *Advances in Applied Science Research*,2(1):105-11017 (2011).

14.Buihongvan,Phamvanben,Hoangvannhat, *Communications in Physics* vol.22 No,2(2012).

15.Pawar M J,, Nimkar S D, Nandurka P R,Tale A S,Deshmukh S B,Chaure S S, *Chalcogenide letters*, Vol.7 No2 (Feb 2010),P 139-143.