

## Structural and Photoluminescent study of Glutathione ZnS:Ce Nanoparticles

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### Abstract

Using microwave method synthesis of uncapped and GSH capped ZnS doped with trivalent Ce ions. The effect of GSH as a capping agent on the structural and optical activity was studied at different concentrations. The presence of GSH on the ZnS:Ce surface was identified by spectroscopic techniques like FTIR. Increase in the concentration of GSH helped us for the synthesis of small sized ZnS:Ce nanoparticles. Information regarding structure and particle size was collected from XRD patterns the nanoparticles showed ZnS cubic structure with size between 3.5-3.0 nm. The cubical nature of these nanoparticles was further confirmed by lattice fringes and SAED patterns with bright circular rings. Effect of capping agent was studied by TEM images, where the size was found to be 8 nm for uncapped and 4 nm for capped nanoparticles with spherical nature. EDAX measurement showed the incorporation of Ce ions in the -doped ZnS nanoparticles and quantum confinement was observed from absorption spectra through blue-shift with reduction in the size of these nanoparticles. Photoluminescence studies for the entire investigated samples displayed two emission bands one in UV (360 nm) and the other at visible region (600 nm). The result showed enhanced luminescence property was observed in the case of capped nanoparticles compare to uncapped.

**Keywords:** ZnS nanoparticles, Glutathione, Photoluminescence

## Introduction

Semiconductor nanoparticles are one of the most challenging classes of new materials constituting an active field of research. Owing to quantum size effects and surface effects, nanoparticles can display novel optical, electronic, magnetic, chemical, and structural properties that might find many important technological applications in the fields of catalysis, and biological labels, due to their unique properties [1]. In contrast to II-IV semiconductor materials zinc both in their O and S forms are safer in terms of toxicity i.e. its nontoxic and biocompatible, which makes them potential agent in biological field [2]. Doped form of ZnO nanoparticles with transition and inner transition metals have been investigated in the biological field which proved to be an efficient antimicrobial agent [3]. A few reports have been presented with respect to ZnS doped with d and f block element towards biological field [4,5]. The luminescent properties of ZnS can be tuned by doping with various transition metals ( $Mn^{2+}$ ,  $Cu^{2+}$ , etc.) and rare-earth metals ( $Ce^{3+}$ ,  $Er^{3+}$ ,  $Tb^{3+}$ , etc.) [6–8]. Among the rare earth metal ions,  $Ce^{3+}$  is one of the most interesting dopant, it possesses a unique optical characteristics. Furthermore, doping of cerium reduces the particle size of nanomaterials and also increases the surface area [9,10]. The current study reports on a facile strategy to tailor glutathione capping agents to improve the solubility, stability, and biocompatibility of cerium doped nanoparticles. Glutathione (GSH;  $\gamma$ -Glu-Cys-Gly) is a very special tripeptide having two  $-COOH$  groups, one  $-NH_2$  group, and one  $-SH$  group. Because noble metals have a high affinity for S, the GSH molecule can be an effective capping ligand for their synthesis. These surface passivated rare earth bimolecular (GSH) capped

inorganic group of nanoparticles with suitable surfactant, avoid the agglomeration and also improve the optical properties of the nanoparticles.

The Surface modified doped material recently [11] studied the optical and physical properties of Cu doped ZnS nanoparticles capped with mercaptopropionic acid (MPA) where they reported that capped nanoparticles proved to show improved physical properties. As per literature survey improved antimicrobial activity of Cu doped ZnS nanoparticles capped with different capping agents such as mercaptosuccinic acid (MSA) and sodium citrate (SC) was reported [12]. In Previous our reserch group reported the surface passivated Biotin capped Gd: ZnS nanoparticles which showed high activity against *K. Pneumonia* at the conc. of 10 µg/ml and also enhance the luminescence property [13]. The less no of article reported the synthesis of different concentration of Ce doped ZnS nanoparticles and surface modified nanoparticles [14]. Recently reported the synthesis of water-soluble Pd nanoparticles capped with glutathione was the bimolecular capping agent and enhancement of structural property [15].The importance of these synthesized biomolecule (GSH) semiconductors has gathered our attention for the surface modification of Ce doped ZnS nanoparticles. In this article rare earth doped Semiconductors nanoparticles synthesized by microwave method, using glutathione as bimolecular capping agent. The effect of biomolecule (GSH ) on the optical and structural property was studied and also their biological property was investigated.

## **Experimental section**

### ***Materials used***

All the chemical reagents were of analytical grade and were used without further purification. Materials to synthesize GSH capped Ce doped ZnS nanoparticles, we have used the

following materials, zinc acetate dehydrate ( $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ), Cerium(III) chloride hepta hydrate [ $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ ], Sodium sulfide ( $9\text{H}_2\text{O}$ ) and GSH were used directly as received from sigma Aldrich. Acid washed glassware's were used in this experimental work, Deionized water was used throughout the process as reaction medium in all the synthesis steps for dilution and sample preparation.

### **Nanoparticles synthesis**

Microwave irradiation technique was employed for the synthesis GSH capped Cerium-doped zinc sulfide ( $\text{ZnS}:\text{Ce}$ ) nanoparticles. Synthesis is the important step in the studies of powder nanoparticles in a typical procedure. Fabrication Starts with various concentrations (0.025 M), (0.05 M) (0.075 M) and (0.1M) of GSH capping agent stirring for 15 min dissolved in 10 ml of deionized water taken in RB flask. Freshly, prepared aqueous solution of 0.1 M of Zinc acetate ( $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ) added to the 50 ml (water + methanol) was sonicated for 5 min and added to above RB flask containing GSH solution and 10 ml of 0.05 M aqueous solution of Cerium(III) chloride added to the above solution and stirred at room temperature for 15min. The solutions were then sonicated for 10 min. A high-intensity ultrasonic bath (Branson 3510) is used for ultrasonic irradiation. Under continuous stirring 0.1 M of 50 ml  $\text{Na}_2\text{S}$  solution was slowly dropped into the above solution. Afterward, micro oven fitted with condenser and irradiated at 720 Watt for 20 min. which results in formation of white precipitate. The finally product was separate from round bottom flask. The formed precipitates were centrifuged (4000 rpm, 10 min) and the residue was washed several times with distilled water and absolute ethanol. Finally, the powder is dried at  $60^\circ\text{C}$  under vacuum for two hour for characterization process.

The uncapped ZnS:Ce nanoparticles was also fabricated with the help of same above procedure in the absence of capping agent.

### ***Characterization***

Microwave synthesized powder sample was characterized by X-ray diffraction(XRD), patterns of the powdered samples were recorded using an X'pert PRO diffractometer with Cu– Ka radiation ( $\lambda = 1.54063 \text{ \AA}$ ). The crystallite size was estimated using the Scherrer equation. The optical transmission/absorption spectra of the samples were recorded in deionized water, using a UV-1650PC Shimadzu spectrometer in the range of 210- 801 nm at room temperature. Transmission electron microscopy (TEM), high resolution transmission electron microscope (HRTEM) and selected area electron diffraction (SAED) images for uncapped and capped Ce doped ZnS nanoparticles were recorded on Philips TECNAI F20 microscope. Fluorescence measurements were performed on a RF-5301PC Spectrophotometer. Emission (350-700 nm) spectra were recorded under 292 nm at room temperature. Fourier transform infrared spectroscopy (FTIR, Shimadzu 8400 S Model) of the powder samples were recorded in the range of  $4000\text{-}501 \text{ cm}^{-1}$  at room temperature in KBr pellets. The frequency of microwave was 9.89 GHz, and a 100 kHz field modulation was used.

## **Result and discussion**

### ***XRD analysis***

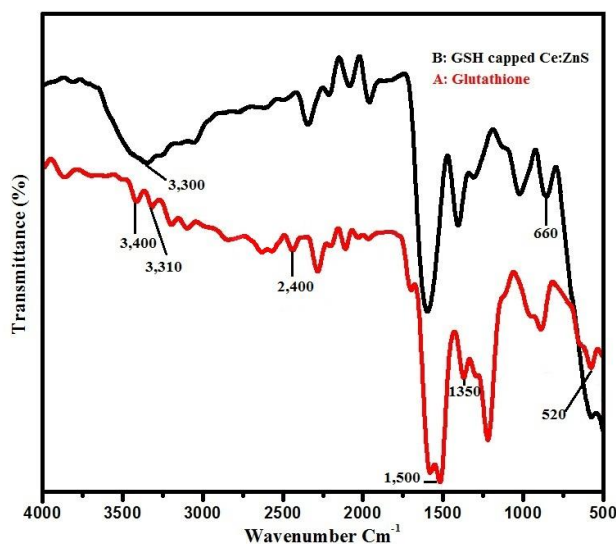
Wide angle X-ray diffraction spectra of GSH capped Ce doped ZnS nanoparticles synthesized at different concentration were shown in Fig. 1 in the range of  $20$  to  $60^\circ$ . X-ray diffraction is used to investigate the phase and crystallite size of the GSH capped Ce doped ZnS

nanoparticles. Fig. 1 shows the wide-angle X-ray diffraction (XRD) pattern of bare ZnS: Ce nanoparticles (A), (B) (0.025), (C) (0.05), (D) (0.075) and GSH capped ZnS: Ce nanoparticles (0.1M) (E). All samples showed reflections from (111), (220) and (311) plane confirming the Cubic (zinc-blend) phase. The broadening of the diffraction peaks indicates the nanocrystalline nature of the sample. The broadening of the diffraction peaks indicates the very fine size of the grains of the sample. This broadness is increased for the capped particles due to decrease of the particles size. Here confirming the high purity of the synthesized product. No extra peaks observed in the spectra, indicating the single phased nature of the samples. It indicated that surface capping agent were not disturbed ZnS lattice. Fig. 1 shows a perfect match with (JCPDS Card No. 36-1450) the cubic zinc blende phase of the GSH capped ZnS:Ce nanoparticles and no reflections and other impurities were identified in the pattern, indicating the high purity of the final product. The broadening of diffraction peaks confirmed that the crystallites were nano sized. The crystallite size of the nanoparticles can be estimated by Debye-Scherrer's equation, [13] and was found to be about 5.6 nm in the case of the bare ZnS:Ce nanoparticles and 3.8-3.1 nm for capped ZnS:Ce nanoparticles with different concentration of GSH (0.025 M, 0.05 M, 0.075 & 0.1M). These results were in good agreement with the observed TEM results. The XRD peaks of the capped nanoparticles systems were broadened as compared to bare ZnS:Ce nanoparticles, which clearly supports the formation of the capped ZnS:Ce nanostructures.

### ***FT-IR study***

FTIR spectral measurements have been made in the scan range of 4000- 510  $\text{cm}^{-1}$ . FTIR spectra of the pure GSH (A) and prepared (B) GSH capped Ce doped ZnS nanoparticles were shown in Fig 1. FTIR peaks were assigned to samples at room temperature. This technique

provides the principle to identify the possibility of capping on the surface of ZnS:Ce nanoparticles. The spectra related to pure GSH, showed absorption peaks around  $3310\text{ cm}^{-1}$  &  $3400\text{ cm}^{-1}$  which was assigned to  $-\text{NH}$  and  $-\text{OH}$  stretching vibrations respectively. A small sharp band at  $1502$ ,  $1355\text{ cm}^{-1}$  was due to C-H stretching. However, the S-H vibration observed at  $2420\text{ cm}^{-1}$  of the free GSH ligand [15]. In the ZnS:Ce nanoparticles are capped with GSH confirms the FTIR spectra, the broad peak at  $3310\text{ cm}^{-1}$  was appeared for  $-\text{NH}$  and  $-\text{OH}$  stretching vibrations. The peak at  $2512\text{ cm}^{-1}$  was not clearly observed because of the SH group was bond on the surface of the ZnS:Ce nanoparticles. This is a clear indication that the GSH was deprotonated and coordinated to the surface of the ZnS:Ce nanoparticle through the sulphur. The S-S stretch vibration appearing in  $528\text{ cm}^{-1}$  range confirms breakage of S-H bond and formation of S-S bond on surface on GSH capped Ce:ZnS nanoparticles. A spectral band appearing at around  $660\text{ cm}^{-1}$  can be ascribed to ZnS vibration [16].

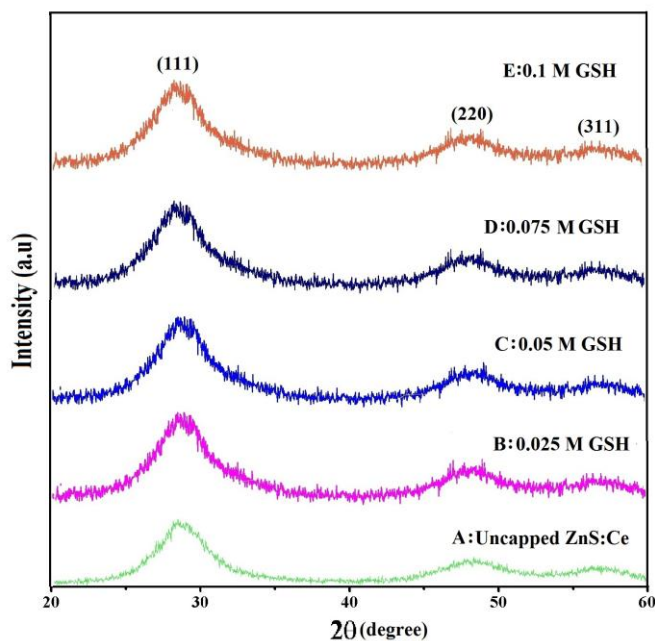


**Fig-1:** FTIR spectra; A: Glutathione and B: GSH capped Ce doped ZnS nanoparticles

**Fig-1: EDAX Spectra of Ce doped ZnS nanoparticles*****Optical studies***

Optical absorption spectra of bare and different concentration of GSH capped ZnS:Ce nanoparticles have been analyzed in deionized water and the spectra were shown in Fig 2. UV-Visible spectra are very much helpful in identifying the band gap and particle size of the semiconductor nanomaterials. Shows the room temperature optical absorption spectra of the different concentration of GSH (0.025 M, 0.05 M, 0.075M & 0.1M) capped ZnS:Ce nanoparticles analyzed in the region 200-700 nm. The absorption characteristics were measured in a quartz cuvette by dispersing these nanoparticles in ethanol. The absorption peaks were observed range of wavelength around 322 nm for bare ZnS:Ce nanoparticles and 310, 303, 298 and 290 nm for the samples prepared with different concentration of GSH (0.025 M, 0.05 M, 0.075 & 0.1M) capped ZnS:Ce nanoparticles. This peak are attributed to the electron-hole pairs caused by the quantum confinement, that is, an exciton energy level. These absorption peaks were at shorter wavelength (blue shifted) compared to bulk ZnS (345 nm), suggesting the nanometer-sized formation of ZnS:Ce. The band gap energy of the nanoparticles were calculated from a simple energy wave equation  $E=hc/\lambda$ . The band gap energy for bare ZnS:Ce was 3.85 eV and 4.00 eV(0.025 M), 4.09 eV(0.05 M), 4.16 eV( 0.075 M) and 4.27 eV(0.1 M) capped nanoparticles as shown in the Fig. 2. All the samples showed band gap value larger than that of bulk ZnS, 3.68 eV [18].





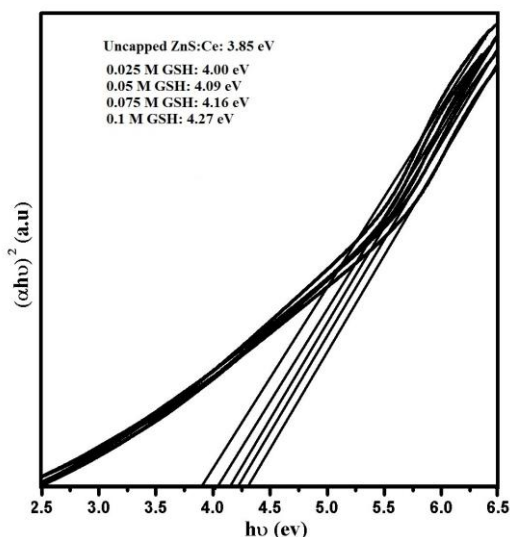
**Fig-2:** Calculation of Optical band gap from the UV- visible absorption spectra

Approximate sizes for these nanoparticles have been calculated using the Brus equation [19]. The particle sizes were determined as 3.68 nm for (0.025M), 3.38 nm for (0.05 M), 3.19 nm for (0.075 M), 2.95 nm for (0.1M) and bare ZnS:Ce nanoparticles 4.91 nm respectively. These values were comparable to those obtained from XRD studies, as shown in Table 1. The particle size for bare ZnS:Ce nanoparticles and different concentration of GSH capped Ce doped ZnS nanoparticles based on the peaks position from the optical absorbance spectra. The increase in the optical band gap and decrease in particle size using different concentration of GSH capping agent. Optical band gap from the UV- visible absorption spectra at different concentration GSH capped and bare Ce doped ZnS nanoparticles have been calculated from the absorption spectra by using the relation  $\alpha(h\nu)^2 = C(h\nu - E_g)$ . To measure the optical energy band gap a graph of

$(ah\nu)^2$  versus the  $(h\nu)$  have been plotted, where,  $a$  is the absorption coefficient [20,22]. The extrapolation of the tangent line to  $(ah\nu)^2 = 0$  axis gives the value of the optical energy band gap.

**Table-1:** Comparison of uncapped and capped Ce doped ZnS nanoparticles of the particle size from XRD, Optical band gap.

GSH concentration	Crystalline size (nm) from XRD pattern	Wavelength (nm)	Particle size (nm) from Optical analysis	Optical band gap (eV)
Uncapped ZnS:Ce	5.6 nm	322	4.91 nm	3.85
ZnS:Ce/ GSH 0.025 M	3.8 nm	310	3.68 nm	4.00
ZnS:Ce/ GSH 0.05 M	3.6 nm	303	3.38 nm	4.09
ZnS:Cu/ GSH 0.075 M	3.3 nm	298	3.11 nm	4.16
ZnS:Cu/ GSH 0.1 M	3.1 nm	290	2.95 nm	4.27

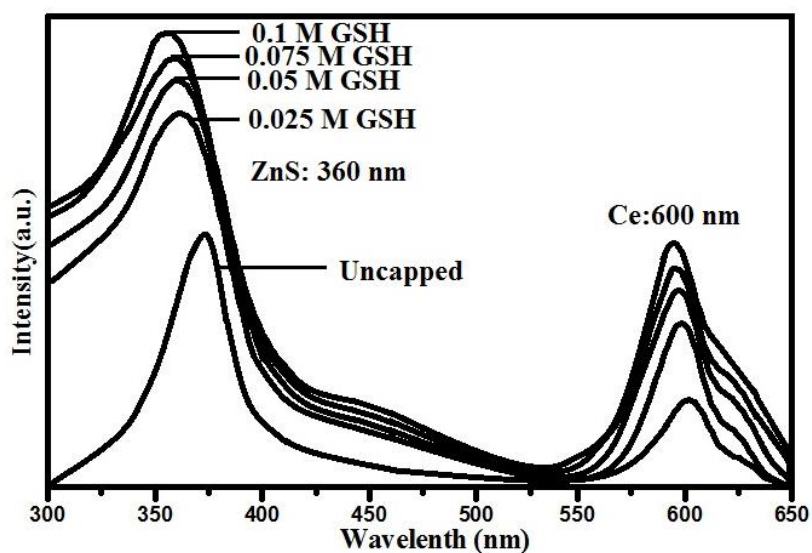


**Fig-3:** Optical energy band gap

### *Photoluminescence study*

The PL spectra of the uncapped and (GSH)-capped ZnS:Ce nanoparticles were shown in Fig.4 recorded at room temperature upon excitation wavelength at 290 nm. PL spectra showed emission peaks in the range of 300-600 nm. The PL spectra of uncapped and various levels of GSH capped samples, two different emission bands are dominant in the PL spectra. In our results characteristic UV band-edge and visible band emissions were observed for the uncapped and capped samples of Ce doped ZnS nanoparticles. The ZnS nanoparticles exhibit a broad blue emission could be due to the recombination of electrons at sulfur vacancy donor level with holes at the zinc vacancy acceptor level [23]. We consider that blue emission of ZnS has been completely quenched and two spectral features, one at UV region (360 nm) and other at visible region (600 nm) are generated due to the 5d-4f transition in  $Ce^{3+}$  ions [24, 25]. The quenching of the ZnS emission and enhancement of the Ce emission demonstrate that ZnS nanoparticles absorbed energy from the excitation source and transferred it nonradiatively to luminescent

centers ( $\text{Ce}^{3+}$  ions). Observed similar type of UV and visible bands for ZnS:Ce. Occasionally, on transition metal ion doping ZnS may exhibit emission bands in the UV and visible regions. Such optical emission was obtained by Murugadoss *et al.*, on surfactant assisted  $\text{Mn}^{2+}$  doped ZnS nanocrystals [26]. As observed from PL spectra in regards of intensity the uncapped nanoparticles are showing weak intensity in comparison to the capped nanoparticles. This concludes the influence of GSH biomolecule is the surface of the nanocrystals i.e. surface improvement. The emission peaks correlated to ZnS:Ce nanoparticles were blue shifted in comparison to uncapped nanoparticles, which point towards the decrease in the particle size with the increase in the GSH capping concentration. Which was also been examined by the characterization techniques of XRD and TEM.



**Fig-4:** PL spectra of the uncapped and (GSH)-capped ZnS:Ce nanoparticles

## Conclusion

This article shows that uncapped and GSH capped Ce doped ZnS nanoparticles synthesized by using microwave method. The effect of capping agent on the structural and

optical properties ZnS:Ce nanoparticles were performed. XRD pattern exhibited the cubic zinc blende structure and particle sizes were in the range of 5.6 nm for uncapped and GSH capped ZnS:Ce is found to be in the range of 3.8 to 3.1 nm. The Particle size of the ZnS:Ce nanoparticles decreased with the increase in the GSH concentration. TEM images indicated that the growth particles were spherical in shape. Band gap was found to increase with capping in comparison to uncapped nanoparticles which is due to quantum confinement effect. Photoluminescence studies for the entire investigated samples displayed two emission bands one at UV region (360 nm) and the other at visible region (600 nm). These emission bands with respect to GSH concentration were blue shifted with enhancement in the intensity with respect to uncapped nanoparticles. PL intensity of capped sample is higher in comparison to uncapped samples, which has been explained on the basis of better passivation in capped nanoparticles as compared to uncapped ones.

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