Synthesis and Characterization of water soluble ZnS: Ce, Cu co-doped Nanoparticles: Effect of EDTA Concentration

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Abstract: *Ce, Cu co-doped ZnS nanoparticles were synthesized through a facile chemical precipitation method using Ethylenediaminetetraacetic acid (EDTA) as the capping agent. The prepared nanoparticles were characterized by X- ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X – ray spectroscopy (EDAX), diffuse Reflectance spectroscopy (DRS), photoluminescence (PL) and raman spectroscopic techniques. The synthesized nanoparticles have a Zinc blende structure with average sizes of about 2-3 nm as determined by X-ray diffraction. It is observed that the particle size decreases with increasing capping agent concentration. SEM and TEM analysis showed the surface morphology of the prepared samples. EDAX analysis confirms the presence of corresponding elemental peaks. DRS studies show that the effective band gap energy increases with increasing capping agent concentration. It was evident from photoluminescence studies that the emission becomes more intensive as the size of the particles is reduced with increasing capping agent concentration. Raman studies revealed the absence of impurities and effective doping of EDTA capped ZnS nanoparticles co-doped with Ce and Cu.*

Keywords: Capping agent, Photoluminescence, XRD, SEM, Raman studies

1. Introduction

Semiconductor nanoparticles possess novel optical and electronic properties, which are potentially useful for technological applications, compared to the corresponding bulk materials. Luminescence of rare-earth doped systems mainly reflects the properties of the dopant. ZnS nanoparticles doped with transition metal ions and rare earth ions have different optical properties compared with conventional bulk materials. In recent years, II-VI semiconductor nanoparticles such as ZnS finds potential applications in optics, photoelectronics, Spintronics, sensors, catalysts, bio labels, lasers etc., because of their high luminescence quantum efficiency, purity and high chemical stability [1-6]. ZnS nanocrystals doped with rare-earth ions and transition metal ions are used extensively as photoluminescence (PL) and electroluminescence (EL) devices. For nanoparticles prepared by solution-based chemical methods, a capping agent, which adsorbs to the nanoparticle surface, is generally added both to control the size of the nanoparticles and to prevent agglomeration of the synthesized particles [7]. Among the different kinds of stabilizers used for the preparation of doped ZnS nanoparticles, the water soluble polymer such as EDTA has significant importance. The energy transfer efficiency has been found to increase with the concentration of EDTA or dopants. This study brings out a new sensitizer (energy donor) activator (energy acceptor) type relation between the polymeric capping agent and luminescent semiconducting nanoparticles [8]. Various researchers have reported wide variety techniques, including chemical precipitation method [8], solvothermal process [9], UV irradiation [10], sol–gel method [11], and colloidal microemulsion[12] for the preparation of semiconductor nanoparticles.

In this present study, we reported a simple soft chemical method namely chemical co-precipitation technique for the synthesis of uncapped and EDTA - encapsulated ZnS: Ce, Cu nanoparticles. This method was adopted, because it is a low cost and the dopent concentration can be easily attained. Structural, compositional, morphological, optical and luminescence studies of the prepared samples were carried out by X- ray diffraction (XRD), Energy dispersive X – ray spectroscopy (EDS), scanning electron microscopy (SEM), Diffuse Reflectance spectroscopy (DRS), Fourier transform infrared (FTIR), Photoluminescence (PL) and Raman spectroscopic techniques.

2. Experimental Details

All chemicals were of analytical reagent grade and were used without further purification. Cerium (2 at.%) and copper (4 at.%) co-doped ZnS nanoparticles were prepared by a simple, cost effective facile chemical co-precipitation method with Ethylenediaminetetraacetic acid (EDTA) as capping agent. The reactants were Zn $(CH_3COO)_2{\bullet}2H_2O$, $CeCl_3{\bullet}7H_2O$ (2 at.%), Cu $(CH_3COO)_2{\bullet}H_2O$ (4 at.%), Na_2S and EDTA. Ultrapure de-ionized water was used as the reaction medium in all the synthesis steps. In a typical synthesis, desired molar proportions of Zn $(CH_3COO)_2{\bullet}2H_2O$, $CeCl_3{\bullet}7H_2O$ (2 at.%) and $Cu(CH_3COO)_2{\bullet}H_2O$ (4 at.%) each in 50 ml were dissolved in ultrapure de-ionized water. Appropriate amount of stabilizer EDTA (0, 2, 4 at.%) was added to control the growth of the nanoparticles during the reaction. Later stirring the solution for 60 min, Na_2S solution was drop wisely added to the solution at room temperature under constant stirring. Stirring was continued for four hours to get fine precipitation. The obtained precipitate was washed with de-ionized water for several times. Finally, the powders were vacuum dried for 3 hours at 80^{o}C to get Ce, Cu co-doped ZnS nanoparticles.

The as synthesized nanopowders were characterized by studying the structure, composition, surface morphology and optical properties. The X-ray diffraction patterns of the samples were collected on a Rigaku D X-ray diffractometer with the Cu-Kα radiation (λ=1.5406 °A). Morphology and elemental composition of the prepared samples were analyzed through EDAX using Oxford Inca Penta FeTX3 EDS instrument attached to Carl Zeiss EVO MA 15 Scanning Electron Microscope. Raman Spectroscopic studies of the as prepared samples were carried out using LabRam HR800 Raman Spectrometer. DRS studies were carried out using Carey-5E UV–VIS–NIR lambda-950 spectrometer. Photoluminescence spectra were recorded in the wavelength range of 400–650 nm using PTI (Photon Technology International) Fluorimeter with a Xe-arc lamp of power 60 W and an excitation wavelength of 320 nm was used. The Fourier transform infrared (FTIR) spectroscopic measurements were recorded on Perkin Elmer spectrometer (spectra GX) in the range 4000–450 cm^{-1}.

3. Results and Discussion

3.1 Structural Analysis

Figure 1 represents the XRD patterns of uncapped ZnS: Ce, Cu nanoparticles and EDTA (2 and 4 at.%) capped ZnS: Ce, Cu nanoparticles. All the samples are well-crystallized, and the diffraction peaks can be indexed to cubic (fcc) ZnS (JCPDS card no. 80-0020).

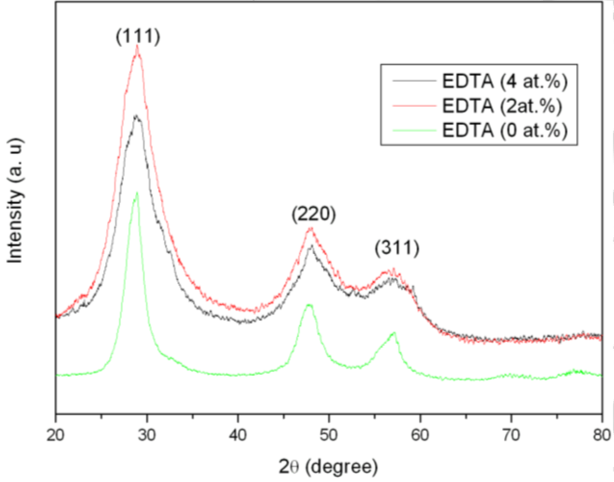


Figure 1: uncapped and EDTA (2 and 4 at.%) capped ZnS: Ce, Cu nanoparticles

It has been observed from Figure 1 that there are three most preferred orientations namely (1 1 1), (2 2 0) and (3 1 1). The broad peaks in the XRD spectra are due to their nanocrystalline nature of the samples. From the XRD spectra it is also observed that no diffraction peaks corresponding to impurity phases are detected. The average particle size calculated by Debye Scherrer's equation [a] for Ce, Cu co-doped ZnS nanoparticles lies in the range of 2-3 nm as in table(1).

$$D = \frac{0.94\lambda}{\beta_{hkl}\cos\theta} \qquad \text{(a)}$$

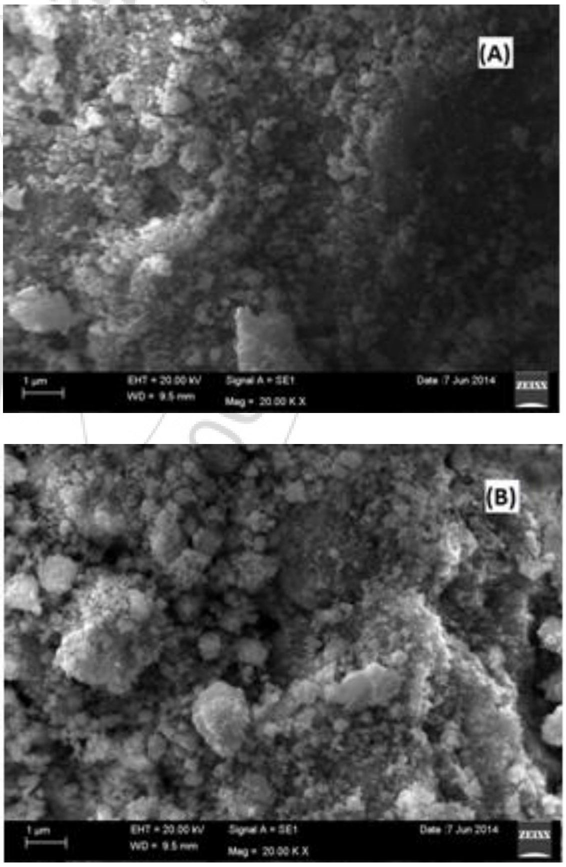
Where, D is the average particle size and β_{hkl} is full width at half maximum of XRD peak expressed in radians and θ is the position of the diffraction peak. The average particle size of the samples was calculated by Debye Scherrer's equation (a) and tabulated as shown in Table1.

Table 1: Average Particle size of EDTA capped Ce, Cu co-doped ZnS nanoparticles.

S.No	*Capping agent concentration (at.%)*	*Particle size(nm)*
1	Uncapped ZnS: Ce, Cu	6.84
2	EDTA (2 at.%)	5.14
3	EDTA (4 at.%)	6.42

3.2 Morphological and Compositional Analysis

Figure 2 shows the morphology of Ce, Cu co-doped ZnS nanoparticles capped with EDTA. Figures 2(A), 2(B) and 2(C) show the SEM images of uncapped ZnS: Ce, Cu nanoparticles and EDTA (2 and 4 at.%) capped ZnS: Ce, Cu nanoparticles respectively. From SEM images it is clearly observed that the particle agglomeration is decreased with EDTA (2 at.%) capping and the particles are homogeneously distributed as in Figures 2(a), 2(b) and 2(c).



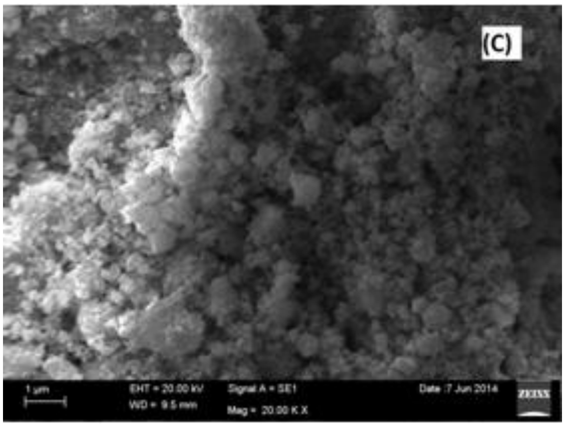


Figure 2.SEM image of uncapped and EDTA (2 and 4 at.%) capped ZnS: Ce, Cu nanoparticles.

The particles observed from the SEM images are nearly spherical in shape and this is further confirmed by the TEM image of EDTA (2 at .%) capped ZnS: Ce, Cu nanoparticles shown in Figure 3. From the TEM micrograph, it is evident that the morphology of the sample seems to be nearly spherical in nature and the estimated particle size is of the order of 5-6 nm and is in good agreement with that of XRD result.

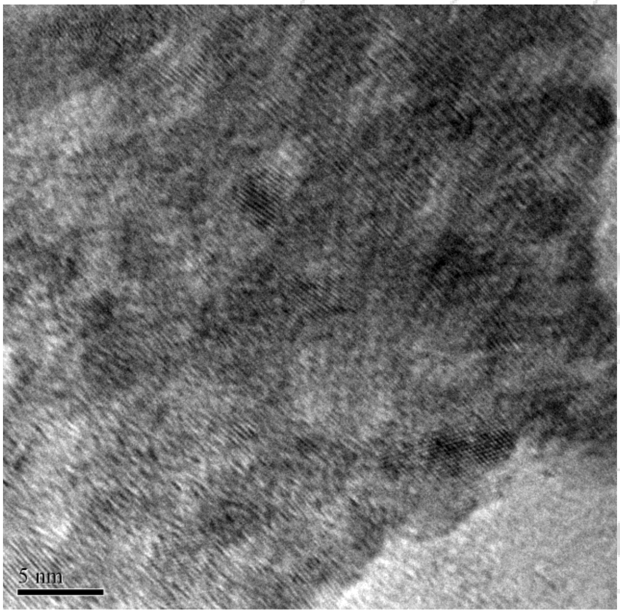


Figure 3:TEM image of EDTA (2 at %) capped ZnS: Ce, Cu nanoparticles.

The chemical composition analysis of the Ce, Cu co-doped ZnS nanoparticles is done by EDAX technique. Figures 4 shows the EDAX spectra of EDTA (2 at.%) capped ZnS: Ce**,** Cu nanoparticles.

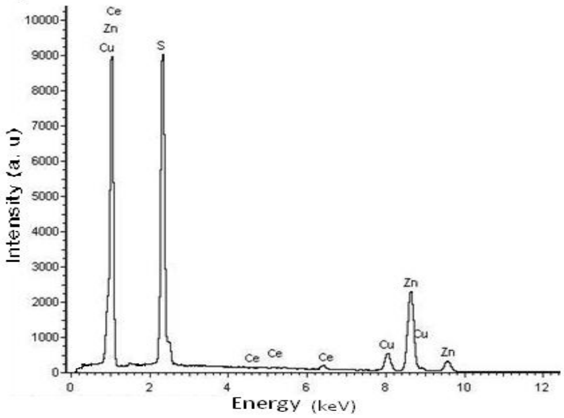


Figure 4: Representative EDS spectrum of EDTA (2 at.%) capped Ce, Cu co-doped ZnS nanoparticles

The EDAX spectra of ZnS: Ce, Cu nanoparticles shown in Figure 4 confirmed that the samples are composed of Zn, Ce, Cu and S elements without any impurities.

3.3 DRS Studies

Figure 5 shows the Diffuse Reflectance Spectrum of uncapped and EDTA (2 and 4 at.%) capped ZnS: Ce, Cu nanoparticles.. All spectra were recorded at room temperature in the wavelength range of 200–800 nm . It is observed that the spectra of the samples shifted towards higher energy (blue shift) as the capping agent concentration increased.

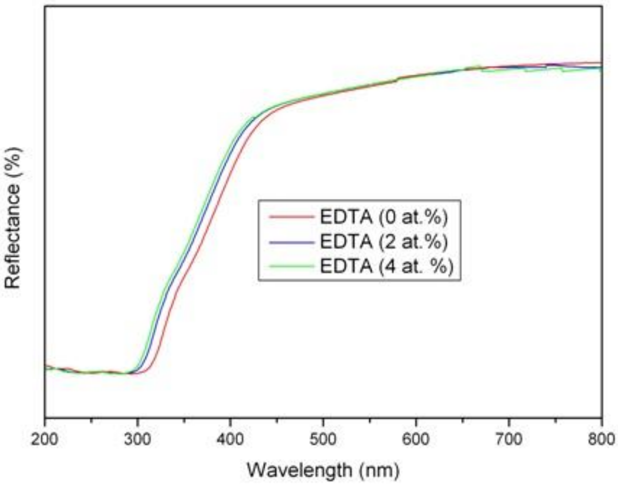


Figure 5: Diffuse reflectance spectra of uncapped (EDTA (0 at %) and EDTA capped (2, 4 at.%) ZnS: Ce, Cu nanoparticles

For analysis purposes the diffuse-reflectance (R) of the sample can be related to the Kubelka–Munk function F(R) by the relation $F(R) = (1-R)^2/2R$ [13]. The band gap of the present samples was estimated from the diffuse-reflectance spectra by plotting the square of the Kubelka–Munk function $F(R)^2$ versus energy and extrapolating the linear part of the curve to $F(R)^2 = 0$, as shown in Figure 6.

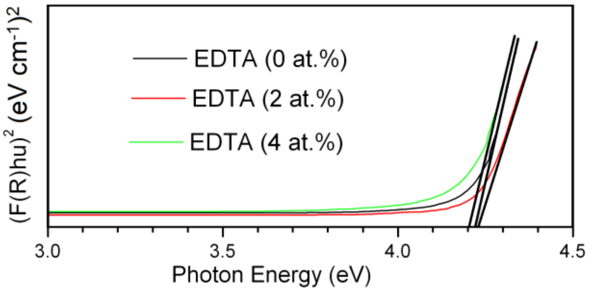


Figure 6: Kubelka–Munk plots and band gap energy estimation for the uncapped and EDTA (2, 4 at. %) capped ZnS: Ce, Cu nanoparticles

The band gap values estimated from DRS spectra are given in Table 2. The band-gap of the samples increases with increase in the EDTA (2 at.%) concentration and decreases at 4 at.% of EDTA as in Figure 6.

Table 2: Optical band gap values for uncapped and EDTA (2, 4 at. %) capped ZnS: Ce, Cu nanoparticles

S.No	EDTA concentration (at.%)	Band gap (eV)
1	Uncapped ZnS: Ce, Cu	4.20
2	EDTA (2 at.%)	4.21
3	EDTA (4 at.%)	4.18

3.4 Photoluminescence Studies

Figure 7 shows the PL spectrum of uncapped and EDTA (2, 4 at. %) capped ZnS: Ce, Cu nanoparticles. The PL spectra was recorded at room temperature with an excitation wavelength of 320 nm.. From the PL spectra of ZnS nanoparticles co-doped with $Ce^{3+}$and Cu^{2+} ions, the emission peaks are observed at 540–550nm and is well supported by the PL studies of P.Yang et al. [14]. However, they have not studied the effect of capping agent on ZnS nanoparticles co-activated with rare-earth ions and Cu^{2+} ions. In this study, we observed that the emission intensity is much higher for 2 at.% of EDTA and is lesser for 4 at.% of EDTA and a blue shift in the spectra is observed.

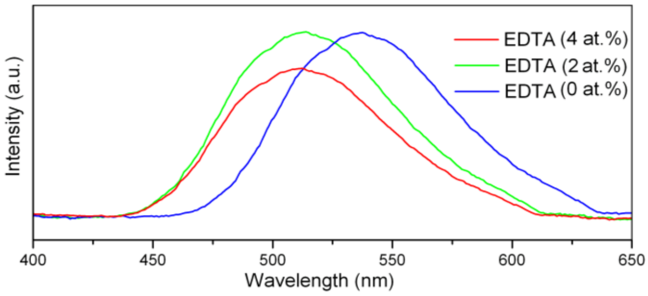


Figure 7: Photoluminescence spectra of uncapped and EDTA (2, 4 at. %) capped ZnS: Ce, Cu nanoparticles.

As composite luminescence center may trap electrons and holes, the fluorescence efficiencies are decreased and the glow peaks shift towards longer wavelength and the luminescent spectra of co-doped samples are remarkably different from those of Cu^{2+} doped, rare-earth metallic ion-doped and pure ZnS nanocrystallites. Because the novel composite luminescent centers enhance the fluorescence quantum field of ZnS nanoparticles, more electrons and holes could be excited and radiative recombination is enhanced. Since EDTA is acted as capping agent the shift in the spectra is attributed to the decrease in particle size.

3.5 Raman Spectroscopy

Raman spectra of uncapped and EDTA (2, 4 at. %) capped ZnS: Ce, Cu nanoparticles recorded in the frequency range 200 - 450 cm^{-1} are shown in Figure 8. The Raman spectrum of undoped ZnS nanoparticles exhibits strong but broad peaks at 276 and 351cm^{-1}.Asymmetric broadening in the Raman bands of Ce^{3+} and Cu^{2+} ions co-doped ZnS nanoparticles and EDTA capped ZnS: Ce, Cu nanoparticles is due to phonon confinement effect and the possible reason for the Raman shift is the ionic radius of $Ce^{3+}$is higher than that of Zn^{2+}, lattice defects get introduced or intrinsic host lattice defects are activated when Ce^{3+}ions are incorporated. The Ce^{3+}ions and Cu^{2+} ions tend to occupy the substitutional cationic sites resulting in host lattice defects. Further, no additional Raman modes due to Ce, Cu impurities are observed in co-doped ZnS: Ce, Cu nanoparticles. Also, No additional peaks were observed due to the presence of capping agent which reveals the absence of impurity phases.

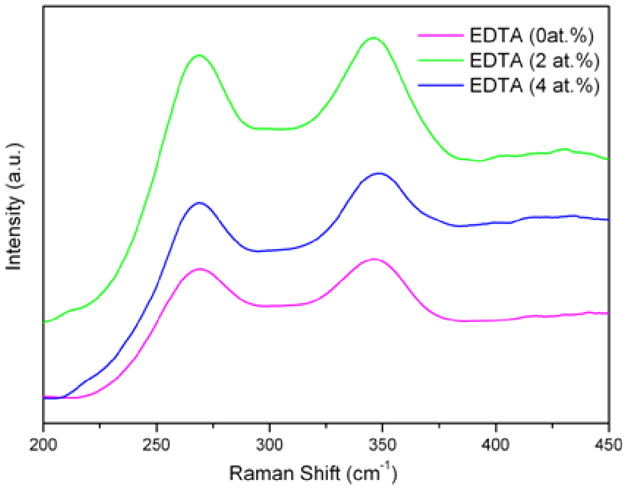


Figure 8: Raman spectra of uncapped ZnS: Ce, Cu and EDTA capped (2, 4 at.%) ZnS: Ce, Cu nanoparticles

In the case of large surface-to-volume ratio, surface scattering contributes more to the Raman signal than the volume scattering. The frequency shift of the Raman bands towards lower frequency side could be due to large surface to volume ratio. Therefore, the frequency shifts of the TO and LO modes observed in the present samples may be attributed to the smaller size and larger surface-to-volume ratio compared with that of the undoped ZnS. They represent Transverse Optical (TO) and Longitudinal Optical (LO) zone center phonons of cubic ZnS crystals respectively and these are similar to Brafman and Mitra [15] reports.

3.6 Conclusions

In summary, uncapped ZnS: Ce, Cu and EDTA capped (2, 4 at.%) ZnS: Ce, Cu nanoparticles have been successfully synthesized by chemical co-precipitation method at room temperature. X-ray diffraction (XRD) measurements showed that the uncapped and EDTA capped (2, 4 at.%) ZnS: Ce, Cu nanoparticles have cubic zinc blende structure. Also decrease in particle size with 2 at.% of EDTA is observed from particle size calculations using Debye Scherrer's equation and is further supported by TEM analysis.The morphology and composition of uncapped and EDTA capped (2, 4 at.%) ZnS: Ce, Cu nanoparticles were successfully studied by scanning electron microscopy, transmission electron microscopy and energy dispersive X-ray spectroscopy respectively. The observed blue-shift in the absorption maxima is a measure of increasing band gap, attributed to the presence of smaller crystallites due to the quantum confinement effect and the effect of capping agent. From the PL spectra of ZnS nanoparticles co-doped with $Ce^{3+}$and Cu^{2+} ions and EDTA capped ZnS: Ce, Cu nanoparticles the emission peaks are observed at 540–550nm. And a blue shift in the PL peaks was observed with increasing capping agent concentration. Uncapped ZnS: Ce, Cu and EDTA capped (2, 4 at.%) ZnS: Ce, Cu nanoparticles showed Raman peaks at 276 and 351cm^{-1} and the TO mode and LO mode of samples exhibited a red shift and asymmetric broadening indicating phonon confinement effects. No additional peaks were observed due to impurities.

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