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Undoped and Metal Doped ZnS Nanoparticles by Precipitation Method

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Abstract

Nanoparticles of undoped and metal (Sn^{2+} and Cu^{2+}) doped individually and combined with ZnS have been synthesised using triethylamine by precipitation. X-ray diffraction and optical absorption measurements have been made on nanoparticles of pure and metal doped ZnS. The studies reveal that the metal doped ZnS does not modify the cubic structure and the average crystallite size is found to be in the range of 6 - 15 nm. The undoped ZnS nanoparticles have higher optical absorption in the visible region than the metal doped ZnS and the allowed direct band gap energy is found to increase in metal doped samples.

Keywords: ZnS, nanoparticles, triethylamine, XRD, UV-Visible

Introduction

Nanosized inorganic semiconducting materials have been generating an extensive interest in recent years owing to their structure, chemical and physical properties which are different from those of the bulk materials. ZnS is one such material that has wide band gap energy of about 3.5 - 3.8 eV at room temperature. Nanocrystals doped with optically active luminescence centers create new opportunities for luminescent study and applications of nanoscale materials [1]. Doping of ZnS can modify its properties, especially in the case of transition metal co-activated ZnS nanoparticles which form a new class of luminescence materials. Nanostructured ZnS materials have attracted much research interest due to their excellent properties in luminescence and photochemistry [2] and also ZnS has many applications in the areas of solar cells, sensors, transducers, optical coating, flat panel displays and light emitting materials [3-7]. Different methods have been used to prepare ZnS nanoparticles including the microwave assisted method [8], hydrothermal method [9], mechanochemical synthesis [10] and precipitation method [11]. Recently, several authors have been reported Cu^{2+}, Sn^{2+}, $Pb^{2+}$and Mn^{2+} doped ZnS nanoparticles with different capping agents [2-5,12-14]. Among the different synthetic strategies the precipitation approach has attracted more attention due to its distinct advantages in having simple reaction conditions and effective control over the size and shape of the nanoparticles by systematically adjusting the reactant mole ratio [11].

According to our literature review, triethylamine capped ZnS nanoparticles have not been presented elsewhere. Hence, the objective of this study is to synthesize ZnS nanoparticles and metal doped (Sn^{2+} and Cu^{2+}) individually and co-doped. Structural and optical absorption have been made on nanoparticles of undoped and metal doped ZnS using XRD and UV-Visible spectroscopy.

Materials and methods

AR grade $ZnCl_2$, $Na_2S.xH_2O$, $SnCl_2.2H_2O$, $CuSO_4.5H_2O$ and triethylamine were used for synthesis. In a typical procedure an aqueous bath of 1 M zinc chloride (50 ml) and 1 M sodium sulfide (50 ml) was mixed with distilled water and then the solution was stirred for about 10 min while 10 ml of triethylamine solution was added slowly to the solution. The solution was again continuously stirred at 60 °C for 3 h, after which a white precipitate was obtained. The precipitate was filtered and thoroughly washed several times using water and methanol to remove impurities. Finally, the precipitate was dried at room temperature for 24 h. Similarly 0.1 M tin(II) chloride and 0.1 M copper sulfate solution were individually and combined with the ZnS solution. Then the remaining steps used for undoped ZnS were repeated, it results in a brown precipitate obtained for Sn^{2+} co-doped ZnS while a green precipitate was obtained for Cu^{2+} doped ZnS.

The structural characteristics of the undoped and metal doped ZnS nanoparticles were carried out by analyzing the X-ray diffraction (XRD) patterns using Cu Kα radiation in the range of 2θ = 10° - 80° with an X' Pert PRO diffractometer (PANalytical, Netherlands). A JEOL-Scanning Electron Microscopy (SEM) (JSM - 5610 LV) was used to record the micrograph for the samples. Optical absorption studies were carried out using a UV-visible spectrometer (UV2202) between 300 - 800 nm.

Results and discussion

The XRD patterns of undoped ZnS, Sn^{2+} and Cu^{2+} doped individually and combined with ZnS nanoparticles are shown in **Figure 1**. The XRD pattern of undoped ZnS nanoparticles show 3 distinct prominent peaks at 2θ = 28.81°, 48.14° and 56.27° which corresponds to the (1 1 1), (2 2 0) and (3 1 1) planes respectively of cubic ZnS (JCPDS card No. 05-0566). The broadening of the peaks indicates typical nanocrystalline characteristics of the samples which presumably are very small in size. The result is in agreement with the earlier report on ZnS by Ummartyotin *et al*. [15].

The XRD patterns of Sn^{2+} and Cu^{2+} doped individually and combined with ZnS also having prominent peaks at 2θ = 28.59°, 47.57° and 56.34° which corresponds to (1 1 1), (2 2 0) and (3 1 1) planes respectively of cubic ZnS (JCPDS card No. 05-0566). However, the intensity of the major crystalline peak at 2θ = 28.61° much reduced in comparison to the undoped ZnS which may indicate competition between the Sn^{2+} and Cu^{2+} ions to replace the small Zn^{2+} ions in the lattice. It is also important to note that the following prominent peak are shifted to lower angles at 2θ = 47.57° in comparison to the undoped ZnS at 48.14°. This is due to the substitution of smaller size Zn^{2+} ions (0.74 Å) by either bigger size Sn^{2+} ion (0.99 Å) or Cu^{2+} ion (1.28 Å) in the Zn^{2+} lattice site [13].

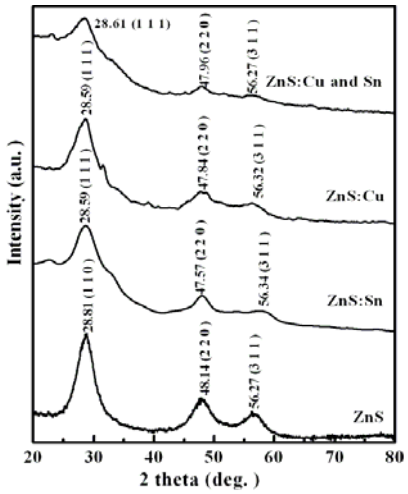

Figure 1 XRD patterns of undoped and metal doped ZnS nanoparticles.

It is observed from the XRD analysis, that the doping of Sn^{2+} and Cu^{2+} ions either individually or together with ZnS does not modify its structure. In addition to this, the obtained products are free from impurities.

Average crystallite size of undoped and metal doped ZnS nanoparticles are calculated using the Debye-Scherrer's equation [16] and the results are given in **Table 1**.

$$D = K \lambda / \beta \cos \theta \quad (1)$$

where, D is the mean grain size, K is constant, λ is the X-ray's wavelength (1.5406 Å), β is the full width at half maximum and θ the Bragg's diffraction angle.

Dislocations are the imperfections in a crystal and associated with the mis-registry of the lattice in one part of the crystal with respect to another part. Unlike vacancies and interstitial atoms, dislocations are not equilibrium imperfections. In fact, the growth mechanism involving dislocations is a matter of importance. The dislocation densities are given by the Williamson and Smallman's relation. $\delta = n/D^2$, where δ is dislocation density, n is a factor, which equals unity, giving minimum dislocation density and D is the crystallite size [17-19]. **Table 1** gives the crystallite size and dislocation density of all prepared samples.

Table 1 Crystallite size and dislocation density of undoped and metal doped ZnS.

Name of the samples	**Crystallite size (nm)**	**Dislocation density (10^{14} lin/m^2)**
ZnS	10.18	9.65
ZnS:Sn^{2+}	6.18	26.18
ZnS:Cu^{2+}	14.84	4.55
ZnS:Sn^{2+} & Cu^{2+}	15.40	4.22

On comparing with the other capping agents (EDTA, polyphosphate and mercaptoacetic acid) the triethylamine yields higher particle sizes. However which is lower than that of thiourea capped ZnS [2,3,12,13].

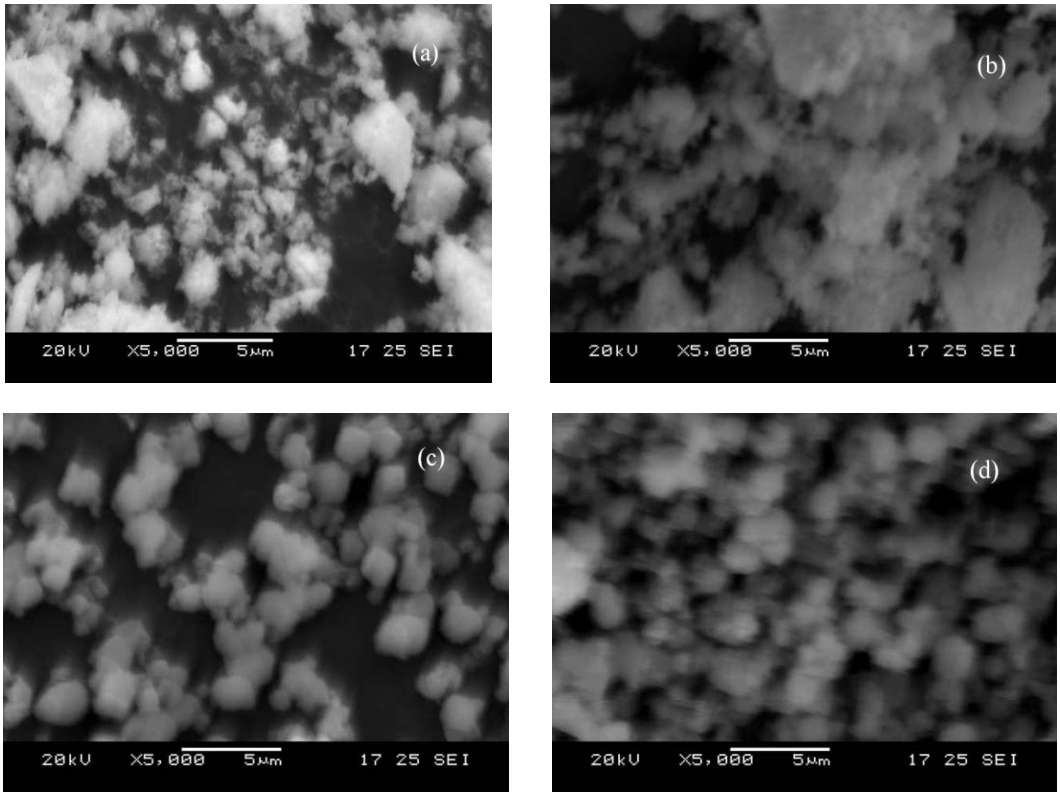

Figure 2 SEM images of (a) Undoped, (b) Cu^{2+}, (c) Sn^{2+} and (d) co-doped ZnS nanoparticles.

The SEM micrographs of undoped, Sn^{2+}, Cu^{2+} individually doped and combined with ZnS are shown in **Figures 2a - d**. In the SEM images of undoped ZnS and metal doped, coalescence between grains are clearly seen with homogeneous fine spherical and polygonal particles. The particles somehow formed compact morphology and are densely packed. Average size particles are found to be less than 1 μm. The Sn^{2+} doped ZnS shows less dense than compares with other samples.

Figure 3 shows the optical absorption spectra of undoped, Sn^{2+}, Cu^{2+} doped individually and combined with ZnS nanoparticles. It is clear from the absorption spectra that the absorption edges found in the range of 290 - 298 nm, indicates blue-shifting from the bulk ZnS that shows absorption at 340 nm [1]. The blue-shift absorption edge is due to quantum confinement of the excitons present in the sample, resulting in a more discrete energy spectrum of the individual nanoparticles.

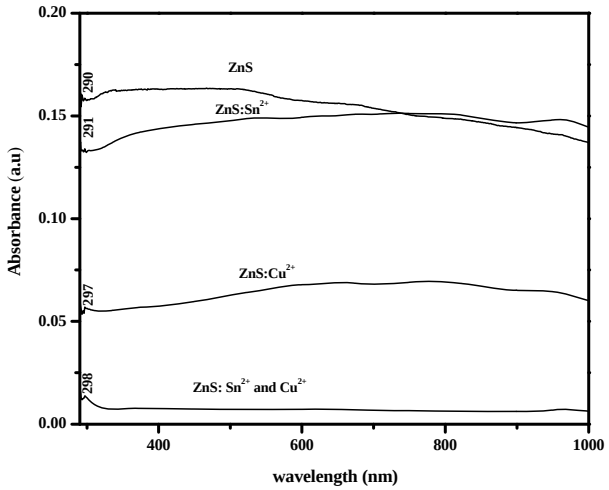

Figure 3 UV-Visible absorption spectra of undoped and metal doped ZnS nanoparticles.

It is observed that the undoped ZnS nanoparticles have higher optical absorption in the visible region than the doped ZnS nanoparticles. The effect of the quantum confinement on impurity critically depends on the size of the host crystal. As the size of the host decreases, the degree of confinement and its effect increases. The confinement of the atomic impurity achieved in a nanocrystalline size host permit the energy transfer efficiently to the atom. The addition of Sn^{2+} to ZnS causes a decrease in particle size as well as a shifting of absorption peaks from 290 to 291 nm indicating that the dopant Sn^{2+} forms a new energy level in the band structure of ZnS.

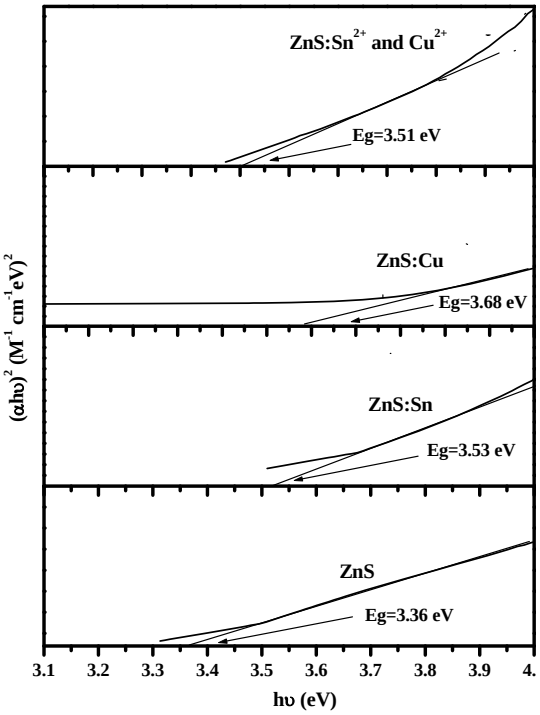

Figure 4 Band gap energy of undoped and metal doped ZnS nanoparticles.

The fundamental absorption, which corresponds to electron excitation from the valence band to conduction band, can be used to determine the value of the optical band gap. The relationship between the absorption coefficient (α) and incident photon energy (hν) can be written as;

$$(\alpha h\nu) = A\,(h\nu - E_g)^n \quad (2)$$

where A is a constant and E_g is the band gap. n is an index that can assume values of (1/2, 2), depending on the nature of electronic transitions. For the direct allowed transitions, n has a value of 1/2 while for indirect allowed transitions n = 2. Here the transitions are direct so we take n = 1/2.

The optical band gap values are calculated by extrapolating the straight line portion of $(\alpha h\nu)^2$ vs. hν graph (**Figure 4**). From the figure, the undoped ZnS shows less band gap energy than that of metal doped ZnS.

The average crystallite size of the nanocolliods can be determined by using a mathematical model of effective mass approximation as suggested by Brus [9] who used the following equation to describe the crystallite size (r, radius) as a function of peak absorbance wavelength (λp) for undoped, doped and co-doped ZnS nanocrystals. This mathematical model is scarcely reported for determination of crystallite size from the UV-Visible analysis.

$$\mathrm{R(nm)} = \frac{\{-0.293 + (40.1970 + 13620/\lambda\mathrm{p})\}}{\{7.34 + 2481.6/\lambda\mathrm{p}\}}$$

From the **Table 2**, the crystallite size of the undoped ZnS was found to be 1.90 nm which is lower than that of metal doped ZnS particles. However, the calculated values are much lower than the result of the XRD study. Triethylamine capped ZnS shows a lower band gap energy than that of polyphosphate capped and mercaptoethanol capped ZnS [12,20].

Table 2 Band gap energy and crystallite size of the doped and metal doped ZnS particles.

Name of the samples	Band gap energy (eV)	Crystallite size (nm)
ZnS	3.36	1.90
ZnS:Sn	3.53	2.06
ZnS:Cu	3.68	1.91
ZnS: Sn^{2+}&Cu^{2+}	3.51	2.09

Conclusions

Nanoparticles of undoped ZnS and metal (Sn^{2+} and Cu^{2+}) doped individually and combined with ZnS nanoparticles were prepared by precipitation. From the XRD analysis, the undoped and metal doped ZnS shows pure cubic structure and the effect of dopants do not modify the structure of ZnS. From the UV-Visible analysis, undoped ZnS nanoparticles exhibit higher optical absorption in the visible region in comparison to the metal doped ZnS nanoparticles except when Sn^{2+} is a dopant. The band gap energy of the undoped ZnS is found to be 3.36 eV when compared to the doped ZnS nanoparticles.

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