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EFFECT OF Sn^{2+} DOPING ON OPTICAL PROPERTIES OF THIOUREA CAPPED ZnS NANOPARTICLES

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Here we are reporting the synthesis of $Zn_{1-x}Sn_xS$ (x = 0, 0.1, 0.2, 0.3) nanoparticles and their photoluminescence properties. $Zn_{1-x}Sn_xS$ nanoparticles were synthesized by using thiourea as a capping agent. All the samples were characterized by X-ray diffraction technique. XRD patterns show the particle size in the range 12-24.5 nm. It was found that, the addition of Sn^{2+} ions causes the change in UV and PL spectra of ZnS nanoparticles. A broad and intense emission peak occurs at 460 nm for $Zn_{0.8}Sn_{0.2}S$ nanoparticles.

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1. Introduction

The special functionality of materials on the nanoscale has been known for some time. Increasing possibilities in tailoring the applications of nanomaterials had renewed the interest in nanotechnology. The size dependent optical and electronic properties of nanoparticles has been proposed in view of novel physical properties [1,2]. The size dependence of the band gap is the most identified aspect of quantum confinement in semiconductors; as the particles size decreases the band gap increases. The variation in the properties of nanoparticles is mainly due to two factors, namely the increase in the surface to volume ratio and change in the electronic structure of the material due to quantum confinement effects. As the particle size decreases, the quantum confinement effects begin to occur.

Most of the II-VI semiconductors (ZnS, ZnO, CdS, and CdO etc) can form, with some degree of stability in bulk, the wurtzite crystal structure. This crystal structure offers several benefits to the formation of and the physical properties of nanomaterials. Because of their uses in optoelectronic and semiconducting applications, II-VI semiconductors have recently been the focus of intense research in nanomaterials. The II-VI semiconductors are typically wide band gap materials, serving as efficient light emitters. Though nanostructures are formed out of II-VI semiconductors with interesting properties, the main focus of this investigation is ZnS nanostructures.

ZnS with wurtzite structure is a direct wide band gap (3.7 eV) semiconductor [1-4], that is one of the most important materials in photonics owing to its high transmittance in visible range and its high index of refraction (about 2.2). ZnS is also an important phosphor host lattice material used in electroluminescent devices (ELD). This is because of its large band gap that is enough to emit visible light without absorption and the efficient transport of high energy electrons. It is the materials of reference to test several theoretical models in condensed matter physics [5,6]. The present investigation is based on the synthesis of urea capped ZnS nanoparticles and their structural properties are discussed. The effect of Sn^{2+} doping on optical properties of ZnS nanoparticles is also presented.

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2. Experimental

Method of synthesis is an important step in studies of nanomaterials. Various methods are being used for synthesis of nanoparticles of metal chalcogenides. A slight change in synthesis conditions can create a valuable change in the morphological, structural optical and other properties of materials. In this work we have synthesized ZnS nanoparticles maintaining the same physical condition during the synthesis of all samples. The ternary alloyed $Zn_{1-x}Sn_xS$ (x = 0, 0.1, 0.2, 0.3) nanoparticles were synthesized from aqueous solutions zinc chloride, stannous chloride, thiourea and sodium sulfide. To the 0.1 M aqueous solution of Zinc chloride, ammonium hydroxide solution was added slowly to form the viscous solution of metal hydroxide. The resultant mixture was stirred followed by the addition of sodium sulfide solution. This solution was kept for stirring at 45°C for 2 h. In order to avoid the agglomeration of ZnS particles, solution of thiourea was added to this solution and a stirring on hot plate was continued for few hours. The reaction mixture was kept on hot plate at 120°C. The obtained precipitate was washed thoroughly five times in double distilled water and then separated by centrifuge and finally air dried. A similar process was followed for synthesis of Sn-doped ZnS nanocrystals. Dried $Zn_{1-x}Sn_xS$ powders were characterized by X-ray diffraction (XRD) analysis. The optical properties of the nanoparticles have been studied by UV-visible (UV-vis) absorption spectroscopy and photoluminescence (PL) to further assess their quality.

3. Results and discussion

All the powders with composition $Zn_{1-x}Sn_xS$ (x = 0, 0.1, 0.2 and 0.3) were characterized by X-ray diffraction technique. The crystallite size (D) was calculated using Scherrer equation (Eq. 1);

$$D = 0.9\lambda/\beta\cos\theta \tag{1}$$

where, λ is a wavelength of the radiation, β is full width at half maxima (FWHM) and θ is the diffraction angle. XRD patterns of $Zn_{1-x}Sn_xS$ powders indicate the formation of a complete solid solution for the addition of Sn up to x = 0.2 For the sample $Zn_{0.7}Sn_{0.3}S$, separate peaks were observed for tin sulfide indicating its immiscibility at the higher concentration x = 0.3. The XRD pattern of $Zn_{0.8}Sn_{0.2}S$ is only presented in figure 1. Figure 1 exhibit three prominent peaks correspond to planes (111), (220) and (311). The broadness of peaks indicates the nanocrystalline behavior of the $Zn_{0.8}Sn_{0.2}S$ particles. The average grain size of the $Zn_{1-x}Sn_xS$ particles calculated from the most intense peaks is in the range of 12-25 nm (Table 1). Figure 2 depicts the effect of Sn concentration (x) on the grain size of $Zn_{1-x}Sn_xS$. It can be seen that, as the Sn concentration increases from x = 0-0.2, grain size decreases and again found to be increased for x = 0.3. From the results, it was assumed that, the added quantity of thiourea is enough to prevent the agglomeration of particles. It was remarkably noted that, the diffraction peaks shifts towards the larger angles as the concentration of Sn^{2+} in ZnS increases. It could be due to the replacement of smaller Zn^{2+} ions (0.74 Å) by the bigger ion Sn^{2+} (0.99 Å).

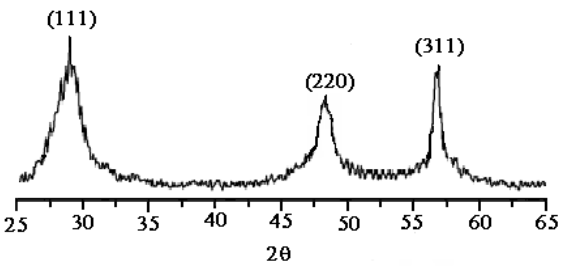

Fig. 1 XRD pattern of $Zn_{0.8}Sn_{0.2}S$ powders.

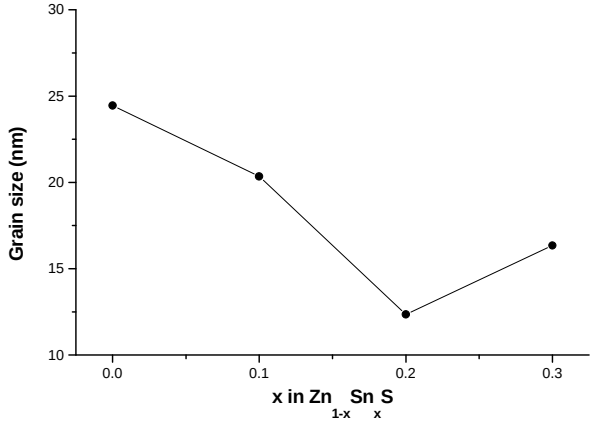

Fig. 2 Variation in grain size of $Zn_{1-x}Sn_xS$ nanoparticles as a function of Sn concentration (x).

Table 1 Absorbance and grain size $Zn_{1-x}Sn_xS$ nanomaterials.

Composition	Sample code	Absorbance (nm)	Grain size (nm)
$Zn_{1-x}Sn_xS$	G-I	290	*24.45*
$Zn_{0.9}Sn_{0.1}S$	G-II	299	*20.35*
$Zn_{0.8}Sn_{0.2}S$	G-III	309	*12.36*
$Zn_{0.7}Sn_{0.3}S$	*G-IV*	*295*	*15.34*

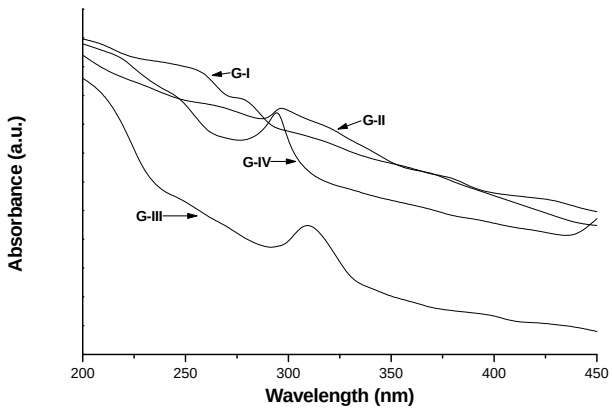

Fig. 3 UV-visible absorption spectrum of $Zn_{1-x}Sn_xS$ (x = 0, 0.1, 0.2 and 0.3) nanoparticles.

Fig. 3 shows UV-visible spectra of $Zn_{1-x}Sn_xS$ with different concentration of Sn. The spectrum of $Zn_{1-x}Sn_xS$ shows the absorbance in the range of 290-309 nm. The absorption peak at 309 nm is blue shifted compared to the bulk ZnS for which the absorption peak is at 345 nm. The blue-shifted absorption edge is due to the quantum confinement of the excitons present in the

sample, resulting in a more discrete energy spectrum of the individual nanoparticles. The broadening of the absorption spectrum is mainly due to the quantum confinement of the $Zn_{1-x}Sn_xS$ particles. 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 nanoparticles causes the decrease in particle size as well as the shifting of absorption peaks from 290 to 309 nm indicating that doped Sn^{2+} forms a new energy level in the band structure of ZnS.

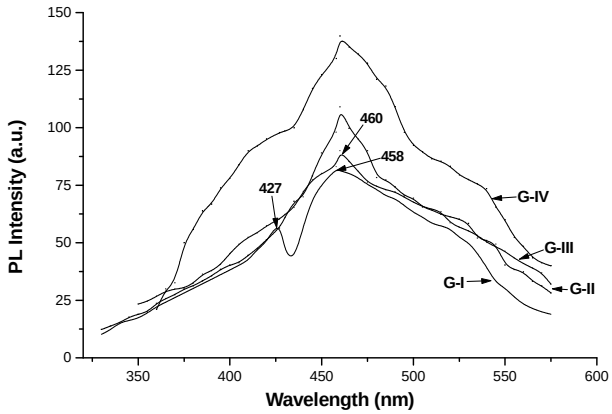

Fig. 4 Photoluminescence spectrum of $Zn_{1-x}Sn_xS$ (x = 0, 0.1, 0.2 and 0.3) nanoparticles

The photoluminescence spectra of $Zn_{1-x}Sn_xS$ nanomaterials were measured at room temperature is shown in Figure 4. The PL spectra of undoped ZnS shows two peaks positioned at 427 nm and 458 nm. The peak at 427 nm for undoped ZnS resulting from the transition of electrons from shallow states near the conduction band to sulfur vacancies present near the valence band. Similar results were reported by Becker et al. [7] and Lu et al. [8]. Murase et al. [9] have reported the emission spectra at 450 nm attributed to the zinc vacancies. In our study we have found an intense peak at 460 nm for Sn^{2+} doped ZnS nanoparticles. In PL spectra of $Zn_{1-x}Sn_xS$ nanomaterials, there is no shifting of the peaks while there is an increase in the peak intensity with addition of dopant. One can see that, with increase in the concentration up to x = 0.2, the intensities the of PL peaks increase.

4. Conclusions

We have successfully synthesized the $Zn_{1-x}Sn_xS$ (x = 0.0-0.3) nanoparticles by using thiourea as one of the capping agent. The particle size was calculated by XRD analysis. The size of nanoparticles was found to decrease with Sn^{2+} concentration. The room temperature photoluminescence shows a broad and intense peak at 460 nm but the concentration of Sn^{2+} ions causes the change in intensity at the same wavelength. There is a further need to study the system in order to enhance the optical properties by manipulating the particle size of ZnS and loading the new and suitable dopants.

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References

[1] D. Denzler, M. Olschewski, K.Sattler, J.Appl.Phys. **84**, 2841 (1998).
[2] B. S. Zou, R.B. Little, J.P. Wang, M.A. L-Sayed, Int .J. Quantum Chem.**72**, 439 (1999).
[3] X.Wang, Y. Ding, C.J. Summers, Z.L.Wang, J. Phys. Chem. B **108**, 8773 (2004).
[4] A. Narayanaswamy, H.F. Xu, N. Pradhan, M. Kim, X. Peng, J. Am. Chem. Soc. **128**, 10310 (2006).
[5] W.Q. Peng, S.C. Qu, G.W. Cong, Z.G.Wang, Cryst. Growth Des. **6**, 1518 (2006).
[6] Z.P. Sun, L. Liu, L. Zhang, D.Z. Jia, Nanotechnology. **17**, 2266 (2006).
[7] W. G. Becker, A. J. Bard, J. Phys. Chem. **87**, 4888 (1983).
[8] H.-Y. Lu, S.-Y. Chu, S.-S. Tan, J. Cryst. Growth. **269**, 385 (2004).
[9] N. Murase, R. Jagannathan, Y. Kanematsu, M. Watanabe, A. Kurita, H.Hirata, T. Yazawa, T. Kushida, J. Phys. Chem. B **103**, 754 (1999).