

Investigations on ZnS nanoparticles based on synthesis temperature for optoelectronic device applications

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ZnS nanoparticles were synthesized by chemical co-precipitation method at 273K (ice temperature) and 373K (100°C) from homogenous solutions of zinc acetate and sodium sulfide. Two sets of ZnS nanoparticles were obtained one, using thiophenol as capping agent and the other, with no capping agent and the results were compared. Morphological studies were carried out using Scanning Electron Microscopy (SEM). X-ray diffraction (XRD) studies revealed the phase singularity of ZnS particles with zincblende structure with the lattice parameter in the range of 5.2-5.5 Å. The mean crystallite sizes were in the range of 1.4nm-6nm. Samples prepared in the absence of template at lower preparation temperature had lower grain size. Atomic Force Microscopy (AFM) studies confirmed the particle size is in the same range. The estimated values of average strain and dislocation density indicated that the particles formed at lower temperature were less strained. Optical absorption studies indicated blue shift of the absorption edge with band gap values in the range of 4.2-4.4eV which are higher than the bulk value of 3.6eV, depicting the nano size of the present ZnS particles.

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1. Introduction

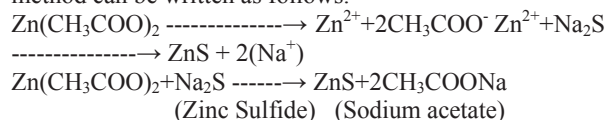
Nanomaterials have attracted considerable attention of the scientific community owing to the novel properties they exhibit because of the large surface to volume ratio compared to their bulk counter parts [1-5]. Nanosized particles of semi conducting compounds in particular display grain size dependent optoelectronic properties, due to the size quantization effects [6]. The photo emission wavelengths, the band gap and lattice parameter are strongly dependent on the grain size rendering the tailorable of these properties as functions of grain size possible. Such unique tunability can not be achieved in bulk semiconductors. The biggest hurdle in nanotechnology seems to be production of uniform sized nanoparticles and the control of grain size in a few nanometer range with considerable reproducibility. In this direction voluminous research has been undertaken in the past decade. Research on II-VI semi conducting compounds with wide band gaps has been under taken by a number of workers in the recent past. Among II-VI compound semiconductors ZnS is one of the most promising materials because of its wide band gap (~3.68eV) [7-8], large exciton binding energy(40meV)[9] and high index of refraction (2.27 at 1µm)[10]. ZnS is less toxic and more environmental safe than other chalcogenide materials[11]. Due to nontoxic nature, ZnS nanoparticles are used in determination of nucleic acids using the resonance light scattering method, biomolecular labeling [12-13] and have more potential applications like solar cells[14], laser devices[15], light emitting diodes[16] biological detection, electroluminescence devices, phosphors, optical sensors, optoelectronic devices, flat-panel displays [17]. For synthesis of ZnS nanoparticles a number of methods are

available such as solid state reaction method[18], simple solvothermal approach[19], hydrothermal method[20], chemical precipitation method [7,21], Electro-explosion of Wire(EEW)[22], Biological synthesis [23] and laser ablation [24]. Among these methods chemical co-precipitation method is widely used for the preparation of colloidal nanoparticles because of its several advantages like cheap raw materials, easy handling, capable of producing high purity samples and also the cluster formation is less compared to the other methods[4], since they form particles of much smaller size with higher surface area than those reported by other methods. Chemical co-precipitation technique using different templates for grain size control appears to be a versatile technique for preparation of semi conducting nanoparticles of high purity. In spite of these, grain size control still remains an unsolved problem. In view of these, in the present study ZnS nanoparticles were synthesized by chemical co-precipitation method at 273K and 373K using zinc acetate and sodium sulfide as the starting materials with thiophenol as capping agent and also with no capping agent. This is a preliminary experiment the authors have tried to examine whether the use of hazardous chemicals as templates can be dispensed with and a lower preparation temperature can be opted for to achieve the same result. The synthesized samples were characterized by SEM, XRD, AFM and optical absorption studies. The results of these investigations are presented in this paper.

2. Experimental

In the present study zinc acetate and sodium sulfide were used as source materials for synthesizing ZnS nanoparticles. 0.1M solution of zinc acetate and sodium

sulfide were prepared dissolved in 100ml of methanol. Aqueous solution of sodium sulfide and 2ml of thiophenol were taken in a beaker and it is placed in a constant temperature bath. The temperature of the bath can be set to a desired value. Zinc acetate solution was taken in a burette, it was added drop by drop to the reaction beaker under constant stirring. The color of the solution became white as the reaction progressed. The reaction continued for about 24 hours till a fine precipitate was formed. Finally the precipitate was filtered out separately and subsequently washed thoroughly with de-ionized water and methanol for removing the additional impurities formed during the preparation process. A similar process was followed for the synthesis of ZnS nanoparticles with no capping agent. The precipitate of nanoparticles was dried using micro wave oven at 60°C for 6h. As already mentioned the nanoparticles were synthesized at two temperatures, 273K and 373K. The ZnS nanoparticles thus obtained were subjected to the following characterization studies. The exchange reaction of the above synthesis method can be written as follows.



Structural investigations were done by “Seifert 3003 TT X-Ray diffractometer”. The phase purity, crystal structure, particle size, lattice parameter, strain, dislocation density of the samples were analyzed by using Cu-K α operating at 20ma employing a scanning rate of 2⁰ min⁻¹ with a wave length of 1.542 Å⁻¹ in the range 20-70 degrees. Morphological studies were carried out using Scanning Electron Microscopy (SEM) with EDAX attachment (Model CARL-ZEISS EVO MA 15). Optical spectra were recorded using Carey-5E UV-VIS-NIR lambda 950 spectrometer.

3. Results and discussion

The synthesized samples were characterized by Energy Dispersive Analysis of X-rays (EDAX) for the estimation the various chemical species present in the samples. EDAX spectra for the as-prepared ZnS samples are shown in Fig.1.

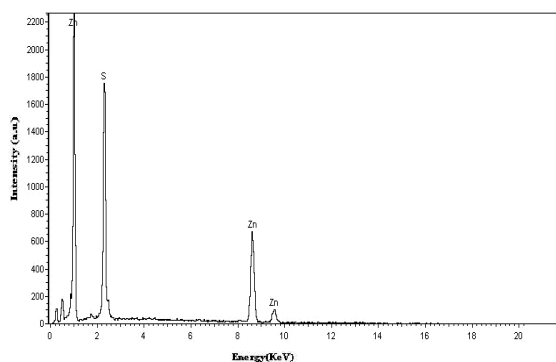


Fig.1. EDAX spectra of ZnS nanoparticles

Fig.2. shows the SEM images of ZnS nanoparticles formed at 373K and 273K in the absence of any capping agent and thiophenol as the capping agent. The SEM images indicate that the ZnS nanoparticles have a narrow size distribution of about 10nm. These images also depict agglomeration of particles with more or less spherical morphology. It is obvious that in the samples formed at 273K agglomeration of particles is less and the particle size also is less.

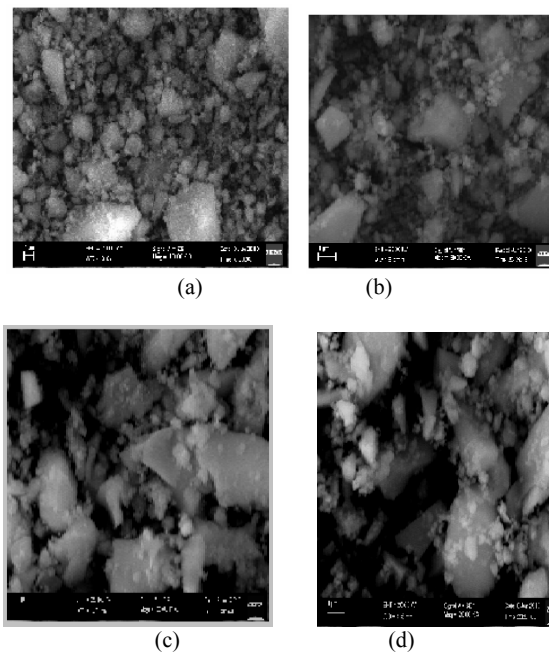


Fig.2 SEM images of ZnS nanoparticles synthesized at 273K and 373K, (a) Synthesized at 273K with no capping agent, (b) Synthesized at 273K with Thiophenol as capping agent, (c) Synthesized at 373K with no capping agent, (d) Synthesized at 373K with Thiophenol as capping agent

Fig. 3. shows the XRD patterns obtained in the present study. The broadening and intensities of the XRD peaks indicate the formation of nano sized ZnS particles. The peaks observed in the XRD patterns match well with those of the cubic ZnS [20, 25, 26] reported in the standard JCPDS (80-0020). Absence of extra peaks in the XRD indicate that there are no impurities present in the samples. The mean crystallite size in the samples was calculated using Scherrer formula [27-29]

$$D = 0.89 \lambda / \beta \cos \theta \quad (1)$$

where D is the average particle size, λ is wavelength of the Cu-K α irradiation, β is the full width at half maximum intensity of the diffraction peak and θ is diffraction angle for the (111) planes of cubic ZnS. It was also observed that as temperature increased the particle size slightly increased [30]. The grain size values are given in Table.1. XRD broadening could be due to other contributions like strain and stress which will be discussed later. The lattice

parameter 'a' of the unit cell is calculated according to the relation [20].

$$1/d^2 = 1/a^2 (h^2 + k^2 + l^2) \quad (2)$$

where d is the interplanar spacing of the atomic planes as determined from the position of the peak (111), lattice parameter is estimated in the range of 5.0 Å - 5.3 Å respectively for samples formed at 373K and 273K. These values are smaller compared to the bulk value of 5.4 Å. As already mentioned the XRD peak broadening could also be due to the strain in addition to the crystallite size of the particles. Hence an attempt has been made to estimate the average strain (ϵ) of the ZnS nanoparticles using Stokes-Wilson equation

$$\epsilon_{st} = \beta / 4 \tan \theta \quad (3)$$

The dislocation density (δ) was also calculated from the relation [31, 32]

$$\delta = 15\epsilon / aD \quad (4)$$

where ϵ = average strain, a = lattice parameter and D = average grain size. The average strains and the dislocation densities values are given at Table.1. The lattice parameter, strain, and dislocation density are less for samples formed at 273K (ice temperature) compared to those formed at 373K.

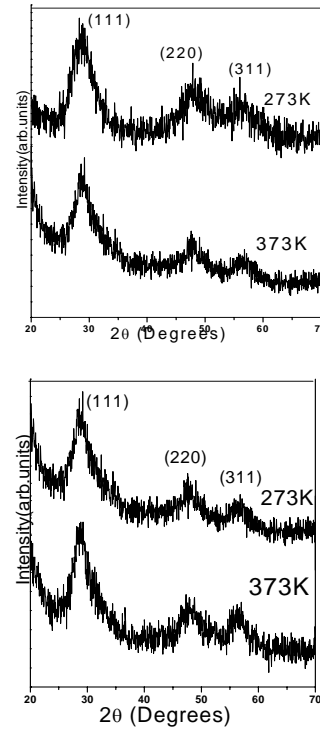


Fig.3. XRD spectra of ZnS nanoparticles synthesized at 273K and 373K. (a) XRD spectra of ZnS with no capping agent, (b) With Thiophenol as capping agent.

Table: 1 Grain size, lattice parameter, strain and dislocation density of ZnS nanoparticles with and with no capping agents at 273K and 373K.

No.	Sample	Grainsize (nm)	Strain	Dislocation density (lines/Å)	Lattice parameter (Å)
1	ZnS at 273K	2.5	0.043	0.38	5.2
2	ZnS at 373K	3.9	0.046	0.42	5.3
3	ZnS thiophenol capped at 273K	2.8	0.059	0.70	5.3
4	ZnS thiophenol capped at 373K	3.4	0.065	0.84	5.5

Table. 2 Grain size, Average roughness, RMS roughness and band gap energies of ZnS nanoparticles with and with no capping agents at 273K and 373K.

No.	Sample	Grainsize from AFM (nm)	Average Roughness(nm)	RMS rough ness (nm)	Band gap (eV)
1	ZnS at 273K	1.455	0.143	0.197	4.329
2	ZnS at 373K	6.509	1.168	1.422	4.300
3	ZnS thiophenol capped at 273K	3.258	0.539	0.702	4.320
4	ZnS thiophenol capped at 373K	6.079	0.837	1.079	4.310

Morphology of all ZnS samples was studied using AFM. Fig 4(a) and 4(b), shows the two-dimensional and three-dimensional AFM images of the nanoparticles synthesized in the absence of any capping agent at 273K and 373K, Fig 4(c) & 4(d) shows the AFM images of thiophenol capped ZnS nanoparticles synthesized at 273K and 373K respectively.

The ZnS particles are seen to be evenly distributed with little aggregation of the particles and partially ordered arrangement, with an average size in between 1.4nm-6nm and the values are given at Table.2. The average roughness of all samples varied in the range 0.1-1.2nm and the RMS rough ness varies in between 0.1-1.4nm.

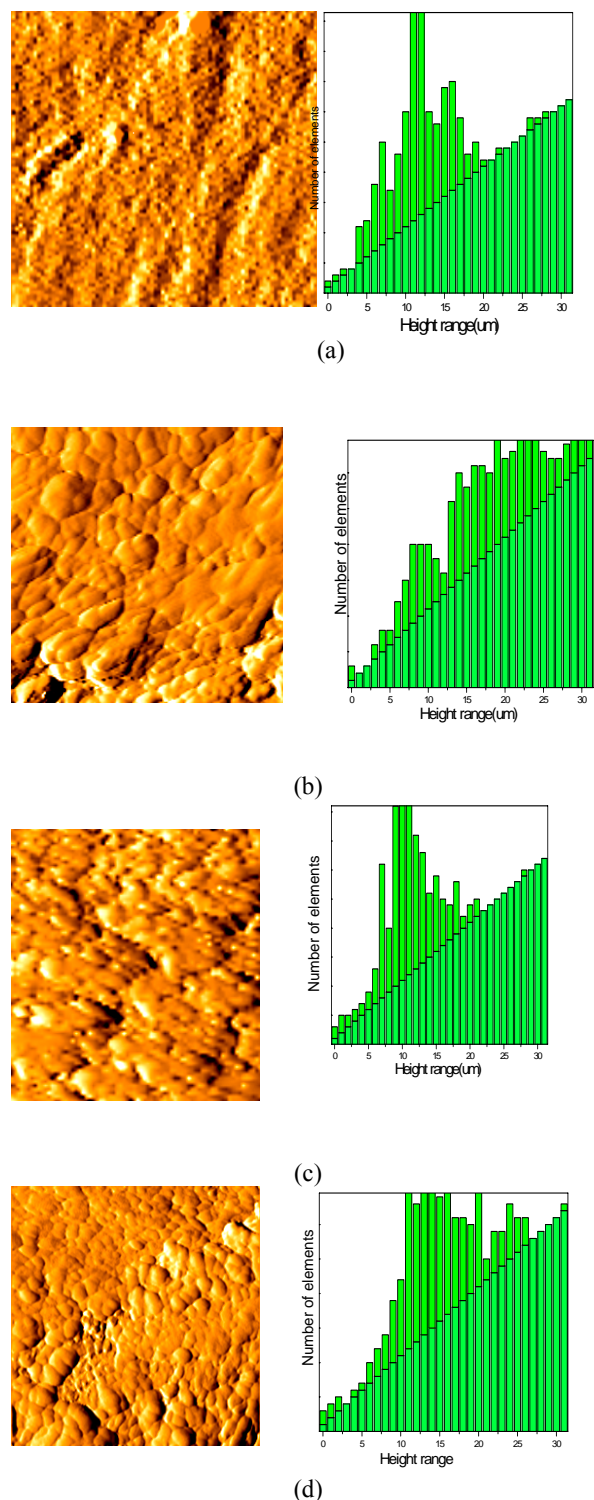


Fig. 4. (a) AFM image and Histogram of ZnS nanoparticles at 273K with no capping agent, (b) AFM Image and histogram of ZnS nanoparticles at 373K with no capping agent, (c) AFM image and histogram of ZnS nano particles at 273K thiophenol as capping agent, (d) AFM image and Histogram of ZnS nano particles at 373K thiophenol as capping agent.

The optical absorption spectra of ZnS nano powders were recorded using Carey-5E UV-VIS-NIR spectrometer in the wave length range of 200nm-800nm. The optical absorption spectra of ZnS at 373K and 273K nanoparticles are shown in Fig 5(a). The spectra reveal that the absorption is uniform in the visible range (390-800nm). The corresponding band gap values are given at Table.2. The band gap energy values are in the range of 4.2eV - 4.3eV which are larger than the bulk value of ZnS (3.6eV). The absorption edge is shifting towards shorter wavelength (blue shift) with decreasing particle size [33]. It has been observed that optical absorption does not occur at surface states and therefore these do not affect the absorption spectra [7]. Thus the absorption spectra indicate that the effective band gap increases with decreasing particle size. Blue shift is characteristic of nanoparticles is observed for both sets of samples. This blue shift is attributed to the quantum size effect due to the small size (1-6nm) of the synthesized nanoparticles. Which is lower than Bohr exciton diameter (~5nm). Optical excitation of electrons across the band gap is a strongly allowed transition, producing an abrupt increase in absorptivity at the wavelength corresponding to the band gap energy.

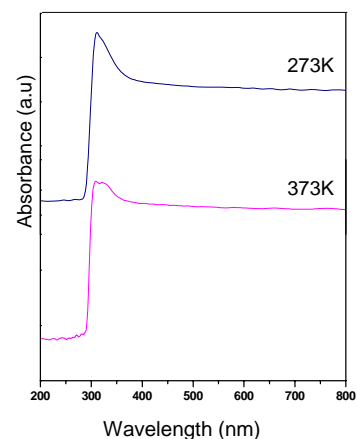


Fig 5(a). Optical absorption spectra of ZnS with no capping agent.

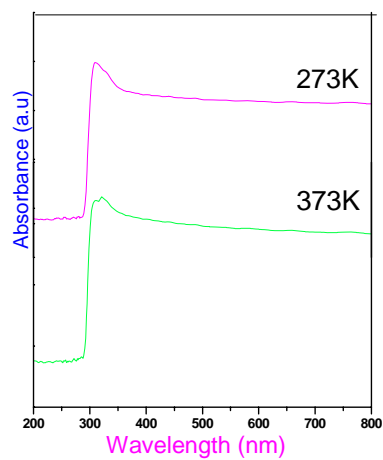


Fig 5(b). Optical absorption spectra of ZnS with thiophenol as capping agent.

4. Conclusions

ZnS nanoparticles were synthesized by chemical co-precipitation method at 273K and also at 373K using thiophenol as a template and with no template. XRD and AFM results indicated that lower synthesis temperature resulted in lower grain size and less strained particles. Size dependent blue shift of absorption edge is attributed to the quantum size effect. The present study suggests that lower synthesis temperatures may be opted for grain size control of nanoparticles in place of harmful templates. More studies in a wider range of synthesis temperature are needed to confirm and understand the particle size control mechanism at low synthesis temperatures.

Acknowledgements

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