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Effect of Temperature on Different Properties of ZnS Nanocrystals Prepared by Chemical Method

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Abstract: *Pure Zinc sulphide nanocrystals were synthesized by simple chemical Coprecipitation method. Samples were calcinated at two different temperatures in muffle furnace followed by furnace cooling up to room temperature. XRD analysis confirms that all samples have hexagonal structure with no impurity phases. The lattice parameter, Volume of unit cell, X-ray density and grain size were calculated by using XRD data. The SEM study confirms that, the crystals are agglomerates. The optical energy band gap of ZnS samples were estimated using UV-Visible absorption analysis. The FTIR spectra are carried out to analyze the chemical composition and quality of the compound and peaks*
Keywords: *ZnS; Nanocrystals; Precipitation; SEM; FTIR*

I. Introduction

Zinc Sulphide (ZnS) is an important II-VI group inorganic semiconducting material. It is found that ZnS has very excellent transmission property with refractive index of 2.27 at 1µm [1]. Zinc sulphide is a wide band gap semiconducting material for cubic zinc blend and hexagonal wrutzite structural phases at 300K [2, 3]. ZnS is one of the most important semiconductor nanomaterials which are useful in the applications in electronics, optoelectronics, catalyst and medicine [3]. ZnS Nanocrystals (NCs) are perfectly gained by hydrothermal and ultrasonic radiations method are have cubic Zinc blend structure [4].

ZnS is very known semiconducting nanomaterial which has considerable attraction because of its band gap, for this purpose it is also widely used in flat panel displays, electroluminescent windows [5]. In recent few years, research is going towards the nanostructure materials specially nanostructure semiconducting materials, which are exhibit their extra ordinary physical and chemical properties in comparison with their bulky form, such as energy absorption, size dependent variation of band gap [6].

Summarizing from the literature survey, there are several methods available for synthesis of semiconducting Nanocrystals (NCs). Using these methods different structures of ZnS are reported, as hexagonal wrutzite by hydrothermal method [7]. Different sizes of Quantum Dots (QDs) / Nanocrystals (NCs) have been prepared by wet chemical route [8].

In this work, a simple chemical method especially Coprecipitation method were used to prepare ZnS Nanocrystals which are calcinated at different two temperature. Our results show that temperature plays an important role in the preparation of ZnS Nanocrystals and also affect the size of crystals. After optimizing the various conditions and parameters Zinc Sulphide Nanocrystals were obtained.

II. Experimental

2.1 Preparation of ZnS Nanocrystals

The hexagonal nanocrystalline ZnS compound were obtained by the simple chemical method i.e. Coprecipitation method as follows. The reactants used for synthesis for ZnS were Zinc acetate and sodium sulphide of analytical grade and ratio of (1:1) molar solution of each reactant were dissolved separately in the mixture of methanol and double distilled water and stirrer for 30 min at room temperature. The freshly prepared aqueous solutions of these chemicals were used for preparation ZnS nanocrystals. Then completely dissolved solution of sodium sulphide was added drop wise into zinc acetate solution under the continuous stirring. The milky white precipitates were obtained which indicate that formation of ZnS compound. In the post synthesis steps, obtained precipitate was kept at constant stirring for 3hrs. Afterwards obtained precipitates were filtered and washed several times with deionised water and then dried at 150º C for 12 hrs. Then dried sample were grinded for 30 min and calcinated at two different temperatures i.e. at 300º C and 500º C for 4 hr.

Table 1. Prepared sample details.

Sample	Material Prepared	Molar Concentration (Zn:S)	Calcinated Temperature
S_1	ZnS	1:1	300º C
S_2	ZnS	1:1	500º C

2.2 Characterization of ZnS Nanocrystals

The X-ray diffraction (XRD) measurement of ZnS Nanocrystals taken by RIGAKU Miniflex X-Ray Diffractometer, Scanning Electron Microscopy was carried out by Hitachi S-4800 Type-II Field Emission SEM to study the surface morphology, absorption spectra of ZnS crystals were recorded with UV- Visible spectrophotometer (UV 1800 series, Shimadzu), Fourier transform infra red spectra (FTIR) of crystals were recorded by Perkin Elmer Spectrum Version 10.03.06 (Range 4000 – 400 cm^{-1}).

III. Results And Discussion

3.1 X- ray diffraction measurement

The XRD pattern of synthesized Pure ZnS nanocrystals of sample S_1 is shown in figure 1. The spectra shows the different diffraction peaks at 2θ values of 27.93, 32.27, 47.03, 55.9, 69.12 and 76.46 corresponding to (1,0,4), (1,0,21), (2,0,3), (1,1,26) and (2,1,4) planes which confirm the hexagonal structure of present investigations with JCPDS card No. 01-074-5013. Similarly XRD pattern of sample S_2 is shown in figure 2. The different diffraction peaks at 2θ values are 26.19, 27.69, 30.18, 33.48, 35.31, 46.72, 55.60 and 68.23 to (1, 0, 0), (0, 0, 2), (1, 0, 1), (1, 0, 2), (1, 1, 0), (2, 0, 0), (2, 0, 2) and (1, 0, 4) planes which are also confirm the Wurtzite hexagonal structure JCPDS card No. 00-036-1450. No extra peaks related to any impurity were observed which indicates that the quality of the product as well as synthesized method. The broad peaks in the XRD pattern are perfectly indexed the presence of ZnS nanocrystals.

It is observed from XRD pattern that the intensity and number of peaks of sample S_1 is lower than sample S_2 that confirms the effect of temperature on the structural properties of the ZnS. The data calculated from XRD pattern are listed in table 1.

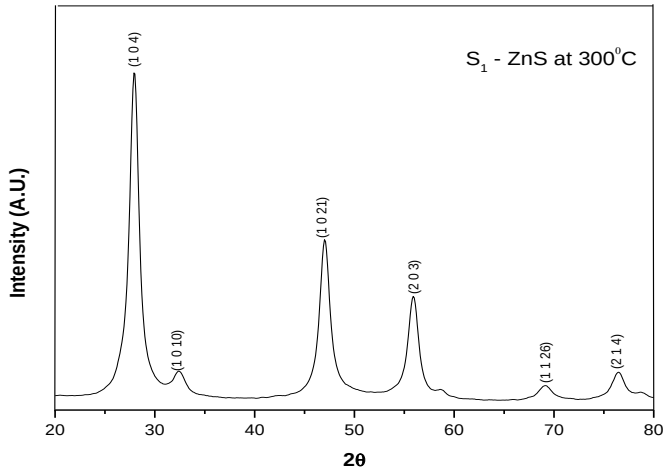

Figure 1. XRD patterns of the ZnS nanocrystals for samples S_1

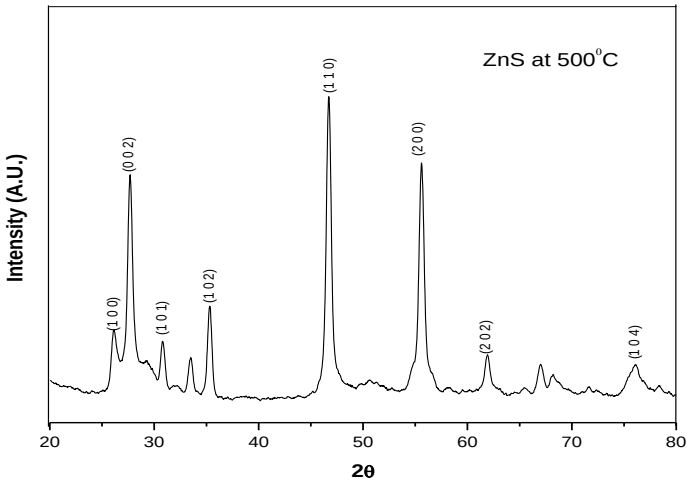

Figure 2. XRD patterns of the ZnS nanocrystals for samples S_2

The broadening of XRD peaks attributed nano-sized formation of prepared ZnS samples. The average crystallite size was estimated from Debye-Scherrer's formula [9],

$$D = \frac{K\lambda}{\beta \cos\theta}$$

Where, D is the crystalline size, β (in radian) is full width at half maxima (FWHM) of diffraction peak, K is the geometric constant factor (0.89), $\boldsymbol{\lambda}$ is the wavelength in nanometer, θ is known as Bragg's diffraction angle measured in radian also. It is observed that the average grain size of ZnS nanocrystal sample S_1 is 7.87 nm while sample S_2 is 21.98 nm. From this it is clear that temperature affect the average crystallite size i.e. size increase with higher calcination temperature. It is observed that the grain size and X-ray density increases while Volume of unit cell decreases with incease in temprature of ZnS. It is indicates the temperature play an important role in the structural properties of ZnS nanocrystals.

Table 2. The lattice parameters, volume, x-ray density and grain size of ZnS samples.

Samples	Lattice parameters in (A^0)		Volume of unit cell in $(A^0)^3$	X- ray density dx (g/cm^3)	Average Grain Size (D) in nm
	a	c			
S_1	3.8199	49.6183	626.99	0.4313	7.87
S_2	3.8209	6.2573	79.1142	3.4181	21.98

3.2 Scanning electron microscopy

The scanning electron microscopy (SEM) image of ZnS samples S_1 is shown in figure 2(a). The SEM micrograph indicates that the morphology of ZnS nanocrystals is large amount of agglomerated. This may due to the calcinations temperature which was 300°C. Figure 2(b) shows SEM image of the ZnS samples S_2 nanocrystals which was calcinated at 500°C. It was found that synthesized ZnS nanocrystals of sample S_1 were quite uniform in size. It is observed that the nearly spherical crystals are varying with their sizes due to temperature effect. The grain boundaries of observed morphology of approximately uniform size distributed, which plays an important role in measurement of optical properties of synthesized ZnS nanocrystals.

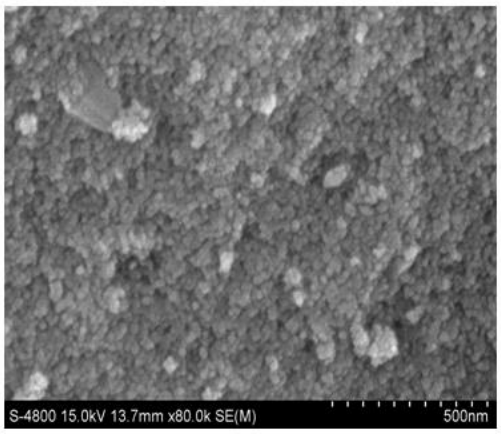

Figure 2a. SEM image of samples S_1.

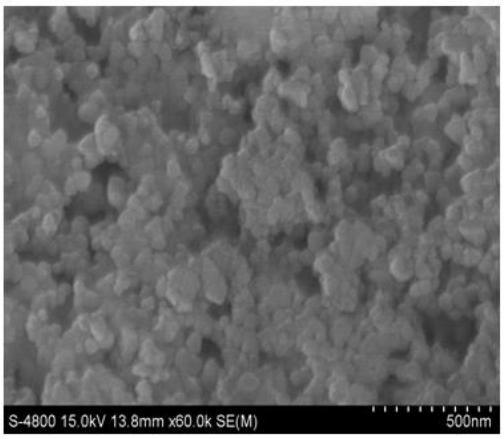

Figure 2a. SEM image of samples S_2

3.3 UV-Visible measurement

The energy band gap of synthesized ZnS nanocrystals were calculated using UV-Vis analysis in the wavelength range 200-800 nm at room temperature. Figure 3 shows the absorption plot of samples S_1 and S_2 ZnS nanocrystals. The band gap value of the prepared S_1 and S_2 ZnS nanocrystals were estimated by intersection point of tangent of the absorption edge with wavelength. The values of calculated band gap of S_1 and S_2 ZnS nanocrystals are about 3.75 eV and 3.59 eV which are comparable to the standard energy band gap of ZnS i.e. 3.7 eV. It is observed that energy band gap decreases with increasing temperature. This supports the increment in grain size with temperature and also confirms the temperature plays an important in the optical properties of synthesized ZnS nanocrystals.

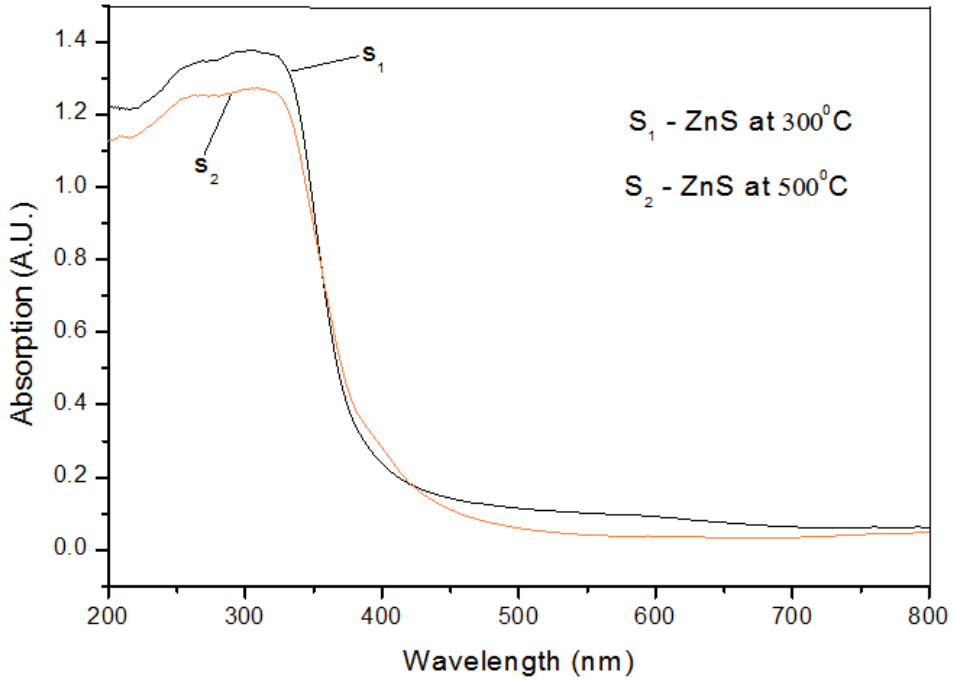

Figure 3. Plot of wavelength (nm) versus Absorption (A. U.) of S_1 and S_2.

3.4 Fourier Transform Infra-red measurement

The FTIR spectra are carried out to analyze the composition and quality of the compound with the help of Perkin Elmer Spectrum Version 10.03.06 (Range 4000 – 400 cm^{-1}) S_1 and S_2 samples are calcinated 300°C and 500°C respectively for 4hrs exhibit characteristic peaks. FTIR spectra for ZnS samples S_1 and S_2 are assigned at room temperature shown in figure 4(a, b) and are listed in table 2.

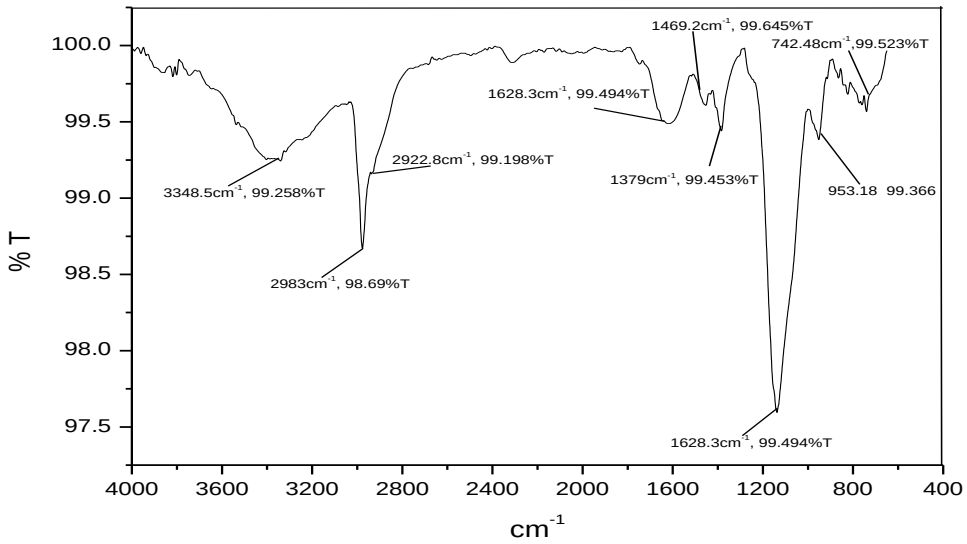

Figure 4a. FTIR spectra of ZnS nanocrystals of samples S_1.

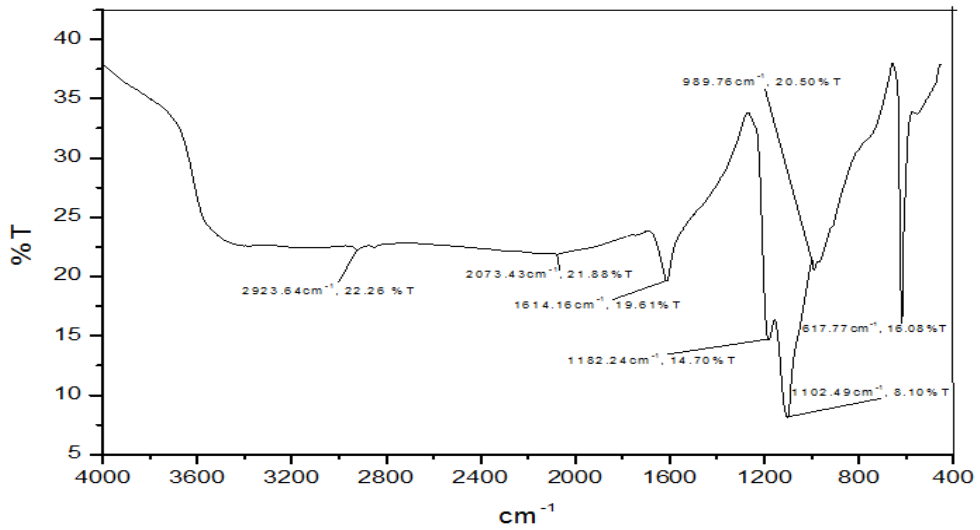

Figure 4b. FTIR spectra of ZnS nanocrystals of samples S_2.

Table 3. FTIR peaks and their assignments for ZnS nanocrystals sample S_1 and S_2.

Assignments	Wave number (cm^{-1}) for ZnS Sample S_1	Wave number (cm^{-1}) for ZnS Sample S_2
O –H stretching	3348	Absent
C – H stretching	2983	2923
Additional weak band and shoulder	2922	2073
Brownsted acidity	1628	1614
Lewis acidity	Absent	1182
Shoulder with asymmetric stretching	953	989
O-H symmetric bending	742	617

The FTIR spectra for Sample S_1 at 3348 cm^{-1}, 2983 cm^{-1}, 2922 cm^{-1}, 1628 cm^{-1}, 953 cm^{-1}, 742 cm^{-1} and some other associated peaks are shown in figure 4a. The peaks appeared at 3348 cm^{-1}, 2983 cm^{-1}, 2922 cm^{-1}, 1628 cm^{-1}, 953 cm^{-1}, 742 cm^{-1} indicates that the presence of CH stretching, additional weak band and shoulder, Lewis acidity (C=C bond), shoulder with asymmetric stretching respectively. The peaks for Sample S_2 at 2923 cm^{-1}, 2073 cm^{-1}, 1614 cm^{-1}, 1182 cm^{-1}, 989 cm^{-1}, 617 cm^{-1}, and some other associated peaks are shown in figure 4b. The peaks appeared at 2923 cm^{-1}, 2073 cm^{-1}, 1614 cm^{-1}, 1182 cm^{-1}, 989 cm^{-1}, 617 cm^{-1} indicates that the presence of OH stretching, Brownsted acidity i.e. vibration of Zn – S, shoulder with asymmetric stretching, OH symmetric bending respectively. The peaks at 3348 cm^{-1} are assigned to OH mode in H_2O molecules. This peak may be due to water present in samples S_1 which were calcinated at 300° C. The O-H stretching absent in sample S_2 and Lewis acidity is absent in sample S_1 clearly indicates that the effect of temperature on ZnS. From this study it is clear that the temperature plays an important role in ZnS nanocrystals synthesized by precipitation method.

IV. Conclusion

The effect of temperature on structural, morphological, optical and chemical properties of ZnS nanocrystals prepared by Coprecipitation method was studied. From XRD studies it is confirmed that samples S_1 and S_2 having wrutzite hexagonal structural with different symmetry.

It is observed that from SEM images that the agglomeration is high in sample S_1 than Sample S_2. It is also found that grain size increases and energy band gap decreases with increasing temperature indicate that temperature plays an important role in structural, morphological and optical properties of ZnS nanocrystals.

The prominent IR peaks of sample S_1 and S_2 were analyzed and assigned. The present of OH stretching in sample S_2 and Lewis acidity in sample S_1. This indicates that change in temperature affects on the chemical composition and quality of the compound.

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