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Effect of Hydrothermal Reaction Temperatures on Structural and Optical Properties of ZnS Nanoparticles

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ABSTRACT

A ZnS nanoparticle was prepared using hydrothermal interaction of zinc acetate with Thiourea in different reaction temperatures (170°C, 180°C, 185°C, 190°C). The structural characterization of synthesized nanoparticle was determined by X-ray diffraction (XRD) which showed a hexagonal structural of ZnS. Scanning electron microscopy (SEM) and energy dispersive spectrum (EDS) analysis were confirmed that the morphology and elemental analysis was formed ZnS nanoparticle. Absorption study has been carried out using UV-VIS spectrophotometer to determine the band gap of ZnS nanoparticle. The optical energy band gap was changed at values equal to (4.16, 4.46, 4.1 and 4.35eV) with different hydrothermal temperatures at (170°C, 180°C, 185°C and 190°C) respectively. However, these values of energy gaps for ZnS nanoparticles are blue shift and larger than that bulk value due to quantum confinement. Fourier Transform Infrared Spectra (FTIR) is recorded in an FTIR spectrometer to verify the presence of ZnS powder. The particle size of ZnS calculated was ranged between 3.5 to 3.9 nm according to Sherrer's equation and the results were compatible when using Effective Mass Approximation (EMA).

Keywords: hydrothermal method, ZnS nanoparticles, XRD, EMA, FTIR.

INTRODUCTION

The semiconductor of Group II-VI compound has very important because of their important unique properties and potential application [1]. ZnS is an important group II-VI semiconductor material with a wide band gap of 3.54 eV at room temperature [2].Because of its wide band gap, it has a high index of reflection and high transmittance in the visible range particularly suitable for host material for a large variety of dopants. Unique properties at the Nano scale and low toxicity made ZnS very interesting by a lot of researchers [3-6]. It has also been widely used in devise applications like filed effect transistor, optical sensor and coating, electroluminescence displays and light emitting material [7-8]. There are several methods to synthesize ZnS nanoparticles such as sol-gel [9], chemical vapors deposition [10], chemical co- precipitation method [11] and hydrothermal method [12]. The hydrothermal method is one of the economical and cost effective methods which can synthesis of nano crystal with different reaction parameters of the sample at a definite temperatures and high vapors pressures. What distinguishes this method also is that the resulting material be of very high purity exceeding the purity of the raw materials used, by varying temperature and pressure control, which are opening conditions for the growth of the crystal and the expulsion of impurities. [13-14].

Experimental Part

The current method of work to prepare the zinc sulfate nanoparticles is hydrothermal at different reaction temperature. A 6.58g of zinc acetate [Zn $(CH_3COO)_2 2H_2O$] were zinc source was dissolved in distilled water and stirred at room temperature then 2.2g of Thiourea [CH_4N_2S]

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as a sulfide source was also dissolved in distilled water and stirred at room temperature. The above reagent were mixed together and poured in to Teflon – lined autoclave, then the autoclave was sealed and maintained at different reaction temperature (170°C, 180°C, 185°C, 190°C) for 2 hours. The products were then washed using water and alcohol for removing impurities. The filtered material dried at room temperatures. The white powder formed was collected for characterization. The X-ray diffraction of all the samples were obtained with Cu-kα radiation of wavelength 1.5406 °A, the optical absorption was recorded using (SHIMADZU. UV-3100).

Results and discussion:

X-ray Diffraction (XRD)

The Figure 1 show that the effect of reaction temperatures on XRD of ZnS nanoparticle.

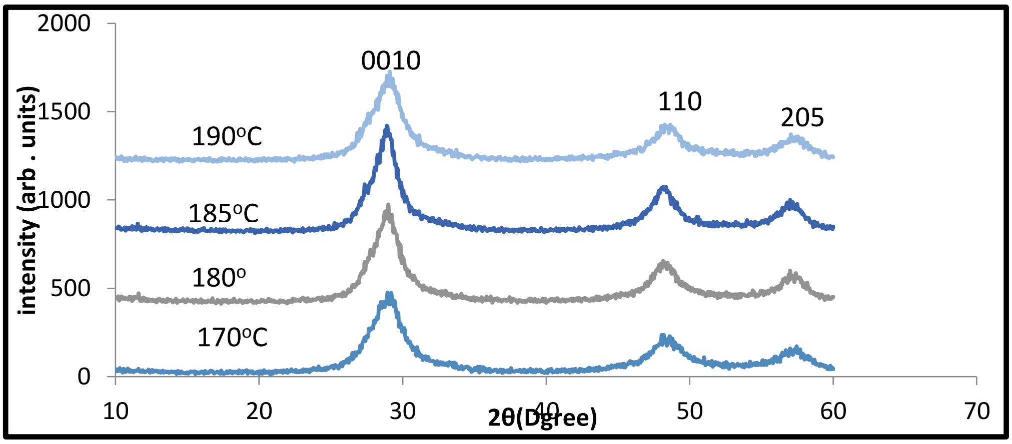


Figure (1) XRD of ZnS nanoparticle using hydrothermal method at different reaction temperature

The XRD patterns display the formed of ZnS nanoparticle, where all diffraction peaks is well indexed to the standard diffraction pattern of wurtzite-10H hexagonal ZnS phases which matches well in JCPDS – card (12-0688). It also can be observed that the diffraction peaks corresponds to the (0010), (110), and (205) lattice planes. All peaks of were broad which indicates the formed of ZnS was in nano size. The diffraction angle of the ZnS nanoparticle (170°C, 180°C, 185°C, 190°C) was shifted slightly toward to high value of 2θ. The increase of diffraction angle can be expected to lattice contraction occur because of higher surface to volume ratio.

The lattice parameters (a) and (c) were calculated according to equation below.

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2} \qquad \cdots (1)$$

Where d is the Interplaner spacing of the crystal planes, h, k and l are Miller indices, (a, c) are lattice constant. The diffraction peaks in XRD pattern of ZnS hexagonal-10H structured with lattice parameters of a = 3.82 °A and c = 31.2 °A which are different of the present result according to Figs. 2 and 3 display the calculating lattice constant (a) and (c) of ZnS with reaction temperature using hydrothermal method. It is shown that the reaction temperature is played on important parameters to prepare ZnS hydrothermally. The calculated lattice constants are close to standard when the reaction temperature increased and reached at optimum value at 185°C as shown in Figs. 2 and 3.

The crystallite size of the sample is calculated using Scherer's formula.

$$D = \frac{k\,\lambda}{\beta \cos\theta} \qquad \cdots (2)$$

Where D is the average crystal size, K is the proportionality constant with a value taken to be 0.9, λ is the wavelength of the Cu- K_a (1.54056 °A), θ is the angle of diffraction and β is the width at half maximum in radians of XRD peaks.

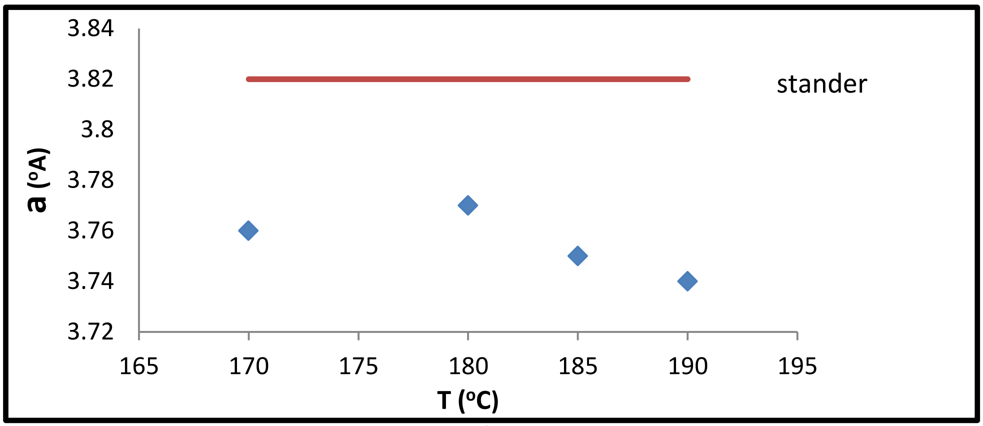
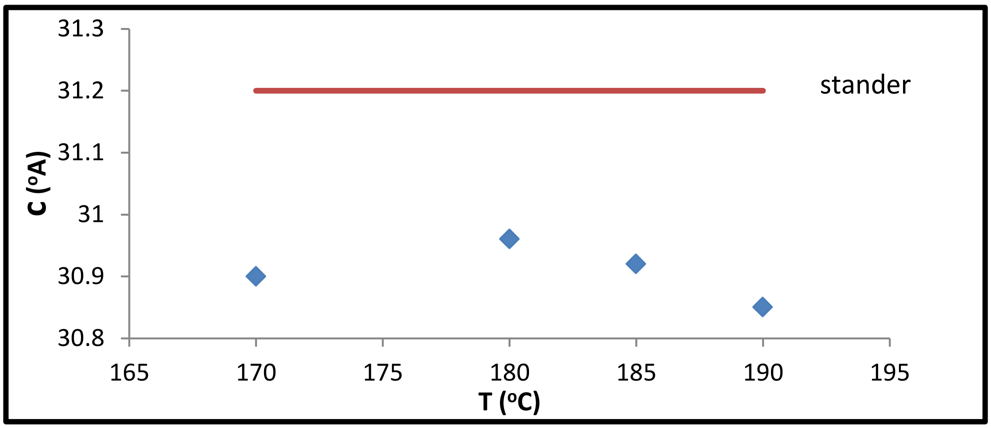


Figure (2) lattice constant (a) of ZnS with reaction temperature



Figure(3). Lattice constant (c) of ZnS with reaction temperatures

To understand the departure of lattice constants of ZnS from the standard as shown in Fig.2 and 3.It shows the lattice parameters (a, c) change with changing hydrothermal temperatures due to compressive strains indicated results of the reduced lattice parameters of the crystal.The lattice strains (e_{cc}) and (e_{aa}) in the lattice along the c-axis and a- axis of ZnS nanoparticle has estimated from the lattice parameters using equation [15].

$$e_{aa} = \frac{a - a_o}{a_o} \qquad \cdots (3)$$

$$e_{cc} = \frac{c - c_o}{c_o} \qquad \cdots (4)$$

Where (c) and (a) is the lattice parameter of ZnS nanoparticle calculated from XRD pattern, (c_o) and (a_o) is the lattice parameter for the ZnS bulk for hexagonal crystal.The lattice strains (e_{aa}, e_{cc}) have negative value due to compression stresses along a-axis and c-axis .It shows the lattice strains (e_{aa}, e_{cc}) have high value at 180°C. While it decreases with increasing hydrothermal temperatures at (185°C, 190°C) are shown in Table (1).XRD broadening could also be due to the strain in addition to the crystalline size of the particle, thus attempt has been mad to estimate the average strain of the ZnS nanoparticle using stokes – Wilson equation(5).

$$\text{Strain } (\varepsilon) = \frac{\beta}{4\tan\theta} \qquad \ldots (5)$$

The Dislocation density (δ) was also determined from the relation (6) [16].

$$\delta = \frac{15\varepsilon}{aD} \qquad \ldots(6)$$

Where (ε) is average strain, a is lattice parameter, D is average particle size.

Table (1) characteristics of ZnS nanoparticles estimated from XRD Data

Hydrothermal Temperatures (^oC)	2 Theta (deg)	Interplaner Spacing d (^{o}A)	Grain Size (nm)	Lattice Constant (^{o}A)		Average Strain		Average Dislocation Density		Lattice Strain	
				a	c	$\varepsilon_{str(a)}$	$\varepsilon_{str(c)}$	δ_a	δ_c	e_{aa}	e_{cc}
170	28.866	3.0904	3.83	3.76	30.9	0.0191	0.035	0.0017	0.037	-0.015	-0.0096
	48.466	1.8767									
	57.151	1.6104									
180	28.846	3.0925	3.56	3.77	30.96	0.0199	0.038	0.0018	0.043	-0.013	-0.0076
	48.204	1.8863									
	57.116	1.6113									
185	28.809	3.0964	3.99	3.75	30.92	0.018	0.034	0.00155	0.033	-0.018	-0.0089
	48.164	1.8877									
	56.994	1.6145									
190	28.911	3.0857	3.76	3.74	30.85	0.0182	0.036	0.00156	0.038	-0.020	-0.0112
	48.427	1.8781									
	57.231	1.6083									

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy gives qualitative information about the way in which the adsorbed surfactant molecules are bound to the surface of ZnS nanoparticle. FTIR spectra of the ZnS Nanoparticles were recorded in the range from 100 to 4000cm^{-1}.Fig. 4 shows the FTIR spectra of as prepared ZnS nanoparticles

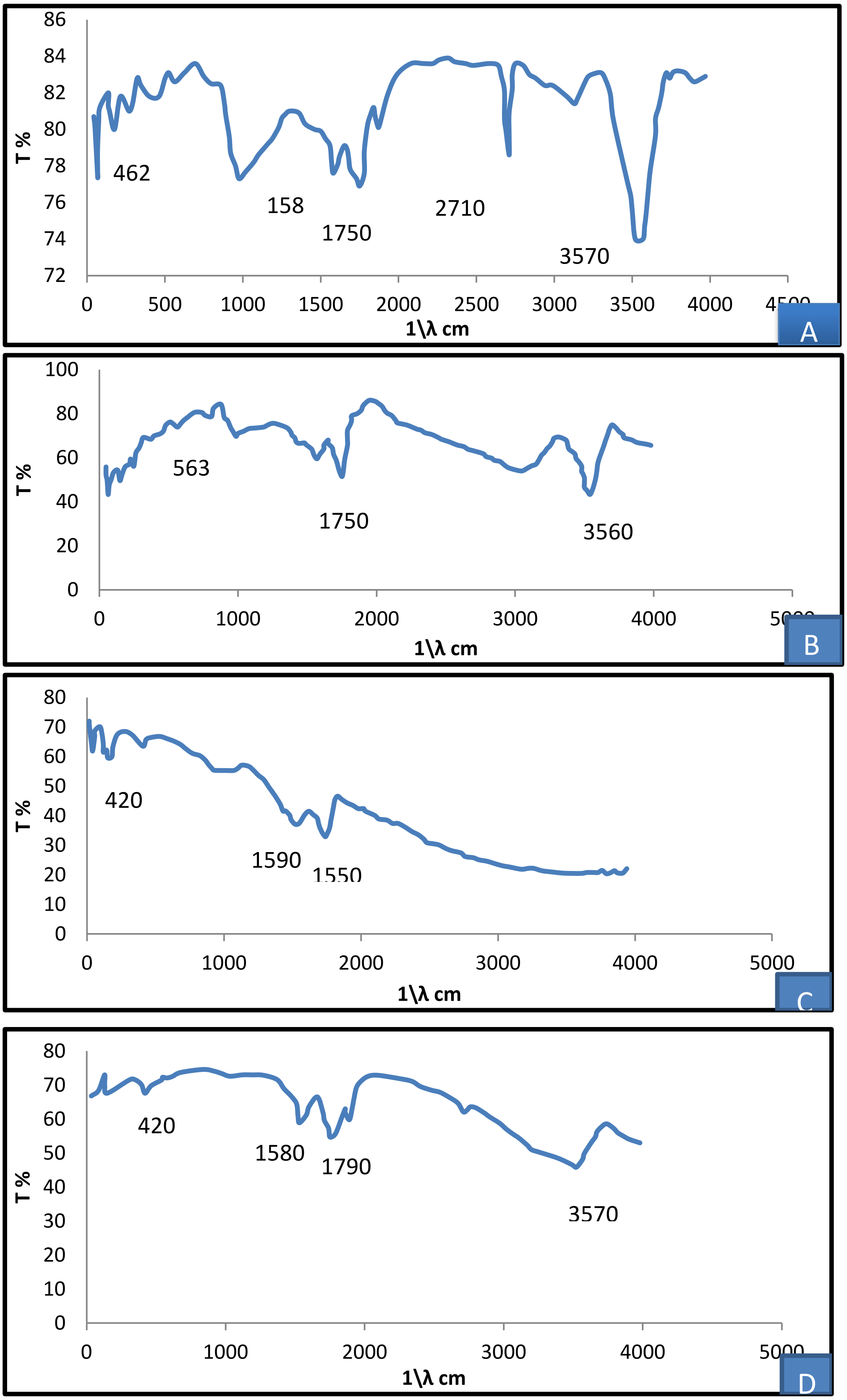


Figure (4) FTIR of ZnS nanoparticles before annealing (500oC at (A) 170°C (B) 180°C (C) 185°C (D) 190°C

The FTIR spectra of ZnS nanoparticles are measured at different hydrothermal temperatures. The broad peak at 3570cm^{-1} corresponding to O-H stretching vibration indicates existence of water in the surface of nanoparticle, the peak at 1750cm^{-1} and 1550cm^{-1} correspond to stretching vibration of C=O and C-H group in acetate [17] , the peak at 563cm^{-1} (stretching) [18] and 420 cm^{-1} corresponds to Zn – S bending, the peaks 1580cm^{-1} correspond to N-H bend and 1590cm^{-1} corresponds to C=C stretching.

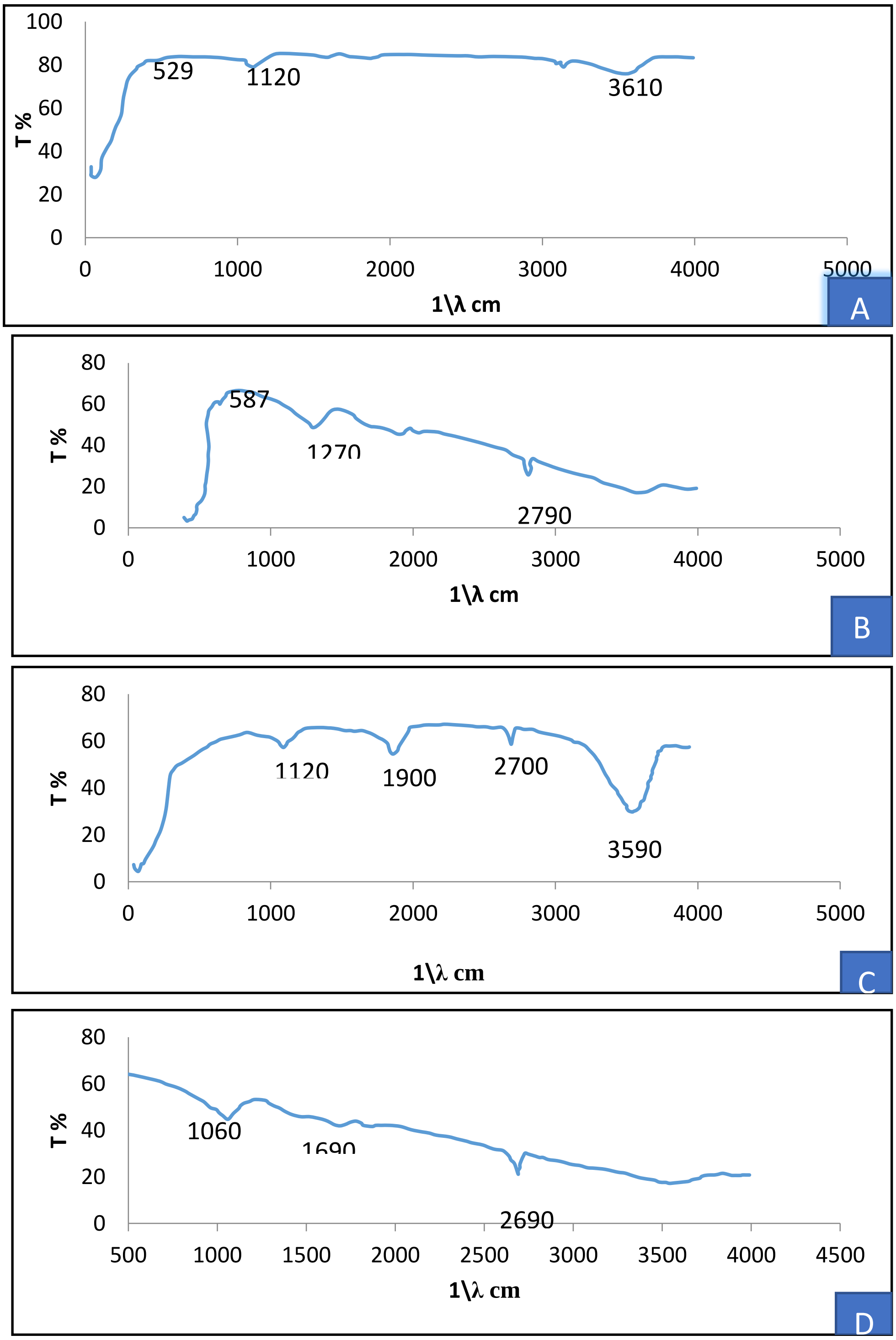


Figure (5) FTIR of ZnS nanoparticles after annealing (500°C) (A) 170°C (B) 180°C (C) 185°C (D) 190°C

Fig 5 shows the FTIR for ZnS NPs after annealing powder to 500^{O}C. The absorption bands are almost similar with before annealing expect the ZnS band at 587cm^{-1} is negligible shifting due to annealing for ZnS nanoparticles and 2690 cm^{-1} corresponds C-Hstretching vibration, the peaks1690cm^{-1} corresponds N-H stretching vibration [19] which are show in Table 2.

Table (2) FTIR of ZnS nanoparticles

Wave number cm^{-1}		Bond
Before annealing	After annealing	
420		Zn –S bending
563	587	Zn-S stretching
1580	1690	N-H bending
1590		C=C stretching
1750		C=O stretching
3570	3610 3590	O-H stretching
	2690	C-Hstretching

Scanning Electron Microscopy (SEM)

The SEM images have been studied of the particle morphology and size distribution for the synthesized ZnS nanoparticle. SEM images of ZnS nanoparticles prepared at different hydrothermal temperatures (170^{o}C, 180^{o}C, 185^{o}C, 190^{o}C) are shown in Fig (6). At different hydrothermal temperatures, it shows all the SEM micrographs were spherical and agglomeration due to drying process. The average particle sizes were (180nm) which agrees with reference [20]. The sizes of the particles were high than the values found from XRD data. At 180^{o}C it shows the particle size is small and homogenous than other hydrothermal temperatures.

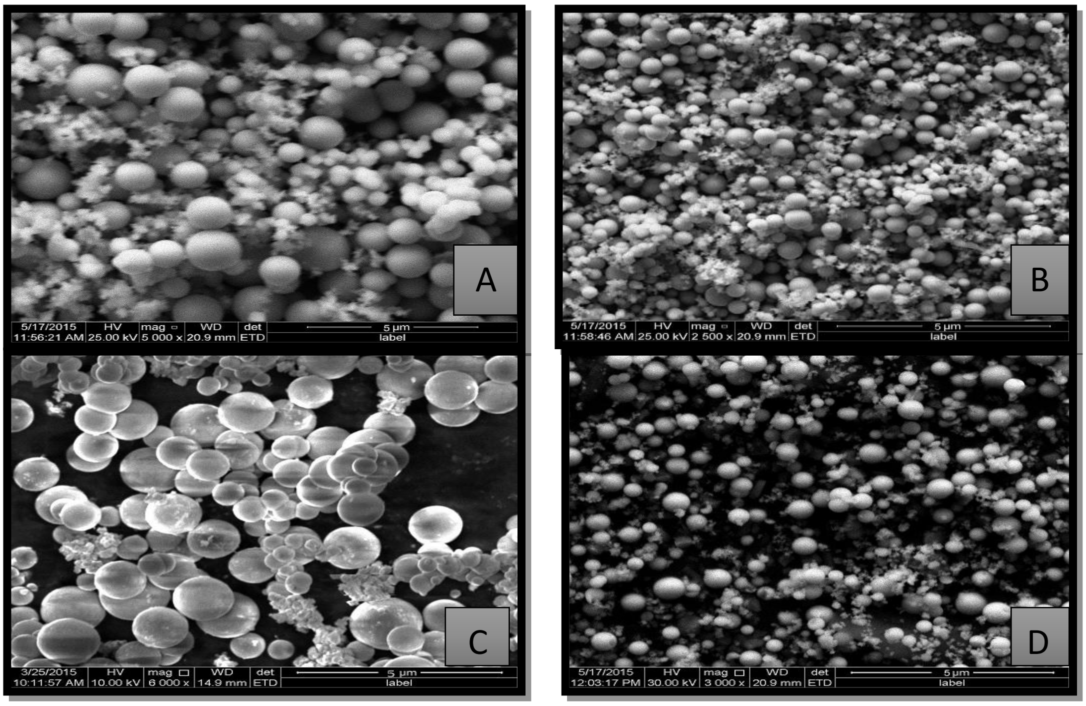
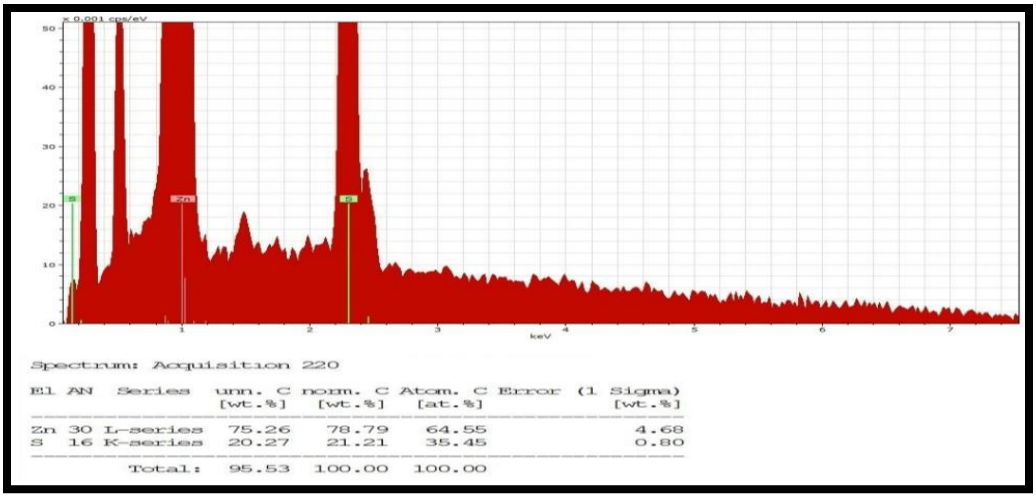


Figure (6) SEM of ZnS nanoparticles at hydrothermal temperatures (A) 170^{o}C (B) 180^{o}C (C) 185^{o}C (D) 190^{o}C

The contradiction associated with the size of ZnS nanoparticles found from XRD and SEM may be because the SEM shows the horizontal dimension of the particles, whereas the XRD gives the regularity in the atomic arrangement. Perhaps the horizontal dimension is of order of a few ten of nanometers, but the individual nanoparticle with regular atomic lattice extended only up to a few nanometers [20].

EDX analysis of smaller crystallite samples were performed to find their elemental composition. Fig (7) where the elements data are shown in Table Fig (7). These data confirm that the prepared powder consists only of ZnS compound.



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Spectrum: Acquisition 220

El AN  Series   unn. C norm. C Atom. C Error (1 Sigma)
                [wt.%]  [wt.%]  [at.%]         [wt.%]
------------------------------------------------------
Zn 30 L-series  75.26   78.79   64.55            4.68
S  16 K-series  20.27   21.21   35.45            0.80
------------------------------------------------------
        Total:  95.53  100.00  100.00
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Figure (7) EDX of ZnS nanoparticles

UV-Vis spectroscopies

The optical properties of ZnS nanoparticles are determined from absorption of different hydrothermal temperatures (170^{o}C, 180^{o}C, 185^{o}C, 190^{o}C) in wavelength range (200-900nm). The study of optical absorption is important to understand the behavior of semiconductor nanoparticle. Optical excitation of electron across the band gap is strongly allowed producing an abrupt increase in absorption at the wavelength corresponding to the band gap energy (Eg). This advantage of the optical spectrum is known as the optical absorption edge. High – quality ZnS structures have well ultraviolet optical properties at room temperature. Fig (8) shows the optical absorption spectra of ZnS nanoparticle, the absorption edge was obtained at shorter wavelength compared to the absorption edge of the bulk material due to the increases in the band gap as a result of the quantum confinement effect as well as the discrete energy band.

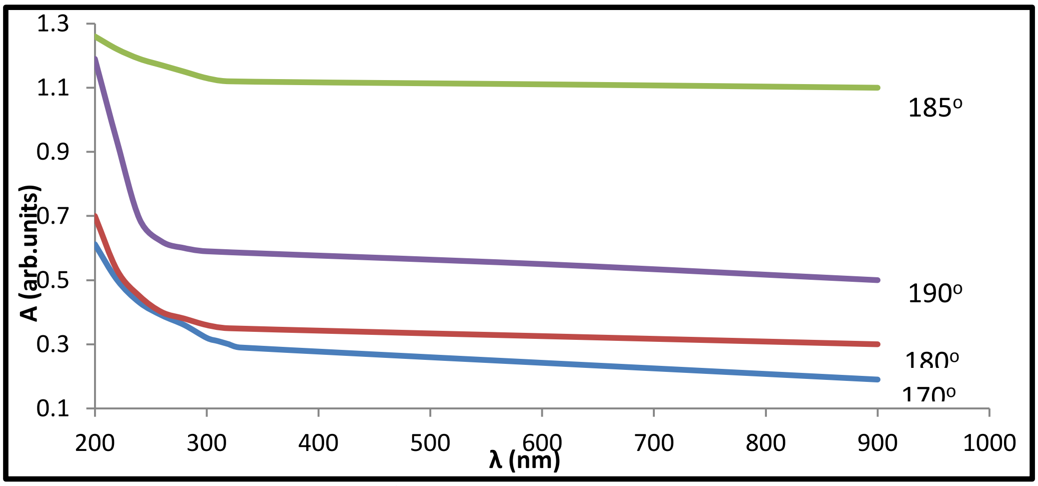
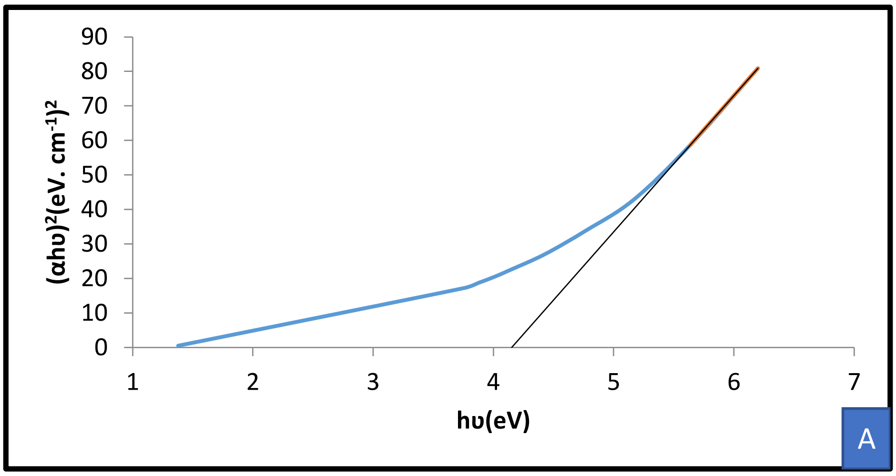


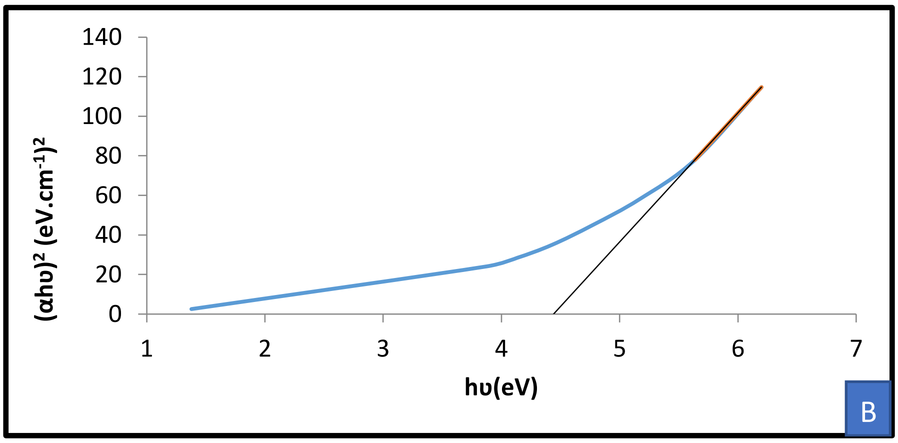
Figure (8) Absorption spectra of ZnS nanoparticles at hydrothermal temperatures

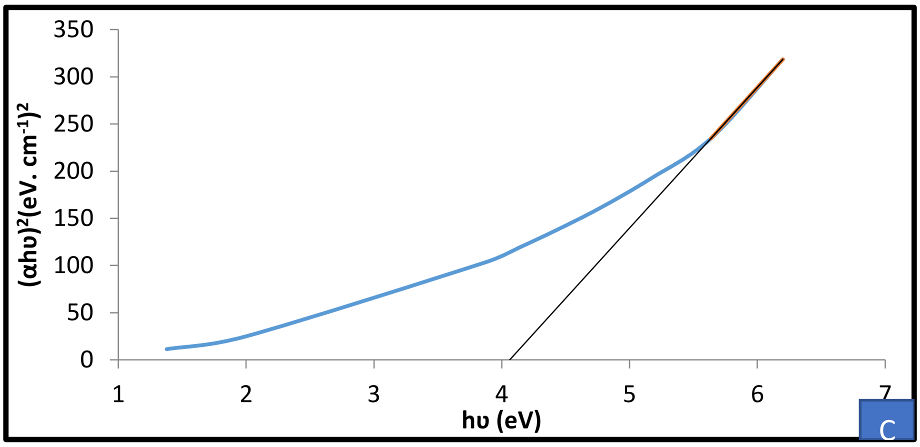
The band gap energyof synthesized ZnS nanoparticles have been determined by using the Tauc's relation [21].

$$\alpha h\upsilon = A\,(h\upsilon - E_g)^{1/2} \qquad \dots(5)$$

Where A is constant, hυ is photon energy, Eg is optical band gap of the nanoparticle, α is absorption coefficient. Fig (9) shows the optical band gap of ZnS nanoparticles is high and blue shifted than the bulk (3.9eV) due to quantum confinement where the particle size in Nano rang. The optical band gap change with increasing the hydrothermal temperatures. At 180°C it has the largest value of energy gap and less value of grain size due to quantum confinement .Bur's has proposed a theoretical model relating the effective band gap of material with the particle size. The simple model predicting the variation of exaction energy with particle size is based on the effective mass approximation. The lowest excited state of the crystallite is assumed to be the ground state of an electron hole pair, the ground state energy of an exaction or increase in effective band gap as a function of the particle size is determined from relation (6). Table (3) shows the energy gap for different hydrothermal temperatures are changed with particle size from Bur's equation. It shows at 180oC has less value of particle size from Bur's and grain size from Scherrer and larger value of energy gap due to effect quantum confinement. While at 185°C it has largest value of particle size from Bur's and grain size from Scherrer and less value of energy gap.







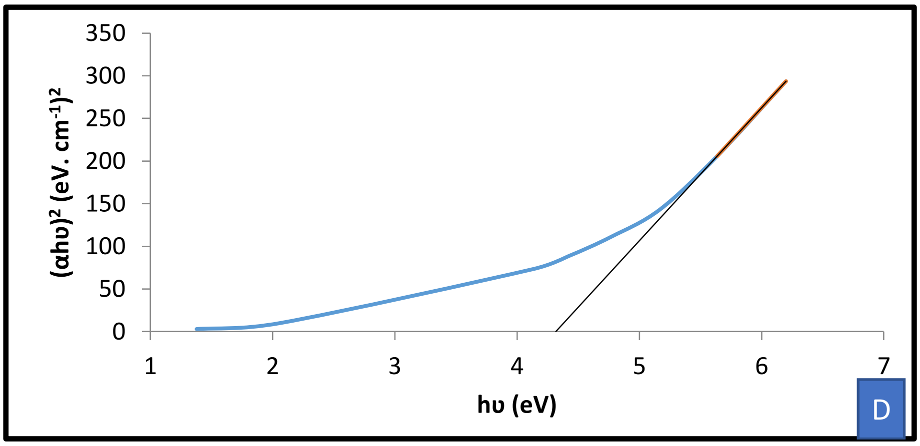


Figure (9) .(αhυ) ^{2} as a function of photon energy of ZnS nanoparticles at (A) 170°C (B) 180°C (C) 185°C (D) 190°C

The particle size calculated from Bru's equation [22].

$$\Delta E = \frac{\hbar^2\pi^2}{2\,r^2}\left(\frac{1}{m^*{}_e} + \frac{1}{m^*{}_h}\right) - \frac{1.8\,e^2}{4\pi\varepsilon_o\varepsilon_r r} \qquad \cdots(6)$$

Where the first term is the bulk band gap energy, the second the kinetic energy of both the electron and the hole in a spherical box. The third term is based on the Columbic attraction between the electron and the hole and the last one corresponds to the correlation between two particles.

Figure (10) UV-Vis spectroscopies

Table(3). Band gap and comparison of particle size estimated by EMA formula and XRD

Reaction Temperatures(^{o}C)	Energy gap(eV)	Particle size from Brus Eq(nm)
170	4.15	3.3
180	4.45	2.2
185	4.1	3.7
190	4.35	2.4

CONCLUSION

1-The ZnS nanoparticles were prepared using hydrothermal method which showed the adoption of sizes on the hydrothermal temperatures.

2-The XRD showed that the ZnS nanoparticles have hexagonal structures and the lattice parameters (a, c) are less than standard values.

3-The optimal hydrothermal temperature was 180^{o}C because it has less value of grain size than larger band gap.

4-The lattice strains (e_a, e_c) of pure and doped ZnS have negative values due to compression stresses along a-axis and c-axis.

5-The ZnS groups were found in different hydrothermal temperatures as a result from FTIR spectroscopy.

6-The SEM and TEM spectroscopy of pure and doped ZnS were exhibits spherical and agglomeration of particles.

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