زانکۆی سەلاحەدین – هەولێر

Salahadin university – erbil

Optical properties of ZnS-NPs prepared by hydrothermal technique

Research project

Submitted to department of physics in partial fulfilment of the
requirements for the degree of BSc in physics

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Abstract

In this research, zinc sulfide nanoparticles (NPs) were synthesized by simple and efficient methods. These approaches include hydrothermal methods. Zinc nitrate hexahydrate $(Zn(NO_3)_2).6H_2O$ were used as Zn sources, and theoria was used as a S source. The nanoparticles were created at three different temperatures, and the optical properties of ZnS nanoparticles (transmission, absorption, and energy band gap) were observed by UV-vis spectroscopy. First, the transmittance spectra measured at wavelength range (200–1100 nm) show that it increases as the temperature increases, the absorbance spectra measured at wavelength range (200–1100 nm) show that it is high at the invisible near infrared region and low at the ultraviolet region at all temperatures; the UV–vis spectra show that by increasing the amount of sulfur source and increasing the reaction time, λ max shifts towards lower wavelengths, and the band gap is in the range of 3.8–3.9 eV for all of the samples.

Chapter One (General Introduction)

1.1- Introduction

Nano structures are materials that in at least one dimension are less than 100 nm (N karrim et al 2010). Zinc (Zn), chemical element, a low-melting metal of Group 12 (IIb, or zinc group) of the periodic table, that is essential to life and is one of the most widely used metals (T editors of encyclopedia 2022). Sulfate, also spelled Sulphate, any of numerous chemical compounds related to sulfuric acid, H_2SO_4. One group of these derivatives is composed of salts containing the sulfate ion, SO_4^{2-}, and positively charged ions such as those of sodium, magnesium, or ammonium; a second group is composed of esters, in which the hydrogen atoms of sulfuric acid have been replaced by carbon-containing combining groups such as methyl (CH_3) or ethyl (C_2H_5) (T editors of encyclopedia 2022). Zinc sulfide (ZnS) is the inorganic compound Semiconductor, with yellow-white color (zhan et al 2014). In many years research has been made in order to find the characteristic properties on nano materials and nano particles (zhan et al 2014) stated that Zns has the following properties. Their structure is cubic and sometimes hexagonal, in electricity it's a N type semiconductor and its optical energy band gap is wide nearly 3.4 ev . some of its applications are used in solar cell systems ,optoelectronic devices and X-ray detectors (N karrim et al 2010). ZnS nanostructures have gained a lot of attention that can be attributed to the properties arising from their size in the nanometer range (Gupta et al., 1997). Nanobelts (Jiang et al., 2003; Meng et al., 2003), nanowires (Zhu et al., 2003; Verna et al., 1995), nanocables, nanorods, nanocable- aligned tetra pods, nanoparticles (Sugimoto et al., 1998). the electrodeposition of ZnS thin films from an aqueous solution using zinc sulphate, sodium thiosulfate and triethanolamine solutions at room temperature. In order to get good quality ZnS thin films, the preparative parameters such as deposition time (15, 30 and 60 min) and deposition potential (−1.0, −1.1 and −1.3 versus SCE) were optimized. The deposited thin films were characterized by X-ray diffraction and atomic force microscopy for their structural and surface morphological characteristics, respectively (N karrim et al. 2010).

1.2 - Structure and properties of ZnS:

Zinc sulfide (ZnS) is a highly important semiconductor material which belongs to the group of II–VI wide band gap semiconductors. In nature, ZnS is a white- to yellow-colored powder or crystal (O'Hare et.al, 2007). It exists in two crystallographic forms having cubic (sphalerite or zincblende) or hexagonal (wurtzite) crystal structure as show in Fig. (1.1) (Scott, and Barnes, 1972). The hexagonal form is a thermodynamically metastable phase, which is usually stable at very high temperature, while the cubic form is more thermodynamically stable phase at low temperature (O'Hare et.al, 2007). ZnS has a direct transition type band structure. The cubic form has a band gap of 3.54 – 3.6 eV, whereas the band gap of hexagonal form is the highest being 3.74 –3.87 eV (Shao, et.al, 2003).. ZnS exhibits high transparency over the wide spectrum region between 380 nm and 25 µm. The electrical resistivity is in the order of 10^4 Ω.cm with n-type electrical conductivity. It can be doped as both n-type and p-type semiconductor, which is unusual for the II–VI semiconductors (Hoa, et.al, 2009).

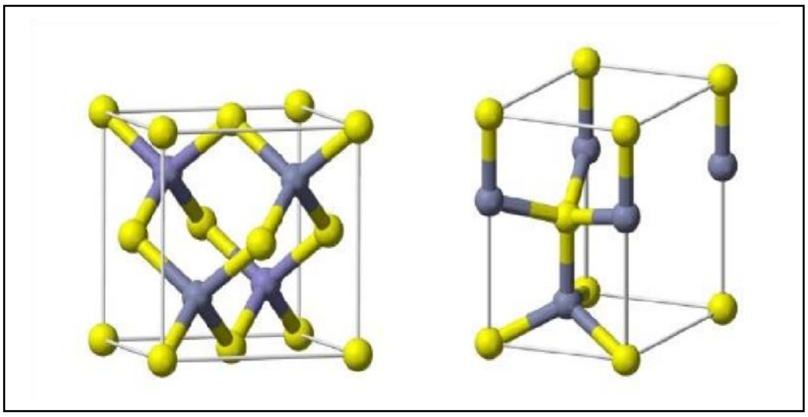


Fig. (1.1): The schematic diagrams of the zinc blende (left) and wurtzite (right) crystal structures of ZnS.

1.3 - Aims of the work:

The main aims of the present work are:

1. Preparation of zinc sulfide (ZnS)-NPs by hydrothermal technique.
2. Prepare ZnS-NPs at different growth temperature in order to obtain the optimized and better quality powder.
3. Study the effect of the growth temperature on the optical prepared of the prepared NPs.

Chapter Two

Experimental Techniques and Characterization Tools

2.1 Introduction

This chapter is divided into two sections. The first consists of a description of the experimental techniques used in this study to fabricate ZnS-NPs using the hydrothermal method. In this method, Zn (NO3) and theoria (cs(NH2)2 with deionized (DI) water are used as a stratifying material, and the effect of temperature on the growth of hydrothermal at three different temperatures (100, 140, 180 0C) has been studied. Lastly, using UV-VIS spectroscopy, the optical properties of the prepared powder have been evaluated. The complete experimental procedure is depicted in Figure 3.1.

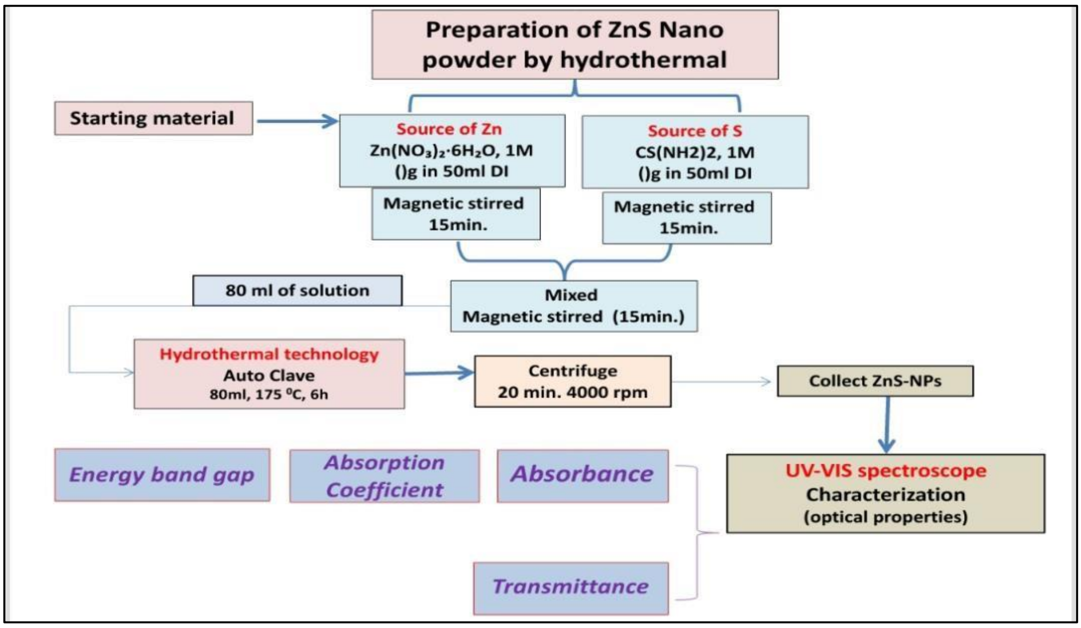


Fig. 3.1 Experimental procedures flowchart.

Part One

ZnS-NPs Preparation

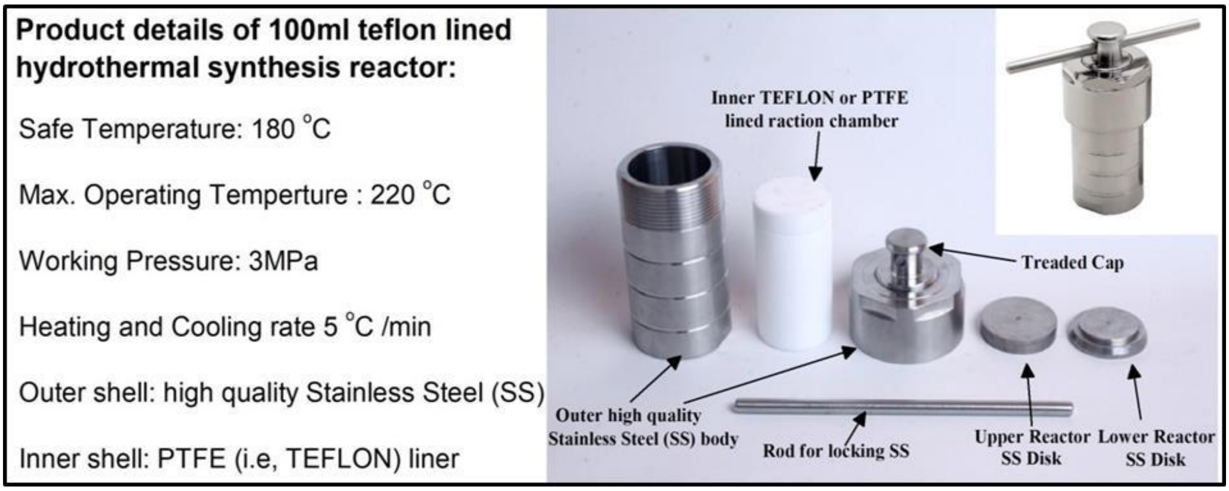
2.2- Hydrothermal/Solvothermal Technique

Hydrothermal method is one of the most common and effective synthetic routes to fabricate the nanomaterial with a variety of morphologies. Hydrothermal synthesis is a heterogeneous chemical reaction in the presence of aqueous solvents (water) above 100˚C at pressures greater than 1 atmosphere in a closed system in order to dissolve and recrystallize materials which are relatively insoluble under normal conditions. Meanwhile solvothermal is totally similar to the hydrothermal method, the only difference between them is the use of non-aqueous (organic) solvent such as ethanol, methanol, etc. instead of water (Li et al., 2015).

2.3- Instruments for Hydrothermal/Solvothermal Processes

A vessel/container (lined reaction chamber) with stand highly corrosive solvent at high temperature and pressure is the main part of a hydrothermal/solvothermal set up, which is known as autoclave reactor (Wang, 2003).. The reactions take place in steel autoclaves, and inside is the Teflon vessels in the range 100-220˚C. Teflon is an inert material, so it does not get into the reaction with the starting materials. Teflon vessels are filled with the starting materials (transition metal oxide, organic component, secondary metal salt, and phosphoric acid) with the reaction solution (water was used for hydrothermal and organic solution used for solvothermal process). To provide enough pressure, minimum 50% of the reaction cup is filled with the solvent. Then, Teflon vessels are placed in steel autoclaves and putted in the oven (Shock, et al., 1992). The reactions are kept for some hours or some days at a constant temperature above 100˚C. The system is sealed well in order to avoid any solvent leakage during heating process. The sealed autoclave is kept into the electrically heated oven for providing desired temperature. On application of the desired hydrothermal synthesis temperature, an autogenously pressure is generated within the autoclave. At the end of the required reaction time, the reaction cups are cooled slowly to room temperature. Crystals that have best quality and size are formed in this cooling period. After that, the products are washed several times with pure water in order to remove the solvent traces from the products (Li et al., 2015).

In this work, a 100 ml Teflon reactor (Model: Tefic Biotech) was used, as shown in Fig.. The reactor consists of inner Teflon or (PTFE) lined reaction chamber shelled with high quality Stainless Steel (SS) body. Also, upper and lower reactor Stainless Steel (SS) disk to cover the upper and bottom of Teflon chamber which closed with stainless steel cup engraved from inside supplier with treaded cup for well sealing.



Product details of 100ml teflon lined hydrothermal synthesis reactor:

Safe Temperature: 180 °C

Max. Operating Temperture : 220 °C

Working Pressure: 3MPa

Heating and Cooling rate 5 °C /min

Outer shell: high quality Stainless Steel (SS)

Inner shell: PTFE (i.e, TEFLON) liner

Fig. 3.4 Teflon lined autoclave 100 mL shows (Steel autoclave and Teflon vessel) with Product details

In hydrothermal synthesis, the grain size, particle morphology, microstructure, and phase composition can be controlled by tuning parameters such as temperature, process duration, and pH of the solution (Zhou et al., 2008). Furthermore, the reaction media plays an important role since the properties of the solvent can be adjusted by modifying the type and volume ratio of the solvent, where the solvothermal process named due to the type changing of the solvent (Deng et al., 2002).

2.4- Solutions Preparation

To create a solution and extract the nano powder from it we used two materials the first one was **$CS(NH_2)_2$** we used (1.9)g of it and add it into (50)ml water and stirred it for 15 minutes on the magnetic stirrer without heat , then we used the second one which is **$Zn(NO_3)_2{\cdot}6H_2O$** we added (7.43)g into (50)ml water and stirred it for 15 minutes on the magnetic stirrer without heat , then we mixed both solutions and stirred it for 20 minutes on the magnetic stirrer without heat , after that we put it inside the Teflon and put it inside the oven for 6 hours .

Part Two

Measurements and Analytical Techniques

The optical property study forms a considerable part while evaluating a thin film performance. The photon absorption, transmission characteristics, directs and indirect band-gap evaluation is some of the important parameters that are determined to characterize a thin film.

The optical transmittance (T%) and absorbance (A%) spectra of the samples were carried out at room temperature by (Shimadzu UV-VIS mini 1240) spectrophotometer in the wavelength range (200-1100 nm). The spectral distributions of transmittance for the ZnS-NPs were determined. The following steps can be used to calculate the optical measurements:

-The absorption coefficient(α)can be computed from the absorbance spectrum using the formula (Schroder, 2006):

$$\alpha = 4\pi k/\lambda, \quad \ldots\ldots\ldots\ldots\ldots\ldots.. \quad (1)$$

- The photon energy (hv) as a function of wavelength is calculated by (Islam, 1997):

$$hv = hc/\lambda \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots. \quad (2)$$

Where (λ) is the wavelength of the incident light.

The general band gap formula is given as (Schroder, 2006):

$$a(hv) = B\ (hv - Eg)\gamma \ \ldots\ldots\ldots\ldots\ldots\ldots..(3)$$

Where(B) is an energy-independent proportionality constant, and $\gamma = 1/2, 3/2, 2, 3$ for direct allowed, direct forbidden, indirect allowed, and indirect forbidden transitions respectively.(Eg) is the band gap energy.

-The band gap energy can be obtained by extrapolating the linear portion of $[a(hv)]^2$ vs. (hv) curve to zero absorption, where this is the usual method for the determination of the value of the energy band gap from absorption spectra (Schroder, 2006), and (Marinkovic, 2013).

Chapter three

Result and discussion

3.1- Introduction:

The optical characterization of prepared Nano-podwer gives information about the physical properties such as the band gap energy and band structure, etc... To study the optical properties of the films, the optical transmittance and absorption spectra of the all films were prepared at different temperatures (100, 140, 180 ^{o}C) by hydrothermal method.

3.2 -The transmittance spectra:

The optical transmittance spectra of ZnS-NPs prepared at different temperatures were measured at room temperature in the wavelength range of (200 - 1100) nm, as shown in Fig (3.1). From this figure it’s observed that the percentage of transmission increase with increase the temperature in the low absorption region, this is attributed to improvement in perfection and stoichiometry of the films.

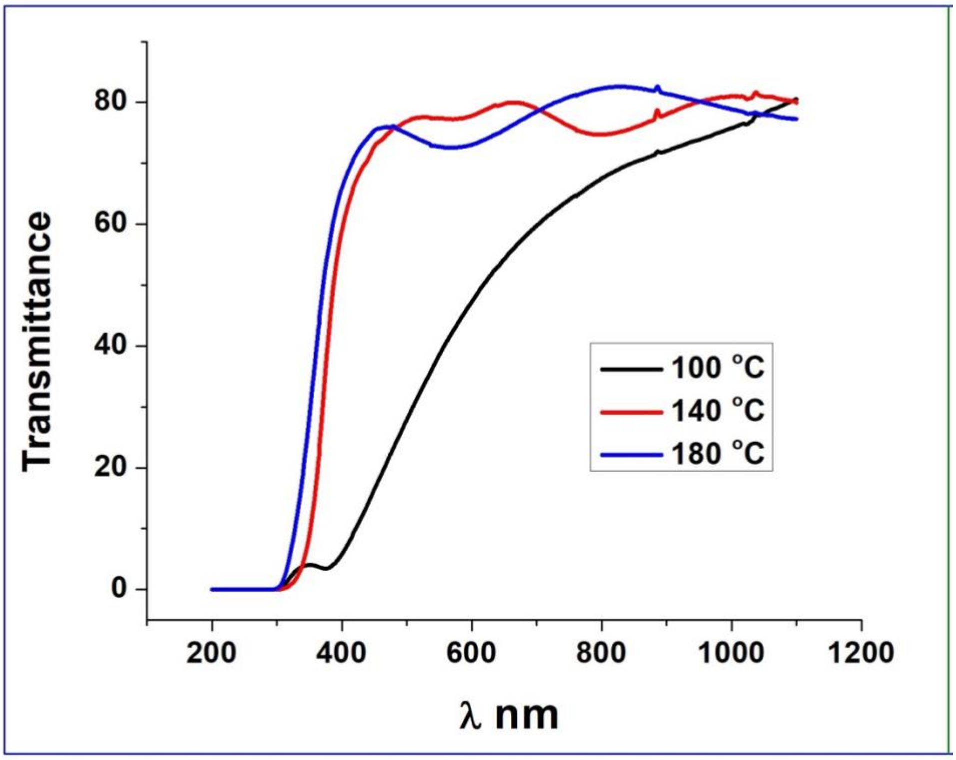


Fig. (3.1): Transmittance spectra versus wavelength for ZnS-NPs at different temperature.

3.3 - The absorbance spectra:

The optical absorbance spectra of ZnS-NPs prepared at different temperatures were measured at room temperature in the wavelength range of (200 - 1100) nm, as shown in Fig. (3.2). From this figure it was observed that the absorption is high at invisible near infrared region , however the absorption is low at ultraviolet region, at all temperatures it has the most absorption rate near the infrared region then the absorption rate decreases as we go to the ultraviolet region.

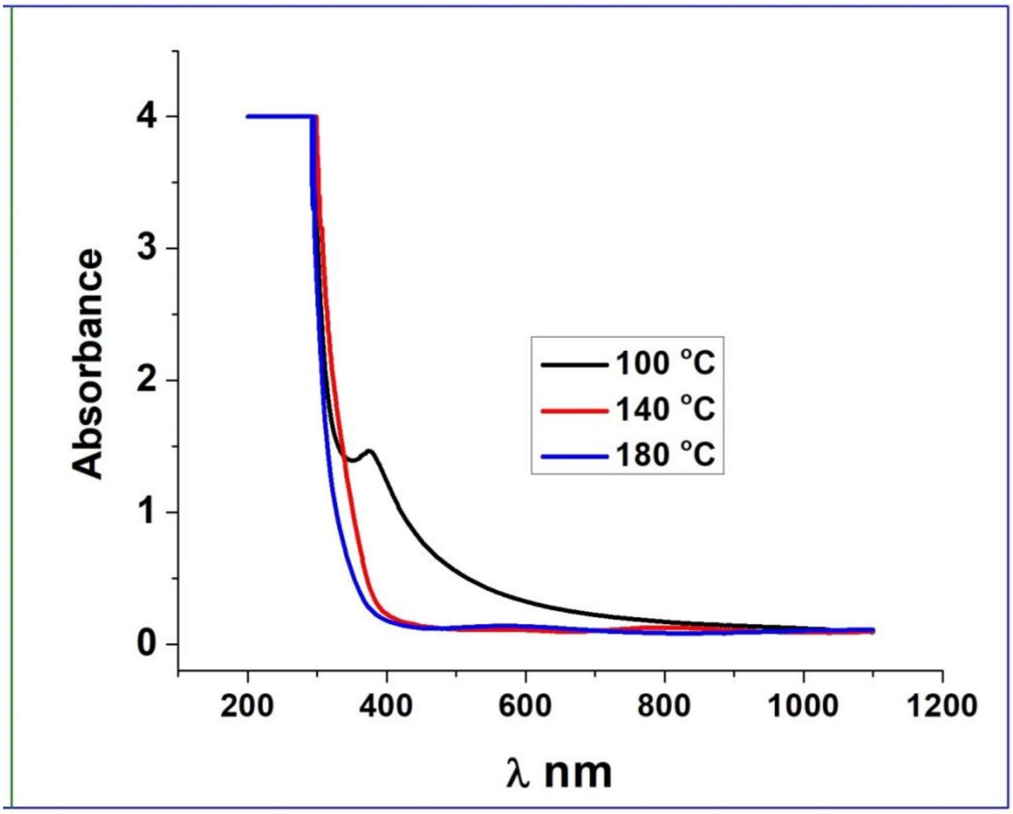


Fig. (3.2): absorbance spectra versus wavelength for ZnS-NPs at different temperature.

3.4 - The optical absorption coefficient spectra:

The optical absorbance coefficient of ZnS-NPs was calculated by using equation (1). Fig.(3.3) shows the variation of absorption coefficient α against wavelength for three different growth temperatures. The α exhibits a steep rise for all samples near the absorption edge. The α is nearly similar to absorption which shows that the transition must correspond to a direct electronic transition.

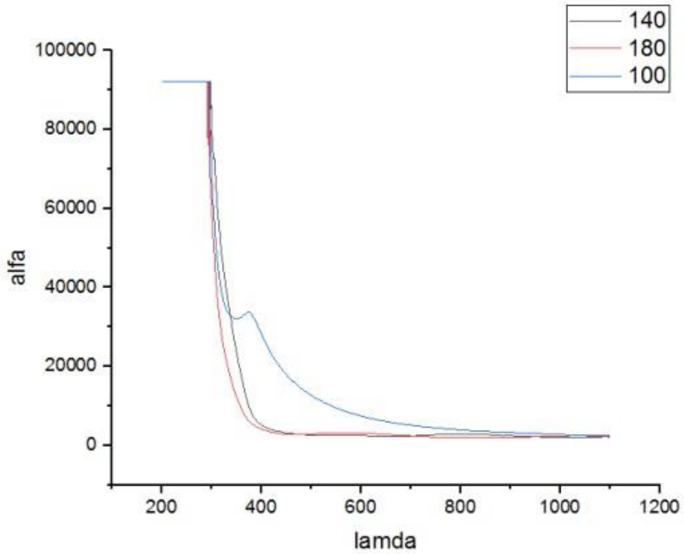


Fig. (3.3): Absorption coefficient versus wavelength for ZnS-NPs ***at different temperature.***

3.5 - The optical band gap energy:

The data point near the absorption edge can be used to determine the band gap (E_g) of the samples using equation ($\alpha h v = (h v - Eg)$). Fig. (3.4) shows the variation of [$\alpha h v^2$] against (hv) for ZnS-NPs prepared by hydrothermal technique at different temperatures. the plots near the absorption edge indicates that ZnS-NPs is a direct band gap nature. The band gap is determined by extrapolating the straight line portion of the graph to the energy axis at α=0. Our results lie in the range of (3.9 eV), which is a good agreement with other researchers. The band gap energy was found to be (3.93eV) at[180c] and (3.80eV) at[140c] and (3.91) at [100c] .

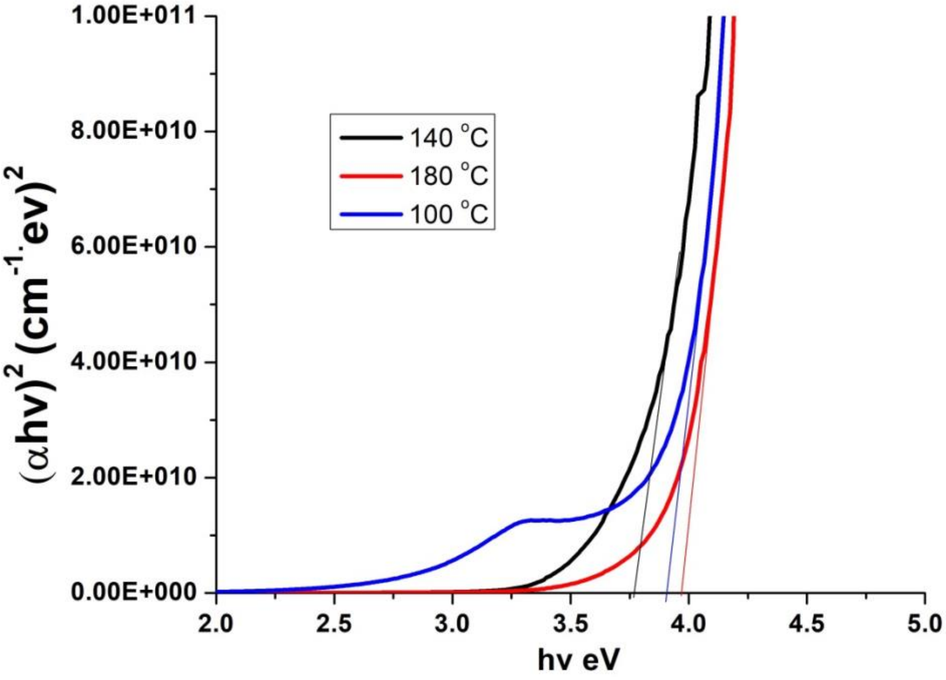


Fig. (3.4): Variation of α(hν)^2 with photon energy for ZnS-NPs at different temperature.

From table (3.1), it's clearly observed that the direct band gap energy increase as the deposition temperature increase. This increase of energy gap with growth temperature is similar to the work done by (Vahid sabaghi, fatemeh davar, and zeinab fereshteh), (sonima mohan, mini vellakkat, arun aravid, and reka u) , (Tran Thi Quynh Hoa, Le Van Vu, Ta Dinh Canh and Nguyen Ngoc Long) where they used hydrothermal technique, the values of determind optical gap for investigated samples are listed in table (3.1).

Table (3.1): values of determined optical energy band gap for ZnS-NPs prepared by hydrothermal method

Researcher	Energy band gap (ev)	method

Vahid	4.38	hydrothermal
Vahid	4.33	hydrothermal
Sonima mohan	3.14	Hydrothermal Uv anylysis
Sonima mohan	3.18	Hydrothermal
		Uv analysis
Tran thi quynh hoa	3.76	Hydrothermal
Tran thi quynh hoa	3.74	Hydrothermal

Chapter Four

Conclusions and Suggestions

4.1- **Conclusions**:

- In this research we have successfully created Zns nanopowder using (Zinc netrite) and (theoria) at three different tempreatures by hydrothermal method.

- We measured the transmittance spectra at different teampreatures in wavelength range (200-1100 nm), we observed that the percentage of transmission increases as we increase teampreature in low absorption region.
- we measured the absorbance spectra at three different tempreatures in wavelength range (200-1100nm) , we observed that the absorption is high at invisible near infrared region, but the absorption is low at ultraviolet region, at all tempreatures the most absorption rate is near infrared region absorption rate decreases as we go to the ultraviolet region.
- We successfully determined the energy band gap for the ZnS-Nps at three different tempreatures (100,140,180), our results showed that the energy gap at (100c) is (3.91ev) , at (140c) is (3.80ev), and at (180c) is (3.93ev). which tells as it has a direct band gap nature, and it increases as the deposition of temperature increases.

4.2- **Suggestions:**

In this research we used hydrothermal method, we suggest for future researchers can use other methods like chemical vapor deposition, thermal evaporation, hydrothermal synthesis, solvothermal method, pulsed laser ablation, and conventional Sol-Gel method and many more , we can also use ZnS-NPs as a window layer for solar cell application.

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