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EFFECT OF HE-NE AND DIODE LASER INDUCED NANOPOWDER *ZINC SULFIDE (ZnS)*

J.Thabithal[1] and N.Ravi[2]

[1]*M.Phil.Physics, St.Joseph's College (Autonomous), Trichy-2.*
[2]*Department of Physics, St.Joseph's College (Autonomous), Trichy-2.*

ABSTRACT: ***Materials have unique optical, electronic or mechanical properties, with the structure at the nano scale. The major advantage of laser processing is that it produces a better quality product with minimum distortion at a high rate. In this work we investigated the nanopowder zinc sulfide and its dealing with He-Ne laser and Diode laser are studied. Zinc sulfide or Zinc sulphide (ZnS) is an inorganic compound , where it mainly occurs in the minerals sphalerite and wurtzite. Both sphalerite and wurtzite are intrinsic, wide band gap semiconductors. ZnS is white in color and it is transparent. In this study, we record the impact of laser processing nanopowder zinc sulfide. The laser irradiated samples are characterized and identified by UV-visible absorption, FTIR spectra, Fluorescence Spectroscopy, DLS studies, SEM and X-ray diffraction. In the UV visible spectrum, it certified the presence of ZnS with the average band gap energy 6.14-6.34 eV. From the analysis of XRD and SEM we can say that the nano particle ZnS has the tetrahedral structure and crystalline size in the range of 24.79 nm to 35.04 nm (XRD) and approximately 200 nm diameters and more than 1 µm in length (SEM). From the DLS studies the particle size varies from 93.7 nm to 142.9 nm. At room temperature the excitation wavelength (λ_{exc}) varies between 570.00 nm and 570.29 nm from Fluorescence spectroscopy studies. In the FTIR spectra it has been found various functional groups present in the ZnS. The results of XRD and SEM are nearly equal values.***

KEYWORDS: ZnS, He-Ne laser, Diode laser, FTIR, UV, XRD, DLS, Fluorescence and SEM.

1. INTRODUCTION

A material science based approach towards nanotechnology takes nano material research. The application of nanoparticles of different fields is more important because of their considerable stability. In laser interaction, absorptivity is one of the most significant parameters. The laser processing efficiency, depends on the absorption of the energy by the material [1,2]. Zinc sulfide or Zinc sulphide (ZnS) is an inorganic compound and it also known as zinc blende and wurtzite. It mainly occurs in the minerals sphalerite and wurtzite, which are intrinsic, wide band gap semiconductors. They belong to prototypical II-VI semiconductors [3,4]. The pure form of mineral appears white and it is used as a pigment. It is also used for visible optics and infrared optics as a window. Then it is denser than water and water insoluble. It is also a byproduct of ammonia synthesis using methane .This ZnS phosphors is especially efficient in electro luminescence [5].
In this paper, the spectroscopic studies of laser treated zinc sulfide nanoparticle with different time periods have been investigated. The particle size and structural analysis of the samples are done using scanning electron microscope and X-ray diffractometer . Similarly, Using UV-Vis Spectrometer, absorbance and transmittance has been measured. Also the energy band gap has been calculated. The band gap energy for the sample irradiated with He-Ne and Diode laser increases with increase in temperature. The functional groups for various peaks have been identified using FTIR Spectroscopy. The photoluminescence spectra of ZnS nanoparticles have been determined as Greenish yellow colour at the various excitation wavelengths of five samples. In this paper, the particle size distribution has been investigated by DLS studies for different time periods using He-Ne and Diode laser.[6]

2. EXPERIMENTAL PROCEDURE

Commercially available powder ZnS is used for investigation. Laser irradiations are worked out by using 5.0 mw low power He-Ne gas laser with red light of wavelength 633nm and the Diode laser with green light of wavelength 532nm (Table1). The structure and particle size of the laser irradiated samples are analyzed by X-ray diffractometers and this recorded the intensity as a Bragg's angles function. The optical investigation of the samples such as UV and FTIR studies are performed using Perkin Elmer UV/VIS spectrophotometer (λ 365) and Perkin Elmer FTIR spectrometer. ZnS nano particles are analyzed using SEM (ZEISS SEM instrument) micrographs. In Fluorescence Spectrometry both an excitation and emission spectrum can be measured. The particle size has been studied using DLS studies [7].The properties of ZnS are tabulated (Table2). The procedure has been figured out (Fig1)

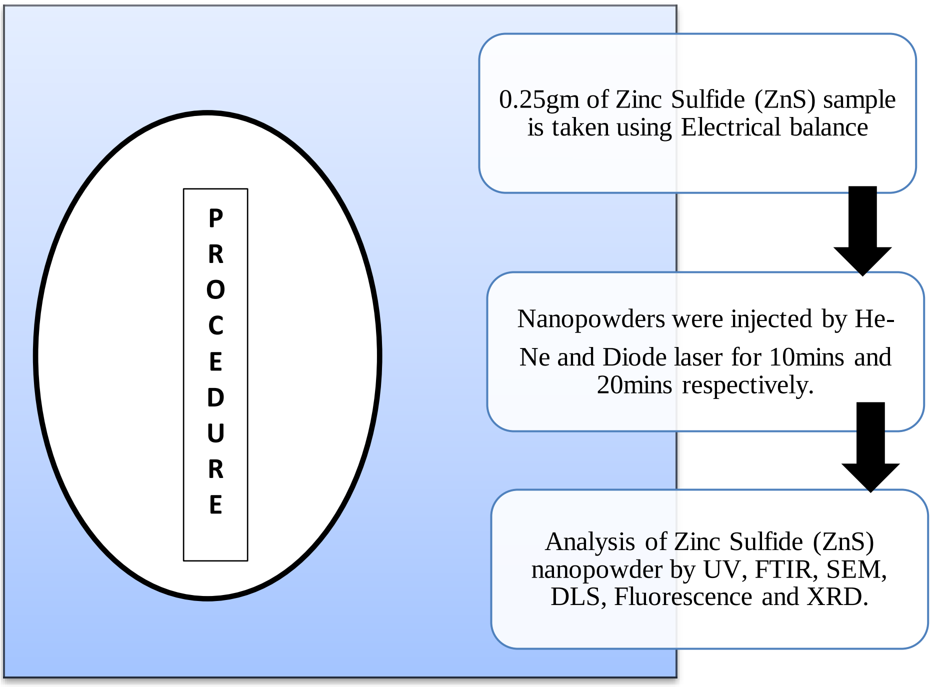
Table 1 Time duration of laser irradiation of samples with different power of laser

SAMPLES	LASER IRRADIATION(sec)	WEIGHT (g)
1	Without laser irradiation	0.25
2	He-Ne laser (10 mins)	0.25
3	He-Ne laser (20 mins)	0.25
4	Diode laser (10 mins)	0.25
5	Diode laser (20 mins)	0.25

Table 2 Properties of ZnS

Parameters	Values
Chemical formula	ZnS
Molar mass	97.474 g/mol
Solubility in water	Negligible
Density	4.090 g/cm^3
Melting point	1850^{o}C
Refractive index	2.3677
Appearance	White crystal

Fig 1 Experimental Flowchart



3. RESULTS AND DISCUSSION

3.1. UV-Vis studies

UV spectroscopy is a type of absorption spectroscopy. The light can be absorbed by the molecule at the ultraviolet range of 200 to 400 nm. Energy of the nano powder with and without laser irradiated can be calculated (Fig 2,3,4,5and6)and tabulated (Table3) as per the absorption spectra, optical constant and band gap energy.[8]

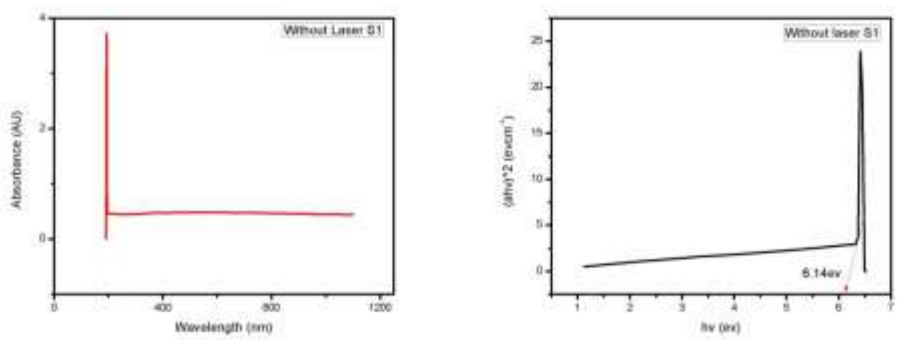


Fig 2 (a) Absorption spectra of ZnS (without laser) and (b) Band gap energy of ZnS (without laser)

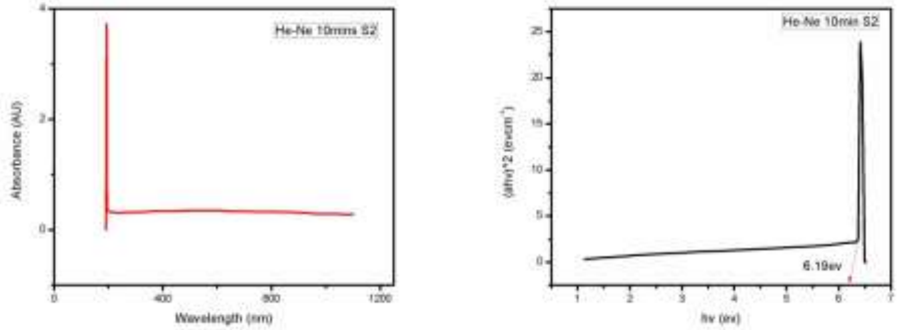


Fig 3 (a) Absorption spectra of ZnS (He-Ne 10 min) and (b) Band gap energy of ZnS (He-Ne 10 min)

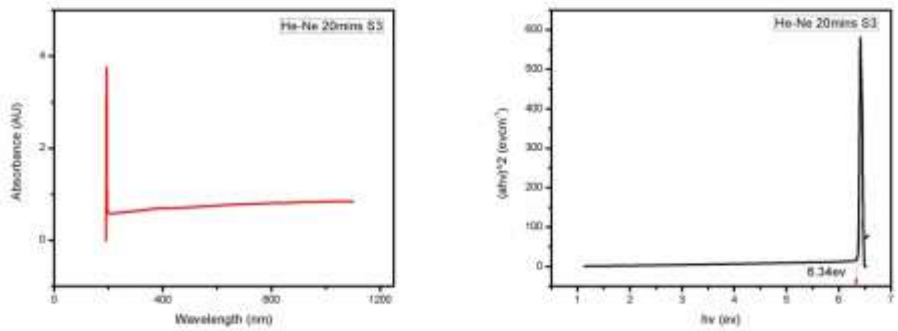


Fig 4 (a) Absorption spectra of ZnS (He-Ne 20 min) and (b) Band gap energy of ZnS (He-Ne 20 min)

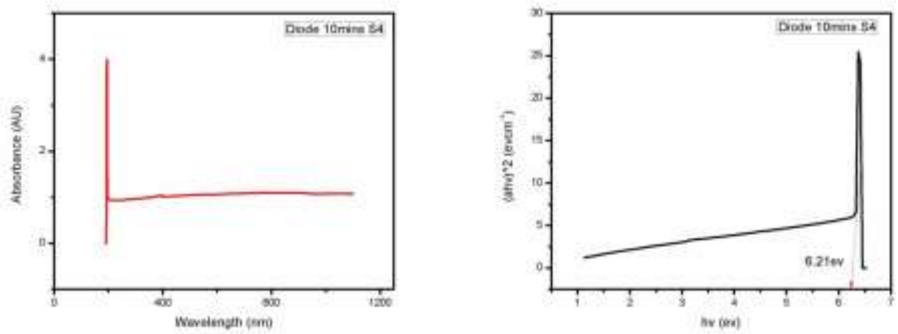


Fig 5 (a) Absorption spectra of ZnS (Diode -10 min) and (b) Band gap energy of ZnS (Diode-10 min)

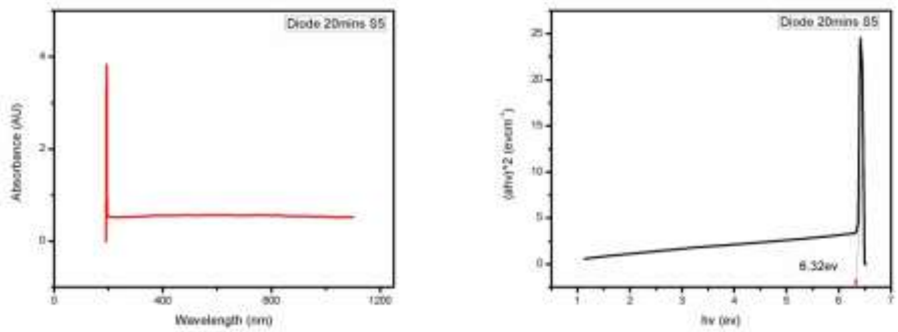


Fig 6 (a) Absorption spectra of ZnS (Diode 20 min) and (b) Band gap energy of ZnS (Diode-20 min)

Table 3 The band gap energy of each sample

SAMPLES	TIME DURATION OF LASER IRRADIATION (sec)	BAND GAP ENERGY (eV)
1	Without laser irradiation	6.14
2	10 mins (He-Ne laser irradiation)	6.19

3	20 mins (He-Ne laser irradiation)	6.34
4	10 mins (Diode laser irradiation)	6.21
5	20 mins (Diode laser irradiation)	6.32

Here, when we compare the band gap energy of sample 2 and sample 4, sample 4 has the greater bandgap energy. Likewise, comparing sample 3 and sample 5, sample 3 has the greater bandgap energy. For without laser sample the bandgap energy is 6.14eV. The maximum bandgap energy is 6.34eV.[9]

3.2 FTIR studies

The FTIR spectrum (Fig .8.9.10and11) of ZnS nanoparticles are given below and the functional groups (Table 4,5,6,7and8) present in the ZnS samples.

Fig 7 FTIR without laser treated ZnS

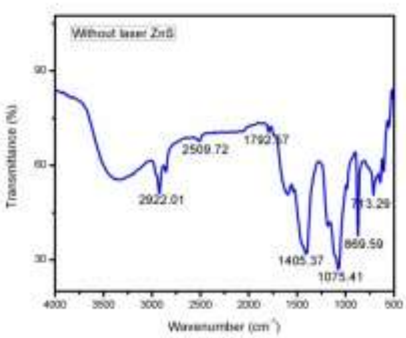


Table 4 FTIR functional analysis without laser Zns

Functional groups	Frequency (cm^{-1})	Vibrations	Intensity
C-H (alkane)	2922.01	Stretching	Medium
O-H (carboxylic acid)	2509.72	Stretching	Strong, Broad
C=O (acid halide)	1792.57	Stretching	Strong
O-H (alcohol)	1405.37	Bending	Medium
C-O (primary alcohol)	1075.41	Stretching	Strong
C-Cl (halo compound)	869.59	Stretching	Strong
C=C (alkene)	713.29	Bending	Strong

Fig 8 He-Ne laser treated 10 min ZnS

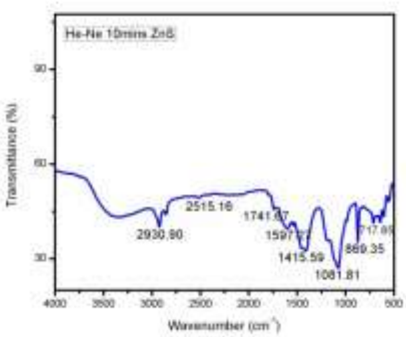


Table 5 FTIR functional analysis (He-Ne-10 min- ZnS)

Functional groups	Frequency (cm^{-1})	Vibrations	Intensity
C-H (alkane)	2930.90	Stretching	Medium
O-H (carboxylic acid)	2515.16	Stretching	Strong, Broad
C=O (acid halide)	1741.67	Stretching	Strong
N-H (amine)	1597.27	Bending	Medium
O-H (alcohol)	1415.59	Bending	Medium
C-O (primary alcohol)	1081.81	Stretching	Strong
C-Cl (halo compound)	869.35	Stretching	Strong
C=C (alkene)	717.85	Bending	Strong

Fig 9 He-Ne laser treated 20 min ZnS

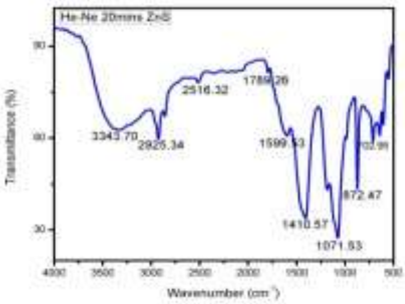


Table 6 FTIR functional analysis (He-Ne-20 min- ZnS)

Functional groups	Frequency (cm^{-1})	Vibrations	Intensity
N-H (secondary amine)	3343.70	Stretching	Medium
C-H (alkane)	2925.34	Stretching	Medium
O-H (carboxylic acid)	2516.32	Stretching	Strong, Broad
C=O (acid halide)	1789.26	Stretching	Strong
N-H (amine)	1599.53	Bending	Medium
O-H (alcohol)	1410.57	Bending	Medium
C-O (primary alcohol)	1071.53	Stretching	Strong
C-Cl (halo compound)	872.47	Stretching	Strong
C=C (alkene)	702.95	Bending	Strong

Fig 10 Diode laser treated 10 min ZnS

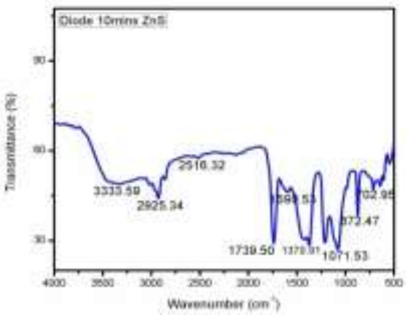


Table 7 FTIR functional analysis (Diode-10 min- ZnS)

Functional groups	Frequency (cm^{-1})	Vibrations	Intensity
N-H (secondary amine)	3333.59	Stretching	Medium
C-H (alkane)	2925.34	Stretching	Medium
O-H (carboxylic acid)	2516.32	Stretching	Strong, Broad
C=O (acid halide)	1739.50	Stretching	Strong
N-H (amine)	1599.53	Bending	Medium
O-H (alcohol)	1370.91	Bending	Medium
C-O (primary alcohol)	1071.53	Stretching	Strong
C-Cl (halo compound)	872.47	Stretching	Strong
C=C (alkene)	702.95	Bending	Strong

Fig 11 Diode laser treated 20 min ZnS

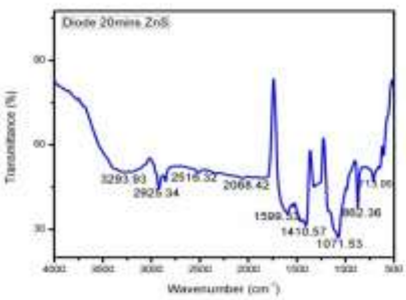


Table 8 FTIR functional analysis (Diode-20 min- ZnS)

Functional groups	Frequency (cm^{-1})	Vibrations	Intensity
N-H (secondary amine)	3293.93	Stretching	Medium
C-H (alkane)	2925.34	Stretching	Medium
O-H (carboxylic acid)	2516.32	Stretching	Strong, Broad
N=C=S (isothiocyanate)	2068.42	Stretching	Strong
N-H (amine)	1599.53	Bending	Medium
O-H (alcohol)	1410.57	Bending	Medium
C-O (primary alcohol)	1071.53	Stretching	Strong
C-Cl (halo compound)	862.36	Stretching	Strong
C=C (alkene)	713.06	Bending	Strong

3.3. XRD analysis

The X ray diffraction pattern (Fig 12,13and14) and crystalline size (Table 9,10 and 11) of with and without laser treated samples are shown below.[10]

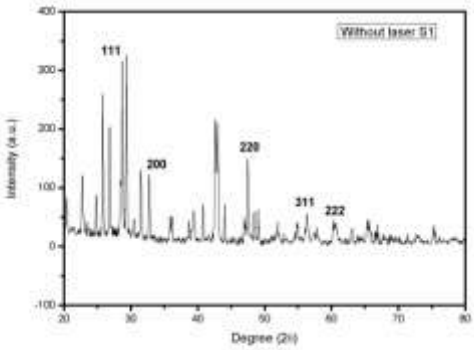


Fig 12 XRD Spectrum Analysis of without laser treated ZnS Nanoparticles

Table 9 Structural Parameters of ZnS nanoparticles without laser irradiation

Position (2Θ)	hkl	FWHM (2Θ)	d-spacing (A˚)	Particle size (nm)
28.72	111	0.32721	3.10740	25.58507
32.82	200	0.13214	2.73279	46.57336
47.46	220	0.27213	1.91493	33.34400
56.37	311	0.27543	1.63348	14.29561
60.24	222	0.40107	1.52564	4.16883

Fig 13 XRD Spectrum Analysis of He-Ne laser Treated 20min ZnS Nanoparticles

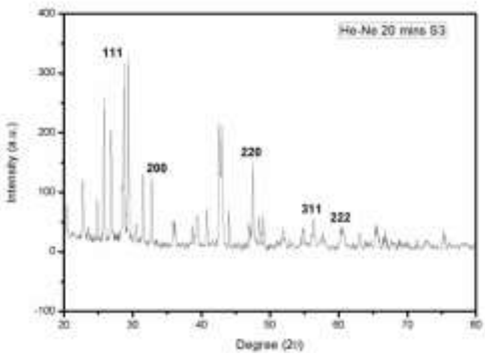


Table 10 Structural Parameters of ZnS nanoparticles He-Ne laser treated with 20mins

Position (2Θ)	hkl	FWHM (2Θ)	d-spacing (A˚)	Particle size (nm)
28.74	111	0.32054	3.10092	46.31639
32.82	200	0.17782	2.72841	46.61629
47.54	220	0.26034	1.91299	34.59993
60.54	311	0.64347	1.53385	21.49382
70.98	222	2.34055	1.31030	13.53909

Fig 14 XRD Spectrum Analysis of Diode laser Treated 20min ZnS Nanoparticles

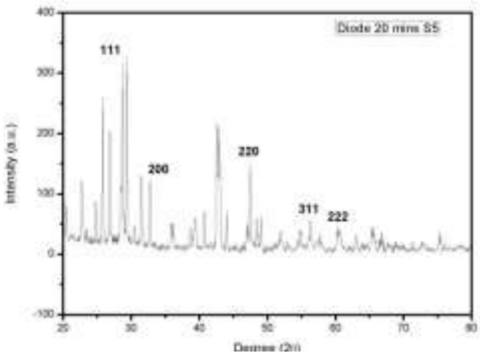


Table 11 Structural Parameters of ZnS nanoparticles Diode laser treated with 20mins

Position (2Θ)	hkl	FWHM (2Θ)	d-spacing (A˚)	Particle size (nm)
28.76	111	0.17707	3.10253	25.06189
32.78	200	0.17764	2.73092	62.67433
47.52	220	0.25087	1.91380	31.88997
56.32	311	0.41925	1.63430	32.72383
60.52	222	0.67933	1.53506	22.89974

The X-ray diffraction studies with and without laser irradiation of zinc sulfide is given in the following session. The powder X-ray diffraction studies were performed at Alagappa university science center in Karaikudi. A beam voltage of 40KV and a beam current 30 mA were used. The data were collected in the 2θ range (10-80) with continuous scan speed of 0.2 deg/min. The average particle size (D) was determined and (Table12) calculated using the Scherrer's equation.

$$D= K\lambda / \beta\cos\theta$$

Where D is the crystallite size, K is the shape factor, being equal to 0.9 , λ is the X-ray wavelength, β is the full width at half maximum of the diffraction peak, and . θ is the Bragg diffraction angle in degree.[11]

Table 12 crystallite grain size of ZnS samples

S.NO.	SAMPLES	GRAIN SIZE IN nm
1	Without laser ZnS	24.793374
2	HeNe laser 20min ZnS	32.513104
3	Diode laser 20 min ZnS	35.049952

3.4. FLUORESCENCE SPECTROSCOPY

In this photoluminescence spectral (Fig 15,16,17,18and19) studies of the ZnS nanoparticle, the excitation wavelength (λ_{exc}) are in the range (Table13) about 570.00nm to 570.29nm at room temperature. Visible light is usually defined as having wavelengths in the range of 400nm to 700nm. Hence the colour spectrum of the ZnS nanoparticle has been insistented as greenish yellow.[12,13]

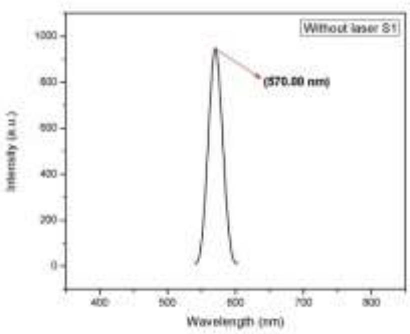


Fig 15 Without laser

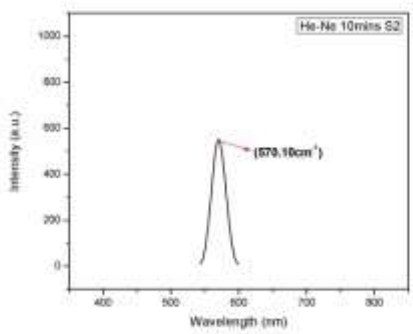


Fig 16 He-Ne laser 10mins

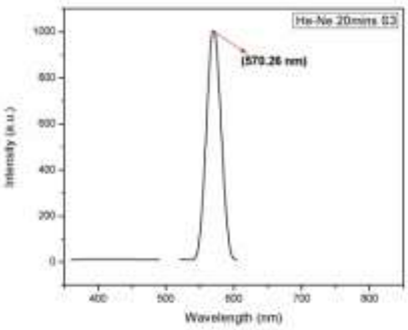


Fig 17 He-Ne laser 20mins

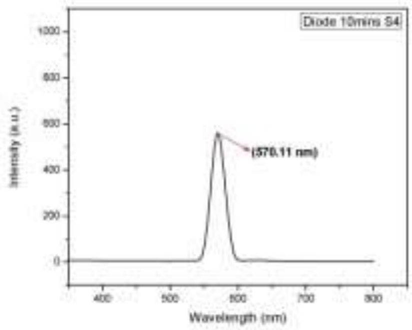


Fig 18 Diode laser 10mins

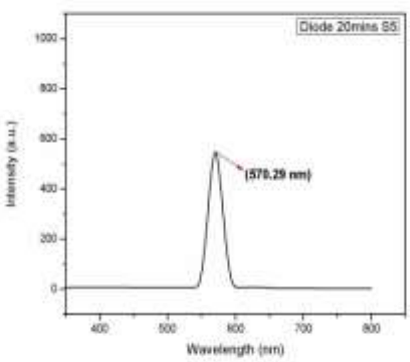


Fig 19 Diode laser 20mins

Table 13 Excitation Wavelength variation of Photoluminescence Spectra

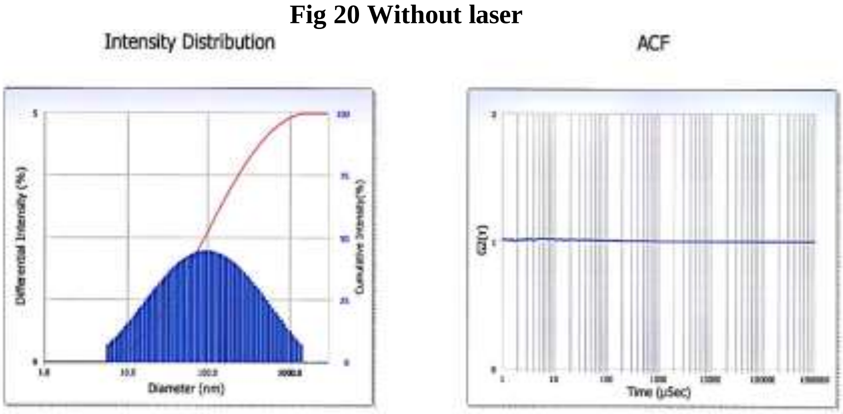
Sample	Laser Irradiation (sec)	Excitation wavelength (λ_{exc}) (nm)
1	Without laser	570.00
2	He-Ne (10mins)	570.10
3	He-Ne (20mins)	570.26
4	Diode (10mins)	570.11
5	Diode (20mins)	570.29

3.5 DLS (Dynamic Light Scattering) Studies

With and without laser treated samples of ZnS nanoparticles the particle size distribution has been studied (Fig 20,21,22,23and24) using DLS analysis. The particle size varies from 93.7nm to 142.9nm.[14]

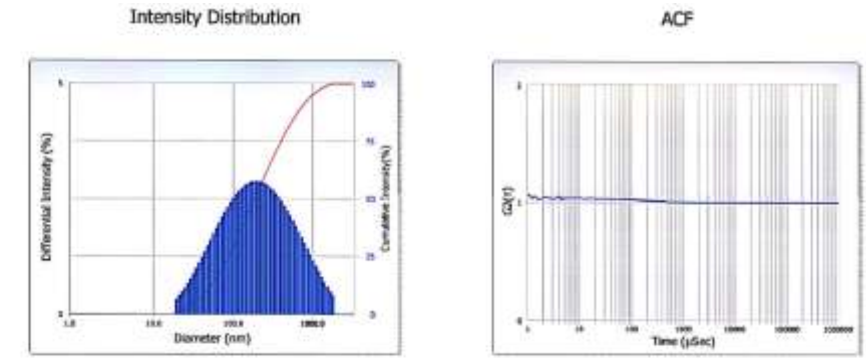
Sample 1

Fig 20 Without laser



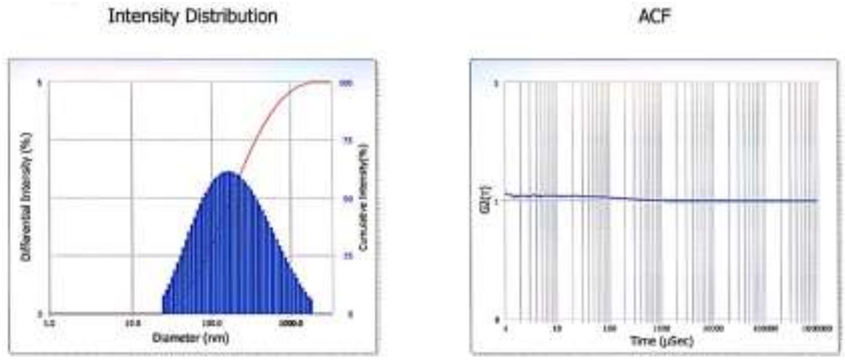
Sample 2

Fig 21 He-Ne laser 10mins



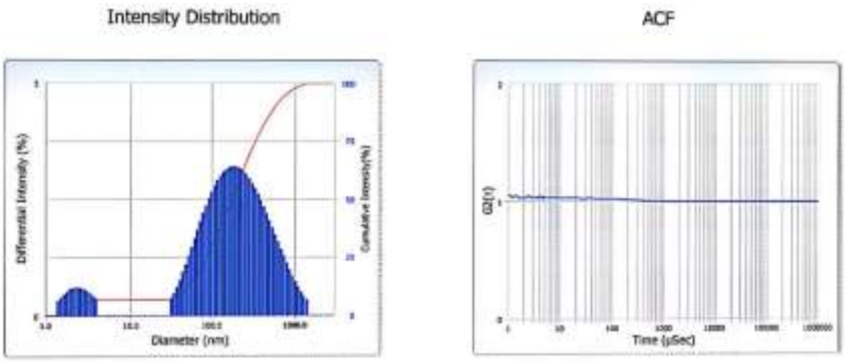
Sample 3

Fig 22 He-Ne laser 20mins



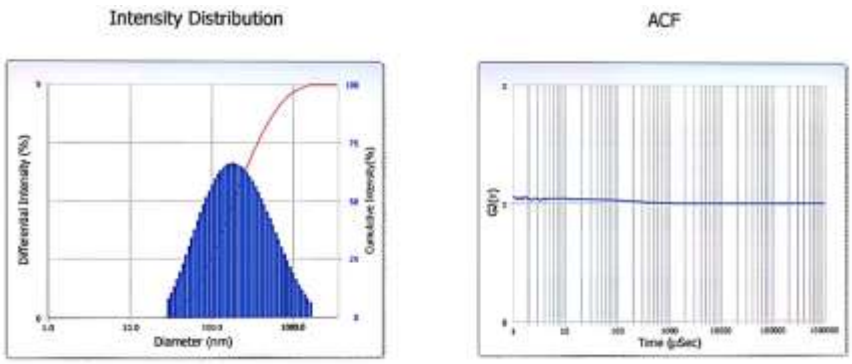
Sample 4

Fig 23 Diode laser 10mins



Sample 5

Fig 24 Diode laser 20mins

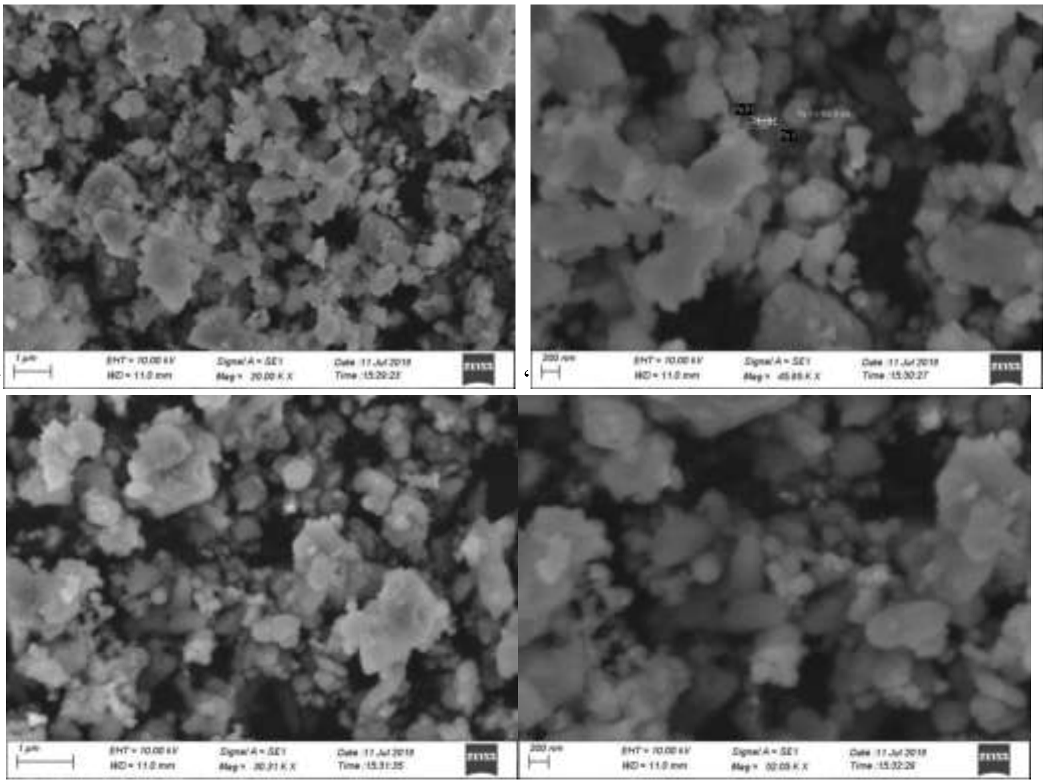


Dynamic light scattering (DLS) studies revealed that the particle size distribution of Zinc Sulphide ZnS nano-particles are 93.7nm(sample-1), 117.3nm(sample-2), 138.3nm (sample- 3), 118.1nm (sample- 4) and 142.9nm (sample- 5).

3.6 SEM Analysis

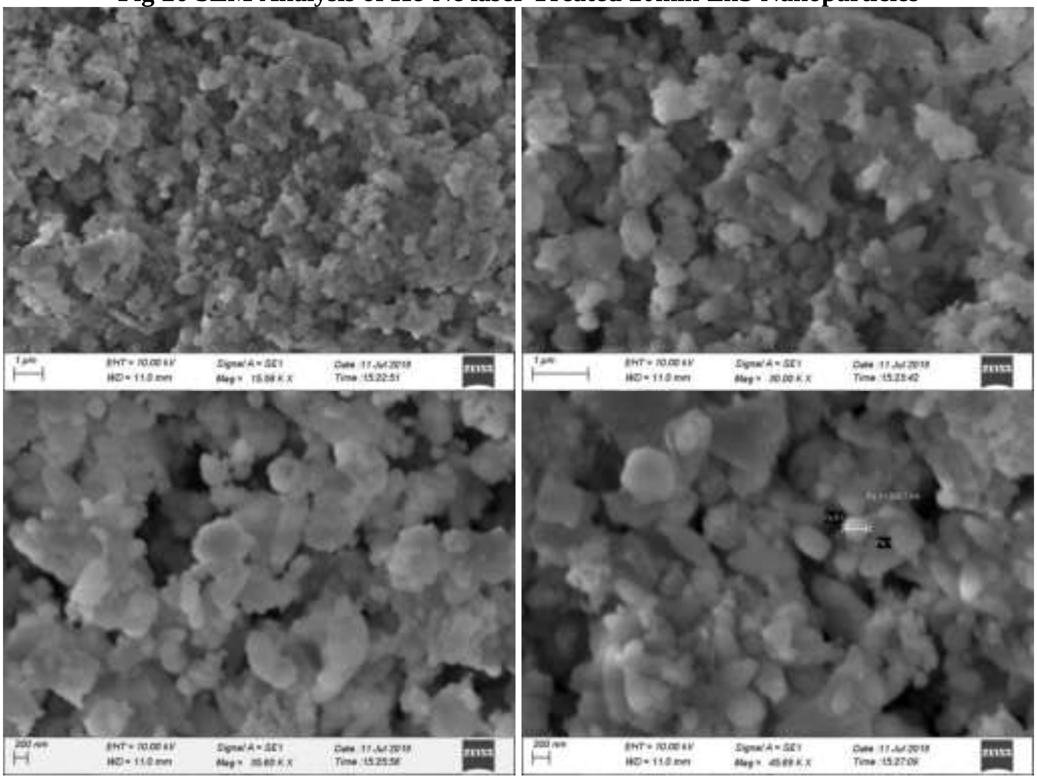
The SEM Analysis (Fig 25,26and27) of with and without laser treated samples are shown.[15]

Fig 25 SEM Analysis of without laser treated ZnS Nanoparticles



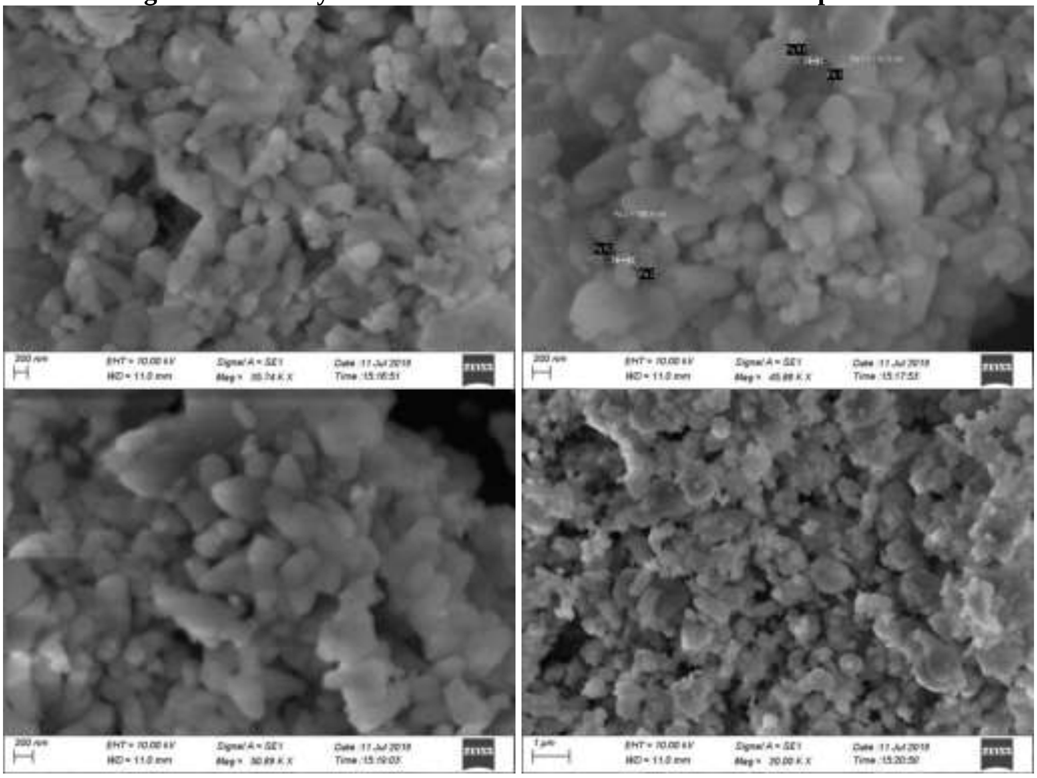
Utilizing this simple and high return method we could develop nano structures of around 196.8–200 nm diameter and more than 1 µm length.

Fig 26 SEM Analysis of He-Ne laser Treated 20min ZnS Nanoparticles



Utilizing this simple and high return method we could develop nano structures of around 200–280.7 nm diameter and more than 1 µm length.

Fig 27 SEM Analysis of Diode laser Treated 20min ZnS Nanoparticles



Utilizing this simple and high return method we could develop nano structures of around 196.4–200 nm diameter and more than 1 µm length. SEM analysis of Zinc sulfide (ZnS) Nano Particle, it is observed that the particles are in the tetrahedral structure[16] . The average particle size (Table14) observed in both SEM and XRD measurements are slightly different values.

Table 14 shows the comparative study of particle size of Zinc sulfide nano particles

S.NO	SAMPLE	XRD Crystallite(nm)	SEM Particle (nm)
1	Without laser irradiation	24.793374	196.8–200
2	20 minutes(with He-Ne laser irradiation)	32.513104	200–280.7
3	20 minutes (with Diode laser irradiation)	35.049952	196.4–200

4. CONCLUSION

In this, we investigated and reported the effect of laser He-Ne and Diode induced nanoparticles zinc sulfide. The results observed are given below:

a. From the UV spectrum studies, we observed band gap energy for He-Ne and Diode laser treated samples (values vary from 6.14-6.34eV). The maximum band gap energy value is from sample 3 that is He-Ne 20 mins .
b. The functional group for different peaks observed from FTIR Spectrum for various samples were analysed .From the FTIR spectrum the wavelength ,vibration ,intensity and which group presented in the sample are analysed.
c. From the X-ray diffraction studies we observed the structure of Zinc sulphide nanoparticle is the tetrahedral structure.
d. From the X-ray diffraction studies, the crystallite gain size of the samples calculated are 24.79 nm(without laser),32.51 nm(He-Ne laser 20mins),35.05 nm(Diode laser 20 mins).
e. The photoluminescence spectra exhibits the Greenish yellow spectrum at the excitation wavelength (λ_{exc}) ranges about 570.00 nm to 570.29 nm using Fluorescence Spectroscopy.
f. The distribution of particle size varies from 93.7nm(sample-1), 117.3nm(sample-2), 138.3nm (sample- 3), 118.1nm (sample- 4) and 142.9nm (sample- 5) using DLS Studies.
g. From the SEM analysis of Zinc sulfide(**ZnS**) nanoparticles ,we observed that the particles are in the tetrahedral structure .The particle sizes are in the range about 196.8–200nm(without laser),200–280.7 nm(He-Ne laser 20mins), 196.4–200nm(Diode laser 20mins)
h. In general, when the laser power with increased time exposure gives improved result in band gap energy as well as in grain size structure.
i. The average particle size observed in both SEM and XRD measurements are nearly equal value.

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