

# Synthesis and Characterization of ZnS Nanoparticles Doped by L- arginine

N. S. Tank<sup>1</sup>, K. D. Parikh<sup>2\*</sup>, B. V. Jogiya<sup>3\*</sup> and M. J. Joshi<sup>1</sup>

<sup>1</sup>Department of Physics, Saurashtra University, Rajkot, 360 005, India.

<sup>2</sup> Department of Physics, Gujarat Arts and Science College, Ahmedabad, 380,006, India.

<sup>3</sup>Regional Forensic Science Laboratory, Rajkot, 360,005, India.

\*Corresponding author: [ketandparikh@yahoo.co.in](mailto:ketandparikh@yahoo.co.in) and [bhoomika.cpi@gmail.com](mailto:bhoomika.cpi@gmail.com)

## Abstract

ZnS nanoparticles are successfully synthesized via the co-precipitation method. The powder XRD confirmed the cubic crystal structure for all the samples. TEM image indicated spherical shape with its size in the range of 10 nm -20 nm. The HRTEM shows nano sized nature of the particles. The FT-IR spectrum indicates the presence of N-H rocking and stretching, C=C group, C=O carbonyl group (keton group), and C-N vibration, C=O stretching in L-arginine doped samples. The thermogram suggested that decomposition of the samples occurs by three stages and almost equal amount of final residue at the final stage due to least amount of amino acid entered in to parent structure of ZnS. The EDAX analysis is done confirm the presence of L-arginine in ZnS nanoparticles.

**Keywords:** ZnS, L-arginine doped ZnS, nano particles, powder XRD, FT-IR, TEM, TGA and EDAX.

Date of Submission: 12-05-2022

Date of Acceptance: 27-05-2022

## I. Introduction

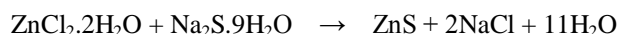
Semiconductor nanoparticles continue to receive much attention due to unique optical and electronic properties which are not present in bulk materials that are dependent on a variety of material properties, such as size, shape and composition. Semiconductor nanocrystals, whose electronic and optical properties are tunable, have aroused considerable interest as technologically important materials. The size dependence of the band gap is the most identified aspect of quantum confinement in semiconductors; the band gap increases as the size of the particles decreases. An extremely active and prolific field in nanomaterials is finding ways to control size and morphology of the nanoparticles since the properties and applications of the nanoparticles are largely dependent on their size and morphology. As a typical non toxic wide band gap semiconductor material of the II-VI group, ZnS has been used as optical devices, such as ultraviolet light emitting diodes [1-3], flat panel displays [4, 5], solar cells [6], and optical sensors [7]. ZnS crystallizes in the zinc-blende (ZB) structures at room temperature with a band gap of 3.68 eV or 3.77 eV respectively [8]. ZnS with a band gap of 3.68 eV corresponds to ultraviolet radiation for optical interband transition. Wide-band gap semiconductors such as ZnS are ideal materials for the study of discrete states in the gap. Visible luminescence can originate only from transitions involving these localized states. The reported luminescence spectrum and absorption in ZnS both show an emission peak at around 420 nm [9-11]. Bulk and nano-scale ZnS crystals have been successfully synthesized by various methods and their properties have been investigated [12-15].

These general preparation techniques include the precipitation method, sol-gel, reverse micelle method, microwave method, hydrothermal process, wet-chemical method, spray pyrolysis, etc. At the nanoparticle sizes of a semiconductor, the energy gap (band gap) increases, and the optical spectrum is shifted toward the short-wavelength region [16] and some of their physical properties differ noticeably from those of the corresponding bulk material. These properties of nanocrystals make them an interesting category of material for optoelectronic applications. In the present study, ZnS and also doping of L-arginine nano particles were synthesized by wet chemical process. This nanoparticles were characterized by various techniques such as Power XRD, FT-IR spectroscopy, TGA-DSC, TEM and EDXA.

## II. Experimental

(1) Nano-sized particles of ZnS crystals were prepared by co-precipitation reaction using ZnCl<sub>2</sub> and sodium sulfide (Na<sub>2</sub>S). All of the reagents were analytical grade in purity and used without further purification, and the deionized water was used as a solvent. The ZnS nanoparticles were prepared in the following sequence: 1M ZnCl<sub>2</sub> was added to 100 ml of deionized water under continuous stirring for 30 min. Then, 1M Na<sub>2</sub>S was

added to 100 ml of deionized water. The Na<sub>2</sub>S solution was then poured into ZnCl<sub>2</sub> solution. After the reaction was completed, a white precipitate formed. Then this mixture was centrifuged at 300 rpm for 30 min and dried at 110 °C for 24 h in air. We can get white fine powder of ZnS nano particles. The chemical reaction of ZnS nanoparticles as under,



(2) In present investigation ZnSD1: 0.25 M L- arginine doping in ZnS nano particle. The ZnSD1: doped 0.25M L-arginine nanoparticles were prepared in the following sequence: 1M ZnCl<sub>2</sub> was added to 100 ml of deionized water under continuous stirring for 30 min. Then, 1M Na<sub>2</sub>S was added to 100 ml of deionized water. The Na<sub>2</sub>S solution was then poured into ZnCl<sub>2</sub> solution. Then after drop wise solution of 0.25M L-arginine in 50 ml was added in this solution.

(3) In present investigation ZnSD2: 0.5 M L-arginine doping in ZnS nanoparticle.

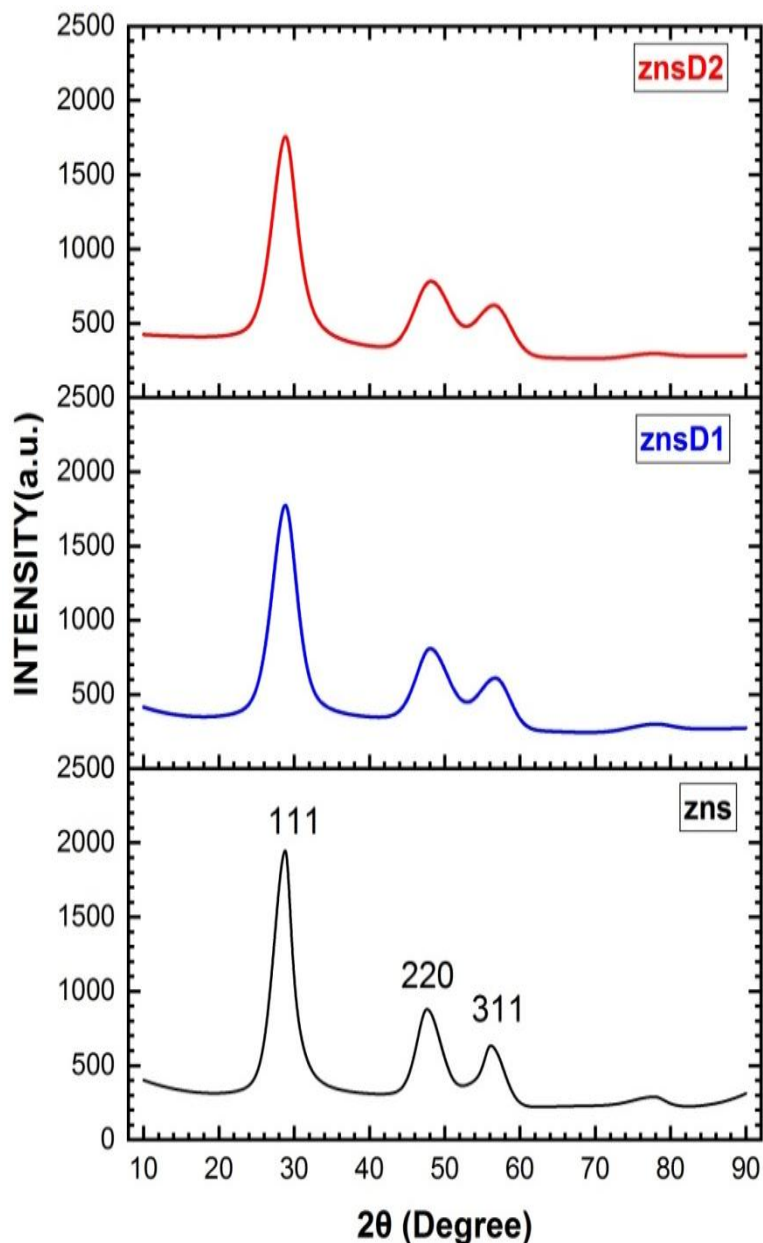
The ZnSD2: doped 0.50M L-arginine ZnSD2 nanoparticles were prepared in the following sequence: 1M ZnCl<sub>2</sub> was added to 100 ml of deionized water under continuous stirring for 30 min. Then, 1M Na<sub>2</sub>S was added to 100 ml of deionized water. The Na<sub>2</sub>S solution was then poured into ZnCl<sub>2</sub> solution. Then after dropped wise solution of 0.50M L-arginine in 50 ml was added in this solution.

### III. Result And Discussion

#### ***Powder X-ray Diffraction Study:***

Powder X-ray Diffraction (XRD) is perhaps the most widely used X-ray diffraction technique for characterizing inorganic and organic crystalline materials. As the name suggests, the sample is usually in a powder form, consisting of fine grains of single crystalline material to be studied. The technique is also used widely for studying particles in liquid suspensions or poly-crystalline solids (bulk or thin film materials). The term 'powder' really means that the crystalline domains are randomly oriented in the sample. Therefore, when the 2-D diffraction pattern is recorded, it shows concentric rings of scattering peaks corresponding to the various *d* spacing in the crystal lattice. The positions and the intensities of the peaks are used for identifying the underlying structure (or phase) of the material. The method has been traditionally used for phase identification, quantitative analysis and the determination of structure imperfections.

In recent years, applications have been extended to new areas, such as the determination of crystal structures and the extraction of three-dimensional micro-structural properties. From the measurement of diffracted peak positions in XRD one can characterize homogeneous and inhomogeneous strains. The significant broadening of the XRD pattern peaks reveals the smaller size of the particles. The similar results are reported by Tank et al. [17]. In the present investigation ZnS and with doped amino acid nanoparticles were analyzed by JAPAN RIGAKU, with Cu-K $\alpha$  radiation. The crystal structure was determined by computer software Powder-X. Figure 1 shows that ZnS sample with doped crystallize in cubic symmetry with lattice parameter  $a = 5.368\text{\AA}$  and unit cell volume  $V = 154.7157\text{\AA}^3$ . The three different peaks of the sample correspond to the lattice planes of (111), (220), and (311), which match very well with the cubic zinc blend structure (JCPDS No. 05-0566). Table 1 indicates the unit-cell parameter's of ZnS, ZnSD1 and ZnSD2 nanoparticles. This all nanoparticles have cubic system and unit cell values are closely matching with the reported values [18]. It is seen from figure 1 that the XRD peaks become slightly broader in the doped samples it suggests the nano sized nature of the samples. The normal diffraction line is of a finite width due to certain factors such as the finite line width of the excitation source and imperfections in the focusing geometry. The width of the diffraction peak is determined by the number planes present in the crystallites.



**Figure 1.** Powder XRD pattern of ZnS sample with doped amino acid showing the corresponding miller indices of diffraction planes.

❖ **Using Scherrer’s Formula:**

In the present investigation the average particle size of ZnS, ZnSD1 and ZnSD2 nanoparticles are calculated by using the Scherrer’s formula [19], which is as follows:

$$D = \frac{k\lambda}{\beta \cos\theta} \dots \dots \dots (1)$$

Where,  $\lambda$  = Wave length of Source = 1.54178 Å for Cu K $\alpha$ , D = Average crystallite size,  $\beta$  is the full width at half maximum (FWHM) of that peak in radian.

From powder XRD the average particle size of ZnS, ZnSD1 and ZnSD2 nanoparticles are 14.05 nm, 14.66 nm and 14.65 nm, respectively, calculated by using Scherrer’s formula. From this characterisation one can conclude that there is no effect of doping amino acid on average particle size.

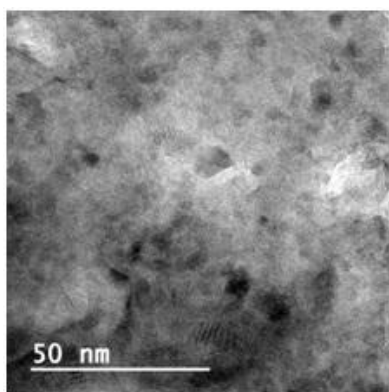
**Table 1:** Unit cell parameters of ZnS, ZnSD1 and ZnSD2 nanoparticles.

Sample Codes	a (Å)	b (Å)	c (Å)	$\alpha$	$\beta$	$\gamma$
ZnS nanoparticles	5.368	5.368	5.368	90	90	90
ZnS D1 nanoparticles	5.305	5.305	5.305	90	90	90
ZnS D2 nanoparticles	5.356	5.356	5.356	90	90	90

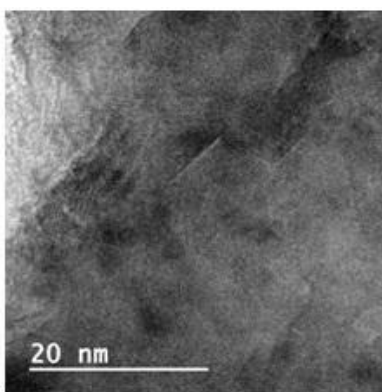
**Transmission electron microscopy studies:**

The Transmission Electron Microscopy (TEM) and the high-resolution transmission electron microscopy (HR-TEM) are the popular techniques for characterization of nanoparticles. TEM images give an immediate visualization of the particles which provides direct information of the size, shape, dispersion, structure and morphology of nano-systems. TEM images usually complement to XRD data and also enable to observe details at a nanometer scale. However, it should be noted that this technique gives image of a very small section of the material.

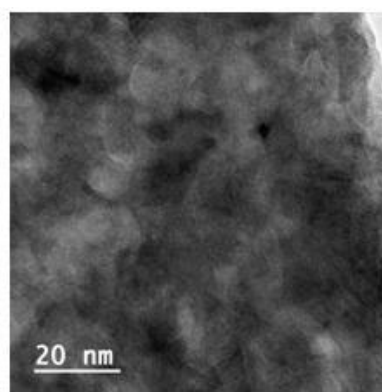
In the present study, TEM analysis was carried out (at Sprint Testing Lab, Mumbai, Son JEOL JEM 2100), where the material was dispersed in acetone and put on the grid. Bright field TEM images of ZnS, ZnSD1 and ZnSD2 nanoparticles are shown in the figure 2, figure 3 and figure 4, respectively. Figure 2 displays the TEM image of large number of assembled ZnS nanoparticles with almost uniform shape and size. It can be observed that the particles are of spherical shape with it size in the range of 5nm - 20nm [20]. All figures shows size of particle in the range of 10-20 nm and the slight reduction is observed with the increasing content of L- arginine.



**Figure 2:** TEM image of ZnS



**Figure 3:** TEM image of ZnSD1



**Figure 4:** TEM image of ZnSD2

**FT-IR spectroscopy studies:**

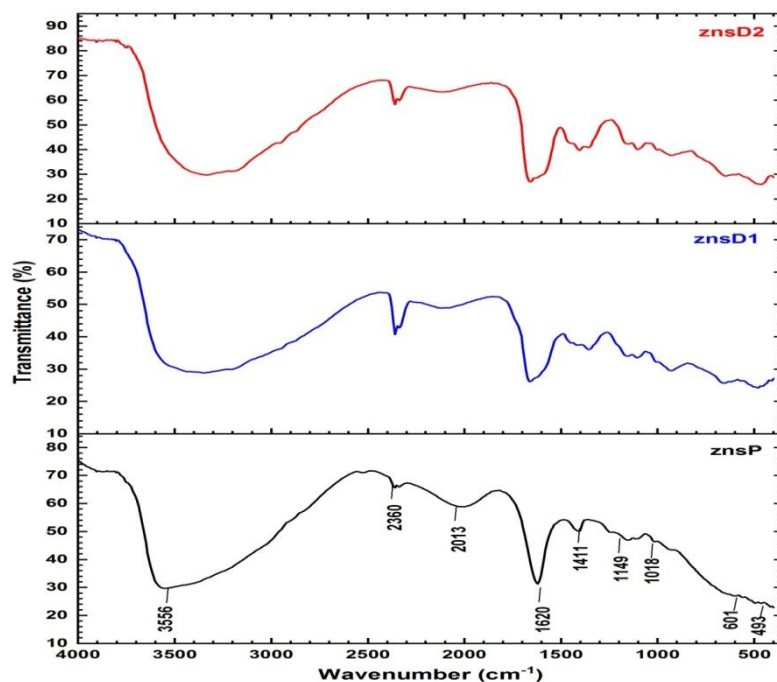
Fourier Transform Infrared (FT-IR) spectroscopy takes advantage of IR active behavior of the samples. It observes the vibrational modes of the molecular bonds present within the samples in an infrared spectrum. The absorption or transmittance peaks of these vibration modes correspond to the frequencies of vibrations between bonds of the atoms making up the material. From the characteristic absorption or transmittance peaks at particular wave number range, different functional groups present in the compound can be identified. There will be an interaction of IR radiation with the molecule if the dipole moment changes due to vibration.

Hence, such mode of vibration is said to be IR active. One can observe increase in amplitude of vibration when energy is transferred to the molecule if the frequency of radiation matches with the frequency of a particular vibration. The frequency of vibration can be obtained from Hooke’s law:

$$v = \frac{1}{2\pi c} \sqrt{\frac{K}{\mu}} \dots \dots \dots (2)$$

Where,  $v$  is the vibrational frequency,  $c$  is velocity of light,  $K$  is the force constant and  $\mu$  is reduced mass. So, from the characteristic bands of certain vibrational frequencies in the IR spectra, one can get structural information about the molecule.

Infrared (IR) spectroscopy is an excellent tool for both qualitative and quantitative analysis [21- 23]. FT-IR spectroscopy is the further advancement of IR spectroscopy by using the mathematical concept of Fourier Transform through proper electronic circuit and computer interfacing.



**Figure 5:** FT-IR spectra for ZnS, ZnSD1 and ZnSD2 nanoparticles.

In the present work, the FTIR studies were carried out using SHIMADZU make FTIR-8400 spectrometer at Department of Chemistry, Saurashtra University, Rajkot in the frequency range of 4000 to 400  $\text{cm}^{-1}$  by properly mixing the sample with spectroscopic grade KBr. Figure 5 shows the room temperature FTIR spectra of, ZnSD1 and ZnSD2 nanoparticles. The presence of water of hydration is primarily confirmed with the presence of a sharp dip at 3556  $\text{cm}^{-1}$ , which is regarded due to O-H stretching. The broad absorption peaks in a range of 3100  $\text{cm}^{-1}$ –3600  $\text{cm}^{-1}$  correspond to O–H stretching modes arising from the absorption of water on the surface of nanoparticles via –COOH group [23-24]. It is slightly sifted shown in the graph of ZnSD1 and ZnSD2. A broad dip of absorption at 1620  $\text{cm}^{-1}$ , and 1149  $\text{cm}^{-1}$  indicates the presence of more than one C=O bond, while the absorptions at 1411  $\text{cm}^{-1}$  due to C=C in enol or keto forms. The absorptions at 1018  $\text{cm}^{-1}$  is due to C–N bond and the absorptions between 400  $\text{cm}^{-1}$  to 600  $\text{cm}^{-1}$  show the presences of oxygen-metal bond.

#### **Thermal analysis:**

Thermo gravimetric analysis (TGA) is a very useful technique to assess the thermal stability of various substances; many workers have demonstrated its usefulness [25-27]. In TGA, the weight of a sample in a controlled atmosphere is recorded continuously as a function of temperature or time, as the temperature of the sample is increased (usually linearly with time). A plot of mass or mass percent as a function of temperature is called a thermogram, or a thermal decomposition curve, or a pyrolysis curve. Often a pyrolysis occurs through many-stepped mechanisms, where the temperature ranges for each step overlap, resulting in irregular weight-temperature curve that may be difficult to analyze. Also, in many cases the trace follows a characteristics path common to a wide range of decomposition processes, which includes many polymer pyrolysis.

In the present study it is clearly seen that the first stage of decomposition occurs before 100° C may be due to the presence water content in the sample. Then, between 200° C to 500° C the gradual decrease in weight is observed. The third stage of decomposition occurs at 500° C to 700° C which completes later in the samples ZnSD1 and ZnSD2 probably the some content of amino acid decomposes later resulted in the phenomena. In each sample the decomposition takes place by three steps, however there is almost negligible difference in the final residue at the final stage may be caused by least amount of amino acid content succeed in entering or attaching the parent ZnS structure, which is further supported by EDAX analysis data.

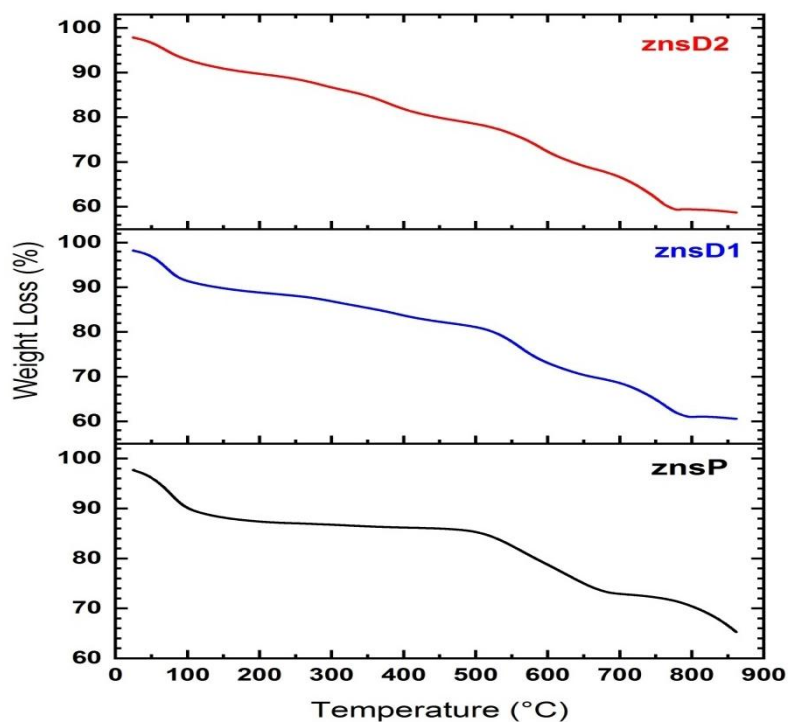


Figure 6: Thermogram of ZnS, ZnSD1 and ZnSD2 nanoparticles.

**EDAX analysis:**

Energy Dispersive X-Ray Analysis (EDAX), referred to as EDS or EDAX, is an x-ray technique used to identify the elemental composition of materials. The EDAX figure shows the presence of C, N, O in the doped samples confirms the successful doping of L-arginine in ZnS nanoparticles.

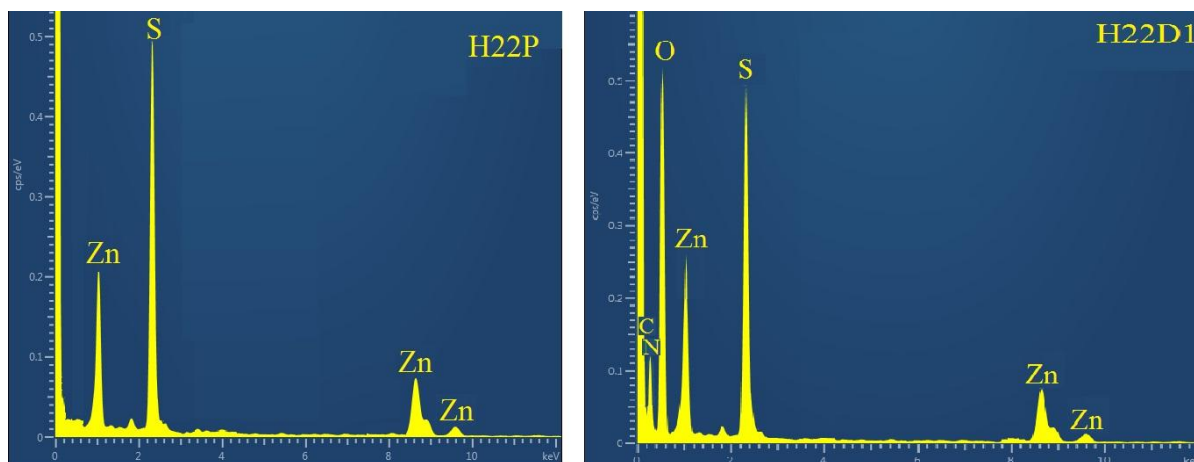


Figure 6: EDAX spectra of ZnS, ZnSD1 nanoparticles.

**IV. Conclusion**

ZnS nanoparticles are successfully synthesized via the co-precipitation method. The powder XRD confirmed the cubic crystal structure same as bulk ZnS nanoparticle. HRTEM image of large number of assembled ZnS nanoparticles with almost uniform shape and size. It can be observed that the particles are of spherical shape with it size in the range of 10 nm to 20 nm. The HRTEM shows the ZnS ZnSD1 and ZnSD2 nanoparticles has nano sized nature of the particles. The FT-IR spectrum indicates the presence of water of hydration, O-H stretching, N-H rocking and stretching, C=C group, C=O carbonyl group (keton group), and C-N vibration, comparing the values of C-N Stretching, C=O stretching and O-H stretching vibration ZnSD1 and ZnSD2 nanoparticles further confirms the successful doping of amino acid in ZnS samples. The EDAX analysis confirmed the successful doping of L-arginine in ZnS nanoparticles. The thermogram of nanoparticles ZnS, ZnSD1 and ZnSD2 suggested decomposition of samples occur by three stages and almost equal amount of final

residue at the final stage may be caused by least amount of amino acid content succeed in entering or attaching the parent ZnS structure, which is further supported by EDAX analysis data.

### References:

- [1]. J. M. Hwang, M. O. Oh, I. Kim, J. K. Lee and C. S. Ha Curr. Appl.Phys. (2005) 531
- [2]. H. Cho, C. Yun, J.-W. Park, and S. Org. Electron. **10** (2009) 1163
- [3]. K. J. Hong, T. S. Jeong, C. J. Yoon, and Y. J. Shin. J. Cryst. Growth **218** (2000) 19
- [4]. M. Yokogawa and N. Chen. J. Crystal Growth, **223** (2001) 369
- [5]. T. Yamamoto, S. Kishimoto and S. Iida, Physica B **916** (2001) 308
- [6]. X. Liu, X. Cai, J. Mao and C. Jin. Appl. Surf. Sci. **183** (2001) 103
- [7]. K. E. Sapsford, T. Pons, I. L. Medntz and H. Mattoussi. Sensors **6** (2006) 925
- [8]. M. Durandurdu. J. Phys. Chem. Solids **70** (2009) 645
- [9]. W. G. Becker and A. J. Bard J. Phys. Chem. **87** (1983)
- [10]. A. Henglein and M. Gutierrez, Ber. Bunsenges. Phys. Chem. **87** (1983) 852
- [11]. H. Weller, U. Koch, M. Gutierrez and A. Henglein 1984 Ber. Bunsenges. Phys. Chem. **88** (1984) 649
- [12]. J. Mu, D. Gu and Z. Xu Mater. Res. Bull. **40** (2005) 2198
- [13]. G. Zhu, K. Drozdowicz-Tomsia, K. McBean, M. R. Phillips and E.M.Goldys Opt. Mater. **29** (2007) 1579
- [14]. R. Kripal, A. K. Gupta, S. K. Mishra, R. K. Srivastava, A. C. Pandey and S. G. Prakash Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy **76** (2010) 523
- [15]. Y. Xu, L. Shi, X. Zhang, K. Wong and Q. Li Micron **42** (2011) 290
- [16]. J. P. Borah and K. C. Sarma Acta Phys. Polon. A **114** (2008) 713
- [17]. N. S. Tank, K. D. Parikh and M. J. Joshi AIP Conferences Proceedings (2017) 1837
- [18]. P. Iranmanesha, S. Saeedniab, and M. Nourzpoora, Chin. Phys. **24** (2015) 046104
- [19]. G. Cao, "Nanostructures and Nanomaterials", Imperial College Press, London (2004)
- [20]. B. Bodo, R. Singha and S. Chandra Das, International Journal of Applied Physics and Mathematics, **2** (2012)
- [21]. G. Socrates, Infrared Characteristics Group Frequencies, John Wiley, Chichester, (1980).
- [22]. R. R. Griffiths; Chemical Infrared Fourier Transform Spectroscopy, Academic Press, New York, (1972).
- [23]. K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, John Wiley 3<sup>rd</sup> Ed **5** (2006) 257
- [24]. N. S. Tank, K. R. Rathod, K. D. Parikh and M. J. Joshi AIP Conferences Proceedings (2016) 1728
- [25]. D. A. Anderson, E. S. Freeman, J. Polymer Sci **54** (1961) 253.
- [26]. H. C. Anderson, S. P. E. Trans **1** (1962) 202.
- [27]. H. D. Anderson Nature **191** (1961) 1088

N. S. Tank, et. al. "Synthesis and Characterization of ZnS Nanoparticles Dopped by L- arginine." *IOSR Journal of Applied Physics (IOSR-JAP)*, 14(03), 2022, pp. 34-40.