Maratha Vidya Prasarak Samaj's

KARMVEER SHANTARAMBAPU KONDAJI WAVARE ARTS,
SCIENCE & COMMERCE COLLEGE, CIDCO, NASHIK

NAAC Re-Accredited 'A' Grade (CGPA 3.20)

A

PROJECT REPORT

ON

# "Synthesis and Characterization of the $Cu_2ZnSnS_4$ Nanoparticles by using Hydrothermal Technique"

Submitted By : **Akshata Dileep Dahivelkar**

Academic Year

2020-2021

Under the Guidance of

**Dr. P.G. Loke**

# Certificate

This is to certify that Miss. **AKSHATA DILEEP DAHIVELKAR,** student of M.Sc. (Physics) has satisfactory completed her project work on **"SYNTHESIS AND CHARACTERIZATION OF THE $Cu_2ZnSnS_4$ NANOPARTICLES BY USING HYDROTHERMAL TECHINQUE"** Towards the partial fulfillment of her M.Sc.(Physics) Semester – IV during Academic year 2020-2021.

Place : Nashik,

Date :

Dr. P. G. Loke

(Project Guide)

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(Head of department)

Internal Examinar

External Examinar

# ACKNOWLEDGEMENT

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In the accomplishment of this project successfully, many people have best owned upon me their blessing and the heart pledged support, this time I am utilizing to thank all the people who have been concerned with this project.

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♦ Akshata Dileep Dahivelkar

# ABSTRACT

Solution-synthesized nanostructured $Cu_2ZnSnS_4$ (CZTS) has attracted significant attention as a promising candidate for use as an efficient and inexpensive photovoltaic energy convertor material. In general, the solution synthesized route involves the use of toxic and explosive chemicals. The present report emphasizes a non-toxic surfactant mediated hydrothermal route for the synthesis of CZTS NPs without the use of toxic chemicals. The physical and chemical properties of the CZTS NPs were studied using X-ray diffraction (XRD), UV visible Spectroscopy (UV vis), Fourier Transform Infrared Spectroscopy (FTIR), Field Emission Scanning Electron Microscopy (FESEM). The XRD spectroscopy result confirmed the formation of single-phase kieserite CZTS NPs. A synthesized sample shows three major peaks at 2θ = 27.00°, 29.09°, 32.77°, 47.79° and 58.95° can be attributed to the diffraction from (101), (112), (200), (220) and (224) planes respectively. From XRD, it shows the particle size is 6nm calculated using Debye Scherrer formula. UV -Visible spectroscopy study gives optical Band gap suggesting CZTS as a good visible light absorbing material. From FTIR analysis it shows the presence of many functional groups like hydroxyl, aldehyde, halo and sulfoxide. Fourier Transform Infrared Spectroscopy (FTIR) shows strong peaks of Aldehyde and Sulfoxide groups present in sample. The peak at 1055.06 $cm^{-1}$ is due to presence of S=O i.e. sulfoxide group. FESEM analysis revealed the formation of well-dispersed CZTS NPs that were 13-14 nm in size. The synthesized CZTS NPs could be used in the form of ink, which could be used to directly coat large area thin film solar cells. Moreover, the probable reaction mechanism for the formation of surfactant assisted CZTS NPs is proposed in present report.

**Keywords:** CZTS Nanoparticles, Hydrothermal, Solar Cells, XRD, FESEM, etc

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# CHAPTER 1

## 1.INTRODUCTION :

$Cu_2ZnSnS_4$ (CZTS) is one of the hopeful materials for the next generation of solar cells due to its Non-toxic and Earth-abundant(Cu: 50 ppm, Zn: 75 ppm, Sn: 2.2 ppm, S:260 ppm)[5]. constituents, good photostability[6], direct band gap energy (~1.5eV), large absorption coefficient (>104 cm-1)[7] and optimal energy band structure, has been widely researched[8]. and Several vacuum and non-vacuum based techniques have been reported for the synthesis of CZTS such as Sputtering, Sol-gel, Electro-deposition [9], Spray Pyrolysis [10], Pulsed Laser Deposition, Co-evaporation, Hydrothermal,[11] Drop casting, etc. CZTS has witnessed a manifold applications in the cuttingedge science and technologies like gas sensors, $H_2$ production, Li-batteries, thermoelectrics, photocatalysis and so on[12].

Hydrothermal synthesis method involves using any one of the many techniques to crystallize substances. It usually does at a high vapor pressure level and using a high-temperature aqueous solution; hence it is termed as ‘Hydro’ + ‘Thermal’ = Hydrothermal method. We have observed natural process for more than 800 years now and the term has geological origins.

Among various non-vacuum based solution synthesis routes, the hydrothermal route is one of the well-known and efficient methods since it is low cost and environmentally friendly [16]. The hydrothermal route can be used to synthesize free standing nanostructures with various morphologies. Moreover, the hydrothermally synthesized CZTS nanocrystals have better crystallinity as compared to other methods. Literatures have shown that variation in reaction duration also plays a vital role in the structure of the thin film materials obtained using hydrothermal synthesis.

$Cu_2ZnSnS_4$ nanoparticles were synthesized by single step hydrothermal method Hydrothermal temperature and time are critical to the formation of single phase $Cu_2ZnSnS_4$ nanoparticles. Raman data suggested that $Cu_2S$ was formed first, Sn and Zn ion were incorporated in the next stage to form $Cu_2ZnSnS_4$. The hydrothermal synthesis possesses remarkable reliability and selectivity as well as high efficiency at low temperature. It does not require any expensive precursors or equipment and can be readily adopted for industrial production processes.

A low cost solar absorbing material with high absorption coefficient and direct band gap has attracted much more attention. Now-a-days copper zinc tin sulphide$Cu_2ZnSnS_4$(CZTS) is a promising material as its constituents are Eco-friendly, Non-toxic, Earth abundant, Low cost and its Absorption Coefficient is also high (~104 cm−1). It is a quaternary p-type semiconducting material[17] which possesses potential to be used in energy harvesting, thermoelectric as well as photocatalytic applications[15]. CZTS was reported by Katagiri for the first time. After that several nanocrystal synthesis methods have been reported, of CZTS such as Microwave, Sol–Gel[18], Solvothermal[14], SILAR, Hot injection[13]. Among these methods, hydrothermal has been widely used due to the simpler procedure, eco-friendly and economical nature. The research is focused on such multifunctional material that can be used in different applications. This boosted our interest for the synthesis of CZTS via hydrothermal route.

Moreover, the hydrothermal growth involves the crystallization of a dissolved solid from a solution by varying the thermodynamic stability of the desired compound by controlling the physical and chemical parameters, such as temperature, pressure and composition of the precursor and surfactants to control the crystal morphology. The reactions that occur in the solution are unique to each hydrothermal system. In the present work, chlorides of zinc, copper and tin were used as starting materials, which offers stability, low toxicity and a relatively low cost. Moreover, the metal chlorides have a strong reducing power. In a hydrothermal process, Cu, Zn, and Sn chlorides dissociate into ions as a function of temperature, and the oxidation–reduction reaction between $Cu_2$+, $Zn_2$+ and $Sn_2$+ inside the hydrothermal autoclave ultimately affords $Cu_2$+, $Zn_2$+ and $Sn_4$+ (cations). In addition, $Na_2S$ will be reduced to $S_2$(anions) ions. However, the system energy increases as a function of temperature. To minimize the system energy, the chalcogenide ions were complexed with metal ions to form stable metal–chalcogenide complexes. This complex can act as a nucleation site that leads to the growth of CZTS NPs.

## 1.1COPPER ZINC TIN SULFIDE (CZTS) PROPERTIES:

- Crystal Properties :

CZTS thin films are usually in a polycrystalline form consisting of Kasterite crystal structures. Kasterite CZTS has highly similar crystal structure with chalcopyrite CIGS where half of indium and (or) gallium is replaced by zinc and the other half by tin. Similar to ZnO or ZnS, the anions and cations in Kasterite CZTS crystals are located in a tetrahedral bonding environment with a stacking model which is similar to zinc blend.

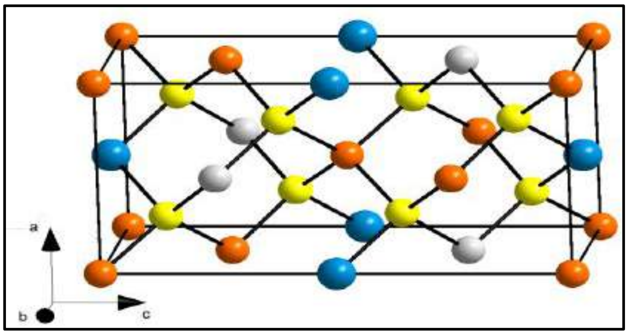


**Fig. 1.1 CZTS crystal structure (Orange: Cu, Grey: Zn, Blue: Sn, Yellow: S)**

➢ Optical Properties :

The optical band gap of stoichiometric Kasterite CZTS was theoretically determined to be 1.50eV. Experimental results demonstrated that band gap of CZTS deposited using different method varied from 1.4eV to 1.5eV. It is commonly recognized that CZTS has an absorption coefficient as high as $10^4 cm^{-1}$. Sol-gel derived CZTS from our group confirmed that the absorption coefficient is higher than the $10^4 cm^{-1}$. In the photon energy range greater than 1.2eV.

➢ Electrical Properties :

In contrast with silicon where either atoms of phosphorous or atoms of boron are intentionally introduced for produced n-type and p-type semiconductors, respectively. CZTS is self-energy doped through a formation of intrinsic defects including vacancies. It was found that the formation of acceptor defects was lower than that of donor defects, which makes n-type doping very difficult in CZTS. The commonly observed p-type conductivity of CZTS comes mainly from the Cu Zn antisite defects, partly explaining why CZTS must be Cu – poor and Zinc – rich to successfully fabricate CZTS powder.

**∆ Advantages :-**

◘ The ability to synthesize substances that are
unstable near the melting point
◘ The ability to synthesize large crystals of high
quality

**∆ Disadvantages : -**

◘ High cost of equipment
◘ The impossibility of observing the crystal as it grows if a steel tube is used.

## 1.2 NANOPARTICLES:

Nanoparticles are particles with at least one dimension smaller than 1 micron and potentially as small as atomic and molecular length scales (~0.2 nm). Nanoparticles can have amorphous orcrystalline form and their surfaces can act as carriers for liquid droplets or gases. To some degree, nanoparticulate matter should be considered a distinct state of matter, in addition to the solid, liquid, gaseous, and plasma states, due to its distinct properties (large surface area and quantum size effects). Examples of materials in crystalline nanoparticle form are fullerenes and carbon nanotubes,while traditional crystalline solid forms are graphite and diamond. Many authors limit the size of nanomaterials to 50 nm or 100 nm, the choice of this upper limit being justified by the fact that some physical properties of nanoparticles approach those of bulk when their size reaches these values. However, this size threshold varies with material type and cannot be the basis for such a classification. A legitimate definition extends this upper size limit to 1 micron, the sub-micronrange being classified as nano.

## 1.3 NANOTECHNOLOGY:

Nanotechnology, which develops materials of dimension smaller than 100 nm, possesses tremendous potential to address many scientific and technological challenges, faced by mankind in a variety of fields. This is in accord with Richard Feynman's speech back in 1959, when he described a vision – ''to synthesize nanoscale building blocks with precisely controlled size and composition, and assemble them into larger structures with unique properties and functions''. This vision has sparked the imagination of a generation of researchers. Nowadays, this small word 'Nano' has become so famous that almost every common person in the society knows 'Nano' being something to be 'very small' although only few of them know its actual meaning. Actually 'Nano' is a Greek word; meaning dwarf. Mathematically a 'Nano' means one billionth. Thus, 1 nm = $10^{-9}$ m. To get a sense of the nano scale, a human hair measures 80,000 nanometers across or just ten hydrogen atoms in a line make up one nanometer. The thing, which is smaller than a nanometer in size, is just a loose atom or small molecule floating in space. Thus, in practice nanostructures are the smallest solid things, which are practically possible to make or ever has made. Any engineered object with at least one of its dimensions less than 100 nm is called as a 'Nanomaterial'. In fact, the nanoscale is unique because it is in the range of the size where the familiar everyday materials properties dominated by quantum mechanical phenomena causing these materials to display many novel and interesting electrical, optical, electronic, magnetic and chemical properties usually not achieved by their bulk counterparts. An overview of the typical dimensional ranges of various materials approaching the nanosize region is shown in below figure

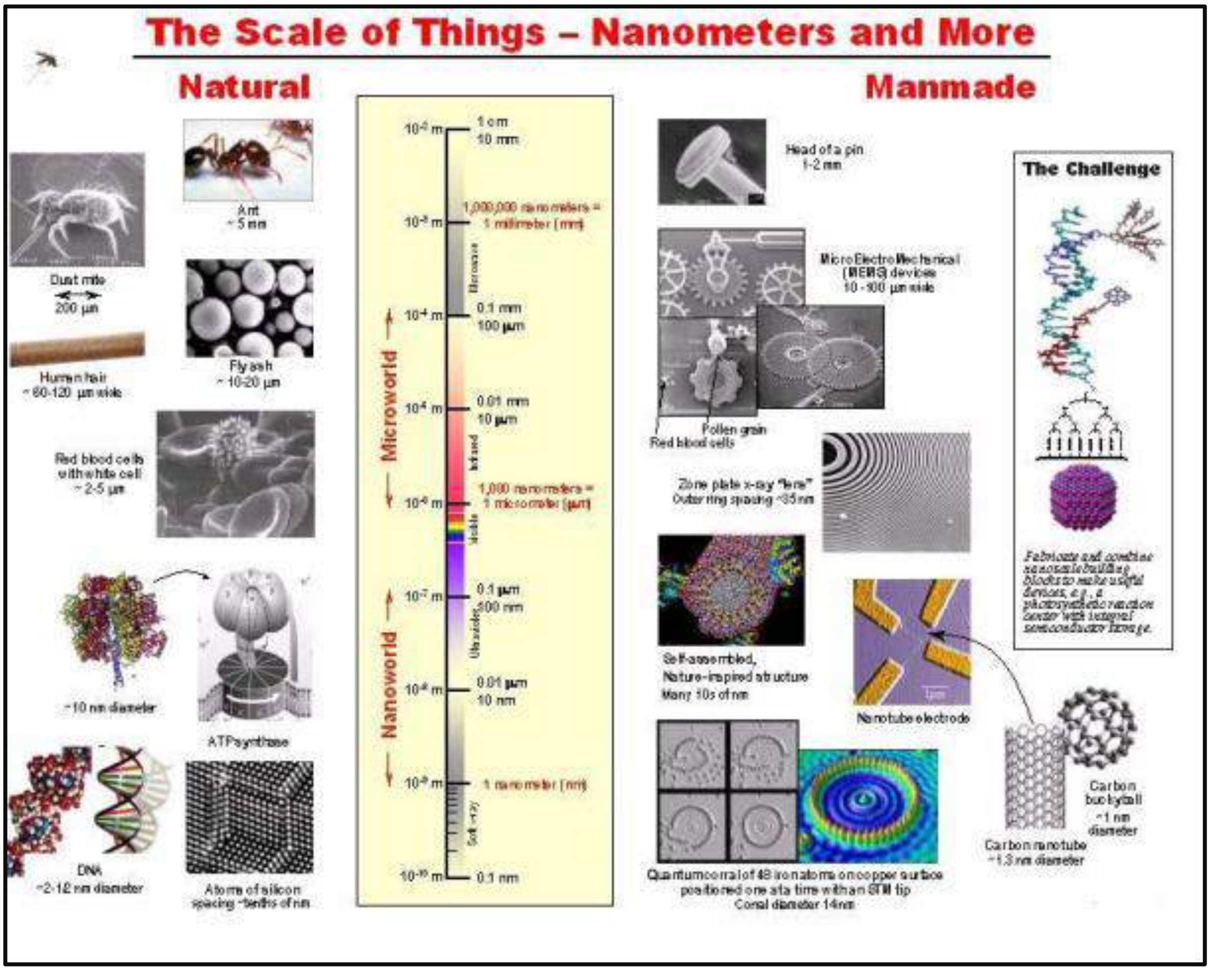


Fig. 1.2 Scale of things

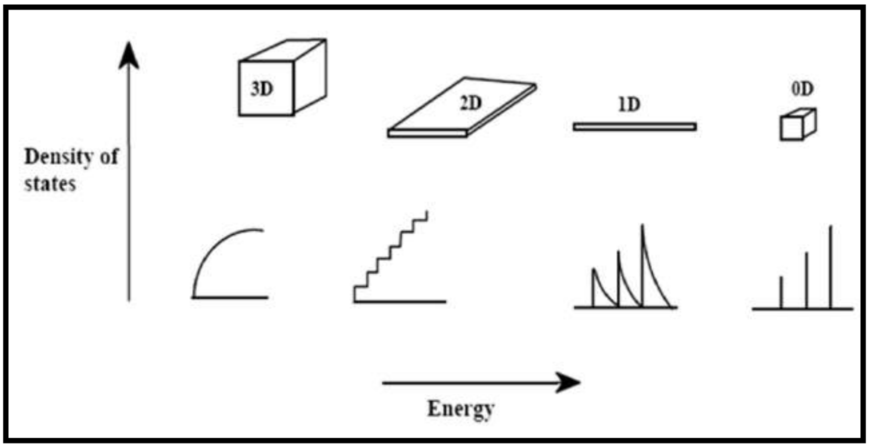
**●Why Nano length scale?**

By patterning matter on the nano scale, it is possible to vary fundamental properties of materials without changing the chemical composition. There are two primary types of nano scale building blocks that may be used for further device fabrication and applications

(i) 0D (e.g., nanoparticles, nanoclusters, nanocrystals)

(ii) 1D (e.g., nanotubes, nanofibers, nanowires)SS

The direct incorporation of these Nano architectures in existing materials to improve their properties is often referred to as incremental nanotechnology. However, the self-assembly of these Nano sized building blocks into 2D (e.g.-films, plates, network) and 3D (e.g.-nanomaterials) architectures may yield entirely new devices and functionalities - referred to as evolutionary nanotechnology.



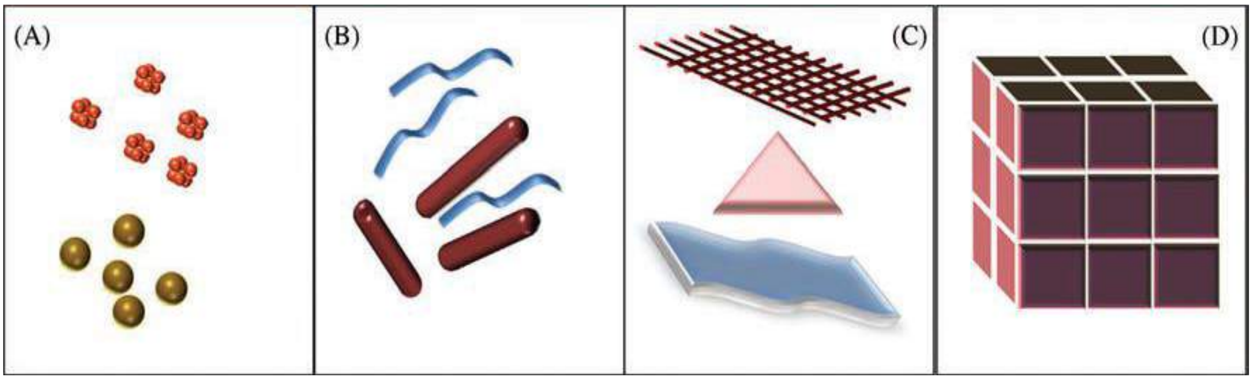


**Fig1.3:-Various kinds of nanomaterials. (A) 0D spheres and clusters. (B) 1D nanofibers, wires, and rods. (C) 2D films, plates, and networks. (D) 3D nanomaterials.**

## 1.4 NANOSCIENCE:

"THERE'S PLENTY OF ROOM AT THE BOTTOM"

Nanoscience is the study of phenomena on a nanometer scale. Atoms are a few tenths of a nanometer in diameter and molecules are typically a few nanometers in size. The smallest structures humans have made have dimensions of a few nanometers and the smallest structures we will ever make will have the dimensions of a few nanometers. This is because as soon as a few atoms are placed next to each other, the resulting structure is a few nanometers in size. The smallest transistors, memory elements, light sources, motors, sensors, lasers, and pumps are all just a few nanometers in size. Nanoscience is the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at a larger scale.

Besides the technological relevance of nanoscience, there is an enormous hype associated with it. Fantastic claims have been made about faster computers, cheap production of goods, and medical breakthroughs. Nanotechnology is expected to appear in products such as tennis rackets, self-cleaning cars, paint, food, cosmetics, and thermal underwear. The European Union is has identified nanotechnology as an important research area and is spending €. The goal of this project is to introduce the concepts of nanoscience so that the issues can be understood and a constructive contribution to the debates can be made.

Nanoscience is a science that describes manipulation of chemical and biological architectures with dimensions in the range from 1 to 100 nanometers. Nanoscience is about developing new chemical and biological nanostructures, uncovering and understanding their characteristics, and ultimately about learning how to organize and join these new nanostructures into larger and more complex functional architectures. It is integrated with nanotechnology because both of them are almost same in use. Nanoscience building blocks ranges from 100 to millions of atoms in a single block.

Nanoscience is a new way of thinking about building up complex materials and machines by exquisite control of the functionality of their matter and its assembling at the nanometer scale. Nanoscience provides a way ahead to the boundaries of every discipline in which it is used. The nano length scale needs the involvement of chemical concepts at the atomic and molecular level. Devices and other functional structures engineered at the nano scale often use light or electrical signals either to interact with the macroscopic world, or because the devices are designed to process information, with electrons and photons. The vision of nanoscience ultimately and finally combines the science, engineering and technology of human made biological entities, which are controlled at the nanometer scale, and then assembled into complex structures. These structures can interact with their surroundings at dimensions ranging from that of molecules to that of humans and beyond it.

## 1.5 APPLICATIONS OF NANOSCIENCE:

- **Nanoscience in food processing**: In food processing Nanoscience is used for improving food ingredients, packaging, flavoring and coloring and safety monitoring .major food processing companies are using nanoscience in testing the chemical reactions and for enhancing preservatives.
- **Nanoscience in medicine**: In the field of medical sciences nanoscience is used to detect the cancerous bacteria in the human body at early stages. Blood thinner used to regulate the blood level and the body also uses nanostructure particles.
- **Nanoscience and automobiles**: In automobile engineering Nanoscience plays important role in making brakes of the vehicle more efficient and soft and for improving the liquids of the disc brakes. In the world of automobile industry, nanoscience is also used for making engines stronger and reliable. Protective nanopaint for cars are made that resist water and dirt**,** resistant to chipping and scratches**,** brighter colors, enhanced gloss to cars all these advancement came into being when nanoscience stepped into field.

- **Influence of nanoscience in our lives**: Nanoscience has a great impact in our lives and lifestyles nanoscience when merged with nanotechnology provided us with the Neuro-electrical machines and other health care devices, which has reduced the death rate in the world. Nanoscience has given us the better way to live and provided us with the exigent and flawless products. Later on we would be definite seeing the more improved products of nanoscience because it has given us the new eye to see and realize the world.
- **Nanotechnology in energy:**Nanotechnogywill play important role in the field of energy. There is considerable amount of research going on to tap hydrogen fuel by spitting water ($H_2O$) using sunlight in presence of nanomaterials (photocatalysts).Hydrogen fuel is essential for a energy source so it can be stored with the help of carbon nanotubes which are now easily available.

# CHAPTER 2

## 2. SYNTHESIS OF NANOMATERIALS:

Last two decades evidenced the exponential growth of activities in the field of nano-science research. Third decade i.e. current time is the start of the new era in the field of nanoscience which includes the directional efforts towards the controlled syntheses of inorganic/organic nanomaterials of specific sizes, different shapes and stiochiometric compositions to get the desired properties in the controlled way. Thus, nanoscience has currently become a frontier field of research with far-reaching implications for the novel technologies. Its projected potential in this respect has led to a significant growth of activity in the fields of a) reproducible growth of nanomaterials with different uniform compositions and controlled shapes and sizes, b) their systematic studies by different reliable techniques such as SPM, TEM, various spectroscopy techniques etc. and c) exploration of these nanomaterials for novel potential technological applications.

There is large number of methods available to synthesize different types of materials in the form of colloids, clusters, powders, tubes, dots, wires, thin films etc. Some of the already existing conventional techniques to synthesize different types of materials are optimized to get novel nanomaterials and some new techniques are developed. Nanotechnology is interdisciplinary subject. There are therefore various chemical, physical, biological and hybrid techniques available to synthesize nanomaterial. The techniques to be used depends upon the material of interest, type of nanostructure viz. zero dimensional( 0D), one dimensional (1D) or two dimensional material (2D), quantity etc.

### 2.1 METHODS OF SYNTHESIS OF NANOMATERIALS:

- **Physical Methods:-**

1. High Energy Ball Milling
2. Melt Mixing
3. Physical Vapour Depositionwith Consolidation
4. Ionized Cluster Beam Deposition
5. Laser Vaporization
6. Laser Pyrolysis
7. Sputter Deposition:-DC & RF Sputtering
8. Chemical Vapour Deposition
9. Electric arc Deposition

- **Chemical Methods:-**

1. Colloids And Colloids in Solution
2. Langmuir-Blodgett (L-B) Methods
3. Micro emulsions
4. Sol-Gel Methods
5. Hydrothermal Methods

- **Biological Methods :-**

1. Synthesis using microorganisms
2. Synthesis using plant extracts
3. Synthesis using DNA

## 2.2 SOME ADVANTAGES OF CHEMICAL SYNTHESIS:

1. Simple techniques
2. Inexpensive, less instrumentation compare to many physical method
3. Low temperature (<350˚C) synthesis
4. Doping of foreign atoms (ions) possible during synthesis
5. Large quantities of the materials can be obtained
6. Variety of sizes and shapes are possible
7. Materials are obtained in the form of liquid but can be converted into dry powder or thin films
8. Self-assembly or patterning is possible

## 2.3 HYDROTHERMAL METHOD:

The hydrothermal technique is becoming one of the most important tools for advanced materials processing, particularly owing to its advantages in the processing of nanostructuralmaterials for a wide variety of technological applications such as electronics, optoelectronics, catalysis, ceramics, magnetic data storage, biomedical, biophotonics, etc. The hydrothermal technique not only helps in processing mono-dispersed and highly homogeneous nanoparticles,but also acts as one of the most attractive techniques for processing nano-hybrid and nano-compositematerials.

The term 'hydrothermal' is purely of geological origin. It was first used by the British geologist, Sir Roderick Murchison (1792-1871) to describe the action of water at elevated temperature and pressure, in bringing about changes in the earth's crust leading to the formation of various rocks and minerals. It is well known that the largest single crystal formed in nature (beryl crystal of >1000 g) and some of the large quantity of single crystals created by man in one experimental run (quartz crystals of several 1000s of g) are both of hydrothermal origin.

Hydrothermal processing can be defined as any heterogeneous reaction in the presence of aqueous solvents or mineralizers under high pressure and temperature conditions to dissolve and recrystallize (recover) materials that are relatively insoluble under ordinary conditions. Definition for the word hydrothermal has undergone several changes from the original Greek meaning of the words 'hydros' meaning water and 'thermos' meaning heat. Recently, Byrappa and Yoshimura define hydrothermal as any heterogeneous chemical reaction in the presence of a solvent (whether aqueous or non-aqueous) above the room temperature and at pressure greater than 1 atm in a closed system. However, there is still some confusion with regard to the very usage of the term hydrothermal.

However, if we look into the history of hydrothermal research, the supercritical fluids were used to synthesize a variety of crystals and mineral species in the late 19th century and the early 20th century itself. So, a majority of researchers now firmly believe that supercritical fluid technology is nothing but an extension of the hydrothermal technique. Hence, here the authors use only the term hydrothermal throughout the text to describe the entire heterogeneous chemical reactions taking place in a closed system in the presence of a solvent, whether it is aqueous ornon-aqueous.Hydrothermal synthesis is normally carried out in steel pressure vessels called'autoclaves' or 'bombs' with or without Teflon liners under controlled temperatureand/or pressure with the reaction in aqueous solutions **Fig.- 2.1 (A) and (B)**.

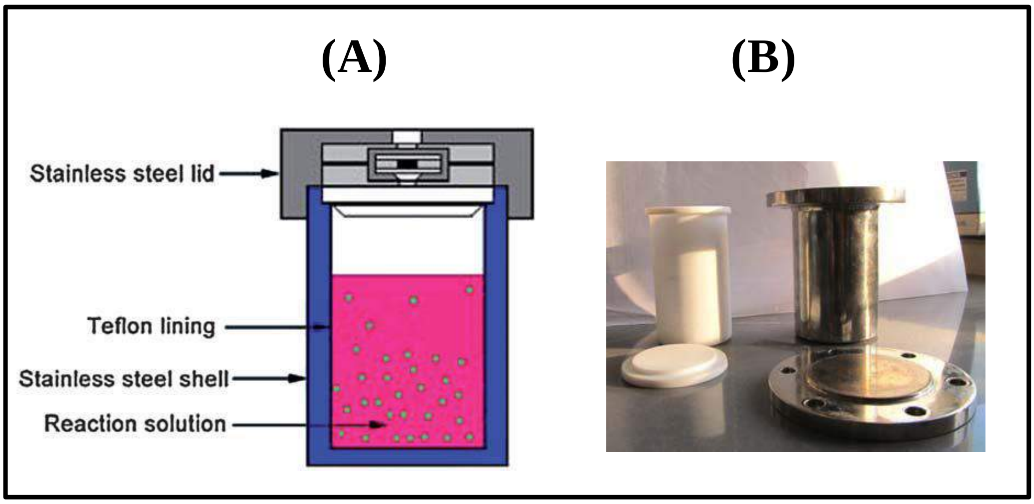


**Figure :**2.3**(A)**A schematic of a Teflon-lined, stainless autoclave (**B**) The photo of Stainless steel autoclave with Teflon liner typically used in the laboratory

The temperature can be above the boiling point of water, attaining the pressure of vapor saturation. The temperature as well as the amount of solution added, mainly deciding the internal pressure produced in the autoclave

Hydrothermal synthesis can be defined as a method of synthesis of single crystal that depends on the solubility of minerals in hot water under high pressure. A method to produce different chemical compounds and materials using closed-system physical and chemical processes flowing in aqueous solutions at temperatures above 100°C and pressures above 1 atm. The method is based on the ability of water and aqueous solutions to dilute at high temperature (500°C) and pressure (10-80 MPa, sometimes up to 300 MPa) substances practically insoluble under normal conditions: some oxides, silicates, sulphides. The main parameters of hydrothermal synthesis, which define both the processes kinetics and the properties of resulting products, are the initial pH of the medium, the duration and temperature of synthesis, and the pressure in the system. The synthesis is carried out in autoclaves which are sealed steel cylinders that can withstand high temperatures and pressure for a long time.

This synthesis method is useful to make a large scale production of nano to micro size particles. In this technique adequate chemical precursor are dissolved in water and placed in steel or any vessel which can withstand high temperature typically upto $300^0$ C and high pressure about 0.01GPa. The vessel known as auto-clave is usually provided with temperature and pressure control and measurement. This method useful to obtain novel shape and size of nanoparticles. This technique becomes useful when it is difficult to dissolve the precursor at low temperature and ordinary temperatures. It is also advantageous to use technique to grow nanoparticles if the material has a high vapour pressure near its melting point or crystalline phases are not stable at melting point. Various oxide, sulphide, carbonate tungstate nano-particles have been synthesized by the hydrothermal technique.

# CHAPTER 3

## 3. CHARACTERIZATION TECHNIQUES:

Nanostructures have attracted huge interest as a rapidly growing class of materials for many applications. Several techniques have been used to characterize the size, crystal structure, elemental composition and a variety of other physical properties of nanoparticles. In several cases, there are physical properties that can be evaluated by more than one technique. Different strengths and limitations of each technique complicate the choice of the most suitable method, while often a combinatorial characterization approach is needed. In addition, given that the significance of nanoparticles in basic research and applications is constantly increasing, it is necessary that researchers from separate fields overcome the challenges in the reproducible and reliable characterization of nanomaterials, after their synthesis and further process (e.g. annealing) stages. The principal objective of this review is to summarize the present knowledge on the use, advances, advantages and weaknesses of a large number of experimental techniques that are available for the characterization of nanoparticles. Different characterization techniques are classified according to the concept/group of the technique used, the information they can provide, or the materials that they are destined for. We describe the main characteristics of the techniques and their operation principles and we give various examples of their use, presenting them in a comparative mode, when possible, in relation to the property studied in each case.

### 3.1 X-ray Diffraction Analysis (XRD) :

XRD technique is exploit to determine structural properties of materials and concern with determination of crystal structure/phase, lattice constants, crystallite size, orientation of single crystals, preferred orientation of polycrystals, defects, strains etc.This information can also help us to identify the unknown phase in the product. This technique is suitable for powders and thin films samples of various materials. High-energy accelerated electrons are made incident on target surface, which could eject core electrons in atoms through the ionization process. When an electron from higher energy orbital fills the shell, characteristic X-ray photons are emitted. This depends on atomic number. Usually targets used in X-ray tubes include Cu and Mo, which emits 8 keV and 14 keV, X-rays with corresponding wavelengths of 1.54 Å and 0.8 Å, respectively. A collimated monochromatic beam of X-rays with a wavelength typically ranging from 0.7 to 2 Å, is incident on a specimen and is diffracted by the crystalline planes in the specimen according to Bragg's equation which places the condition for the constructive interference for the diffracted

X-ray from the successive atomic planes formed by the crystal lattice of the material. The Bragg’s condition is formulated by

$$\mathbf{2d\ sinq = n\lambda} \text{ ------------------------ } \mathbf{(2)}$$

Where **λ** the wavelength of the incident X-ray, d is the interplaner distance, qis the scattering angle and n is an integer-the order of diffraction. The fundamental requirement is the coherence in diffracted X-rays that leads to intense signal.

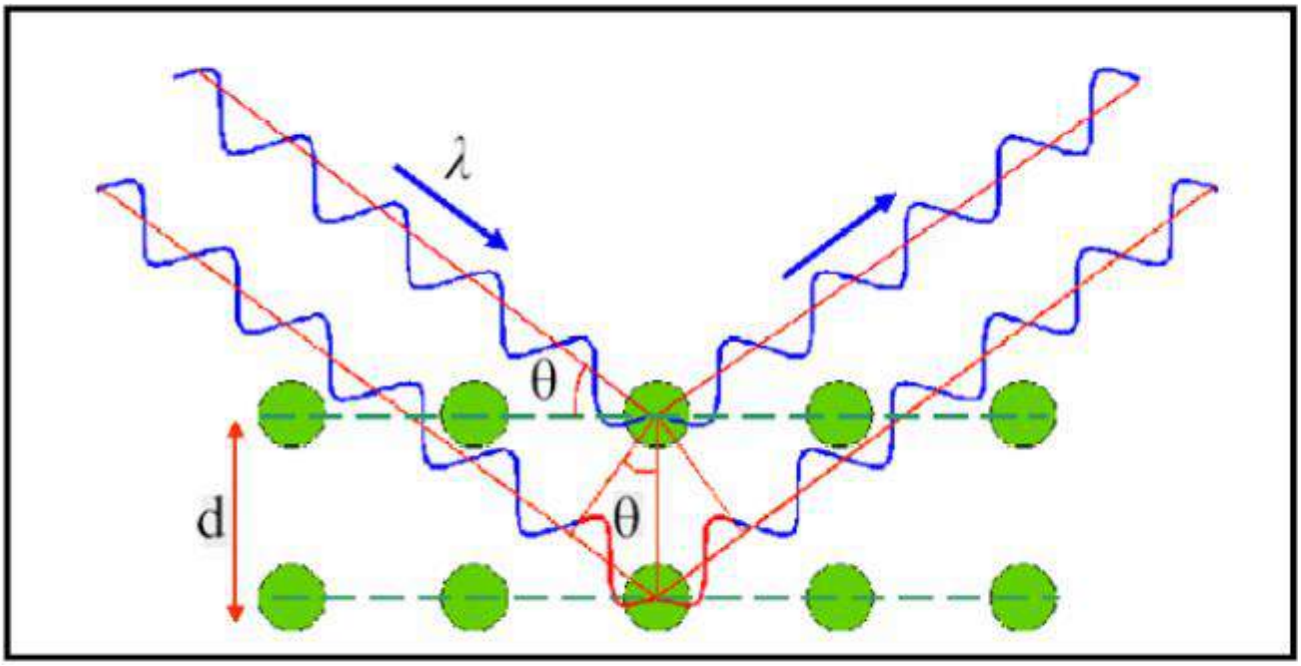


**Figure 3.1** : Representation of Diffraction of X-rays by crystal planes

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The XRD can be taken in various modes such as q-2q scan mode; a monochromatic beam of Xrayis incident on the sample at an angle of q with the sample surface. The detector motion is coupled with the X-ray source in such a way that it always makes an angle 2q with the incident direction of the X-ray beam (**Fig.3.1**). The resulting spectrum is a plot between the intensity recorded by the detector versus 2q. XRD is nondestructive and does not require complicated sample preparation. Nanomaterials have smaller sized crystallites and major strains due to surface effects, causing peak broadening and shifts in the pattern. From the shifts in the peak positions, one can calculate the change in the d-spacing, which is the result of change of lattice constants under strain. The crystallite size (D) is calculated using
Scherrer’s formula:

$$\boldsymbol{D = \frac{K\lambda}{\beta cosq}}$$

Where, k = Scherrer's Constant ≈ 0.9, β = Full Width at Half Maximum (FWHM). However, one should be know the fact that nanoparticles frequently form twinned structures; therefore, Scherrer's formula may produce results different from the actual particle sizes. Only disadvantage of XRD is its sensitivity towards low-Z materials, usually high-Z materials are used. In such cases, electron or neutron diffraction is employed to overcome the low intensity of diffracted X-rays, particularly for low-Z materials. For present study x-ray diffraction measurements were done on (Panalytical expert Pro) with Cu Ka radiation using a Ni filter.

## 3.2 UV-VIS Spectroscopy (UV-Vis) :

Absorption spectroscopy in the UV and visible region has long been an essential tool to the analyst. It measures the intensity of absorption of near-ultraviolet and visible light (wavelength region from 200-800 nm) by a sample. The transitions arise due to molecular and structural changes in the substances being examined, leading to corresponding changes in the ability to absorb light in the UV and visible region of the electromagnetic spectrum. UV and visible light are energetic enough to promote the outer electrons in an atomic, molecular or material system to higher energy levels depending on the specific nature of the electronic states of a given material. Absorption of energy leads to a transition of electron from ground state to excited state. In semiconductors, when the incident photon energy more than or equal to the band gap energy of the material then absorption takes place and signal is recorded by the spectrometer. This spectrometer can operate in two modes (i) transmission and (ii) reflection mode. In transmission mode usually thin films and colloidal nanoparticles well-dispersed in solvent are used. The optical measurements for those nanoparticles which are not dispersible in solvents are done in diffuse reflectance spectra (DRS) mode. Reflectance spectra provide information about the scattering and absorption coefficient of the samples and hence their optical properties. Schematic of UV-Vis spectrometer is shown in **Fig 3.2a.** The light from the deuterium source is alternatively split into one of two beams by a chopper; one beam is passed through the sample and the other through the reference. The detector, which is often a photodiode, alternates between measuring the sample beam and the reference beam (**Fig. 3.2a**). Some double beam instruments have two detectors, and the sample and reference beam are measured at the same time. In other instruments, the two beams pass through a beam chopper which blocks one beam at a time. The source used for the UV and visible light are deuterium and tungsten lamps respectively and the detector used is PMT.

**Intensity of Spectral lines:** There are three key factors that choose the intensity of spectral lines:

**(i) Transition probability:** The possibility of a system in one state changing to another state which is usually governed by selection rules obeying quantum mechanics.

**(ii) Population of states:** The number of atoms/molecules initially in the state from which the transition occurs is also most important deciding factor of intensity of spectral lines. It is governed by the equation:

$$\frac{\boldsymbol{Nupper}}{\boldsymbol{Nlower}} = \mathbf{exp}\left(-\frac{\Delta\mathbf{E}}{\boldsymbol{kBT}}\right)$$

Where ΔE = Eupper - Elower, T= temperature (K), kB = Boltzman's Constant

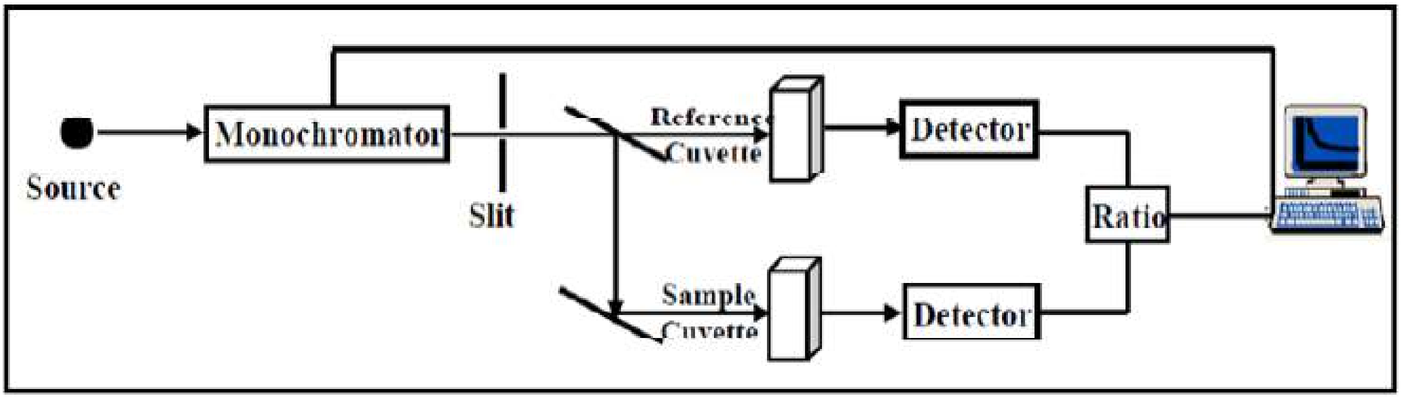


**Figure 3.2(A)**: Schematics of UV-VIS Spectrophotometer

**(iii) Concentration and path length:** Amount of material present giving rise to the spectrum. Clearly if a sample is absorbing energy from a beam of radiation, the more sample then more beam traverses, the more energy will be absorbed from it. Besides the amount of the sample, the concentration of the sample is also deciding factor for the energy absorption. The relationship between concentration (c), path length (l), and the incident and transmitted intensities of radiation, (I0 and I respectively) can be expressed in many ways, The combined Beer-Lambert law is used for quantification of exact concentration of unknown species in a mixture using UV-visspectroscopy. This can be done by drawing a graph of intensities of absorption for different concentrations of the sample and comparing with a standard graph.

$$\mathbf{I / I_0 = exp\ (-kcl)}$$

Where, k = constant, for particular spectroscopic transition under consideration.

$$\mathbf{I / I_0 = 10^{-\varepsilon cl} = T}$$

Where T = transmittance = $I / I_0$, ε= proportionality constant known as the absorptivity or molar absorption coefficient. Inverting above equation and taking logarithms,

$$\mathbf{I_0 / I = 10^{\varepsilon cl}}$$

$$\mathbf{log\ (I_0 / I) = \varepsilon\ c\ l = A}$$

$$\mathbf{A = \varepsilon\ c\ l}$$

Where A = absorbance/optical density, ε = proportionality constant known as the absorptivity or molar absorption coefficient. Thus, absorbance is directly proportional to the concentration, where the path length and molar extinction coefficient is supposed to be constant for the particular measurement.

**Broadening of spectral transitions:** Following are some of the possible sources for the signal broadening:

**(i) Doppler Broadening**: Random motion of particles in the liquids and gases samples causes their absorption and emission frequencies to show a Doppler shift and hence the spectrum lines are broadened. This effect is more pronounced in liquids than gaseous samples. In the case of solids, the motions of the particles are more limited in extent and less random in direction, so that solid phase spectra are often sharp but show evidence of interactions by the splitting of the lines into two or more components.

**(ii) Heisenberg's Uncertainty Principle**: If a system exists in an energy state for a limited time '$\delta t$' seconds, then the energy of that state will be uncertain to an extent '$\delta E$' and is given by $\delta E$ x $\delta t \approx h/2\pi \approx$ 10-34 J.s ,where h = Planck's Constant. Usually life time of excited state is 10-8 sec, i.e. 108 Hz uncertainty in the radiation frequency which is, in fact, small as compared to UV-Vis frequency regime (1014 – 1016 Hz)

**Diffuse Reflectance Measurement using Uv-Vis spectroscopy:** Since light cannot penetrate opaque (solid) samples, it is reflected on the surface of the samples. As shown in the below **Fig.3.2b**, incident light reflected symmetrically with respect to the normal line is called "specular reflection," while incident light scattered in different directions is called "diffuse reflection."

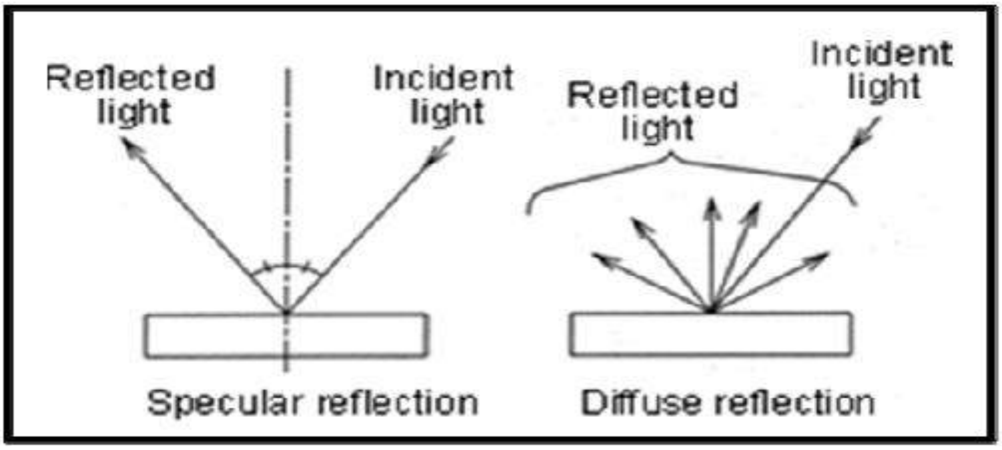


**Figure 3.2(B)**: Schematic of Specular and diffuse reflection

With integrating spheres, measurement is performed by placing the sample in front of the incident light window, and concentrating the light reflected from the sample on the detector using a sphere with a barium sulfate-coated inside. The obtained value becomes the reflectance (relative reflectance) with respect to the reflectance of the reference standard white board, which is taken to be 100%.

When light is directed at the sample at an angle of 0°, specular reflected light exits the integrating sphere and is not detected. As a result, only diffuse reflected light is measured. Models of integrating spheres with different angles of incidence are available, enablingmeasurement of both specular and diffuse reflected light in instances such as these as shown in **Fig 3.2c**.

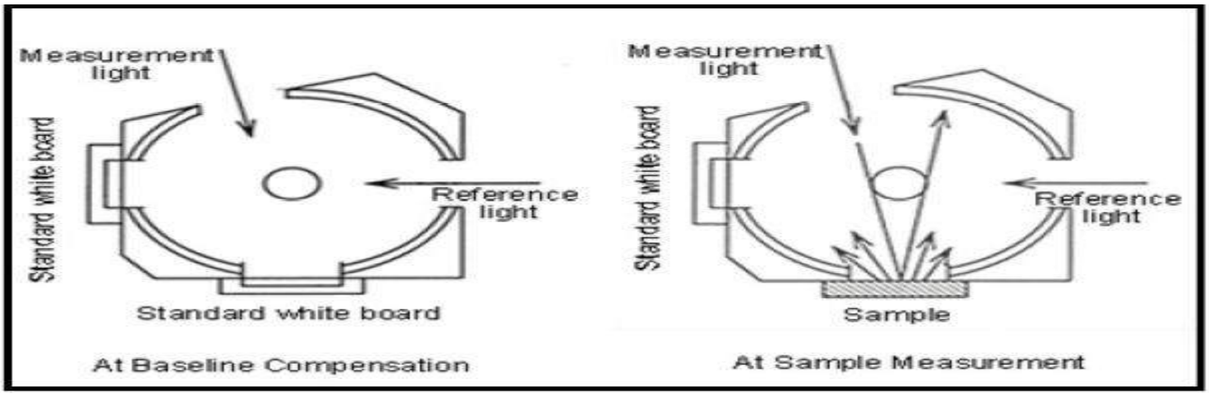


**Figure 3.2(C)**: Measurement of diffuse and specular reflection using an integrating

**Advantages:**

1. Analysis ability and easy to use.

2. In astronomy research, an UV / Vis spectrophotometer helps the scientists to analyze the galaxies, neutron stars, and other celestial objects.

3. A UV spectrum can provide rich information of the velocity and the elements of an astronomical object.

4. In other industries, UV / Vis spectrophotometer also brought the high-tech spectral analysis possibilities.

**Disadvantages:**

1. The stray light of UV-Vis spectrophotometer that caused by the faulty equipment design and other factors could influence spectra measurement accuracy of the absorption in substance.

2. In addition, the electronic circuit design and the detector circuit quality of spectrometer will affect the amount of noise that is coupled into the measurement signal, thereby affecting the measurement accuracy and reduce the sensitivity of the instrument.

## 3.3 Fourier Transform Infrared Spectroscopy (FTIR):

FTIR is a technique that provides information about the chemical bonding or molecular structure of materials, whether organic or inorganic and identifies chemical bonds or functional groups by the absorption of infrared radiation which excites vibrational modes in the bond. The atoms in a molecule do not remain in a fixed relative position and vibrate about their mean position. Owing to this vibrational motion, if there is a periodic change in the dipole moment then such mode of vibration is infrared active. The IR region of the electromagnetic spectrum is 100 μm –1 μm wavelength. The advantage of using FTIR is that the whole spectrum is obtained across the entire frequency range at once with constant resolving power over entire range. A molecule that is exposed to infrared rays absorbs infrared energy at frequencies which are characteristic to that molecule. Each functional group have particular range of vibrational frequencies and are extremely sensitive to the chemical environment and the neighboring, therefore they provide important information about the presence of certain functional groups in the particular sample.

The frequency of vibration is given by the relation

$$\boldsymbol{\nu} = \frac{\mathbf{1}}{\mathbf{2}\pi}\sqrt{\frac{k}{\mu}}$$

Where, k is force constant and μ is a reduced mass Schematic of FTIR spectrophotometer is shown in **Fig 3.3**. The apparatus derives from the classical attempt by Michelson to measure the ‘ether wind’ by determining the velocity of light in two perpendicular directions. A parallel beam of radiation is directed from the source to the interferometer, consisting of the beam splitter B and two mirrors, M1 and M2. The beam splitter is a plate of suitably transparent material (e.g. KBr) so as to reflect just 50% of the radiation falling on it. Thus half the radiation goes to M1, and half to M2, returns from both these mirrors along the same path, and is then recombined to a single beam at the beam splitter. It is well identified that if monochromatic radiation emitted by the source, the recombined beam leaving B shows constructive or destructive interference, depending on the relative path lengths B to M1 and B to M2. Thus if the path lengths are the same or differ by integral multiple of wavelengths, constructive interference gives bright beam leaving B, whereas if the difference is a half integral number of wavelengths, the beam cancels at B. As the mirror M2 is moved smoothly away or towards from B, therefore, a detector sees radiation alternating in intensity It is rather easy to visualize that if the source emits two separate monochromatic frequencies, υ1 and υ2 then interference pattern of υ1 and υ2 would overlay the interference caused by M1 and M2; the detector would see a more complicated intensity fluctuation as M2 is moved, but computing the Fourier transform of the resultant signal is very rapid way of obtaining the original frequencies and intensities emitted by the source.

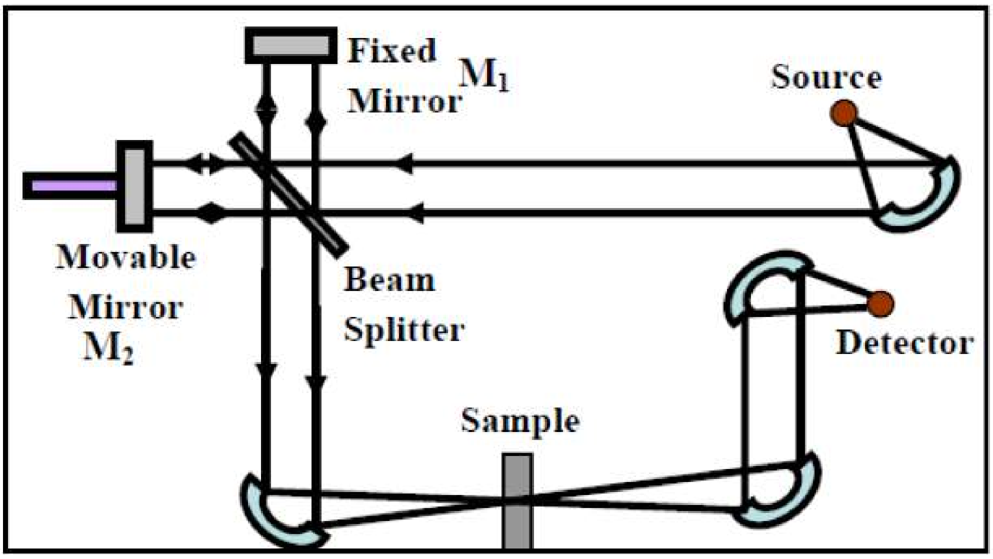


**Figure 3.3**: Schematic of FTIR Spectrophotometer

Taking the process further, even white radiations emitted by the source produces an interference pattern which can be transformed back to the original frequency distribution. The production of a spectrum is a two-stage process: (a) Without a sample in a beam, mirror M2 is moved smoothly over period of time through a distance of about 1 cm, while the detector signal the interferogram is collected into multi-channel computer; the computer carries out the Fourier transformation of the stored data to produce background spectrum. (b) A sample interferogram is recorded in exactly the same way, Fourier transformed, and then rationed against the background spectrum for plotting as transmittance spectrum. Alternatively, the sample and background spectra may each be calculated in absorbance forms and the latter simply subtracted from the former to give an absorbance spectrum of the sample alone. The advantage of using FTIR is that the whole spectrum is obtained across the entire frequency range at once with constant resolving power over entire range. In present study FTIR measurements were performed on a Perkin-Elmer Spectrum One B spectrophotometer over the spectral range of 400– 4000 $cm^{-1}$.

**Advantages:-**

1. We can determine small quantity of analyte.
2. Better sensitivity & brightness.
3. Allows simultaneous measurement over the entire wave number range.
4. Required no slit device.
5. The resolution is better and constant across the entire region under study.
6. High scanning by FT-IR is possible to measure the whole spectrum in a few seconds.
7. The detectors employed are much more sensitive.
8. Photometric accuracy advantage. These instruments employ a He-Ne laser as an internal wavelength calibration standard. These instruments are self-calibrating.

**Disadvantages:-**

1. Cannot detect atoms or monatomic ions-single atomic entities contain no chemical bonds.
2. Cannot detect molecules comprised of two identical atoms symmetric-such as N2 or O2.
3. Aqueous solution is very difficult to analyze-water is strong IR absorber.
4. Complex mixture-samples give rise to complex spectra.

**Application:-**

1. For opaque or cloudy samples.
2. Analysis of raw materials or finished products.
3. Kinetics reaction on the microsecond time-scale.
4. Analysis of chromatographic and the thermo gravimetric sample fractions.
5. Micro-samples. Tiny samples, such as in forensic analysis.
6. Identification of compounds.

## 3.4 Field Emission Scanning Electron Microscopy (FESEM):

Field Emission Scanning Electron Microscopy (**FESEM**) The field emission scanning electron microscope (FE-SEM) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern.

**Principle:**

FESEM is the abbreviation of Field Emission Scanning Electron Microscope. A FESEM is microscope that works with electrons (particles with a negative charge) instead of light. These electrons are liberated by a field emission source. The object is scanned by electrons according to a zig-zag pattern.

Fig 3.4: Field Emission Scanning Electron Microscopy Instrument

**Advantages:**

1. FESEM provides topographical and elemental information at magnifications of 10x to 300,000x, with virtually unlimited depth of field.
2. FESEM produces clearer, less electrostatically distorted images with spatial resolution down to 1 1/2 nanometers – three to six times better.
3. The ability to examine smaller-area contamination spots at electron accelerating voltages compatible with energy dispersive spectroscopy (EDS).
4. Reduced penetration of low-kinetic-energy electrons probes closer to the immediate material surface.
5. High-quality, low-voltage images with negligible electrical charging of samples (accelerating voltages ranging from 0.5 to 30 kilovolts).
6. Essentially no need for placing conducting coatings on insulating materials.
7. For ultra-high-magnification imaging, we use in-lens FESEM.

**Disadvantages:**

1. The size and cost.
2. FESEMs are expensive, large and must be housed in an area free of any possible electric, magnetic or vibration interference.
3. Maintenance involves keeping a steady voltage, currents to electromagnetic coils and circulation of cool water.

**Applications:**

1. Semiconductor device cross section analyses for gate widths, gate oxides, film thicknesses, and construction details
2. Advanced coating thickness and structure uniformity determination
3. Small contamination feature geometry and elemental composition measurement

# CHAPTER 4

## 4. RESULT AND DISCUSSION:

### 4.1 Material Characterizations:

The X-ray diffraction pattern of as synthesized CZTS NPs was recorded in the 2θrange of 10–80°at a scanning rate of 2°/min using Rikagu (Miniflex600, Japan).The ultraviolet-visible (UV-Vis) spectroscopy study of CZTS NPs was carried out by SHIMADZU Spectrophotometer in the range of 200 to 800 nm. The Fourier transform infrared spectrum was recorded by Fourier Transform Infra-red Spectrophotometer (FTIR), SHIMADZU IRAffinity-1. A drop of CZTS NPs solution was placed on freshly prepared KBr disc and scanned between 500 - 4000 $cm^{-1}$. The scanning electronic microscopic images were captured by FESEM (FEI Nova Nano SEM- 450 instrument) with an EDS (Bruker XFlash-6I30).

### 4.2 Molar mass & weight percent calculations:

It is defined as the mass of the given substance divided by the amount of substance.

**Formula:-Weight in gram** $= \frac{\textbf{Concentration} \times \textbf{Molar mass} \times \textbf{Volume}}{\textbf{1000}}$

► **Calculations for CZTS:**

**1) For Copper Chloride**

**Concentration =** 1M (0.02gm); **Molar mass of $CuCl_2$=** 134.45gm/mol

**Weight in gram =** $\frac{2M \times (134.45) \times 100ml}{1000}$

$= \frac{(0.02) \times 134.45 \times 100}{1000}$

= 0.2689gm

**2) For Zinc Chloride**

**Concentration =** 1M (0.01gm); **Molar mass of $ZnCl_2$**= 136.286gm/mol

**Weight in gram** = $\frac{1\text{M}\times(136.286)\times100\text{ml}}{1000}$

$= \frac{(0.01)\times136.286\times100}{1000}$

= 0.1362gm

**3) For Tin Chloride**

**Concentration =** 1M (0.01gm); **Molar mass of $SnCl_2$ =**189.6gm/mol

**Weight in gram** = $\frac{1\text{M}\times(189.6)\times100\text{ml}}{1000}$

$= \frac{(0.01)\times189.6\times100}{1000}$

= 0.1896gm

**4) For Sodium Sulphide**

**Concentration =** 4M (0.04gm); **Molar mass of$Na_2S$ =**78.0452gm/mol

**Weight in gram** = $\frac{4\text{M}\times(78.0452)\times100\text{ml}}{1000}$

$= \frac{(0.04)\times78.0452\times100}{1000}$

= 0.3121gm

## 4.3 Synthesis of CZTS:

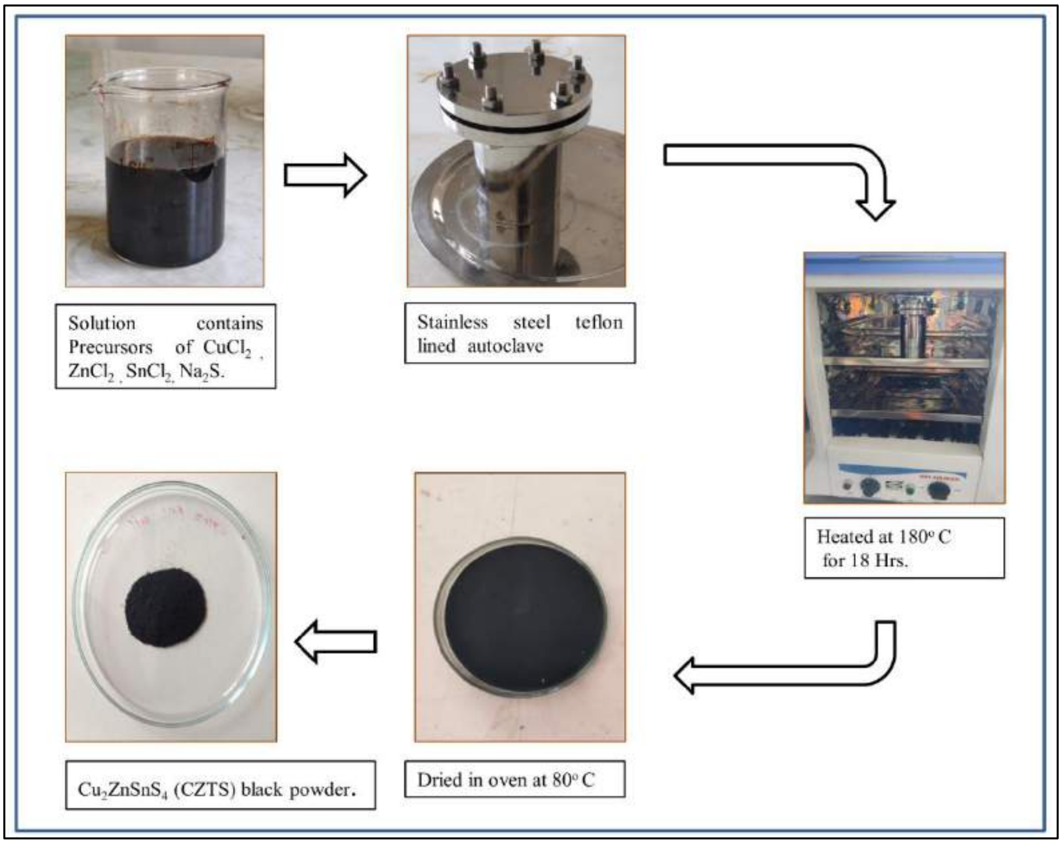


Figure 4.3: Schematic Diagram of Synthesis Process of CZTS composite

The chemicals such as copper chloride ($CuCl_2$), zinc chloride ($ZnCl_2$), tin chloride ($SnCl_2$) and sodium sulphide ($Na_2S$) with a purity level of 99%. All of the chemical reagents were used as received without further purification. In the synthesis route, the precursor solution was prepared from 0.02 M ($CuCl_2$), 0.01 M ($ZnCl_2$), 0.01 M ($SnCl_2$), and 0.04 M ($Na_2S$) in de-ionized water. The obtained precursor solution was maintained in a Teflon-lined stainless steel autoclave. Sealed autoclave was kept in Muffle Furnace at 180°C for 18 h. After natural cooling to room temperature, the nanoparticles were centrifuged and washed with de-ionized water and ethanol several times to remove water soluble impurities and finally drying it at 80°C for 6 h.

## 4.4 XRD:

The XRD patterns of synthesized and annealed samples are shown in Fig. 4.4. A synthesized sample shows three major peaks at 2θ = 27.00°, 29.09°, 32.77°, 47.79° and 58.95° can be attributed to the diffraction from (101), (112), (200), (220) and (224) planes respectively. After annealing intensity of major peaks increases indicating increase in crystalline nature of powder samples. Diffraction peaks match well with the JCPDS data reveal that the synthesized power has kieserite CZTS phase. The Average Particle size of the CZTS nanoparticles was calculated by Debye Scherrer formula which shows size is about 6 nm [18].

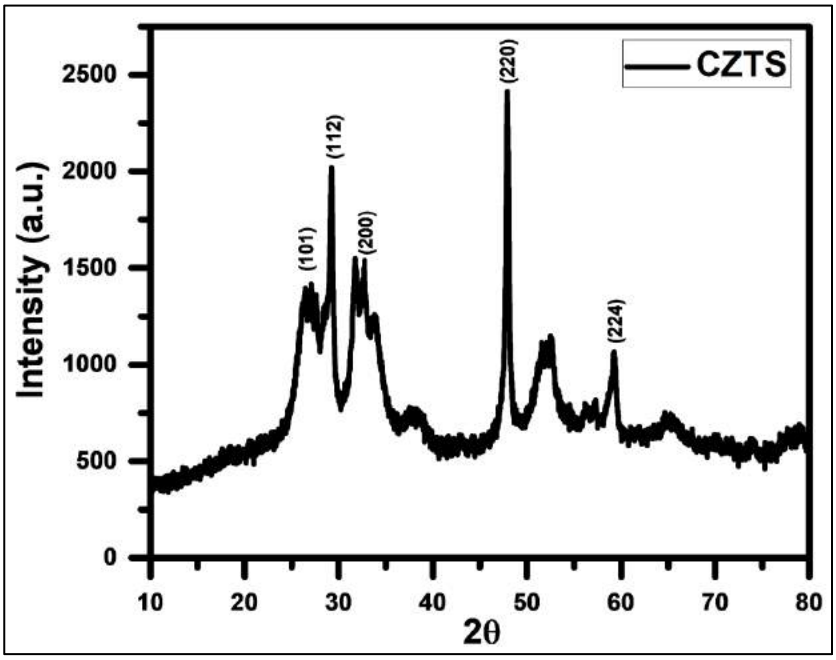


Fig 4.4: XRD Pattern of CZTS nanoparticles

| Peak Position | FWHM | Height | Crystal Size D | Average Distance | Crystal Plane |
|---|---|---|---|---|---|
| **27.0041** | 3.46671 | 793.685 | 2.35673 | | 101 |
| **29.0971** | 0.7431 | 846.09 | 11.0449 | | 112 |
| **32.7702** | 3.61329 | 848.691 | 2.2917 | 6.29684 | 200 |
| **47.7907** | 0.65963 | 1206.77 | 13.1726 | | 220 |
| **58.9535** | 3.48532 | 281.084 | 2.61828 | | 224 |

## 4.5 UV-VIS Spectroscopy:

Figure 4.5 shows the UV vis absorption spectra of CZTS nanoparticles. From figure, it shows that there are some small variations are present in spectra and spectra goes up and down as different wavelength with absorption. The UV vis shows optical properties of the CZTS nanoparticles sample it help to study the material properties with proper results.

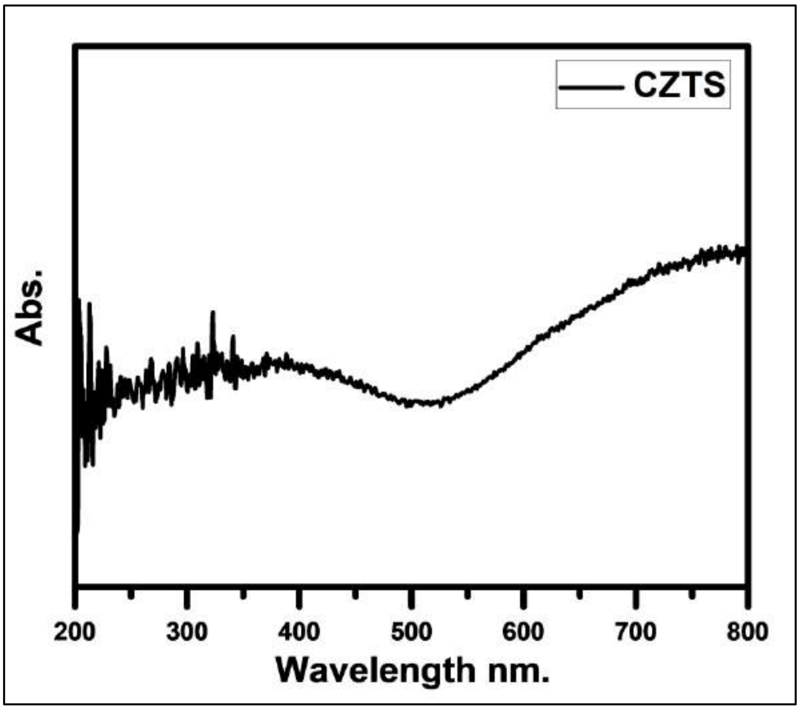


Fig. 4.5: UV vis of CZTS nanoparticles

## 4.6 FTIR:

The vibrational stretching of different bonds present in CZTS was investigated using FTIR spectrophotometer to reveals the presence of various peaks with maxima which exhibits the transmission spectra of CZTS. The peak at 2976 cm$^{-1}$ in the higher energy region is assigned to O-H stretching of absorption of water on the surface of CZTS NPs. The strong peak is observed at 2895 cm$^{-1}$ owing to C-H group. The aldehyde group which is observed at peak 1392 cm$^{-1}$. The C-O stretching vibration shows the intense and strong peak at 1249.87 cm$^{-1}$. The peak at 1055.06 cm$^{-1}$ is due to presence of S=O i.e. sulfoxide group. The small and strong peak at 445.56 cm$^{-1}$indicates the C-Cl Halo compound.

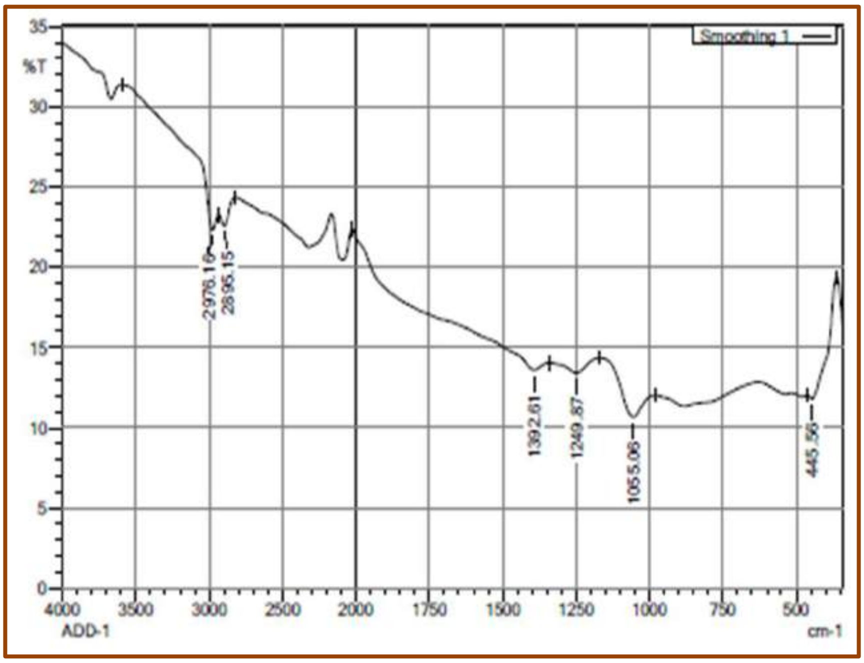


Figure 4.6: FTIR Spectra of CZTS

## 4.7 FESEM:

Field Emission Scanning Electron Microscopy (FESEM) gives morphology, Structural and size and shape of the nanoparticles. From EDAX we can say that all the nanoparticles are perfectly deposited or bounded and detected very well as shown in Figure: Similarly in figure: there is that presence of CZTS. In figure 4.7a shows various FESEM images at different resolution and magnification. Energy dispersive X-ray analysis (EDAX) as shown in the figure 4.7d confirms presence of CZTS without any impurity from figure 4.7e. The Field Emission Scanning Electron Microscopy (FESEM) gives a morphology, wide variety of information and higher resolution with greater energy ranges. The synthesized NPs was observed using this technique and we found that the structure and actual size of the CZTS. By the results of FESEM we obtained that the nanoparticles average size was about 13 nm. There was different ranges used to analyse the morphology that ranges are 50µm, 10 µm, 5 µm, 2 µm, 1 µm, 500nm, 400nm and 200nm. For these nanoparticles to know more EDS was taken and it shows the presence all elements. EDS also shows the coloured image of CZTS detection shown in Fig: 4.7d and 4.7e.

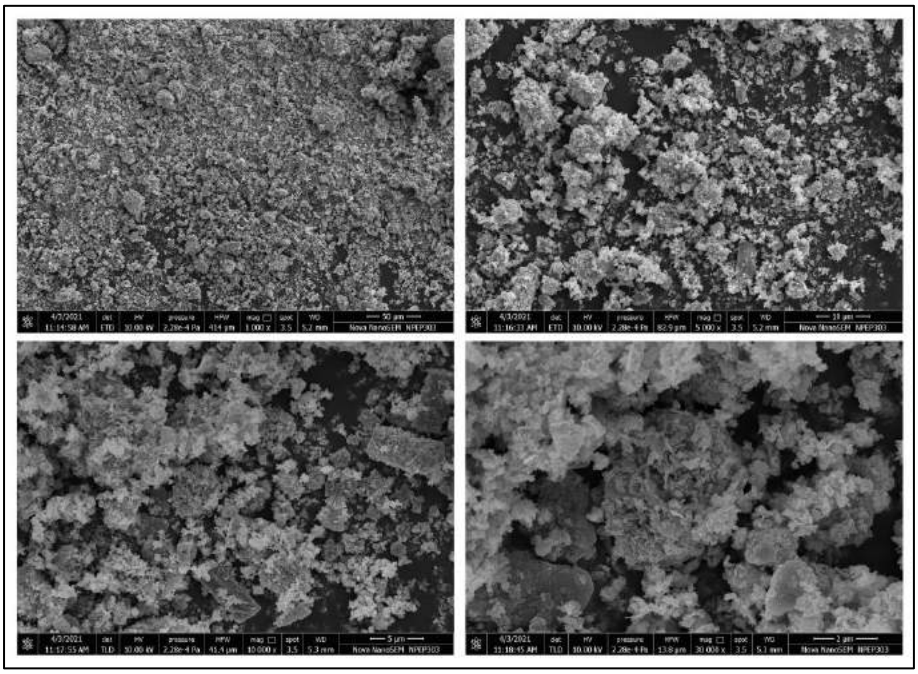


Fig.4.7(A): FESEM of CZTS at the ranges of 50µm, 10 µm, 5 µm, 2 µm

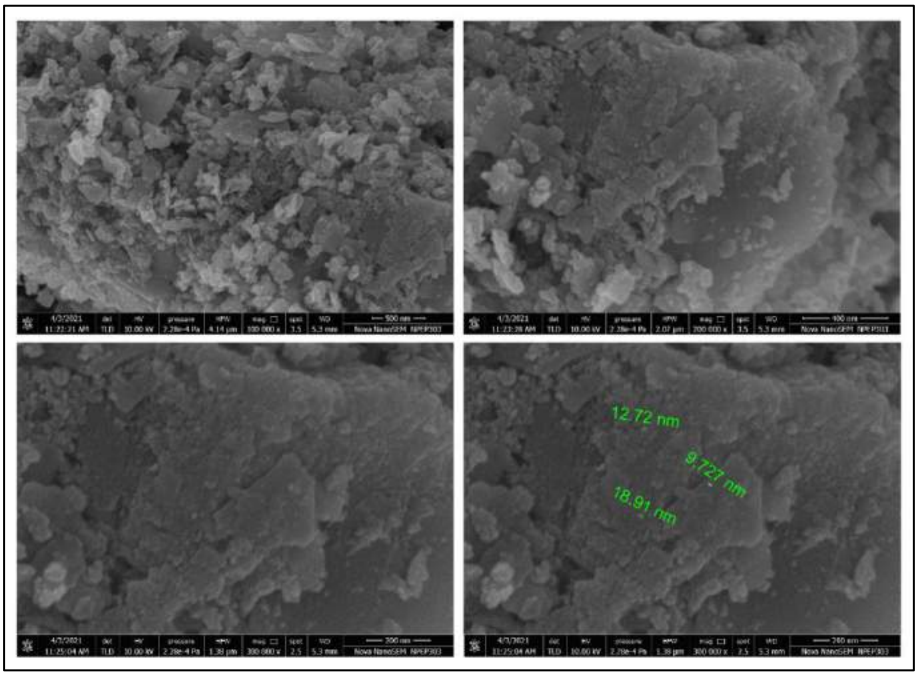


Fig. 4.7(B): FESEM of CZTS at the ranges of 500nm, 400nm, 200nm with particle size

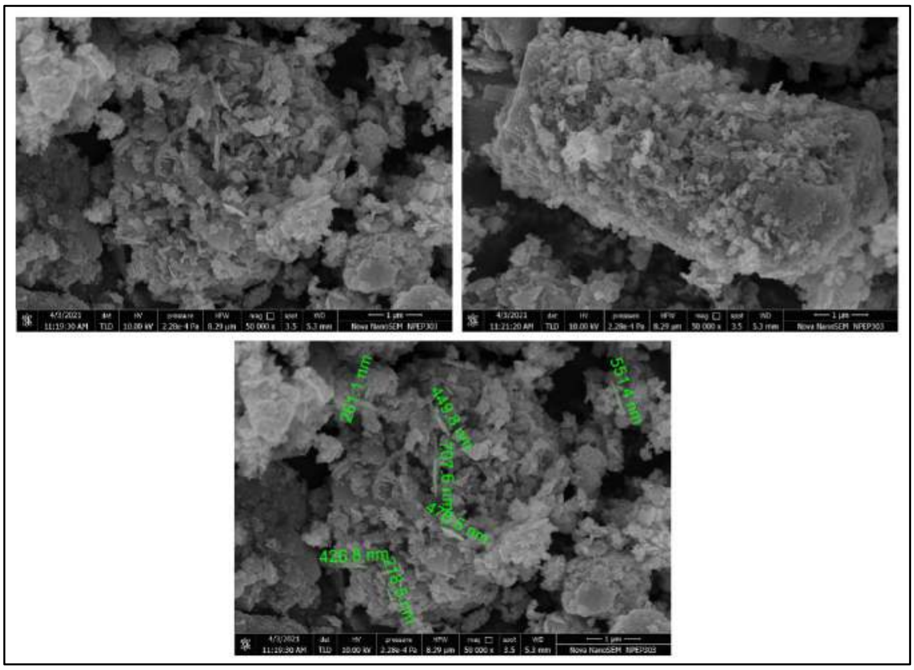


Fig. 4.7(C): FESEM of CZTS at the ranges of 1µm with particle size

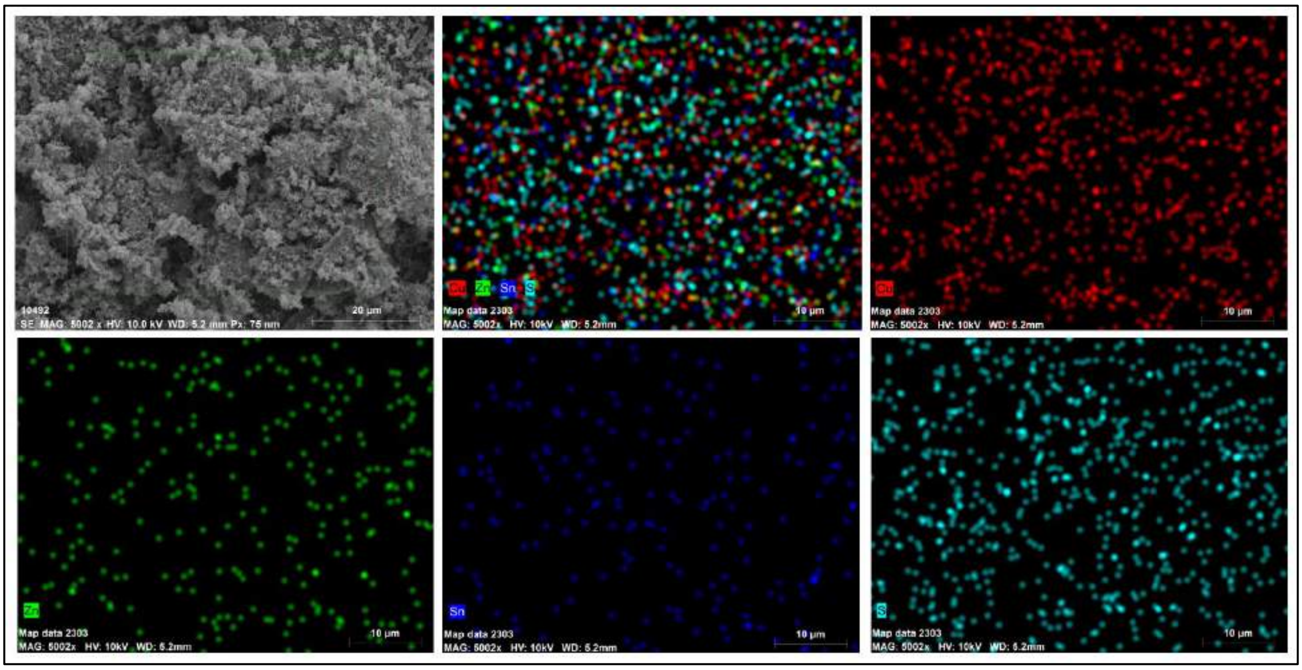
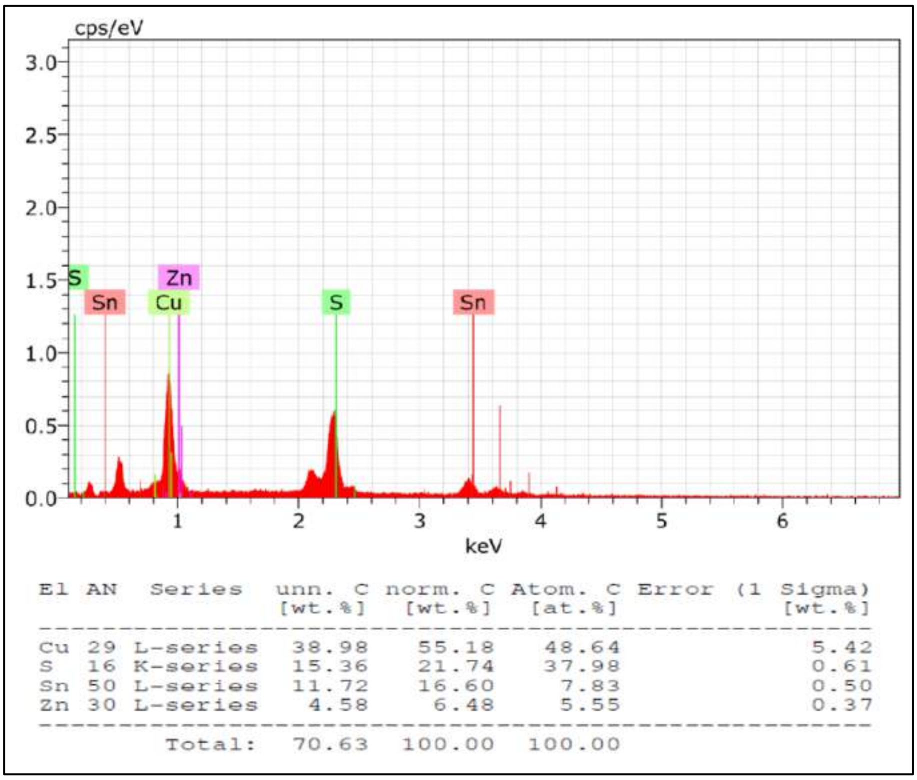


Fig. 4.7(D): EDAX Images of Element Detection at 20µm



```
El AN  Series   unn. C norm. C Atom. C Error (1 Sigma)
                [wt.%]  [wt.%]  [at.%]          [wt.%]
-----------------------------------------------------
Cu 29 L-series  38.98   55.18   48.64             5.42
S  16 K-series  15.36   21.74   37.98             0.61
Sn 50 L-series  11.72   16.60    7.83             0.50
Zn 30 L-series   4.58    6.48    5.55             0.37
-----------------------------------------------------
        Total:  70.63  100.00  100.00
```

Fig. 4.7(E): EDAX pattern of CZTS with table of %

# 5.CONCLUSION & FUTURE PROSPECT:

We have successfully synthesized CZTS nanoparticles using a simple, non-toxic and cost-effective hydrothermal method. Ethanol was used as a surfactant to prevent high agglomeration (for purity) formation of phase kesterite structure with preferred orientation and particle size of 6**nm** was confirmed by X-Ray Diffraction (XRD) analysis. A synthesized sample shows three major peaks at 2θ = 27.00°, 29.09°, 32.77°, 47.79° and 58.95° can be attributed to the diffraction from (101), (112), (200), (220) and (224) planes respectively. UV -Visible spectroscopy study gives optical Band gap suggesting CZTS as a good visible light absorbing material. Fourier Transform Infrared Spectroscopy (FTIR) shows strong peaks of Aldehyde and Sulfoxide groups present in sample. The peak at 1055.06 $cm^{-1}$ is due to presence of S=O i.e. sulfoxide group. Field Emission Electron Microscope (FESEM) along with energy dispersive X-Ray Spectroscopy (EDAX) shows the nanoparticles form CZTS element without any impurity. The simplicity, Eco- Friendliness & Commercial Feasibility of the current synthesis strategy would be beneficial for the production of CZTS based low cost solar cell.

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