# PREPARATION AND CHARACTERIZATION OF ZnO NANORODS THIN FILM ARRAY

*Aphase-I Project report submitted to Kalasalingam Academy of Research and Education in partial fulfillment of the requirements for the degree of*

**Master of Science in Physics**

***Submitted by***

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**Academic Year (2022-23)**

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## DECLARATION BY THE STUDENTS

I hereby declare that the report entitled "**PREPARATION AND CHARACTERIZATION OF UNIFORM SIZE ZnO NANORODS THIN FILM ARRAY"** submitted by me for the Degree of Master of Science in PHYSICS is the result of my original and independent research work carried out under the supervision of **Dr. P. DEVENDRAN**, Department of PHYSICS, Kalasalingam Academy of Research and Education, Krishnankoil and it has not been submitted for the award of any degree, diploma, associate ship, fellowship of any University or Institution.

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## BONAFIDECERTIFICATE

Certified that this Report entitled **"PREPARATION AND CHARACTERIZATION OF UNIFORM SIZE ZnO NANORODS THIN FILM ARRAY "** is the Bonafide work of Ms. D.ASHA JOY (Reg.No.:9921127002) who carried out the research under my supervision. Certified further, that to the best of my knowledge the work reported herein does not form part of any other report or dissertation on the basis of which a degree or award was conferred on an earlier occasion on this or any other scholar.

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## ACKNOWLEDGEMENT

At the outset, I thank GOD ALMIGHTY for showering his blessings on me to carry out this research work successfully.

I am indebted and profusely thankful to my reputable and respectful guide **Dr.P. Devendran, M.Sc., Ph.D.,** Assistant Professor, Department of Physics, Kalasalingam Academy of Research and Education, Anand Nagar, Krishnankoil, for his inspiring guidance, valuable contribution and constant care throughout the period of my research and also for critical reading of the project report.

I would like to express my sincere gratitude to **Dr. S. Saravana kumar**, Head, Department of Physics, Kalasalingam Academy of Research and Education, Anand Nagar, Krishnankoil, for his support and encouragement.

I feel immensely happy to express my gratitude to the management of Kalasalingam Academy of Research and Education, Anand Nagar, Krishnankoil, for their support and help during this investigation.

I wish to thank **Mr. C. Sambathkumar , Mr. K.R. Nagavenkatesh ,** and all other research scholars from the department of physics for their great support.

I am also thankful to all the faculty members in the Department of Physics, Kalasalingam Academy of Research and Education, Anand Nagar, Krishnankoil, for their support, encouragement and help throughout my research period.

Finally, I would like to thank my parents, friends and all my loved ones for their blessings and support.

D. Asha joy

## ABSTRACT

ZnO nanorods have been synthesized by hydrothermal method on sol–gel derived ZnO seeds on ITO substrates. The effect of annealing temperature of seed layers on the morphological, structural and optical properties of ZnO nanorods is systematically investigated. The morphologies of ZnO nanorods investigated By scanning electron microscope-. X-ray diffraction measurement shows that all nanorods possess a strong diffraction peak at 36.34° corresponding to ZnO (101) plane and no impurity phase is observed. The sample functional group analysis was studied by the Fourier Infrared Spectroscopy (FT-IR).

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# CHAPTER-I

## 1.NANOTECHNOLOGY

### 1.1INTRODUCTION

The Greek word “nano” (meaning dwarf) refers to a reduction of size, or time, by$10^{-9}$, which is 1000 times smaller than a micron. One nanometer (nm) is one billionth of a meter and it is also equivalent to ten Angstroms. As such a nanometer is $10^{-9}$ m and it is 10,000 times smaller than the diameter of a human hair. A human hair diameter is about 50 μ m in size, meaning that a50 nm object is about 1/1000 th of the thickness of a hair. One cubic nanometer (nm) is roughly 20 times the volume of an individual atom. A nano size particle compares to a basketball like a basketball to the size of the earth .Figure 1.1 shows size ranges for different nanoscale and microscale objects. It is obvious that nano science and nanotechnology all deal with very-small-sized objects and systems. Officially, the United States National Science Foundation by Roco et al in the year of 1999 defined nanoscience/nanotechnology as studies that deal with materials and systems having the following key properties: (1) Dimension: at least one dimension from 1 to 100 nm. (2) Process: designed with methodologies that show fundamental control over the physical and chemical attributes of molecular scale structures. (3)Building block property: they can be combined to form larger structures. Nanoscience, in a general sense, is quite natural in biological sciences considering that the sizes of many bio- entities we deal with (like DNA, RNA, proteins, enzymes, viruses) fall within the nanoscale range of 1–100 nm. Nanoscale is regarded as a magical point on the dimensional scale: Structures in nano scale(called nanostructures) are considered at the border line of the smallest of human-made devices and the largest molecules of living systems. Our ability to control and manipulate nanostructures will make it possible to exploit new physical, biological, and chemical properties of systems that are intermediate in size, between single atoms, molecules, and bulk materials.

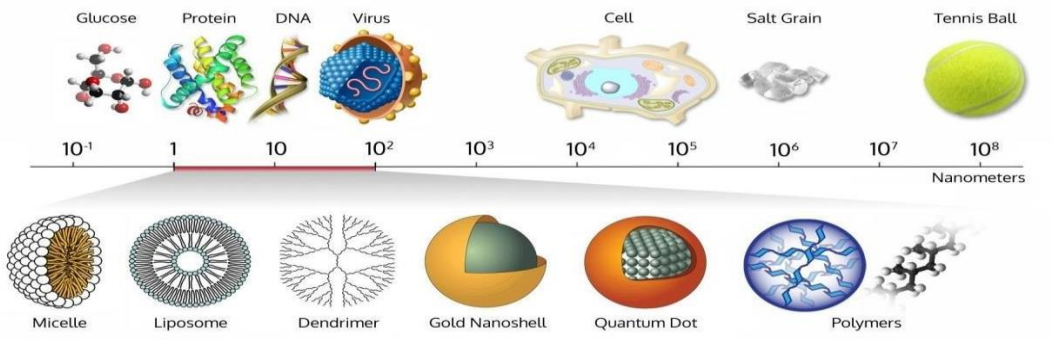


**Figure1.1.SizeandScaleofnanotechnology**

In general, nanotechnology can be understood as a technology of design, fabrication and applications of nanostructures and nanomaterials. Nanotechnology also includes fundamental understanding of physical properties and phenomena of nanomaterials and nanostructures. Study on fundamental relationships between physical properties and phenomena and material dimensions in the nm scale, is also referred to as nano science. To study the unique physical properties and promising applications of nanostructures and nanomaterials, the ability to fabricate and process nanomaterials and nanostructures are the first corner stone in nanotechnology. Nanostructured materials are those with at least one dimension falling in nm scale and include nanoparticles (including quantum dots, when exhibiting quantum effects), nano rods and nano wires and thin films and bulk materials made of nanoscale building blocks or consisting nano scale structures.

### 1.2 History of Nanomaterials

Although we have long been aware of many investigators who have be endealing with "nano"-size dentities, the historic birth of nano technology is commonly credited to Richard P. Feynman. Historically nanotechnology was for the first time formally recognized as a viable field of research with the landmark lecture delivered by Feynman, the famous Noble Laureate physicist, on December 29$^{th}$ 1959 at the annual meeting of the American Physical Society (Feynman 1960). His lecture was entitled "***There's Plenty of Room at the Bottom—An invitation to enter a new field of physics.***" Feynman stated in his lecture that the entire encyclopedia of Britannica could be put on the tip of a needle and, in principle, there is no law preventing such an undertaking. Feynman described then the advances made in this field in the past and he envisioned the future for nanotechnology. His lecture was published in the February1960 issue of Engineering and Science quarterly magazine of California Institute of Technology. In his talk Feynman also described how the laws of nature do not limit our ability to work at the molecular level, atom by atom. Instead, he said, it was our lack of the appropriate equipment and techniques for doing so. Feynman in his lecture talked about "How do we write small?," "Information on a small scale," possibility to have "Better electron microscopes" that could take the image of an atom, doing things small scale through "Miniaturizing the computer," example of which is thin-film formation by chemical vapour deposition, "Rearranging the atoms" to build various nanostructures and nano devices, and behavior of "Atoms in a small world" which included atomic scale. To Fabrication as a bottom up approach is self-assembly of machines from basic chemical building blocks which is considered to be an ideal through which nanotechnology will ultimately be implemented. Top-down approach is assembly by manipulating components with much larger devices which is more readily

achievable using the current technology. It is important to mention that almost all of the ideas presented in Feynman ' s lecture and even more are now under intensive research by numerous nanotechnology investigators all around the world. Today nano phase engineering expands in a rapidly growing number of structural and functional materials, both inorganic and organic, allowing manipulating mechanical, catalytic, electric, magnetic, optical and electronic functions.

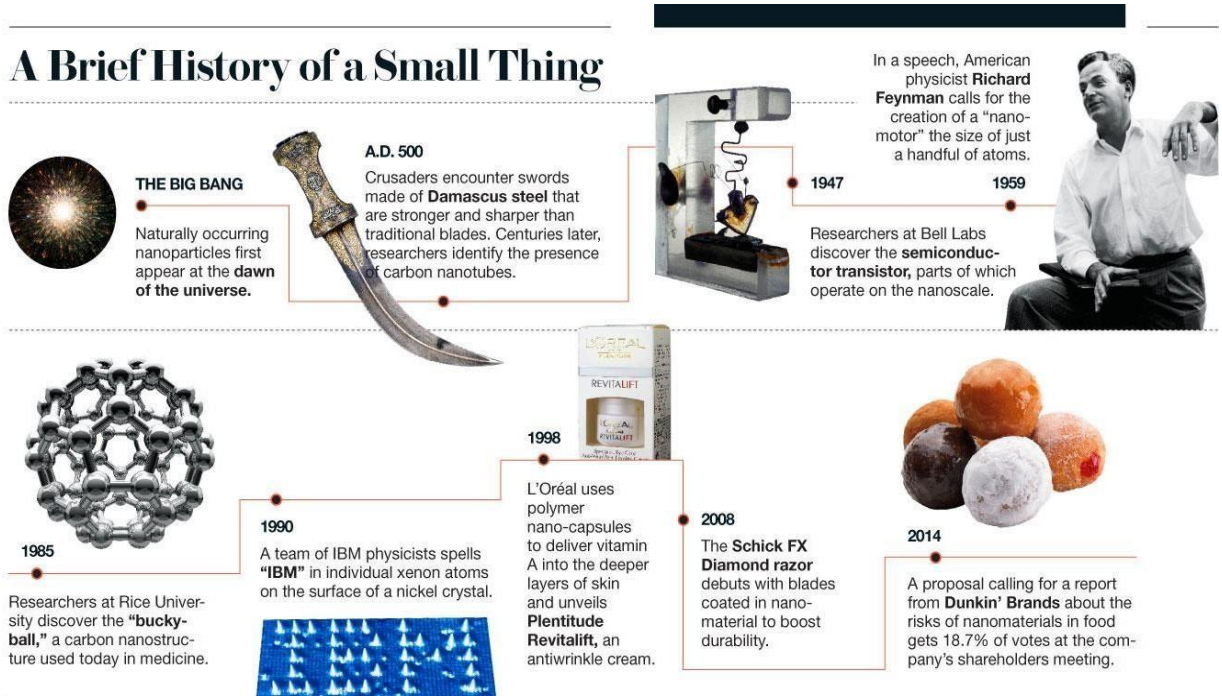


**Figure 1.2 History of nanotechnology**

The production of nano phase or cluster-assembled materials is usually based upon the creation of separated small clusters which they are fused into a bulk-like material or on their embedding into compact liquid or solid matrix materials. e.g. nano phase silicon, which differs from normal silicon in physical and electronic properties, could be applied to macroscopic semiconductor processes to create new devices. For instance, when an ordinary glass is doped with quantized semiconductor "colloids," it becomes a high-performance optical medium with potential applications.

### 1.3 Classification of Nano materials

Nanomaterials have extremely small sizes which have at least one dimension 100 nm or less. Nanomaterials can be nano scale in one dimension (eg. surface films), two dimensions (eg. strands or fibres ), or three dimensions (eg. particles). They can exist in single, fused, aggregated or agglomerated forms with spherical, tubular, and irregular shapes. Common types of nanomaterials include nano tubes, dendrimers, quantum dots and fullerenes. Nanomaterials

have applications in the field of nanotechnology and displays different physical-chemical characteristics from normal chemicals (i.e., silver nano, carbon nano tube, fullerene, photo catalyst, carbon nano, silica). According to Siegel, Nanostructured materials are classified as Zero dimensional, one dimensional, two dimensional, three dimensional nanostructures. Nanomaterials are materials which are characterized by an ultra-fine grain size (< 50 nm) or by a dimensionality limited to 50 nm. Nanomaterials can be created with various modulation dimensionalities as defined by Richard W. Siegel: zero (atomic clusters, filaments and cluster assemblies), one (multi layers), two (ultrafine-grained over layers or buried layers), and three(nano phase materials consisting of equiaxed nanometer sized grains)

### 1.4 Why so much interest in nanomaterials?

These materials have created high interest in recent years by virtue of their unusual mechanical, electrical, optical and magnetic properties. Some examples are given below: Nano phase ceramics are of particular interest because they are more ductile at elevated temperatures as compared to the coarse-grained ceramics. Nano structured semiconductors are known to show various non-linear optical properties. Semiconductor Q-particles also show quantum confinement effects which may lead to special properties, like the luminescence in silicon powders and silicon germanium quantum dots as infrared optoelectronic devices. Nanostructured semiconductors are used as window layers in solar cells. Nano sized metallic powders have been used for the production of gas- tight materials, dense parts and porous coatings. Very small particles have special atomic structures with discrete electronic states, which give rise to special properties in addition to the super-paramagnetism behaviour. Magnetic nano composites have been used for mechanical force transfer (ferro fluids), for high-density information storage and magnetic refrigeration. Nanostructured metal clusters and colloids of mono- or pluri metallic composition have a special impact in catalytic applications. They may serve as precursors for a new type of heterogeneous catalysts (Cortex-catalysts) and have been shown to offer substantial advantages concerning activity, selectivity and lifetime in chemical transformations and electro catalysis (fuel cells). To selective catalysis were also achieved using chiral modifiers on the surface of nanoscale metal particles. Nanostructured metal- oxide thin films are receiving growing attention for the realization of gas sensors ($NO_X$, CO, $CO_2$, $CH_4$ and aromatic hydrocarbons) with enhanced sensitivity and selectivity. Nanostructured metal-oxide applicable for rechargeable batteries for cars and electronic accessorises. Nano crystalline silicon films for highly transparent contacts in thin film solar cell and nano structured titanium oxide porous films for its high transmission and significant surface

area enhancement leading to strong absorption in dye-sensitized solar cells. Polymer- based composites with a high content of inorganic particles leading to a high dielectric constant are interesting materials for photonic band gap structure.

### 1.5 Nanoscience

Nano science 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. Thus, it is the science and technology of small things, in particular things that are less than 100 nm in size termed as nanomaterials. Nanotechnology is the design, characterization, production and application of structures, devices and systems by controlling shape and size at nanometer scale. Nanotechnology uses science on the nanoscale, which occurs at the scale of atoms and molecules. At this scale, traditional boundaries between biology, chemistry and physics are not very distinguishable. Nanotechnology concepts play important roles in all of these disciplines at the macroscopic scale. Nanotechnology, in future will encompass all these disciplinary areas and have understanding basic nano technology concepts will help students understand all sciences. It is a highly interdisciplinary area, meaning that it involves ideas integrated from many traditional disciplines. Scientists working in physics, chemistry, biology, engineering, information technology, metrology and other fields are contributing to today's research breakthroughs in materials. But, one needs to be trained in a discipline so as to take part in this interdisciplinary field. You cannot be interdisciplinary if you do not have home discipline. It is increasingly common to hear people referring to the 'nanotechnology industry', just like the software or mobile phone industries, but will such a thing ever exist? Many of the companies working with nanotechnology are simply applying our knowledge of the nanoscale to existing Industries, whether it is improved drug delivery mechanisms for the pharmaceutical industry or producing nano clay particles for the plastics industry. In fact, nanotechnology is an enabling technology rather than an industry in its own right. No one would ever describe Microsoft or Oracle as being part of the electricity industry, even though without electricity the software industry could not exist. Rather, nanotechnology is a fundamental understanding of how nature works at the atomic scale. New industries will be generated as a result of this understanding, just as the understanding of how electrons can be moved in a conductor by applying a potential difference led to electric lighting, the telephone, computing, the internet and many other industries, all of which would not have been possible without it. While it is possible to buy a packet of nanotechnology, a gram of nano tubes for example, it would have zero intrinsic value. There all value of the nano tubes would be in their application, whether within existing industry, or to enable the creation of a whole new one.

### 1.6 Nano structures

Nanostructures or nanomaterials began exact definition. Somehow, a nano material is something that has a nanoscale dimension. One might define a nano material most broadlyas one which has dimensions larger than that of a molecular cluster but smaller than that of a bulk material, but more importantly has some interesting property that is different from either. So, in a sense, if it quacks like a nano material, it is a nano material. If you have a quantum confinement and a change in band structure and a change in absorption frequency, you are dealing with phenomena on the nanoscale. If you have a suppressed melting point, you are dealing with nanoscale phenomenon and you seek to harness those phenomena for the application in question. Materials and objects with nm scale features are not new nor were they first created by man. There are many examples of nanostructures in nature in the way that plants and animals have evolved. If one thinks of condensation of solar nebula, the initial particles that were formed were probably not well crystallized. They were likely little, poorly crystalline dust grains (nanoparticles), which eventually grew, nucleated, condensed came under pressure and thus started the evolution of planets .The surface chemistry of a planet such as earth involves nanoscale processes. The weathering of rocks is nanoscale corrosion. The whole geochemical cycle then takes these weathered rocks, turns them into sediments. Eventually, the sediments coalesce again and become rocks. The cycle involves primary reaction of particles at the nanoscale. I fone thinks of soil science and agriculture, soil is the most complex nano material-mixed organic, inorganic, biological entities of different sizes. But certainly, much of the transport of nutrients, pollutants, organics and heavy metals takes place at the nanoscale. The nucleation of clouds is a nanoscale phenomenon; ice droplets, sulphuric acid droplets and cloud seeding are nanoscale processes. Thus, nucleation is really a nano science. Any initial solid state or condensed phase reaction starts somewhere and a few atoms do something. In a sense, the start of an earthquake, which may affect hundreds of kilometers, occurs somewhere with the breaking of few chemical bonds. Origin of life and biochemical reactions has probably been mediated by mineral surfaces and very likely by mineral surfaces of small grains. The science and technology of very small materials (less than 100 nm) will be the most profoundly transforming technology of our era. The nano-revolution occurring is attributed not only to the recognition of its potential value but also to the availability of tools that allow scientists to explore the world at the nanoscale and transforming their discoveries into products and services offering practical benefits in our everyday lives. Similar to quantum mechanics, on the nano

metre scale, materials or structures may possess new physical properties or exhibit new physical phenomena. Some of these properties are already known. For example, band gap of semiconductors can be tuned by varying material dimension. There may be many more physical properties not known to us yet. There are thus endless possibilities for improved devices, structures and materials, if we can understand these differences and learn how to control the assembly of small structures. These materials have unique properties because of their small size.

## 1.7Nanomaterials

Nano science and nanotechnology include the areas of synthesis, characterization, exploration of nano structured and nano sized materials. The application of nanomaterials can be historically traced back to even before the generation of modern science and technology. Systematic experiments conducted on nanomaterials had also been started from the known Faraday experiments in the 1857. In the recent years, nanomaterials have steadily received growing interests as a result of their peculiar and fascinating properties and applications superior to their bulk counter parts. A wealth of interesting and new phenomena associated with nanostructures has been found with the best established examples including size dependent excitation and emission. It is generally accepted that the quantum confinement of electrons by the potential well of nano meter size structure may provide one of the most powerful and wonderful means to control the mechanical, electrical, optical, magnetic and thermoelectric properties of a solid state functional materials. When the dimensions of materials are reduced to nanoscale, they demonstrate unique properties, which are different from those of their bulk counterparts. Such features make nanomaterials attractive for unique applications and also at the same time, cause complications in their characterization processes. Therefore, the challenges lie in finding the right characterization techniques that have optimum capabilities. In the past decades, sophisticated instruments for characterization and manipulation, such as scanning electron Microscopy, transmission electron microscopy and scanning probe microscopy became more available for researchers to approach the nano world.Sinceproteinsare10-1000 nm in size and cell walls 1-100 nm thick, their behaviour on encountering a nanomaterialmay be quite different from that seen in relation to bulk materials. Nanocapsules and nanodevices may present new possibilities for drug delivery, gene therapy and medical diagnostics.

## 1.8Nanocomposites

Nanocomposite is a multiphase solid material where one of the phases has one, two or three dimensions of less than 100 nm or structures having nano-scale repeat distances between the

different phases that make up the material. The idea behind Nanocomposite is to use building blocks with dimensions in nm range to design and create new materials with unprecedented flexibility and improvement in their physical properties. In the broadest sense this definition can include colloids, gel sand copolymers, but is more usually taken to mean the solid combination of a bulk matrix and nano-dimensional phase(s) differing in properties due to dissimilarities in structure and chemistry. The mechanical, electrical, thermal, optical, electrochemical, catalytic properties of the nanocomposite will differ markedly from that of the component materials.

### 1.9PropertiesofNanomaterials

The physical properties of nanostructured materials distinction essentially beginning that of the mass materials as the framework size methodologies quantum mechanical scale. Streamlining of morphology, structure, electronic, geometry, optical and mechanical properties of nm sized frameworks be of essential significance for the plan of nanostructures through positive properties. Essentially, reduce in the molecule size opening mass to nanoscale bring about a growth in the amount of surface energy with modifies the bury molecule separating. In light of the fine grain sizes and thus high thickness of Nanocrystalline materials interfaces, show an assortment of properties that are single and commonly remarkably enhanced in connection through those of normal coarse-grained materials. These include stretched quality/hardness, improved pliability/strength, diminished thickness, higher electrical resistivity upgraded diffusivity, lower warm conductivity, decreased versatile modulus, expanded explicit heat, higher coefficient of warm development, and unrivaled delicate attractive properties.

### 1.9.1 Mechanical Properties

The superiority and hardness of the Nanocrystalline materials are 4-5 times more important, when contrasted with the common grained material along with the elastic steady of these materials include been experimental to be decrease by 30% or less. The mechanical properties of solids clearly depend on the thickness of separations, grain size and henceforth interface-to-volume proportion. An improvement in damping limit of a nanostructured strong might be related with grain-limit sliding or with energy dissemination system restricted at inter faces. A lessening in grain size fundamentally influences the yield quality and hardness. The grain limit structure, limit edge, limit sliding and development of separations are significant elements that decide the mechanical properties of nanostructured materials. Grain boundary diffusion and sliding are the input necessities for super plasticity.

### 1.9.2 Optical Properties

Nanocrystalline frameworks have pulled in interests for their novel optical properties, which contrast strikingly from mass gems. With the developing innovation of these resources, it is basic to comprehend the complete reason used for photonic belongings of nanoparticles. The direct and nonlinear optical properties of such materials can be limitedly custom fitted through controlling the precious stone measurements, the science of their surfaces and strategy for synthesis. The size reliance of optical properties has been clarified in the accompanying captions.

### 1.9.3 Luminescence Properties

Luminescence might remain characterized for example the emanation of light from certain substance, when energized with radiations like X-beam/UV/electrons and mechanical pressure/concoction response/electric release/warm warming and so on. The transmitted radiation from a luminescent material is free since warming impact and thus is likewise named as 'chilly emanation'. Optical excitation of semiconductor nanoparticles regularly prompts both band-edge and profound snare radiance. The size reliance of the excitonic or band-edge fluorescence has been examined broadly and can be sensibly clarified by the compelling mass guess. The fluorescence procedure in semiconductor nanoparticles is intricate and most nanoparticles show expansive and Stokes-moved iridescence emerging from the profound snares of surface states. Just bunches with great surface passivation illustrationgreatband-edgeemanation.Photoluminescenceisorderedintotwosorts,contingent on the idea of the ground also the energized states. In a singlet energized express, the electron in the higher energy orbital has the contrary turn direction as another electron in the lower orbital. These paired electrons are understood to be collective. In a triplet express these electrons are unpaired, that is, their twists have a similar direction. Coming back to the ground state from an energized singlet state ensures not require an electron to change its turn direction. A difference in turn direction is required designed for a triplet state to come back to the singlet ground state.

### 1.9.4 Electrical and Electronic Properties

The electrical conductivity of the solids is said by its band structure otherwise electronic structure. On description of semiconductors, the entirely filled valance band and the unoccupied conduction band are isolated by an energy gap(Eg) which is little(3eV). The electrons can be energized since the valence band to conduction band utilizes light otherwise warmness which results in partial conductivity. In envelop the Eg is elevated and the electrical conductivity is

restricted. The important idea of the solids can be inclined by different fundamentals like, temperature and molecule quantity. At the point when the molecule mass is decreases to Nanometer expand the Eg increments and henceforth the conductivity is diminish. On account of metal nanoparticles, the thickness of states in the conduction and valence group are decrease then electronic properties changed completelyThe importance of the electrical resistivity (and consequently conductivity) in nanocomposites can be improved by adjusting the grain size.

### 1.10Applications of Nanomaterials

Development of nanomaterials helps mankind to move towards a bright future. The use of more efficient and better designed materials directly contributes to conservation of natural resources. They offer more precise methods of addressing the problems of mankind. At the nanoscale, properties of materials behave differently and are said to behave under atomic and molecular rules. Researchers are using these unique properties of materials at this small Scale to create new and exciting tools and products in all areas of science and engineering. There are thus endless possibilities for improved devices, structures and materials if we can understand these differences and learn how to control the assembly of small structures.

# CHAPTER-II

# LITERATURE SURVEY AND CHARACTERIZATION TECHNIQUES

## 2.1 Literature Survey

| Synthesis | Precursor material | Morphology | Diameter of ZnO nanostructure | Length of ZnO nanostructure | Ref. |
|---|---|---|---|---|---|
| Hydrothermal process | ZnO and NaOH | Nanorods | 90–200 nm | 1.7–2.1 μm | 1 |
| Wet chemical process | $ZnCl_2$, NaOH | Flower-like nanorods | 200–500 nm | 1.0–1.5 μm | 2 |
| Two-step solution growth | $ZnCl_2$, KOH | ZnO NRs | 150 nm | 4 μm | 3 |
| Hydrothermal | Zinc nitrate, $LiNbO_3$, hexamethylenetriamine, and Polyethyleneimine | Nanorods | 45 nm | 1 $\mu$m | 4 |
| | $Zn(NO_3)_2.6H_2O$ and $C_6H_{12}N_4$ | Nanorods | 30–50 nm | 1.2 μm | 5 |
| | $Zn(NO_3)_2.2H_2O$, NaOH, $K_2SnO_3 \cdot 3H_2O$ and urea | Nanorods | 2.8 nm, 2.5 nm | 26 and 22 nm | 6 |
| | $Zn(NO_3)_2 \cdot 6H_2O$ $C_6H_{12}N_4$ | Nanorods | 30–50 nm | — | 7 |
| | $Zn(NO_3)_2$, NaOH and hexamethylenetetramine | ZnO nanorods | 290–330 nm | 3.2–3.4 μm | 8 |
| Sol-gel | $Zn(CH_3COO)_2 \cdot 2H_2O$, NaOH | Nanorods | 51 and 33 nm | 262, 748, and 470nm | 9 |
| Hydrothermal | $Zn(CH_3COO)_2$, $2H_2O_2$-propanol $C_4H_{11}NO_2$, zinc acetate dehydrate, | Hexagonal Nanorods | 60–70 nm | --- | 10 |

| | | | | | |
|---|---|---|---|---|---|
| | $(CH_2)_6N_4$ | | | | |
| solvothermal method | $Zn(NO_3)_2$ and HMTA | Nanorods | 220 nm | — | 11 |
| Hydrothermal | $Zn(NO_3)_2.6H_2O$ sodium hydroxide and CTAB | ZnO nanorods | 80–150 nm | — | 12 |
| Ultrasonic irradiation | Alumina substrate, $Zn(NO_3)_2 \cdot 6H_2O$, $(CH_2)_6N_4$ | Nanorod (vertically aligned) | 50 nm | 500 nm | 13 |
| Solution method | $Zn(NO_3)$ $6H_2O$, $C_6H_{12}N_4$, $CoSO_4 \cdot 7H_2O$ | ZnO nanorod | 100–300 nm | 1–3 μm | 14 |
| Microwave irradiation | Zinc acetate dihydrate, NaOH | ZnO flower | 200–300 nm | 1.5 μm | 15 |
| Hydrothermal | $Zn(CH_3COOH)_2 \cdot 2H_2$ O, HMTA, CTAB | Hexagonal ZnO nanosheets | 17 nm | 90 nm | 16 |
| Sputtering | 0.01 mol $C_6H_{12}N_4$, in 400 ml DI water | ZnO nanorods | 8–160 nm thick seed layer | — | 17 |
| Solvothermal | $Zn(CH_3COO)_2 \cdot 2H_2O$, methanol, KOH | NRs | 15 nm | 50–120 nm | 18 |

### 2.2 Characterization

By using the various experimental tools used for the characterization of various parameters for ZnO nanorods following different synthesized method include X-Ray Diffraction (XRD) Fourier Transform Infrared Spectroscopy (FTIR), and Scanning Electron Microscope (SEM).

#### 2.2.1 Powder X-ray diffraction analysis

X-ray powder diffraction is a rapid analytical technique primarily used for phase identification of a crystalline material and it can provide information on unit cell dimensions. There is many of X-ray techniques available based on the scatter, emission and absorption properties of X-radiation (X-ray). The two most commonly used methods are X-ray Fluorescence Spectrometry (XRF) and X-Ray Powder Diffractometer (XRPD). Microcrystalline powder is used as

specimen in the XRPD method. This method is suitable for structural determination, where single crystal is not available. Any material which is made up of an ordered array of atoms gives a particular diffraction pattern, the powder XRD is also known as Debye-Scherer method.

**History of the development of powder XRD**

X-rays were discovered by Wilhelm Conrad Roentgen, the first Nobel laureate in physics, in 1895. In 1912, Max von Laue, a German physicist and a Nobel laureate discovered that crystalline substances act as three dimensional diffraction gratings for X-ray wavelengths through to the spacing of planes in a crystal lattice. Both the discoveries gave a powerful tool that could see inside of crystals and allow investigators for detailed determination of crystal structures. This discoveries Changed the dimensions of physics, chemistry, crystallography, mineralogy and medicine. After Laue's pioneering research, the field developed rapidly, most notably by the contribution from a pair of father and son physicists, namely, William Henry Bragg and William Lawrence Bragg, respectively. In 1912-1913, the Bragg developed a well-known Bragg's law, which connects the observed scattering with reflections from evenly spaced planes within the crystal. Following these discoveries two major fields of materials analysis have been developed. One of them is the method of powder XRD, which was devised independently in 1916 by Peter Joseph William Debye, a Nobel laureate, and P. Scherrer in Germany and in 1917 by Hull in United States. In the late 1930s, the powder XRD technique was recognized as a powerful technique for phase identification and chemical analysis. The technique developed steadily and, half a century later, the traditional applications, such as phase identification, the determination of accurate unit-cell dimensions and the analysis of structural imperfections, were well established. There was then a dramatic increase of interest in powder methods during the 1970s, following the introduction by Rietveld in 1967 of his powerful Rietveld method for refining crystal structures from X-ray and neutron powder diffraction data. Powder XRD has become an important tool for rapid identification of polymorphs and new compounds in pharmaceutical industry. Powder XRD opens tremendous possibilities for characterization of materials and stimulates an interdisciplinary dialogue and collaboration among physicists' mineralogists, crystallographers, chemists, pharmacists and material scientist.

**Powder X-ray diffraction instrumentation**

X-ray diffractometer consists of three basic elements: an X-ray tube, a sample holder, and an X-ray detector. X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons toward a target by applying a high voltage, and

bombarding the target material with electrons. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced. These spectra consist of several components, the most common being Kα and Kβ. Kα consists, in part, of Kα1 and Kα2. Kα1 has a slightly shorter wavelength and twice the intensity as Kα2. The specific wavelengths are characteristic of the target material (Cu, Fe, Mo, Cr). Filtering, by foils or crystal monochromator, is required to produce monochromatic X-rays needed for diffraction. Kα1and Kα2 is sufficiently close in wavelength such that a weighted average of the two is used. Copper is the most common target material for powder crystal diffraction, with CuKα radiation of wavelength1.5418Å. These X-rays are collimated and directed onto the sample. As the sample and the detector are rotated, the intensity of the reflected X-rays is recorded. When the geometry of the incident X-rays impinging the sample satisfies the Bragg Equation, constructive interference occurs and a peak in intensity occurs. A detector records and processes this X-ray signal and converts the signal to a count rate, which are then output to a device such as a printer or computer monitor as shown in Figure 3.1.

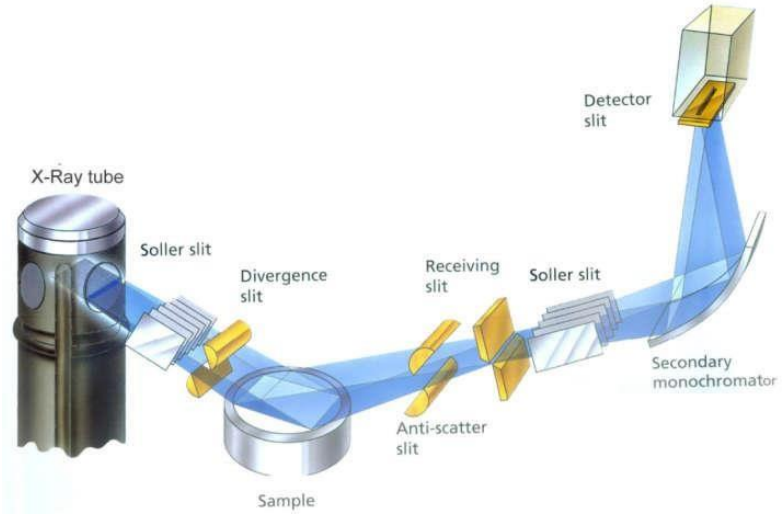


**Figure: 3.1.** The Schematic diagram of Powder X-Ray Diffraction

## Applications

Powder X-ray diffraction is the most widely used one for the identification of unknown crystalline materials (e.g. minerals, inorganic compounds). Determination of unknown solids is critical to studies in geology, environmental science, material science, engineering and biology. It is reliable and powerful tool for crystalline sample identification. It is a non-destructive technique. Ability to analyses mixed phases. For the purpose of simultaneous and quick measurement of the positions and intensities of diffraction lines the diffractometer are advantageous. It is a fast technique (< 20 min) for identification of an unknown sample. In most cases, it provides an unambiguous sample determination. Simplicity in sample preparation, i.e.,

required sample preparation is minimal and extensive sample preparation is notneeded.XRD units are widely available.

### 2.2.2 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared (FT-IR) spectrometry was developed in order to overcome the limitations encountered with dispersive instruments. The main difficulty was the slow scanning process. A method for measuring all of the infrared frequencies simultaneously, rather than individually, was needed. A solution was developed with a very simple optical device called "interferometer". The interferometer produces a unique type of signal which has all of the infrared frequencies encoded into it. The signal can be measured very quickly, usually in the order of one second or so. Thus, the time required per sample is reduced to a matter of a few seconds rather than several minutes. Therefore, FT-IR is the preferred method of infrared spectroscopy.

**FT-IR Spectrometer and Experimental Procedure**

FT-IR spectrometer is a spectral instrument that collects and digitizes the interferogram, performs the Fourier transform function on the interferogram and displays the spectrum. FT-IR spectrometer is the advancement of the dispersivespectrometer.

**Sample Preparation:** Samples for FT-IR can be prepared in a number of ways. Sample crystal can be milled with potassium bromide (KBr) to form a very fine powder. This powder is then compressed into a thin pellet which can be analysed. KBr is transparent in the IR region. Alternatively, solid samples can be dissolved in a solvent such as methylene chloride, and the solution placed onto a single salt plate. The solvent is then evaporated off, leaving a thin film of the original material on the plate. This is called a cast film, which is frequently used for polymer identification. For liquid samples, the easiest is to place one drop of sample between two plates of sodium chloride (salt), which is also transparent to infrared light. The drop forms a thin film between the plates. Multiplex types of instruments employ the mathematical tool of Fourier Transform. The Michelson interferometer, which is the heart of the apparatus of FT-IR spectrometer, is as shown in Figure 2.3. The interferometer requires two mirrors (M1 and M2), an infrared light source, an infrared detector, and a beam splitter(B) made-up of half-silvered mirror.The main components of the FT-IR spectrometers are (1) drive mechanism, (2) beam splitters (3) sources (4) IR detector and (5) signal processor / computer. As shown in Figure 3.2, a parallel beam of radiation is directed from the source to the interferometer. It is well known that the interference patterns are obtained from monochromatic radiation. Radiation from the source strikes the beam splitter and separates into two beams. One beam is transmitted through the beam splitter to the fixed mirror and the

second is reflected off the beam splitter to the moving mirror. The fixed and moving mirrors reflect the radiation back to the beam splitter. Again, half of this reflected radiation is transmitted and half is reflected at the beam splitter, resulting in one beam passing to the detector and the second back to the source. The interference patterns (interferogram) obtained can be transferred back to the original frequency distribution. This can be achieved by a mathematical process known as Fourier Transform. Nowadays, this process is carried out by a computer or microprocessor of the spectrometer. The end result of the Fourier transform is the spectrum of peaks and valleys that is displayed. The resulting absorption pattern can be compared to the millions of patterns that are stored in computer databases, both on-site and remotely via the Internet. If a matching spectrum is obtained, then the identity of the sample compound will be determined.

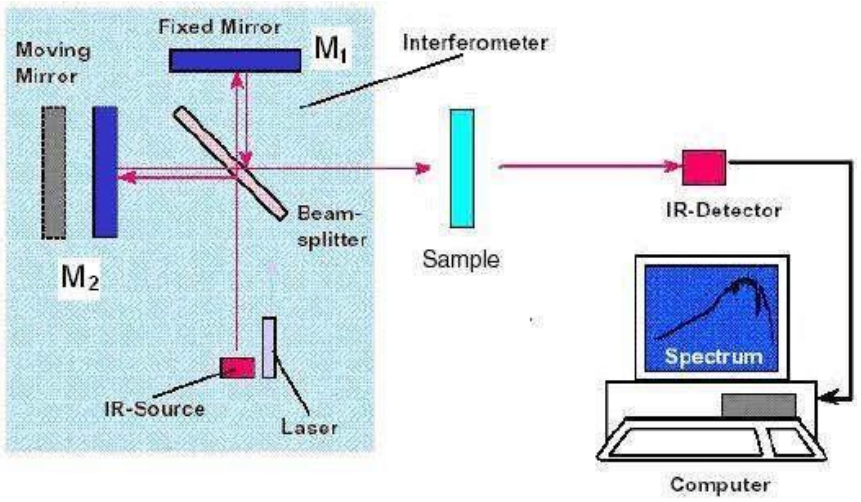


**Figure 3.2 Schematic diagram of FT-IR spectrometer**

FT-IR Spectrometer makes use of all the frequencies from the source simultaneously, rather than sequentially as in dispersive instrument (i.e. grating spectrometer). This feature is called the Multiplex advantage.

### 2.2.3 Scanning Electron Microscope (SEM)

A typical SEM instrument, showing the electron column, sample chamber, EDS detector, electronics console, and visual display monitors**.** The scanning electron microscope uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology, chemical composition, and crystalline structure and orientation of materials making up the sample. In most applications, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that displays spatial variations in these properties. Areas ranging from approximately 1 cm to 5 microns in

width can be imaged in a scanning mode using conventional SEM techniques. The SEM is also capable of performing analyses of selected point locations on the sample; this approach is especially useful in qualitatively or semi- quantitatively determining chemical compositions, crystalline structure, and crystal orientations. The design and function of the SEM is very similar to the EPMA and considerable overlap in capabilities exists between the two instruments.

**Principle**

Accelerated electrons in an SEM carry significant amounts of kinetic energy, and this energy is dissipated as a variety of signals produced by electron sample interaction when the incident electrons are decelerated in the solid sample. These signals include secondary electrons, backscattered electron, diffracted backscattered electrons, photons, visible light, and heat. Secondary electrons and backscattered electrons are commonly used for imaging samples, secondary electrons are most valuable for showing morphology and topography of the samples and backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples.

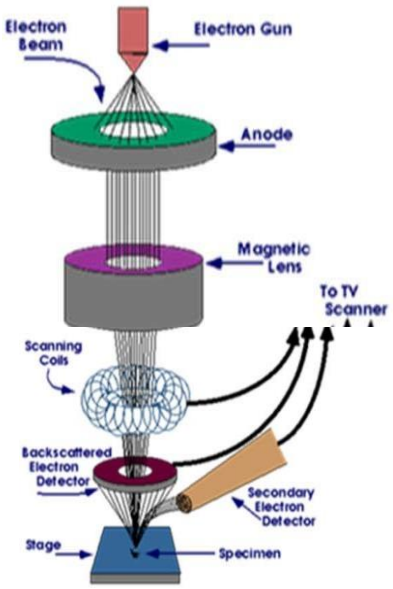


**Fig.3.3. Scanning Electron Microscopy**

X-ray generation is produced by inelastic collisions of the incident electrons with electrons in discrete orbital of atoms in the sample. As the excited electrons return to lower energy states, they yield X-rays that are of a fixed wavelength. Thus, characteristic X-rays are produced for each element in a mineral that is excited by the electron beam. SEM analysis is considered to be

non-destructive. X-ray generated by electron interactions does not lead to volume loss of the sample, so it is possible to analyses the same materials repeatedly.

**Instrumentation**

Essential components of all SEMs include the following

Electron Source (Gun)

Electron Lenses

Sample Stage

Detectors for all signals of interest

Display or Data output devices

SEM always has at least one detector, and most have additional detectors. The specific capabilities of a particular instrument are critically dependent on which detectors it accommodates.

**Application**

The SEM is routinely used to generate high-resolution images of shapes of objects and to show spatial variations in chemical compositions:

Acquiring elemental maps or spot chemical analyses using EDS

Discrimination of phases based on mean atomic number using BSE

Compositional maps based on differences in trace element activators using CL.

The SEM is also widely used to identify phases based on qualitative chemical analysis or crystalline structure. Precise measurement of very small features and objects down to 50 nm in size is also accomplished using the SEM. Backscattered electron images can be used for rapid discrimination of phases in multiphase samples. SEM is equipped with diffracted backscattered electron detectors can be used to examine micro fabric and crystallographic orientation in many materials.

**Strength**

There is arguably no other instrument with the breadth of applications in the study of solid materials that compares with the SEM. The SEM is critical in all fields that require characterization of solid materials. SEM is comparatively easy to operate, with user friendly

intuitive interfaces. Many applications require generate data in digital formats, which are highly portable.

# CHAPTER-III

# EXPERIMENTALANDSYNTHESISMETHOD

## 3.1 INTRODUCTION OF HYDROTHERMALMETHOD

Hydrothermal Synthesis method involves using anyone of the many techniques to crystallize substances. Nanotechnology is one of the most critical factors in it. Advanced sciences rank nanotechnology as one of the driving forces with the potential to revolutionize material science of the current age. For the synthesis of nanoparticles, the process of the hydrothermal method is being increasingly favored globally, by industries and R&D labs alike.

### 3.1.1 Fundamentals of Hydrothermal Method

Hydrothermal synthesis method involves using any one of the many techniques to crystallize substances. It usually does at a high vapour 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. In easy terms, hydrothermal synthesis described as an artificial way to synthesize single-crystal(nanoparticles). Also, it depends on the solubility of aqueous solution under hot water and higher temperature levels. A strong container is used for hydrothermal reactor 'Auto clave,' and fills with a solution. The process wants constant maintenance of temperature difference between the opposing ends of the crystallizing compartment. The end with higher temperature is wherever the solvent dissolved and comparatively cooler, when the nano particle growth takes place.

### 3.1.2 How Hydrothermal Synthesis Work for Nanoparticle

Hydrothermal technique for nano particle synthesis needs using special instrumentation, called Hydrothermal Autoclave Reactor. It is a specific style of strong vessel that we intend to face up to high temperatures and better pressure levels from within. The autoclave reactor consists of thick and steel-walled cylindrical vessels having hermetic sealing. Likewise, this helps it to bear high levels of heat and pressure regularly and safely, for a longtime. Also, the fabric of the autoclave also must be resistant to solvents. While the most vital part of the hydrothermal autoclave reactor is probably the 'closure'. Apart from this, the seals are a successive necessary part of the autoclave. As many hydrothermal processes need to use solutions having a corrosive impact on the interior material of the autoclave. Also, we apply special protective coatings to prevent corrosion. Because we usually design to suit the interior of the autoclave seamlessly and

can either cover the entire interior of the autoclave or part of it.

### 3.2 Advantages of Hydrothermal Synthesis Method for Nanoparticle Synthesis

These are some of the top advantages and advantages of using hydrothermal nanoparticle synthesis methodology, as compared to other ways, for crystallization and synthesis of nanomaterials:

- Abletoproducecrystallinephaseswhicharen'tstableathighertemperaturessafely.
- Grows materials which are known to have a higher vapour pressure as their melting point gets closer.

- Createslarger-sizedandhigh-qualitycrystalsandnanoparticles,withcontrolover their content and composition.

### 3.3 Synthesis Method of ZnO on the glass substrate

#### 3.3.1 Materials

Sulfuric acid ($H_2SO_4$), zinc Nitrate ($Zn(NO3)_2.6.H_2O$), citric acid ($C_6H_8O_7$)were obtained from Merck India. All chemicals were bought as analytical grade and utilized without additional purification. Double distilled (DD) water was used throughout the synthesis. Ethanol was purchased from Sigma Aldrich for washing purposes.

#### 3.3.2SynthesisMethod

The etching process has been done in the ITO glass plate by using Sulfuric acid ($H_2SO_4$), for etching process taking 10 ml of Sulfuric acid added with 30 ml of distilled water in figure 2.1.

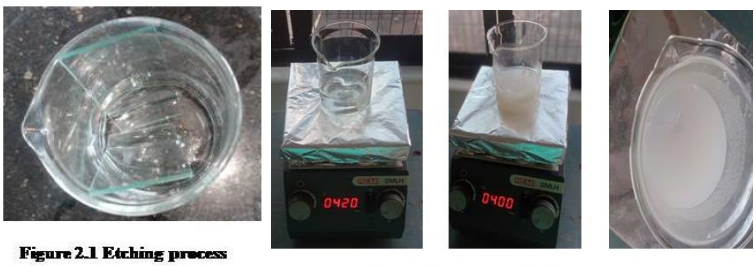


Figure 2.1 Etching process

Figure 2.2 Preparation of ZnO seed solution

**Figure 2.1 etching process**

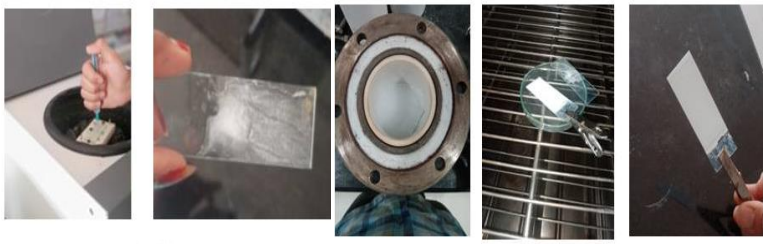

Figure 2.3 Spin coating

Figure 2.4 ZnO thin film

**Figure 2.2 Synthesis of ZnO nanorods**

These two were stirred for 15 min. Then the glass plate was set into the mixed solution. After finishing etching ZnO nanorods array was synthesis in simple hydrothermal route as shown in figure 2.2. First take 0.05 M of Metal source precursor zinc Nitrate ($Zn(NO_3)_2.6.H_2O$) and citric acid, stir separately for 2h with50 ml of distilled water. Adding one after another solution in above zinc Nitrate solution after that the obtained solution was coated on the glass plate by using spin coating method. Then the glass plate was dried in oven for 5 h at 80°C. The glass plate was transferred to the Teflon lined stainless steel autoclave and heated for 12 h at 100°C.At the end ZnO nanorods growth in the ITO glass plate.

# CHAPTER-IV

# RESULT AND DISCUSSION

## 4.1 X-RAY DIFFRACTION

The structure of prepared ZnO were studied by X-ray diffraction (XRD) as shown in Fig. 4.1 The peaks are observed at the 2θ peaks at the range of 33° 36.34°, 48.30°, 55.46°, 62.74°, 65°, 65.86°, 69.86°, and 71.11° corresponding to the planes of (100), (002), (101), (102), (110), (103), (201) and (202) with matching the JCPDS card No. 36-1451. In this XRD pattern 20 to 30° small hump are present which indicates the amorphous nature due to the uses of the glass as a substrate to coat on ZnO prepared nanoparticles. The obtained ZnO nanoparticles (NPs) are corresponds to the wurtzite type.

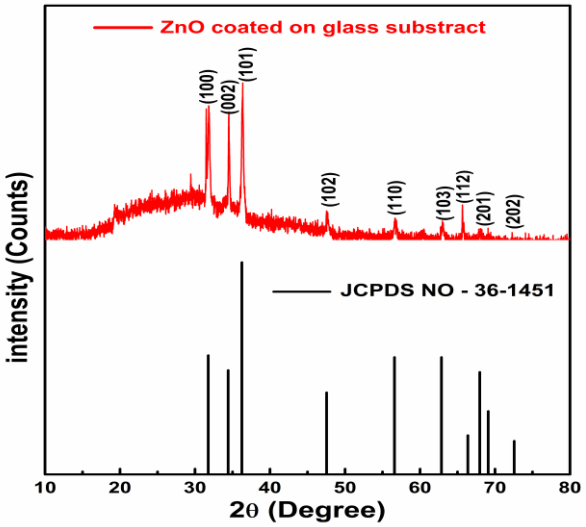


**Fig.1 The XRD pattern of ZnO nanorods**

## 4.2 FT-IR

As the FT-IR spectrum as shown in Figure 4.2 the absorption band around 409 $cm^{-1}$, assigned to the Zn–O stretching vibration modes, which is the typical characteristic band of the pure ZnO. The broad absorption peak round 3537 and 1387 $cm^{-1}$ is attributed to vibrations of OH groups that belongs to the absorption of water molecules on ZnO surface. The peaks around 2385 and 2338 $cm^{-1}$ are due to C-H stretching of the Nitrate.

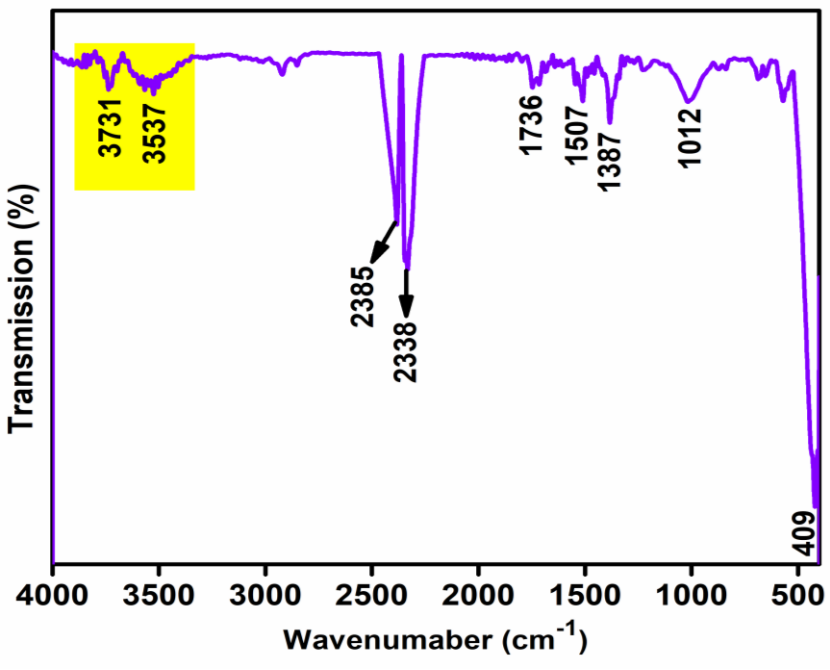


**Fig. 2. The FT-IR spectra of synthesized ZnO NRs**

### 4.3 SEM

Morphological formation of the prepared ZnO Thin film was investigated by SEM analysis. Figure 3 Shows the different magnification of SEM image of ZnO nanorods  The SEM images of. Presence of rod like structured nano particles with less agglomeration was observed in SEM images. the SEM image of nanorods in figure 3 some of the nanorods diameter decreases, but the whole nano rod diameter is not uniform. On the other hand, the crystalline maturity of the nanorods depends on, at least partly, the reaction time.

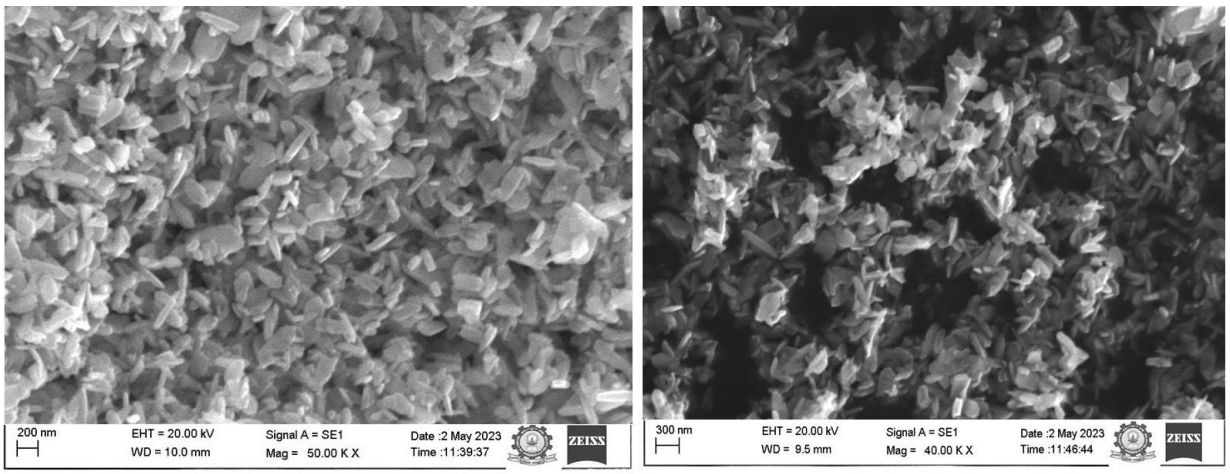


Figure 3 Shows the different magnification of SEM image of ZnO nanorods

# CHAPTER-V

## CONCLUSION

Structural, surface morphology and vibrational properties of ZnO nanorod thin films grown on a ZnO seed layer deposited ITO coated glass substrates were investigated to explore the possibility of producing highly conductive, well electrochemical effective electrodes through a simple low cost process. The XRD, SEM and FT-IR revealed that all the films were grown with c-axis preferred orientations without any degradation of ZnO wurtzite structure. Moreover, further studies on optimization of synthesis condition and sensitization of dye molecules, metal oxide, and non-oxide nanoparticles over these nanorods may help to pave the way for all possible potential applications.

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