A

PROJECT REPORT

on

"Synthesis and Characterization of ZnO nanostructures by Hydrothermal method"

By

Lalit R. Nandre

Under the Guidance of

Dr. A. B. Gawande

Material Research Laboratory

Department of Physics

KARMAVEER SHANTARAM BAPU KONDAJI WAVARE (K.S.K.W)

ARTS, SCIENCE & COMMERCE COLLAGE, CIDCO, NASHIK-422008

2021-2022

Certificate

This is to certify that the project entitled

"Synthesis and Characterization of ZnO nanostructures by Hydrothermal method"

has been successfully completed by

Lalit R. Nandre

Seat no: -------------

During the academic year 2021-22 for fulfilment of

M.Sc-II (Physics) degree

Dr. A. B. Gawande
(Project Guide)

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

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<div style="text-align: right">Lalit R. Nandre</div>

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Chapter 1

INTRODUCTION

1.1 Nanoscience:

The word itself is a combination of nano, from the Greek "nanos" (or Latin "nanus"), meaning "Dwarf", and the word "Science." 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. Nano refers to the 10^{-9} power, or one billionth. In these terms it refers to a meter, or a nanometer, which is on the scale of atomic diameters. For comparison, a human hair is about 100,000 nanometers thick. 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.

1.2 Nanomaterial:

Nanomaterials is a field that takes a materials science-based approach to nanotechnology. It   studies materials with morphological features on the nanoscale, and especially those that have special properties stemming from their nanoscale dimensions. Nanoscale is usually defined as smaller than a one tenth of a micrometer in at least one dimension.

• *Materials with an average grain size less than 100 nanometers (10^{-9} m).*

• *One billion nanometers=one meter*

For comparison, the average width of a human hair is on the order of 100,000 nano meters. A single particle of smoke is in the order of 1,000 nanometers.

The nanomaterials field includes subfields which develop or study materials having unique properties arising from their nanoscale dimensions.

1. Interface and colloid science has given rise to many materials which may be useful in nanotechnology, such as carbon nanotubes and other fullerenes, and various nanoparticles and nanorods. Nanomaterials with fast ion transport are related also to nanoionics and nanoelectronics.

2. Nanoscale materials can also be used for bulk applications; most present commercial applications of nanotechnology are of this flavor.

3. Progress has been made in using these materials for medical applications; see Nanomedicine.

4. Nanoscale materials are sometimes used in solar cells which combats the cost of traditional Silicon solar cells.

1.3 Nanotechnology:

In his now legendary December 20, 1959, lecture *Plenty of Room at the Bottom*, physicist Richard P. Feynman spoke of the possibilities associated with the nascent field of nanotechnology, foreshadowing the revolution that was to come decades latter. Today, Feynman's dream is surely being realized on a grand and global scale. In twenty first century we are poised to make use of it for atomic-level manipulation of matter or engineering at the atomic level for the well being of mankind.

Nanotechnology is defined as the "Engineering of functional systems at the molecular scale". Simply defined, "Nanotechnology is the creation, use or manipulation of matter on the atomic scale". Nanotechnology is an emerging, interdisciplinary field combining principles of chemistry and physics with the engineering principles of mechanical design, structural analysis, computer science, electrical engineering, and system engineering. Built to atomic specification, the products would exhibit order of magnitude improvements in strength, toughness, speed, and efficiency, and be of high quality and low cost. Nanotechnology is the technology of preference to make things small, light and cheap.

Nanotechnology is the study and design of systems at the manometer scale [$0.000000001(10^{-9})$ meter] the scale of atoms and molecules. Human ability to manipulate materials on the nanoscale could revolutionize the way that almost everything is designed and made as nature does it. The field of Nanometer Scale Science and Technology (NSST) is very broad, ranging from nanoparticles, nanoclusters, and mesoscopic systems to individual atoms and molecules and their self-assembly into defined structures such as nanowires or biomolecules. This is a field where the border between the traditional disciplines like physics, chemistry and

biology is no longer detectable and interesting synergies arise, e.g., instruments developed in physics provide the precision and sensitivity to perform specific molecular recognition experiments in biology.

Nanometer-scale traps will be constructed that will be able to remove pollutants from the environment and deactivate chemical warfare agents. Computers with the capabilities of current workstations will be the size of a grain of sand and will be able to operate for decades with the equivalent of a single wristwatch battery. Robotic spacecraft that weigh only a few pounds will be sent out to explore the solar system, and perhaps even the nearest stars. Nanotechnology will change the nature of almost every human made object. The total societal impact of nanotechnology is expected to be greater than the combined influences that the silicon integrated circuit, medical imaging, computer-aided engineering, and man made polymers have had in this century. Significant improvement in performance and changes of manufacturing paradigms will lead to several industrial revolutions in the twenty first century.

Nanometer length scale:

Nanometer (nm) is one-billionth of a meter. For comparison, a single human hair is about 80,000 nm wide, a red blood cell is approximately 7,000 nm wide and a water molecule is almost 0.3nm across.

Why this length scale is so important?

There are five reasons why this length scale is so important:

1. The wavelike properties of electrons inside matter are influenced by variations on the nanometer scale. By patterning matter on the nanometer length scale, it is possible to vary fundamental properties of materials (for instance, melting temperature, magnetization, charge capacity) without changing the chemical composition.

2. The systematic organization of matter on the nanometer length scale is a key feature of biological systems. Nanotechnology promises to allow us to place artificial components and assemblies inside cells, and to make new materials using the self-assembly methods of nature. This is a powerful new combination of materials science and biotechnology.

3. Nanoscale components have very high surface areas, making them ideal for use in composite materials, reacting systems, drug delivery, and energy storage.

4. The finite size of material entities, as compared to the molecular scale, determine an increase of the relative importance of surface tension and local electromagnetic effects, making nanostructure materials harder and less brittle.

5. The interaction wavelength scales of various external wave phenomena become comparable to the material entity size, making materials suitable for various optoelectronic applications.

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, Nano clusters, Nano crystals)

(ii) 1D (*e.g.*, nanotubes, Nano fibers, nanowires)

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*.
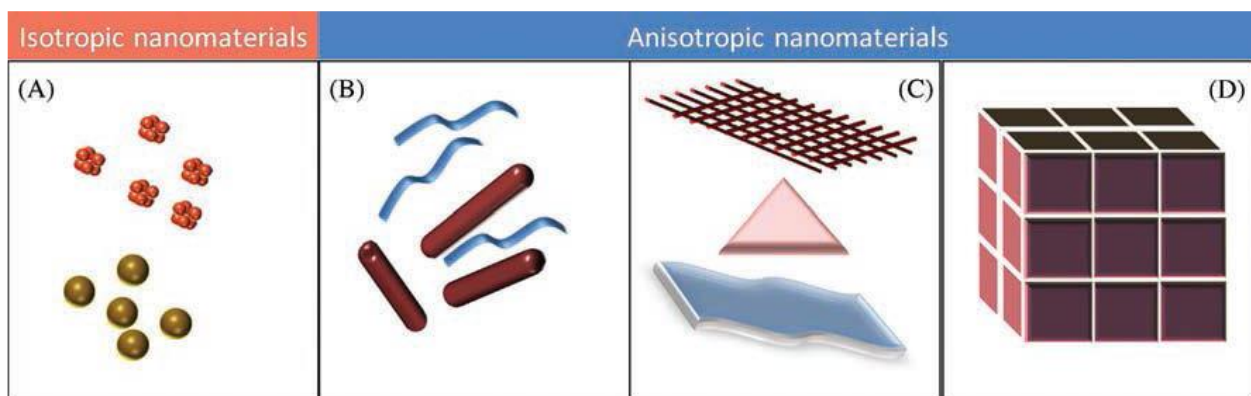

Fig1.1:-Various kinds of nanomaterials. (A) 0D spheres and clusters. (B) 1D nanofibers, wires,

and rods. (C) 2D films, plates, and networks. (D) 3D nanomaterials.

Nanostructure:

A clear distinction between nanostructures and microstructures is given here arbitrarily using length measurements. Nanostructures are defined according to their geometrical dimensions. This definition addresses technical dimensions, induced by external shaping processes, with the key feature being that the shaping, the orientation and the positioning is realized relative to an external reference system, such as the geometry of a substrate. Of less importance is whether this process uses geometrical tools, media or other instruments.

A narrow definition of nanostructures is that they include structures with at least two dimensions below 100nm.   An extended definition also includes structures with one dimension below 100 nm and a

second dimension below 1 μm. Following on from this definition , ultra-thin layers with lateral sub-micrometer structure sizes are also nanostructures.

All spontaneously distributed or spontaneously oriented structures in materials and on surfaces are not incorporated in nanotechnical structures. However, this does not exclude the presence of such structures in Nano technical setups, as long as their dimensions are in accord with the above-mentioned criteria. Also microstructured ultrathin layers are excluded, because they exhibit only one nanometer dimension. Nanodevices are devices with at least one essential functional component that is a nanostructure. Nanosystems consist of several Nano devices that are of importance to the functioning of the whole system.

1.4 Zinc Oxide (ZnO)

Zinc oxide (ZnO), a direct wide band gap (3.37 eV) semiconductor, has stimulated great research interest due to its unique optical and electrical properties that are useful for nanolasers, piezoelectric nanogenerators, solar cells, gas sensors, photocatalyst, and so on. Considerable effort has been devoted to fabricating various ZnO nanostructures, including nanowires, nanorods, nanobelts, nanotubes, nanodisks, and so on, because of their size- or morphology-dependent properties or device performances. Recently, semiconductor photocatalysts on a nanometer scale have become more and more attractive due to their different physical and chemical properties from bulk materials. As one of the most important semiconductor photocatalysts, ZnO has attracted considerable interests because of its high photosensitivity and stability. Due to the fact that a photocatalytic reaction occurs at the interface between catalyst and organic pollutants, the photocatalytic activity of ZnO is strongly dependent on the growth manner of the crystal, and it has been demonstrated that fine-tuning of face orientation could result in optimization of the photocatalytic activity of nanostructured semiconductors. As a polar crystal, ZnO is constructed from a number of positively charged (0001) planes rich in Zn^{2+} ions, alternating with negatively charged (0001) planes rich in O2- ions, stacked along the c axis. Normally, ZnO nuclei tend to aggregate along the c axis resulting in a one dimensional (1D) nanostructure (nanowires, nanobelts, nanorods, and nanotubes) due to electrostatic interaction. Although recent reports have demonstrated that the ZnO nanoplates can be generated by using polymers and surfactants as growth modifiers to suppress crystal growth along the [0001] axis, there still remains a significant challenge to directly prepare two dimensional (2D) ZnO nanoplates or nanosheets as well as to fabricate 3D hierarchical and complex ZnO structures assembled by these nanosheets. Such 3D hierarchical structures combining the features of nanoscaled building blocks not only show unique properties different from those of the monomorphological structures, but also may provide more opportunity for the surface photochemical reaction to realize region-dependent surface reactivity, due to their high specific areas and porous nanostructured surface layers.

Therefore, to develop convenient synthetic strategies to synthesize the hierarchical ZnO microstructures assembled by nanosheets with a larger population of unconventional planes is desirable and significative for exploring the photocatalytic property of ZnO material. Because of its easily controllable condition and relatively cheap equipments, the low temperature synthesis in an aqueous solution is highly desirable and represents an environmentally kind and user-friendly approach, which may be considered to be a relatively green chemical alternative of practical significance. However, various organic additives are usually involved in the synthesis of the hierarchical ZnO microstructures. With the existence of organic additives, there is considerable chance to absorb organicmolecules on the surface of ZnO and thus the efficient surface area decreases, resulting in the decrease in the photodegradation efficiency.

Zinc oxide is an inorganic compound with the formula ZnO. It usually appears as a white powder, nearly insoluble in water. The powder is widely used as an additive into numerous materials and products including plastics, ceramics, glass, cement, rubber (e.g. car tyres), lubricants, paints, ointments, adhesives, sealants, pigments, foods (source of Zn nutrient), batteries, ferrites, fire retardants, etc. ZnO is present in the Earth crust as a mineral zincite; however, most ZnO used commercially is produced synthetically.

In materials science, ZnO is often called a II-VI semiconductor because zinc and oxygen belong to the 2nd and 6th groups of the periodic table, respectively. This semiconductor has several favourable properties: good transparency, high electron mobility, wide band gap, strong room temperature luminescence, etc. Those properties are already used in emerging applications for transparent electrodes in liquid crystal displays and in energy-saving or heat-protecting windows, and electronic applications of ZnO as thin-film transistor.

Zinc oxide (ZnO), a wide band gap (3.4 eV) *II-VI* compound semiconductor, has a stable wurtzite structure with lattice spacing $a = 0.325$ nm and $c = 0.521$ nm. It has attracted intensive research effort for its unique properties and versatile applications in transparent electronics, ultraviolet (UV) light emitters, piezoelectric devices, chemical sensors and spin electronics. ZnO has been proposed to be a more promising UV emitting phosphor than GaN because of its larger exciton binding energy (60 meV). This leads to a reduced UV lasing threshold and yields higher UV emitting efficiency at room Temperature. Surface acoustic wave filters using ZnO films have already been used for video and radio frequency circuits. Piezoelectric ZnO thin film has been fabricated into ultrasonic transducer arrays operating at 100 MHz's. Bulk and thin films of ZnO have demonstrated high sensitivity for toxic gases. An assortment of ZnO nanostructures, such as nanowires, nanotubes, nanorings, and nanotetrapods have been successfully grown via a variety of methods including chemical vapour deposition, thermal evaporation, and electrodeposition, *etc*. These nanostructures have been subjected to electrical transport, UV emission, gas sensing, and ferromagnetic doping studies, and considerable progresses have been achieved. This review presents recent advances on ZnO nanostructures

Compared with bulk materials, low dimensional nanoscale materials, with their large surface area, high surface to volume ratio, and possible quantum confinement effect, exhibit distinct photocatalytic, chemical and thermal properties

1.4.1 Properties of Zinc Oxide (ZnO) nanostrucrure:

1) **Mechanical properties**:

ZnO is a relatively soft material with approximate hardness of 4.5 on the Mohs scale. Its elastic constants are smaller than those of relevant III-V semiconductors, such as GaN. The high heat capacity and heat conductivity, low thermal expansion and high melting temperature of ZnO are beneficial for ceramics. Understanding the mechanical properties of nanostructures is essential for the atomic-scale manipulation and modification of these materials, which have been known to behave differently when the dimensions are reduced from micro to nano scale. Nano wires also provide direct evidence of the mechanism, responsible for the plastic deformation when it undergoes mechanical stretching or compression. Further, it was found that the bond strength of the nanowire is approximately twice that of the bulk metallic bond. Computational studies indicate that the total effective stiffness of the nanowires had a strong dependence on the local arrangement of the atoms.

2) **Chemical properties**

ZnO occurs as white powder known as zinc white or as the mineral zincite. The mineral usually contains manganese and other impurities that confer a yellow to red color.Crystalline zinc oxide is thermochromic, changing from white to yellow when heated and in air reverting to white on cooling. This color change is caused by a small loss of oxygen to the environment at high temperatures to form the non-stoichiometric $Zn_{1+x}O$, where at 800 °C, $x = 0.00007$.

Zinc oxide is an amphoteric oxide. It is nearly insoluble in water and alcohol, but it is soluble in (degraded by) most acids, such as hydrochlori ZnO reacts slowly with fatty acids in oils to produce the corresponding carboxylates, such as oleate or stearate. ZnO forms cement-like products when mixed with a strong aqueous solution of zinc chloride and these are best described as zinc hydroxy chlorides. This cement was used in dentistry

3) Structural and Optical Properties:

ZnO is a key technological material. ZnO is a wide band-gap (3.37 eV) compound emiconductor that is suitable for short wavelength optoelectronic applications. The high exciton binding energy (60meV) in ZnO crystal can ensure efficient excitonic emission at room temperature and room temperature ultraviolet (UV) luminescence has been reported in disordered nanoparticles and thin films. In addition, the lack of a centre of symmetry in wurtzite, combined with large   electromechanical coupling, results in strong piezoelectric and pyroelectric properties and the consequent use of ZnO in mechanical actuators and piezoelectric sensors. Furthermore, ZnO is a versatile functional material that has a diverse group of growth morphologies, such as nanocombs, nanorings, nanohelixes/nanosprings, nanobelts, nanowires and nanocages. These ZnO nanostructures are easily formed even on cheap substrates such as glass and hence they have a promising potential in the nanotechnology future. Finally, ZnO nanostructures are also attractive for biomedical application since it is a bio-safe material and its nanostructure has a large surface area. As well as we know, all these applications definitely originate from its basic properties.

At ambient pressure and temperature, ZnO crystallizes in the wurtzite (B4 type) structure, as shown in figure 2.1. This is a hexagonal lattice, belonging to the space group P63mc with lattice parameters a = 0.3296 and c = 0.52065 nm. The structure of ZnO can be simply described as a number of alternating planes composed of tetrahedrally coordinated O^{2-} and Zn^{2+} ions, stacked alternately along the c-axis (Figure2.1). The tetrahedral coordination in ZnO results in noncentral symmetric structure and consequently piezoelectricity and pyroelectricity.

Another importantcharacteristic of ZnO is polar surfaces. The most common polar surface is the basal plane. The oppositely charged ions produce positively charged Zn-(0001) and negatively charged O-(0001) surfaces, resulting in a normal dipolemoment and spontaneous polarization along the c-axis as well as a divergence in surface energy. To maintain a stable structure, the polar surfaces generally have facets or exhibit massive surface reconstructions, but ZnO-± (0001) are exceptions: they are atomically flat, stable and without reconstruction Efforts to understand the superior stability of the ZnO ± (0001) polar surfaces are at the forefront of research in today's surface physics .
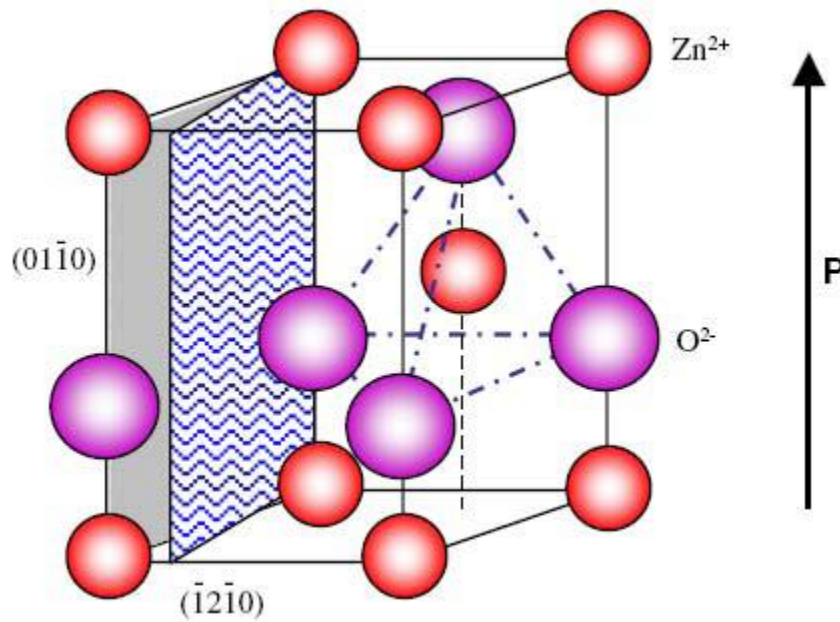
Fig.1.2 The wurtzite structure model of ZnO with tetrahedral coordination of ZnO.

Additional to the wurtzite phase, ZnO is also known to crystallize in the cubic zinc blende and rocksalt (NaCl) structures, which are illustrated in figure 2.Zincblende ZnO is stable only by growth on cubic structures [29–31], while the rocksalt structure is a high-pressure metastable phase forming at ~10 GPa, and cannot be epitaxially stabilized [32]. Theoretical calculations indicate that a fourth phase, cubic cesium chloride, may be possible at extremely high temperatures, however, this phase has yet to be experimentally observed.
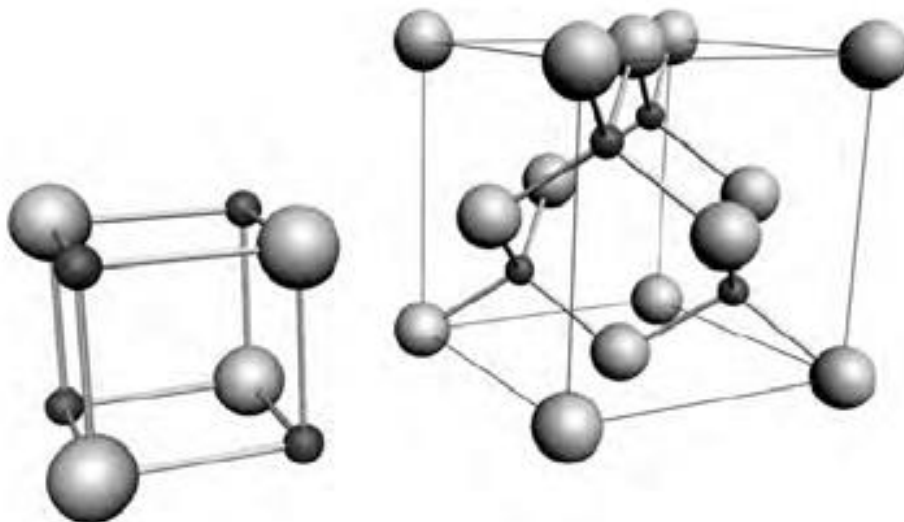

Fig. 1.3 Rock salt (left) and zinc blende (right) phases of ZnO. O atoms are shown as white spheres, Zn atoms as black spheres. Only one unit cell is illustrated for clarity.

4) Electrical Properties:

ZnO has a relatively large directband gap of ~3.3 eV at room temperature. Advantages associated with a large band gap include higher breakdown voltages, ability to sustain large electric fields, lower electronic noise, and high-temperature and high-power operation.Most ZnO has *n*-type character, even in the absence of intentional doping. Nonstoichiometry is typically the origin of n-type character. p-type doping of ZnO remains difficult. This problem originates from low solubility of p-type dopants and their compensation by abundant n-type impurities. This problem is observed with GaN and ZnSe. Controllable n-type doping is easily achieved by substituting Zn with group-III elements such as Al, Ga , In or by substituting oxygen with group-VII elements chlorine or iodine. Piezoelectric properties of ZnO can be used for gas sensing, surface acoustic wave devices, varistors, and transparent thin film transistors. It is also attractive for forming various types of nanorods, nano wires, and nanotubes for observation of quantum effects.

4) Physical Properties:

Table lists the basic physical properties of bulk ZnO. It is worth noting that as the dimension of the semiconductor materials continuously shrinks down to nanometer or even smaller scale, some of their physical properties undergo changes known as the "quantum size effects". For example, quantum confinement increases the band gap energy of quasi-one-dimensional (Q1D) ZnO, which has been confirmed by photoluminescence. Bandgap of ZnO nanoparticles also demonstrates such size dependence. X-ray absorption spectroscopy and scanning photoelectron microscopy reveal the enhancement of surface states with the downsizing of ZnO nanorods.

Properties	Value
Lattice constants	(T = 300 K)
A_0	0.32469 nm
C_0	0.52069 nm
Density	5.606 g/cm3
Melting point	2248 K
Relative dielectric constant	8.66
Gap Energy	3.4 eV, direct
Intrinsic carrier concentration	< 106 cm-3

Exciton binding Energy	60 meV
Electron effective mass	$0.24m_e$
Electron mobility (T = 300 K)	200 cm2/V s
Hole effective mass	$0.59m_e$
Hole mobility (T = 300 K)	5-50 cm2/V s

In addition, the carrier concentration in Q1D systems can be significantly affected by the surface states, as suggested from nanowire chemical sensing studies. Understanding the fundamental physical properties is crucial to the rational design of functional devices. Investigation of the properties of individual ZnO nanostructures is essential for developing their potential as the building blocks for future nanoscale devices. This section will review the up-to-date research progress on the physical properties of ZnO nanostructures, including mechanical, piezoelectric, electrical, optical, magnetic and chemical sensing properties.

1.4.2 Applications of Zinc Oxide (ZnO) nanostrucrure:

Zinc oxide has the richest family of nanostructures among all materials, both in structures and in properties. The nanostructure could have novel application in photocatalytic activity, in hydrogen generation and in biomedical sciences. Here few applications are highlighted

1) Lasing:
Nanostructure with flat ends can be exploited as optical resonant cavities to generatecoherent light on the nanoscale. Huang et al. have demonstrated the room temperature UV lasing ZnO nanowires. The observed lasing action in these nanowires arrays without any fabricated mirror indicates that these single-crystalline faceted nanowires can, indeed, function as natural resonant cavities.

2) Electronics:

ZnO has wide direct band gap (3.37 eV). Therefore, its most common potential applications are in laser diodes and (LEDs). Some optoelectronic applications of ZnO overlap with that of GaN, which has a similar bandgap (~3.4 eV at room temperature). Compared to GaN, ZnO has a larger exciton binding energy (~60 meV, 2.4 times of the room-temperature thermal energy), which results in bright room-temperature emission from ZnO.

ZnO can be combined with GaN for LED-applications. For instance as TCO layer and ZnO nanostructures provide better light outcoupling. Radiation resistance makes ZnO a suitable candidate for space applicationsThe pointed tips of ZnO nanorods result in a strong enhancement of an electric field. Therefore, they can be used as field emitterss toxic compared to the generally used indium tin oxide (ITO).

3) Photoconductivity and Optical Switching:

ZnO epitaxial heterostructures exhibits uniqueluminescence in contrast with that of individual tetra pod ZnO nanostructures, in which the epitaxial interface induces new luminescent properties. This result may inspire great interest in exploring other complicated epitaxial systems and their potential applications in solar energy conversion, photo catalysis and nanodevices in the near future.

1.4. 3 Methods of Preparation of Nanostructures:

There is large number of techniques 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.

1)Physical Methods:-

1. High Energy Ball Milling
2. Melt Mixing
3. Physical Vapour Deposition with 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

2) Chemical Methods:-

1. Colloids and Colloids in Solution

2. Langmuir-Blodgett (L-B) Methods

3. Micro emulsions

4. Sol-Gel Methods

5. Hydrothermal Methods

Hydrothermal method

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, 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 or non-aqueous.

Hydrothermal synthesis for rational design of nanoparticles is still at its infancy and for beyond its maturity even though this traditional approach has been widely explored for the synthesis of various kinds of functional oxides and nonoxide nanomaterials with specific shape and size of new materials. Hydrothermal route can be defined as the use of water as reaction medium is a sealed reaction container when the temperature is raised above 100^0C. Autogenously pressure which is self-developed and not externally applied is generated under mese conditions. The pressure within the sealed reaction container increases dramatically with temperature, but also will depend on other experimental factors, such as the percentage fill of the vessel and any dissolved salts as illustrated in figure 1.4. One remarkable advantage of the use of hydrothermal condition is that it has significant effects on the reactivity of inorganic solids and the solubility of diverse compounds under conditions of elevated pressure and temperatures. Secondly, the chemical reactivity of usually insoluble reagents can be much enhanced and a lot of sluggish solid-state reactions can be initiated under hydrothermal

conditions. In hydrothermal synthesis often higher temperatures above 300ºC are applied and often the reactions take place under supercritical conditions; however, the low temperature route (temperature <250ºC) is usually applied for the synthesis of various well-known functional materials and even in new solids.\
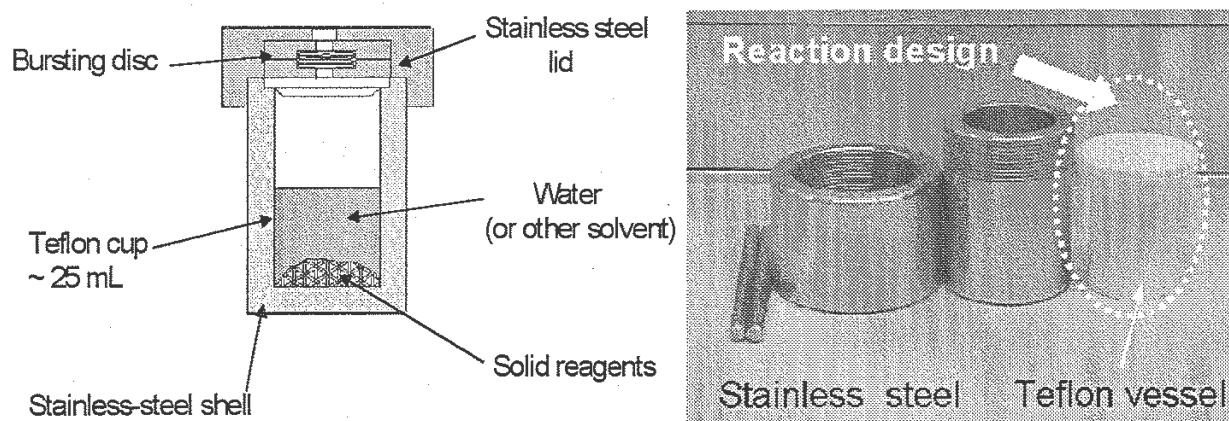

Fig. 1.4 Schematic illustration of a Teflon- lined, stainless autoclave typically used in the labotarory to perform subcritical hydrothermal / solvothermal synthesis. (b) A picture of a set of the autoclave.

 It has to be pointed out that the concepts embodied in hydrothermal process have already been extrapolated to non-aqueous systems and the so called "Solvothermal process" has emerged in which an organic solvent is used as reaction medium instead of water at elevated temperature about its boiling point. Low dimensional nanostructures of oxides are very important for the design of superconductors, semiconductors, sensors and many other devices in a future nanotechnology. Therefore, a general synthetic access is needed for the large-scale preparation of 1D oxide nanostructures. Hydrothermal synthesis method can also generate novel ZnO nanostructures such as nanooparticles, nanorods, nanowires, ZnO nanorod arrays rotor like ZnO by epitaxial growth and novel ZnO superstructures with ring-like nanosheets standing on spindle- like rods. Recently, single crystalline zinc oxide (ZnO) nanorods or nanoplatelets can be even aligned into curved arrangements analogous to the "parachutes" array in a dandelion via a hydrothermal approach. Similarly, hollow ZnO microhemispheres and microspheres can be constructed from 1D ZnO nanorods and 2D thin nanosheets via the hydrothermal approach

Chapter 2
CHARACTERIZATION TECHNIQUE

2.1 X-ray diffraction (XRD)

Basic principle of X –ray generation:

X-ray are electromagnetic radiation with wavelength of the order of 10 nm bombarding a metal with high energy electron generates them.

Crystalline solids consist of a regular, three-dimensional arrangement of atoms in a periodic pattern called a crystal lattice. The internal structure of such solids can be determined using a technique called X-ray diffraction. As you will recall from the Preliminary Course, diffraction is the name given to the phenomenon in which a wave spreads out as it passes through a small aperture or around an obstacle. Diffraction patterns are most intense when the size of the aperture or obstacle is comparable to the size of the wavelength of the wave. Since the wavelength of X-rays is of the order of 10^{-10} m and since the interatomic spacing in solids is of the same order, X-rays produce strong diffraction patterns from crystals. (Note that both neutrons and electrons can be used in place of X-rays.)

The British physicists William and Lawrence Bragg (father & son) applied X-ray diffraction to the study of crystals from about 1912 onwards. A beam of X-rays with a wide range of wavelengths was collimated and directed onto the single crystal specimen under study. A flat film behind the specimen received the diffracted beams. The diffraction pattern consisted of a series of spots of light that indicated the symmetry of the crystal.

William Bragg presented a simple explanation of the diffracted beams from a crystal. He suggested that the X-ray wave's incidents on parallel planes of atoms in the crystal are reflected, with each plane reflecting only a very small fraction of the radiation. The diffracted beams are formed when the reflections from parallel planes of atoms interfere constructively, as in the diagram
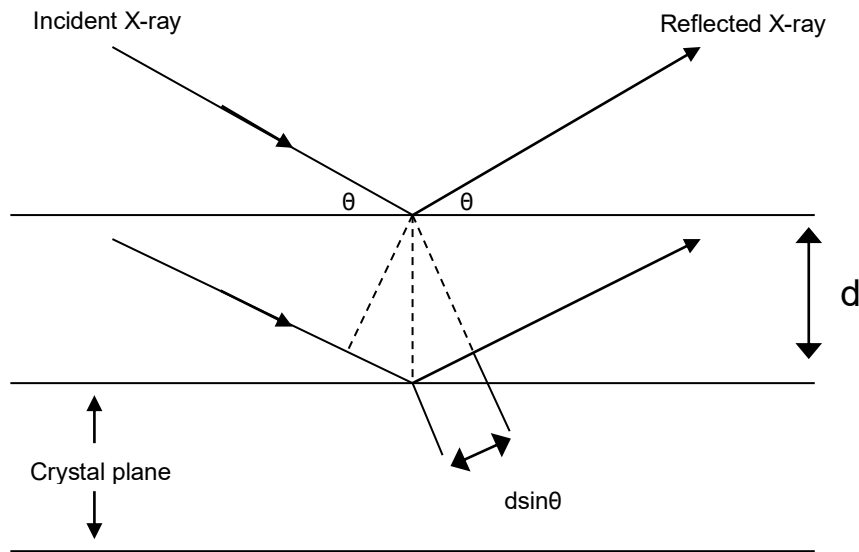
Fig 2.1:-X-rays diffraction from the planes in same direction.

Bragg derived the following formula, now called the Bragg Law, which enables the determination of the interatomic spacing, d, of the atoms in the specimen or the wavelength, l, of the X-rays (depending on what is known):

$$2d \sin\theta = n\lambda$$

where θ = the angle of reflection at which constructive interference occurs and n = the order of diffraction (n = 1, 2 , 3, ….. corresponding to occasions when the path difference d between the two reflected rays in the diagram is an integral number, λ= wavelengths, allowing constructive interference to occur).

The Braggs' contribution to our understanding of crystal structure has had a lasting beneficial impact in many areas of science and engineering. They were pioneers in a field which has allowed us to greatly increase our knowledge and understanding of materials and which has assisted tremendously in the development of new materials. The Braggs received the 1915 Nobel Prize for Physics in recognition of their important contribution to science.

Here XRD was done by the X-ray diffraction of the as milled powder samples were performed using the diffractometer. X-Ray diffraction patterns were recorded from 20° to 90° with a Analytical system diffractometer (Model: DY-1656) using Cu Kα (λ=1.542Ao) with an accelerating voltage of 40 KV. Data were collected with a counting rate of 1°/min. The Kα doublets were well resolved. From XRD, the crystallite size can be found out by using the scherrer's formula,

$$D = \frac{0.9\lambda}{\beta \cos\Theta}$$

Where,

D – Crystallite size

λ – Wavelength (1.54A0),

β - Full maxima half width,

θ- Diffraction angle

X-ray primarily interacts with electrons in atoms, and during the course of the interaction some photon from the incident beam will be deflected away from the direction where they originally travel. The scattered X-ray carry information about the electron distribution in material. However, in the in elastic scattering process (Compton scattering), energy is transferred to the electrons and scattered X-ray will have different wavelength than the incident X-rays. Diffracted waves from different atom can interfere with each other and the resultant intensity distribution is strongly modulated by this interaction. If the atoms are arranged in periodic fashion, as in crystal, the diffracted wave will consist of sharp interference maxima (peaks) with the same symmetry as in the distribution of atom. Measuring the diffraction pattern therefore allows one to deduce the distribution of atom in a material. The peaks in the X-ray diffraction pattern are directly related to the atomic distances.

2.3 **UV-Visible Spectrscopy:**

Diagram of the components of a typical spectrometer is shown in the following diagram. The functioning of this instrument is relatively straightforward. A beam of light from a visible and/or UV light source (colored red) is separated into its component wavelengths by a prism or diffraction grating. Each monochromatic (single wavelength) beam in turn is split into two equal intensity beams by a half-mirrored device. One beam, the sample beam (colored magenta), passes through a small transparent container (cuvette) containing a solution of

the compound being studied in a transparent solvent. The other beam, the reference (colored blue), passes through an identical cuvette containing only the solvent shown in fig 2.3. The intensities of these light beams are then measured by electronic detectors and compared. The intensity of the reference beam, which should have suffered little or no light absorption, is defined as I_0. The intensity of the sample beam is defined as I. Over a short period of time, the spectrometer automatically scans all the component wavelengths in the manner described. The ultraviolet (UV) region scanned is normally from 200 to 400 nm, and the visible portion is from 400 to 800 nm.

If the sample compound does not absorb light of of a given wavelength, $I = I_0$. However, if the sample compound absorbs light then I is less than I_0, and this difference may be plotted on a graph versus wavelength, as shown on the right. Absorption may be presented as **transmittance** ($T = I/I_0$) or **absorbance** ($A = \log I_0/I$). If no absorption has occurred, T = 1.0 and A= 0. Most spectrometers absorbance on the vertical axis, and the commonly observed range is from 0 (100% transmittance) to 2 (1% transmittance). The wavelength of maximum absorbance is a characteristic value, designated as λ_{max}.
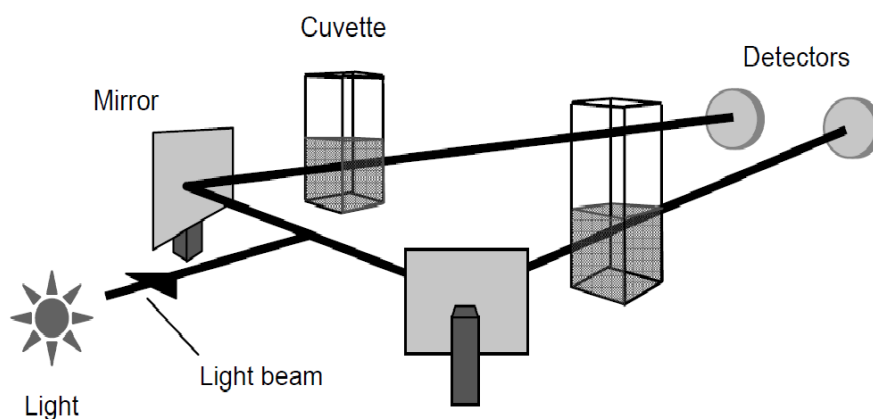

Fig.2.3 -Principle of UV/Vis spectrometer

Different compounds may have very different absorption maxima and absorbances. Intensely absorbing compounds must be examined in dilute solution, so that significant light energy is received by the detector, and this requires the use of completely transparent (non-absorbing) solvents. The most commonly used solvents are water, ethanol, hexane and cyclohexane. Solvents having double or triple bonds, or heavy atoms (e.g. S, Br & I) are generally avoided. Because the absorbance of a sample will be proportional to its molar concentration in the

sample cuvette, a corrected absorption value known as the **molar absorptive** is used when comparing the spectra of different compounds. This is defined as :

Molar Absorptivity,

$$\varepsilon = A/C\, l$$

 Where,

A= absorbance,

C=sample concentration in moles/liter *l* = length of light path through the cuvette in cm.

For the spectrum on the right, a solution of 0.249 mg of the unsaturated aldehyde in 95% ethanol ($1.42 \cdot 10^{-5}$ M) was placed in a 1 cm cuvette for measurement. Using the above formula, $\varepsilon = 36,600$ for the 395 nm peak, and 14,000 for the 255 nm peak. Note that the absorption extends into the visible region of the spectrum, so it is not surprising that this compound is orange colored. Molar absorptivities may be very large for strongly absorbing compounds ($\varepsilon > 10,000$) and very small if absorption is weak ($\varepsilon = 10$ to 100).

Chapter 3

Experimental Section

Materials and Methods

Zinc acetate (Zn (CH$_3$COO)$_2$. 4H$_2$O) Merck) and Sodium hydroxide (NaOH, Merck) were used as the starting materials. All the chemicals were used as recived. Cetyltriammonium bromide (CTAB) was used as the surfactant. All the solutions were prepared using double distilled water during the synthesis.

Synthesis of ZnO :

ZnO nanorods were prepared from Zinc acetate and CTAB in a neutral aqueous solution under hydrothermal conditions. In order to synthesize the ZnO nanorods, First 0.768gm NaOH dissolve in 48 ml of distilled H$_2$O and then 2.1gm zinc acetate dissolve into 96mldistilled.H$_2$O in two separate beakers. This two solution are kept for magnetic stirring for 10 minutes. After some time two separate solutions were added in one beaker. Out of this 42 ml solution is taken and 30 ml of ethanol added in it. In another beaker CTAB of 7.5 gm dissolve in 24 ml of dist H$_2$O and added to above solution. After this solution kept in oven at temperature 80˚C for a 6 hours. After completion of reaction, the autoclave cool at room temparatue and then final product wash with water about 3-4 times by centrifugation process. The final residue kept in vacuum oven at 60 ^{0}C for drying about 10 hours.

Chapter 4

Result and Discussion

4.1 X-Ray diffraction (XRD)

The X-ray diffraction (XRD) studies of the sample was performed by PANalytical X'PERT PRO using Cu Kα radiation. The sample was scanned in 2θ range from 10 to 80°.X-ray diffraction (XRD) study indicate that all the diffraction peaks could be indexed to hexagonal wurtzite ZnO and it is match with reported JCPDS. data Fig. 2 depicts the XRD pattern of ZnO Nanorods while the sharp peaks at 2θ values 34.26^0, 36.24^0, 47.54^0, 56.62^0, 62.9^0, and 68.02^0, with corresponding crystal plane (002), (101), (102), (110), (103), (201) Fig. 4.1 shows the X-ray diffraction pattern of the hydrothermally synthesized ZnO nanorods prepared with C-TAB as capping reagent.
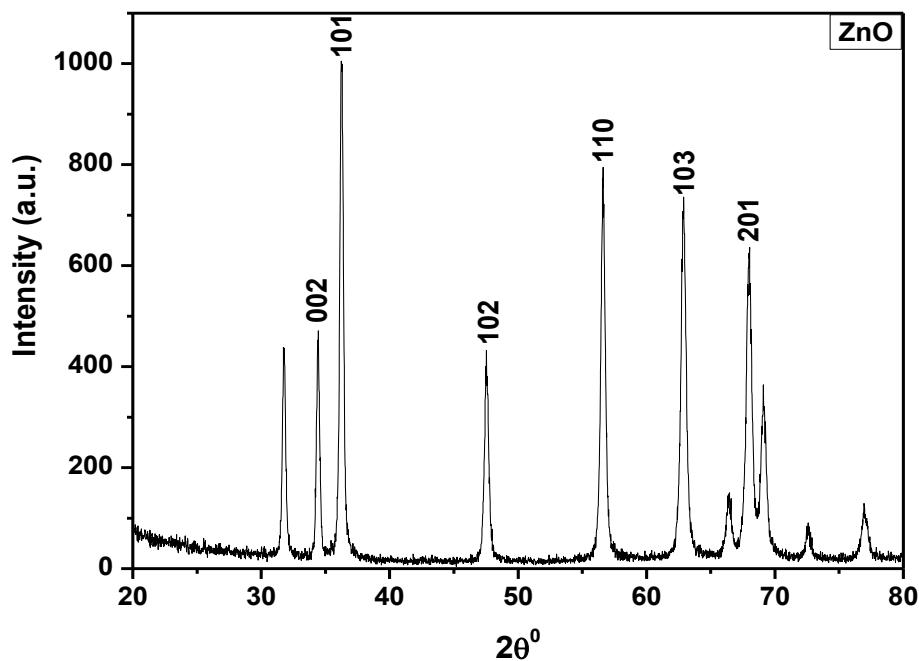

Fig. 4.1 X-ray diffractograms of ZnO nanoparticles

4.2 UV-visible Spectroscopy (UV-Vis)

UV-visible absorption spectrophotometer is standard technique to obtain the band gap which is one of the characteristic properties of the material. It gives the rough idea about the patical size by red or blue shift in the absorption spectra. It also gives the rough idea about the phase formation.UV-Vis spectra of nanocrystalline ZnO powder synthesized by hydrothermal method are shown in Fig.3. The absorption of ZnO nanorod powder showed absorption edge cut off at 381 nm (band gap: 3.25 eV). The band gap obtained is higher than the reported value i.e. 3.37 eV, owing to nanocrystalline nature of the ZnO powders.
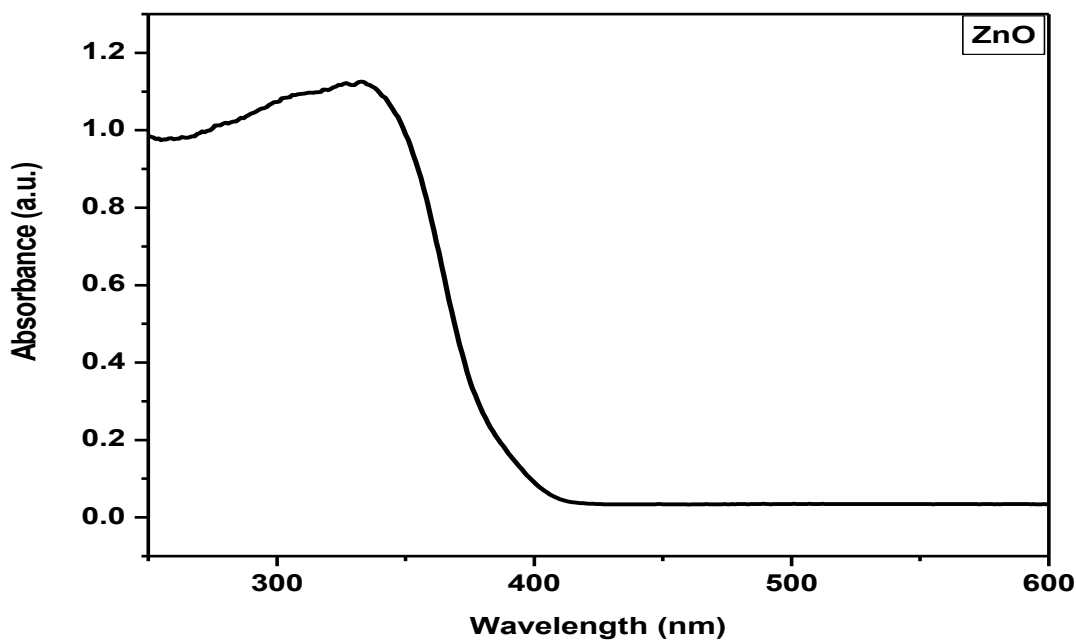
d

Fig. 4.2 UV-DRS spectra of ZnO nanorods

Chapter 5

CONCLUSION

Nanorods of Zinc oxide were successfully synthesized by hydrothermal method using Cetyltriammonium bromide (CTAB) as a capping agent and Zinc acetate as a precursor. The morphological, optical and structural properties of the nanorods were characterized by field-emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), diffuse reflectance spectra (DRS) .FE-SEM images clearly show that the one dimensional nanorods were obtained by using simple hydrothermal method. X-ray diffraction study indicates that all the diffraction peaks could be indexed to hexagonal wurtzite ZnO structure. The band gap energy value observed by diffuse reflectance spectroscopy is 3.25 eV. ZnO is very attractive for various applications such as conductive oxide, antistatic coatings, sensors and touch display panels and high band gap optoelectronic devices.

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