

# **SYNTHESIS AND CHARACTERIZATION OF LEAD DOPED ZINC OXIDE NANOPARTICLES FOR OPTICAL APPLICATIONS**

Project Report submitted to  
St.Joseph's College (Autonomous), Tiruchirappalli-2  
Affiliated to the Bharathidasan University  
in partial fulfillment of the requirements  
for the award of the degree of  
**MASTER OF SCIENCE IN PHYSICS**

By  
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Assistant Professor



**PG & RESEARCH DEPARTMENT OF PHYSICS**  
**St.JOSEPH'S COLLEGE (Autonomous)**  
Special Heritage Status Awarded by UGC, Accredited with 'A++' Grade (4<sup>th</sup> Cycle) by NAAC  
College with Potential for Excellence by UGC, DBT-STAR & DST-FIST Sponsored College  
TIRUCHIRAPPALLI – 620 002, TN  
APRIL-2020

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**Dr. A. J. CLEMENT LOURDURAJ M.Sc., M.Phil., PGDCSA., Ph.D.**  
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**CERTIFICATE**

This is to certify that the project entitled “**Synthesis and Characterization of Lead doped Zinc Oxide Nanoparticles for Optical Applications**” submitted by **Vishnu. S, D.NO.18PPH107** during 2019-2020, at the Department of Physics, St.Joseph's College (Autonomous), Tiruchirappalli – 620 002, and that the project has not previously formed the basis for the award of any PG Degree in Physics or any other similar title to anyone and that the project represents entirely an independent work on the part of the candidate.

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**PROJECT GUIDE**

**Place :**  
**Date :**

**The Project Viva-voce examination held on \_\_\_\_\_ at the Department of Physics,**  
**St. Joseph's College (Autonomous), Tiruchirappalli.**

**Internal Examiner**

**External Examiner**

## **DECLARATION**

I declare that the thesis entitled, “**Synthesis and Characterization of Lead Doped Zinc Oxide Nanoparticles for Optical Applications**” submitted by me for the degree of Master of Science in Physics to St. Joseph’s College (Autonomous), is the result of my original and independent work done in the Post Graduate and Research Department of Physics, St. Joseph’s College, Tiruchirappalli-2, India during 2019-2020 under the supervision and guidance of **Dr.A.J.CLEMENT LOURDURAJ, M.Sc., M.Phil., PGDCSA., Ph.D.**, Assistant Professor in Physics, St. Joseph’s College, Trichy. This work has not previously formed the basis for the award of any degree, diploma, fellowship or other similar titles in this or any other University or other similar institute of higher learning.

**VISHNU. S**

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## **CHAPTER-I**

### **INTRODUCTION ABOUT NANOTECHNOLOGY**



# CHAPTER-I

## INTRODUCTION ABOUT NANOTECHNOLOGY

### 1.1 Introduction:

Nanotechnology is the capacity that able to observe measure, define, control and producing things at nanometer scale. “**There is plenty of room at bottom**” is a famous talk given by renowned scientist **Richard Feymann** in 1959- In this He dealt possibility of synthesis by direct manipulation of atoms which needed nanotechnology concepts.

Nanotechnology is the design, characterization, production and application of structures, devices and systems by controlling shape and size by 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. Yet, nanotechnology concepts play important role in all of these disciplines at the macroscopic scale. Nanotechnology of the future will encompass all these disciplinary areas and understanding basic nanotechnology concepts will help student understand all sciences. It is highly interdisciplinary area, meaning that it involves ideas integrated from many traditional disciplines. Scientists working in physics, chemistry, biology, engineering, information technology, meterology and other fields are contributing 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.

Since nanotechnology must build its devices from atoms and molecules. The upper limit is more or less arbitrary, but it around the size below which phenomena not observed in larger structures; these new phenomena make nanotechnology distinct from other such devices, which are nearly miniaturized versions of that equivalent macroscopic device. It has the potential to change our prospective and expectations and provide us with the capability to resolve global issues. The discovery and use of carbon nanomaterials has allowed the introduction of many new areas of technology in nanomedicine, biosensors and bioelectronics. In recent years, nanotechnology has emerged as a multidisciplinary field, in which gaining a fundamental understanding of the electrical, magnetic, optical

and mechanical properties of nanostructures with wide applications. Also it has the challenging of catalysis, medicine and solar energy conversion and water treatment.

## 1.2 History:

The term ‘nanotechnology’ was first used by Japanese scientists **Norio Taniguchi** in 1974 paper on production technology that creates objects and features on the order of nanometer. The American engineer **K. Eric Drexler** is credited with the development of molecular technology, leading to nanosystems machinery manufacturing.

First, the invention of the **Scanning Tunnelling Microscope** in 1981 which provided unprecedented visualization of individual atoms and bonds, and was successfully used to manipulate individual atoms in 1989. The microscope’s developers **Gerd Binnig and Heinrich Rohrer at IBM Zurich Research Laboratory** received a Nobel Prize in Physics in 1986.

Second, **Fullerenes** were discovered in 1985 by **Hary Kroto, Richard Smalley** who together won Nobel Prize in Chemistry. Smalley investigated in the research field of inorganic and semiconductor clusters using pulsed molecular beams and time of flight mass spectrometry. The discovery of carbon nanotubes is largely attributed to **Sumino Iijima** in 1991 who discovered the multi-walled carbon nanotubes in the insoluble material of arc-burned graphite rods.

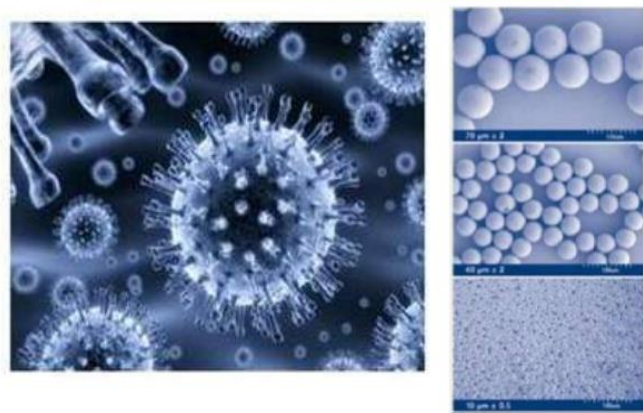
Third, the first **MOSFET** were discovered in 1987, by **Bijan Davari** led an IBM research team demonstrated with a 10 nm gate oxide thickness, using tungsten-gate technology. Multi-gate MOSFETs enabled scaling below 20 nm gate length, starting with the FinFET (fin field-effect transistor), a three-dimensional, non-planar, double-gate MOSFET.

In the early 2000s , the field garnered increased scientific, political and commercial attention that led to both controversy and progress. These products are limited to bulk applications of nanomaterials and do not involve atomic control of matter.

### 1.3 Nanoparticles:

A nanoparticle (or nanopowder or nanocrystal or nanocluster) is a microscopic particles having the dimensions ranging from 1-100 nm. Nanoparticle research is currently an area of intense scientific research, due to a wide area of applications in all aspects such as electrical, magnetic, optical and electronic fields. Nanoparticles are of great effectively bridge bulk materials and atomic or molecular structures.

## NANOPARTICLES



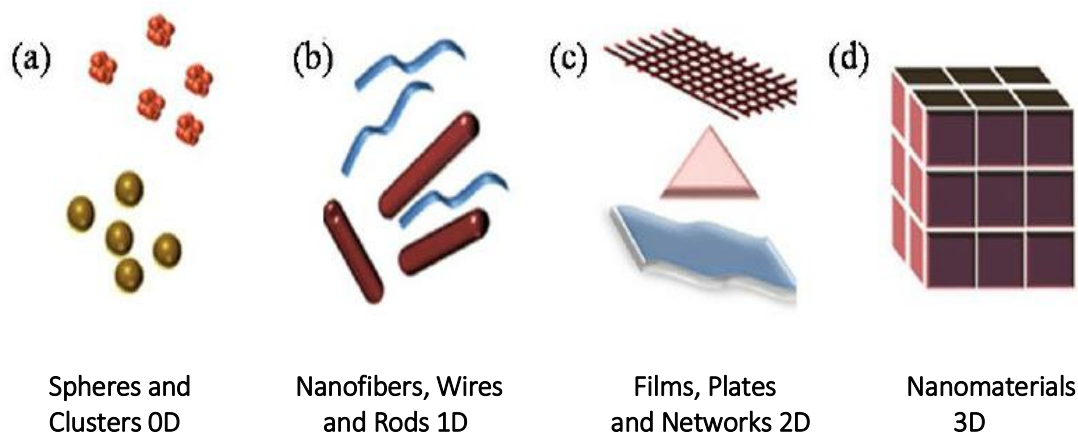
Nanoparticles can be classified according to their size. The reduction of bulk materials to the nano region induces the size dependent effects arising due to:

- Significant increase of the surface-to-volume ratio leading to a large interfacial area.
- Changing in the physic-chemical properties of the interfacial species.
- Changes in the electronic structure and arrangement of the species within the nanoparticles.
- Confinement and quantum size effects.
- For bulk materials larger than one micrometer the percentage of atoms at the surface is minuscule relative to the total number of atoms of the material.
- Copper nanoparticles smaller than 50nm are considered super hard materials because that do not exhibit the same malleability and ductility as bulk copper.
- Nanoparticles often have unexpected visible properties because they are small enough to confine their electrons and produce quantum effects.

## 1.4 Classification of Nanomaterials:

Nanomaterials have extremely small size which is having at least one dimension 100 nm or less. Nanomaterials can be nanoscale in one dimension (eg. Surface films), two dimensions (eg. Strands or fibres), three dimensions (eg. Particles). They can exist in single, fused, aggregated forms with spherical, tubular and irregular shapes. Nanomaterials have applications in the field of nanotechnology and displays different physical chemical characteristics from normal chemicals (i.e., silver nano, carbon nanotube, fullerence, photocatalyst). Common types of nanomaterials are as follows,

- Nanoparticles
- Nanotubes
- Nanowires
- Nanoplates
- Nanodiscs
- Nanofiber



- Accordingly, in zero-dimensional (0D) nanomaterials all the dimensions are measured within the nanoscale (no dimensions are larger than 100nm). Most commonly , 0D nanomaterials are nanoparticles.
- In one-dimensional nanomaterials (1D), one dimension is outside the nanoscale. This class includes nanotubes, nanorods and nanowires.
- In two-dimensional nanomaterials (2D), two dimensions are outside the nanoscale.

- This exhibitsexhibits graphene, nanofilms, nanolayers and nanocoatings.
- Three dimensional (3D) nanomaterials that are not confined to the nanoscale in any dimension. This contains nanowires, nanotubes and nanoparticles.
- Two principle factors cause the properties of nanomaterials to differ significantly from other materials: increased relative surface area and quantum effects. These factors can change or enhance properties such as reactivity, strength and electrical characteristics.

## **1.5 Properties of Nanomaterials:**

The size of the nanomaterials is very hard to imagine that is it's very small of one billionth of a meter ( $10^{-9}$  meters). It exhibits many properties such as physical, chemical, magnetic and optical properties which are follows as:

### ***Physical Properties:***

- Nano-sized condensed matter exhibits some remarkable specific properties that may be significantly different from the physical properties of bulk materials.
- Origins: Large fraction of surface atoms.  
Large surface energy.  
Spatial confinement.  
Reduced imperfections.
- As the size of the particle is very less, shape and aspect ratio.
- Nanomaterials may have a significantly lower melting point due to a large fraction of surface atoms.
- Mechanical strength is due to the reduced probability of defects in the bulk form.
- Nanomaterials exhibits the super plastic behavior.

### ***Mechanical Properties:***

- Mechanical properties of nanomaterials deals with bulk metallic and ceramic materials, influence of grain size, carbon nanotubes based composites.
- It produce macroscopic bodies with a high density and a grain size in the range of less than 100 nm.
- As nanomaterials are stronger, harder and more wear resistant and corrosion resistant, they are mostly used in spark plugs.

- For example: Nano-crystalline carbides are much stronger and harder and are used in micro drills.
- Lower plastic deformation and more brittle.

#### ***Magnetic Properties:***

- Magnetic nanoparticles are the type which can be manipulated and targeted by external magnetic field.
- It has the increase of potential use of nanomaterial based catalysis, data storage and optical fibers.
- Elements like Fe, Co, Ni and their oxides can form magnetic nanomaterials. Iron oxides are commonly used in high electrical resistivity, mechanical hardness and magnetic properties in RF region.
- It depends on the synthesis methods and shapes of the nanoparticles.
- Ferro magnetic and anti ferromagnetic multilayers have been found to exhibit Giant Magneto Resistance (GMR).
- Small particles differ from the bulk in that these atoms will have lower coordination number.
- Metals of sodium and potassium are having the bulk Paramagnetic and cluster Ferromagnetic nature.

#### ***Optical Properties:***

- One of the most fascinating and useful aspects of nanomaterials is optical properties and their applications based on optical detector, laser, sensor, imaging, display, solar cell, photo catalysis and biomedicine.
- It depends on the parameters such as size, shape, surface characteristics and including doping of nanostructures.
- Increase in luminescent efficiency of semiconductors; transparency of nanoparticles.
- Surface Plasmons

Metal nanoparticles like gold and silver have Plasmon frequencies in the visible range.

When white light impinges on metal nanoparticles the wavelength corresponding to the Plasmon frequency is adsorbed.

***Electrical Properties:***

- The electronic structure of nanomaterials is different from its bulk material.
- The density of the energy states in the conduction band changes.
- When the energy spacing between two energy levels is more than  $k_B T$ , energy gap is created.
- Nano clusters of different sizes will have different electronic structures and different energy levels separations.
- The ionization potential at Nano sizes are higher than that for the bulk materials.

**1.6 Applications of Nanomaterials:**

Nanotechnology is finding application in all fields ranging from science to engineering. Nanomaterials are finding many applications such as Medicine, Food, Catalysis, Sensors, Textiles, Cosmetics and Communication engineering.

***Nanomaterials in Medicine:*** Nanotechnologies are new areas of research focusing on matter at the atomic and molecular levels. It focuses on developing many areas of preventing diagnosing and treating various diseases. Nanomaterials shows very high efficiency in destroying cancer cells and clinical trials. Mostly due to the fact that they allow cancer cells to be targeted imaging of tissues, making therapy much easier. One area of interest is creating nanomaterials that are not only efficient, but also well tolerated by the human body. It has the variety of areas such as drugs, medicines, surgery, abnormal conditions and medical robotics. Future medical technology expected to employ nanorobots injected into the patient to perform treatment on a cellular level.

***Nanomaterials in Energy Sector:*** An epoxy containing carbon nanotubes is being used to make windmill blades to increasing the electricity generated by windmills. Stronger and lower weight blades are made possible by the use of nanotube-filled epoxy. *Storing hydrogen for fuel cell powered cars:* Graphene layers to increase the binding energy of hydrogen to the graphene surface in a fuel tank resulting in a higher amount of hydrogen storage. *Clothing that generates electricity:* Piezoelectric nanofibers that are flexible enough into clothing and it turns normal motion into electricity to power your cell phone and other electronic devices. *Improving the performance of batteries:* Companies are currently developing batteries using nanomaterials. One battery can recharged significantly faster than conventional batteries. Some of the Opto-Electronic devices are

OLEDs (organic LEDs), LEDs, solar cells, CCD (Charged Coupled Device), LCD (Liquid Crystal Device) having more broad bandwidth and efficiency.

***Nanomaterials in Kinetic Energy Penetrators:*** Depleted uranium possess a unique self-sharpening mechanism on impact with a target and a lack of non explosive. Nanocrystalline tungsten heavy alloys lend themselves to such a sharp mechanism because of unique deformation such as grain-boundary sliding.

***Nanomaterials in Next Generation Computer Technology:*** Nanomaterials reduced the size of the devices for comfortable such as transistors, resistors and capacitors. By achieving the reduction in their size, the microprocessors which contains these components and can run much faster. Poor dissipation of tremendous amount of heat generated by these microprocessors due to faster speeds; short mean time to failures.

***Nanomaterials in Phosphors:*** Nanocrystalline Zinc selenide, Zinc sulfide and Cadmium sulfide are synthesized by sol-gel technique for improving the resolution of monitors. The resolution of a television or a monitor depends greatly on the size of the pixel. These pixels are generally made of materials called “phosphors” which streams of electrons inside the Cathode Ray Tube (CRT). The use of nanophosphors is to reduce the cost of these displays to render high definition-televvisions and personal computers to be purchased by an average household.

***Nanomaterials in Catalysis:*** Catalysis is the increase in the rate of a chemical reaction due to the participation of an additional substance. It has huge surface area, high proportion of atoms on the surface. It enhanced intrinsic chemical activity as size gets which is likely to changes in crystal shape. As crystal gets smaller anion/cation vacancies can increase thus affecting surface energy; also surface atoms can be distorted in their bonding patterns. It enhanced solubility, sintering at lower T, more adsorptive capacity.

***Nanomaterials in Sensors:*** Biological, chemical or physical sensory points used to convey information about nanoparticles to the macroscopic world. It is very smaller in size, require less power, greater sensitivity and better specificity. Some of the applications are Transportation, Communications, Integrated circuits, medicine, Safety and Aerospace.

***Nanomaterials in Filtration:*** Nanofiltration is a technique that has prospered over the few years. It is applied only in drinking water purification. Process steps such as water softening, decolouring and micro pollutant control. Viruses of dimensions 10-100 nm are



removed by ultrafiltration. It is a low pressure membranes process that separates materials in the range of 0.001 to 0.1  $\mu\text{m}$ . Dissolved salts and colour producing organic compounds are removed by reverse osmosis and nanofiltration.

***Nanomaterials in Food:*** Nanostructured films and packaging materials can prevent the invasion of pathogens and other microorganisms and ensure food safety. Nanosensors embedded in food packages will allow the determination of nutrient content. By adding certain nanoparticles into packaging material and bottles, food packages can be made more light and fire-resistant, with stronger mechanical and thermal performance and controlled gas absorption.

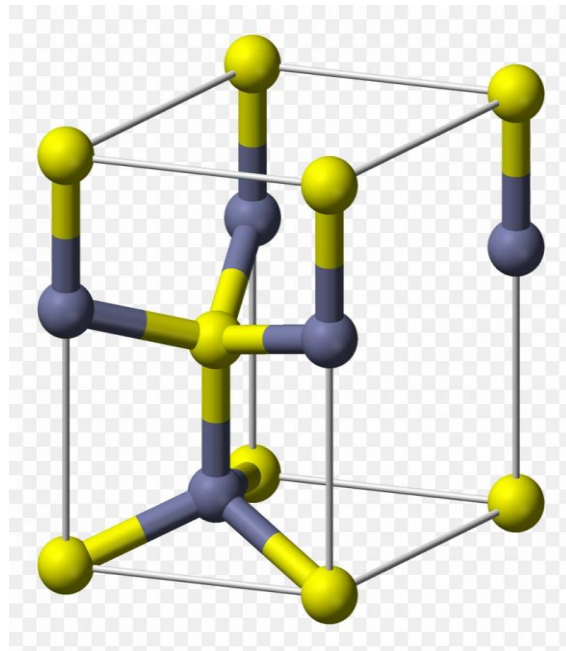
***Nanomaterials in cutting tools:*** Cutting tools are made of nanocrystalline materials such as tungsten carbide, tantalum carbide and titanium carbide are much harder, much more wear-resistant, erosion resistant and last longer than conventional counterparts. They are currently being used in the microdrills. They also enable the manufacturer to machine various materials much faster, thereby increase productivity and reducing manufacturing costs.

## **1.7 Zinc Oxide**

Zinc oxide (ZnO) is rapidly gaining area as a material with excellent possibilities. It is regarded as the key technological material which exhibits semiconducting, piezoelectric and pyroelectric multiple properties. It is a white powder that is insoluble in water. Most ZnO used commercially is synthetic.

- It is semiconductor with a broad band gap of 3.37 eV and large binding energy of 60 meV. It is important function oxide, exhibiting near ultraviolet emission and transparency conductivity.
- It has been demonstrated as a promising electron transfer medium for dye sensitized oxide semiconductor solar cells.
- Zinc oxide nanoparticles exhibit size dependent electronic bandgap energies. The dependence of size gives the many interesting applications, especially by tuning the band gap of semiconductors.
- The wurtzite results in strong piezoelectric property and key property in electromechanical coupled sensors and transducers.

- It is bio-safe and bio-compatible and can be used for biomedical applications without coatings and toxicity. It is non toxic.



**Wurtzite structure**

- Zinc oxide is one of the most important nanomaterials in future research and applications. ZnO will be important for UV optical devices including LEDs, laser diodes, photo detectors and optical sensors.
- ZnO has large bandgap is higher breakdown voltages and ability to sustain large electric field and lower electronic noise.
- High thermal conductivity: used in rubber industry and protect rubber from fungi and UV light.
- ZnO is having high optical transparency and Luminescence in visible and near UV range of spectrum.
- ZnO is commonly found in medical ointments where it is used to treat skin irritations. Other uses are paint pigments, paint coatings and spintronics.
- Future of Zinc oxide is nanostructured growth is heavily researched presently. Its hexagonal lattice can easily match catalyst's lattice structure and facilitate controlled growth patterns. It shows promising signs in the field of

nanotechnology, UV detectors and actuators. It has direct bandgap semiconductor that could replace silicon as the main substrate in chip manufacturing.

- Dual semiconductor and piezoelectric properties.

### **1.8 Why Lead used as a Dopant:**

- Lead is very resistant to corrosion.
- It has the ability to absorb gamma radiation.
- Lead absorbs Electromagnetic radiation of short wavelength, used as a storing radioactive materials.
- The average crystalline size, unit cell volume also increased upto 10% of lead doping.
- The bandgap values of the Pb doped ZnO nanoparticles decreased in comparison to the bandgap value of undoped ZnO nanoparticles.
- Some of the applications widely used for car batteries, lead crystal glass, radiation protection and optical glass.

**CHAPTER-II**  
**LITERATURE SURVEY AND FOCUSED PROBLEM**

## CHAPTER-II

### LITERATURE SURVEY AND FOCUSED PROBLEM

**Kumar et al (2013)** ZnO nanoparticles were prepared using a simple precipitation method. The XRD and EDS analyses clearly indicate that highly pure ZnO is formed. SEM images of ZnO show that the morphology was changed with calcinations temperature. The bandgap of ZnO was decreased by an increase in calcinations temperature, and the absorption maximum is also shifted to higher wavelengths.

**Pradeev raj et al (2016)** ZnO nanoparticles were synthesized by co-precipitation technique. It is found that the typical particle size has enhanced with calcination temperature. The UV-vis spectrum shows that the synthesized nanoparticles have a high absorption between 350 to 410 nm for pure and calcined ZnO NPs. It is found that the bandgap energy value for pure ZnO NPs is 3.70 eV before calcinations and 3.05 eV after calcinations. Decrease in the bandgap energy value and the red shift corresponds to the strong quantum confinement in synthesized ZnO nanoparticles. PL spectra exhibits near band edge levels and significant trap level emission at 377 to 499 nm.

**Hasnidawani et al (2015)** The zinc oxide nanostructure is synthesized by using sol-gel method. The results of ZnO rod like structure is synthesized by sol-gel technique in nanosize range about 84.98 nm. The synthesized ZnO nano powder obtained exhibit good crystallinity.

**Alessio Becheri et al (2007)** The peculiar performance of ZnO nanoparticles as UV absorbers, can be effectively transferred to fabric materials through the applications of ZnO nanoparticles on the surface of cotton and wool fabrics. The result can be exploited for the protection of the body against solar radiation and for other technological applications.

**Naveen Kumar et al (2017)** A uniform hexagonal ZnO nano disc structure of approximately 100 nm were synthesized by wet chemical synthesis at 85°-90°C. Bandgap energy was found to be 3.48 eV. The obtained ZnO nano structure is in great demand due to its large aspect plays a vital role in sensing low concentration of the gas analyte. Thus ZnO nanoparticle semiconducting metal oxide can be used as a wearable sensor.

**Mater et al (2007)** The ZnO nanoparticles is synthesized via sol-gel technique of simple, rapid and high yield. TEM analysis found that sizes of the nanoparticles vary between 38 and 54 nm. ZnO is an n-type semiconductor with a wide bandgap and it varies from 3.34 eV to 3.21 eV. These properties

enable ZnO samples with applications in for renewable energy. This ZnO nanopowder may have potential applications in visible optoelectronic devices, dye sensitized solar cells and sensors.

**Shirsatetal (2016)** ZnO nanoparticles were synthesized by sol-gel method. The secondary bond vibration at 667.03 per cm in FTIR spectrum confirms the production of ZnO nanoparticles. The absorption peak is found to be 361.75 nm. The energy bandgap of a synthesized nanoparticle obtained to be 3.2794 eV.

**Asha etal (2018)** Zinc oxide nanoparticle were synthesized by using a simple hydrothermal method. The x-ray diffraction shows the particle size and found to be 55 nm. The high resolution scanning electron microscope shows the nanorod shape and hexagonal structure. From the UV-visible spectrum zinc oxide nanomaterial has a energy bandgap of 3.027 eV and optical property were studied.

**Kumar etal (2014)** ZnO and Cu doped nanoparticles have been prepared by using chemical precipitation method. X-ray diffraction results that ZnO and Cu doped nanoparticles exhibits cubic zinc blende structure. The average particle size of the nanoparticle is found to be 26-39 nm. The absorption edge of Cu doped ZnO nanoparticles is shifted towards longer wavelength side when compared to that of undoped ZnO and the bandgap is observed to be 4.18-4.23 eV.

**Sathya etal (2016)** Pb doped ZnO semiconductor nanoparticles have been prepared by using chemical precipitation method. XRD analysis confirmed the crystalline size increases continuously up to 10(wt%).tauc's relation confirmed the energy gap decrease as an increase of Pb dopant. FTIR analysis confirms the Pb dopant through the peak shifting from 437cm<sup>-1</sup> to 549cm<sup>-1</sup>. Photoluminescence spectra confirms the Pb dopant diminishes the emission property of ZnO nanoparticles.

**CHAPTER-III**  
**EXPERIMENTAL AND CHARACTERIZATION TECHNIQUES**

## CHAPTER-III

### EXPERIMENTAL AND CHARACTERIZATION TECHNIQUES

#### Experimental techniques

Fabrication of nanomaterials with strict control over size, shape and crystalline structure has become very important for the applications of nanotechnology in numerous fields including catalysis, medicine and electronics. There are two main approaches used for the synthesis of nanoparticles.

- TOP DOWN METHOD
- BOTTOM UP METHOD

#### 3.1 Top down approach:

In this approach, nanoscale devices are created by using larger, externally controlled devices to direct their assembly. The top down approach often uses the traditional workshop or microfabrication methods in which the externally-controlled tools are used to cut, mill and shape materials into the desired shape and order. Attrition and milling for making nanoparticles are typical top-down processes. Example of this kind of approach include the various types of lithographic techniques.

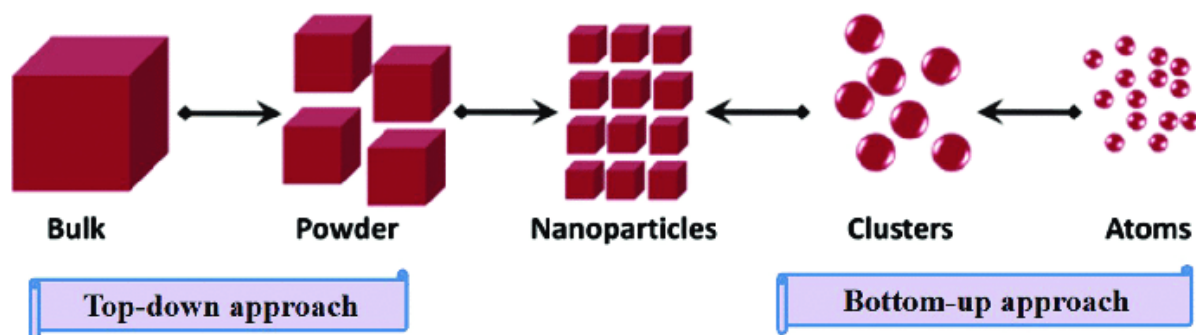


Fig. 3.1 Approaches



### **3.2 Bottom up approach:**

In the bottom-up approach, molecular components arrange themselves into more complex assemblies atom-by-atom, molecule-by-molecule, cluster-by-cluster from the bottom (e.g. growth of a crystal). Molecular components arrange themselves into some useful conformation using the concept of molecular self-assembly. For example, synthesis of nanoparticles by colloid dispersion.

### **3.3 Synthesis Methods:**

Synthesis of dimensionally controlled particles in a large quantities under study their properties to investigate novel application is a preferred activity for research in nanomaterials. There a large number of techniques available to synthesize different types of nanomaterials in the form of colloids, clusters, powders, tubes, rods, wires, thinfilms, 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.

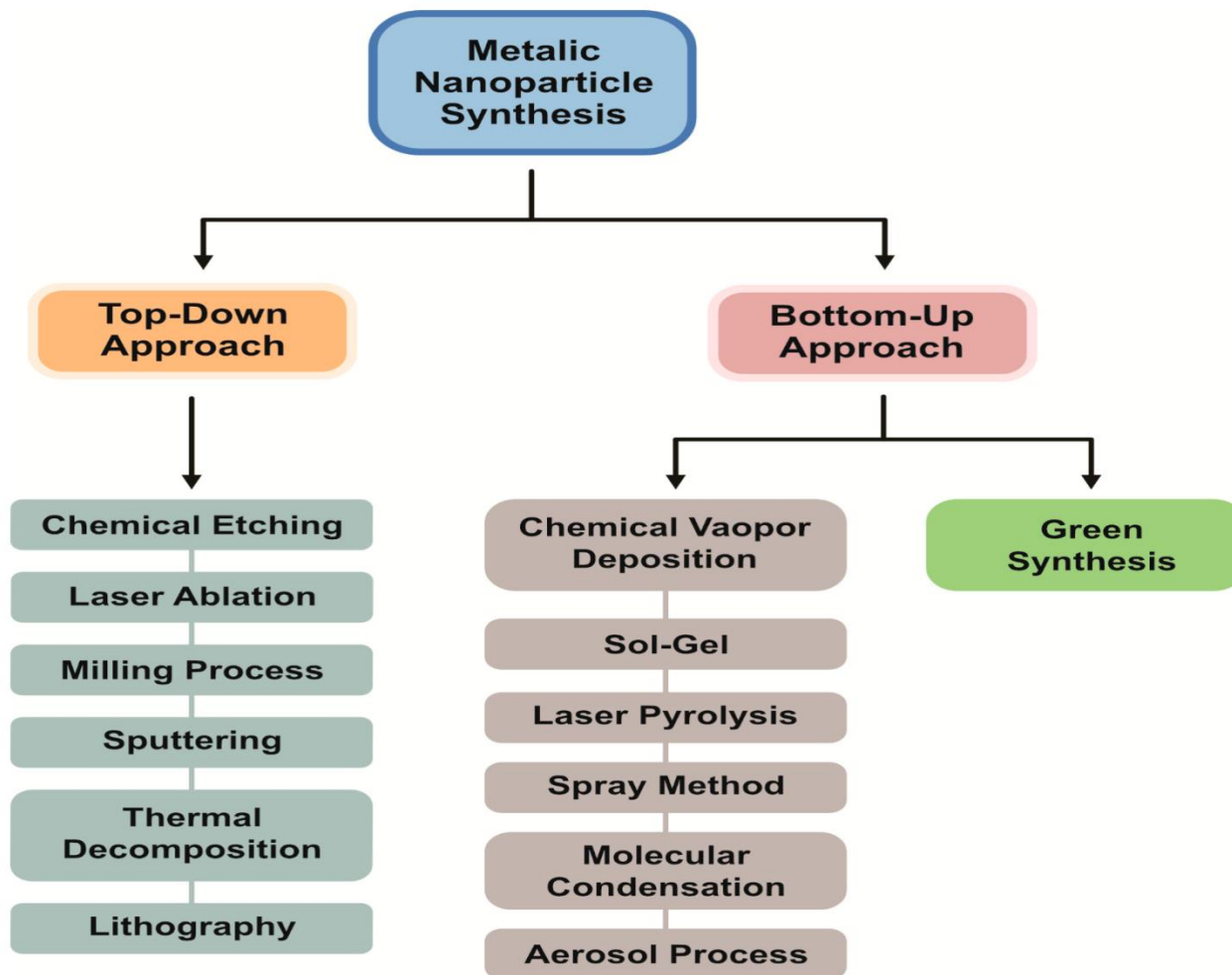


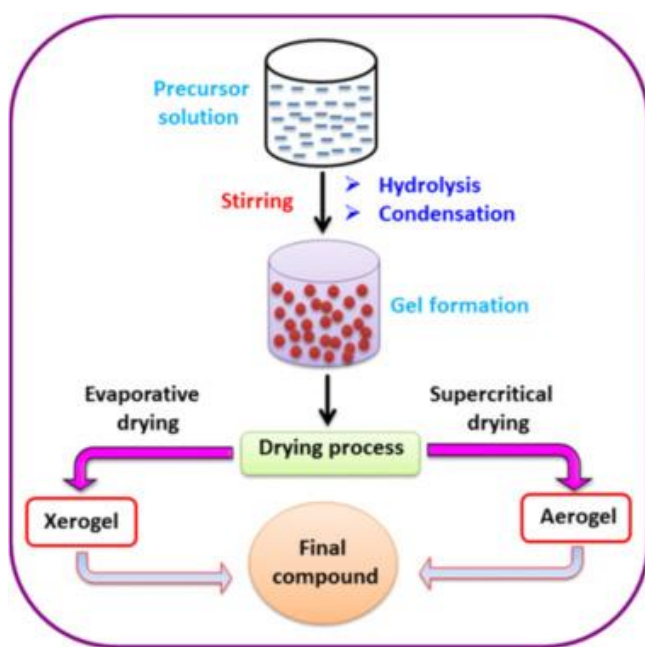
Fig.3.2 Methods of Synthesis

### 3.4 Chemical method:

#### 3.4.1 Sol-Gel Method:

The sol-gel method is a versatile process used for synthesizing various oxide materials. This synthetic method generally allows control of the texture, the chemical, and the morphological properties of the solid. The major advantages of the sol-gel technique molecular scale mixing, high purity of the precursors, and homogeneity of the sol gel products with a high purity of physical, chemical, morphological and chemical properties.

In a typical sol-gel process, a colloidal suspension or a sol is formed from the hydrolysis and polymerization reactions of the precursors, which are usually inorganic metals salts or metal organic compounds such as metal alkoxides. Any factor that affects either or both of these reactions is likely to impact the properties of the gel. These factors, generally referred to as sol-gel parameters, include type of precursors, type of solvent, water content, acid or base content, precursor concentration and temperature. These parameters affect the structure of the initial gel and in turn the properties of the material at all subsequent processing steps. After gelation, the wet gel can be optionally aged in a mother liquor, or in another solvent and washed. The time between the formation of a gel and its drying, known as aging, is also an important parameter. A gel is not static during aging but can continue to undergo hydrolysis and concentration.



**Fig 3.3 sol-gel method**

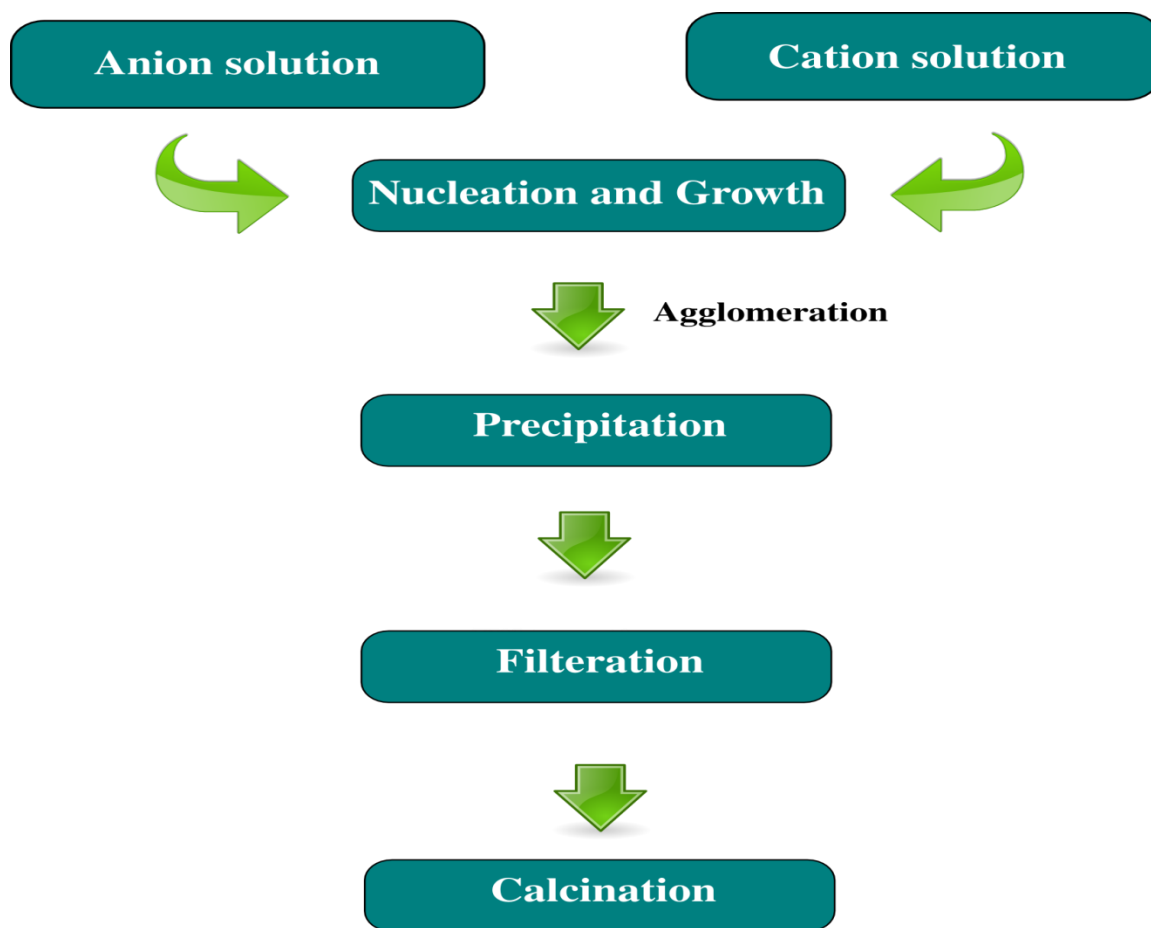
### 3.4.2 Applications of sol-gel method:

Applications for sol-gel process derive from the various special shapes obtained directly from the gel state (monoliths, films, fibers and monosized powders) combined with compositional and microstructural control and low processing temperatures. Compared with other methods, such as the solid-state method, the advantages of using sol-gel process include:

- The use of synthetic chemicals rather than minerals enables high purity materials to be synthesized.
- It involves the use of liquid solutions as mixtures of raw materials. Since the mixing is low viscosity liquids, homogenization can be achieved at a molecular level in a short time.
- Since the precursors are well mixed in the solutions, they are likely to be equally well-mixed at the molecular level when the gel is formed.
- Changing physical characteristics such as pore size distribution and pore volume can be achieved. Incorporating multiple components in a single step can be achieved.
- Producing different physical forms of samples is manageable.

### **3.4.3 Chemical co-precipitation method:**

Co-precipitation is the carrying down by a precipitate of substances normally soluble under the conditions employed. Coprecipitation is an important issue in chemical analysis, where it is often undesirable, but in some cases it can be exploited. In gravimetric analysis, which consists on precipitating the analyte and measuring its mass to determine its concentration or purity, coprecipitation is a problem because desired impurities often coprecipitate with the analyte, resulting in excess mass.



**Fig. 3.4 coprecipitation method**

On the other hand, in the analysis of trace elements, as is often the case in radiochemistry, coprecipitation is often the only way of separating an element. Since the trace element is too dilute to precipitate by conventional means, it is typically coprecipitated with a carrier, a substance that has a similar crystalline structure that can incorporate the desired element. There are three main mechanisms of coprecipitation: inclusion, occlusion and adsorption. An inclusion occurs when the impurity occupies a lattice site in the crystal structure of the carrier, resulting in a crystallographic defect. An adsorbate is an impurity that is weakly bound to the surface of the precipitate. An occlusion occurs when an adsorbed impurity gets physically trapped inside the crystal as it grows.

#### **3.4.4 Hydrothermal method:**

Hydrothermal technique for nanoparticle synthesis needs using special instrumentation called Hydrothermal Autoclave Reactor. It is a specific style strong vessel that we face upto high temperatures and better pressure levels from within. The autoclave reactor consists of thick and steel-walled cylindrical vessels having hermetic sealing. This helps it to bear high levels of heat and pressure regularly and safety for a longer time. It processes need to solutions having a corrosive impact on the interior material of the autoclave and special protective coatings to prevent corrosion. These protective coatings are usually made of gold, platinum, silver, glass and teflon. It able to produce crystalline phases which aren't stable at high temperatures safely. It grows materials which are known to have a high vapor pressure as their melting point gets closer.

#### **3.4.5 Solvothermal method:**

Solvothermal method is very similar to hydrothermal method. Solvothermal method is a method for preparing a variety of materials such as metals, semiconductors, ceramics and polymers. Solvothermal processes can be described as a reaction or a transformation of precursor in presence of a solvent in a close system and at a temperature higher than that the boiling temperature of the solvent. Zinc oxide is an example of a II-VI compound that can be prepared solvothermally and will exhibit quantum dot effects. This involves heating of the reaction in a close vessel called Autoclave. An autoclave is usually constructed from thick stainless steel to withstood the high press and is fitted with a safety wall. It may be lined with teflon. When the autoclave is heated the pressure increases and the water remains liquid above its normal boiling temperature of 373K which is called "superheated water".

#### **3.4.6 Microwave method:**

The principle frequencies of microwave heating are between 900 and 2450 MHz. at lower microwave frequencies, conductive currents flowing within the material due to movement of ionic constituents can transfer energy from microwave field to the material. At higher frequencies, the energy absorption is primarily due to molecules with a permanent dipole which tend to influence of microwave electric field. This reorientation loss mechanism originates from the inability of the polarisation to follow extremely rapid reversal of electric field, so the polarisation lags applied electric field. This ensures that the resulting current density has a component in phase with the field and power is dissipated in the dielectric material.

### 3.5 Characterization Techniques:

#### 3.5.1 Powder XRD analysis:

The German physicist, Max von Laue in 1912, discovered the crystalline substances act as three-dimensional diffraction gratings for wavelengths similar to the spacing of planes in a crystal lattice. X-ray diffraction technique is the study of crystal structures and atomic spacing. X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference when the conditions satisfy

Bragg's Law  $n\lambda = 2d \sin\theta$

This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of  $2\theta$  angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. X-ray diffractometers consist of three basic elements: 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 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. The geometry of an X-ray diffractometer is such that the sample rotates in the path of the collimated X-ray beam at an angle  $\theta$  while X-ray detector is mounted on an arm to collect the diffracted X-rays and rotates an angle of  $2\theta$ .

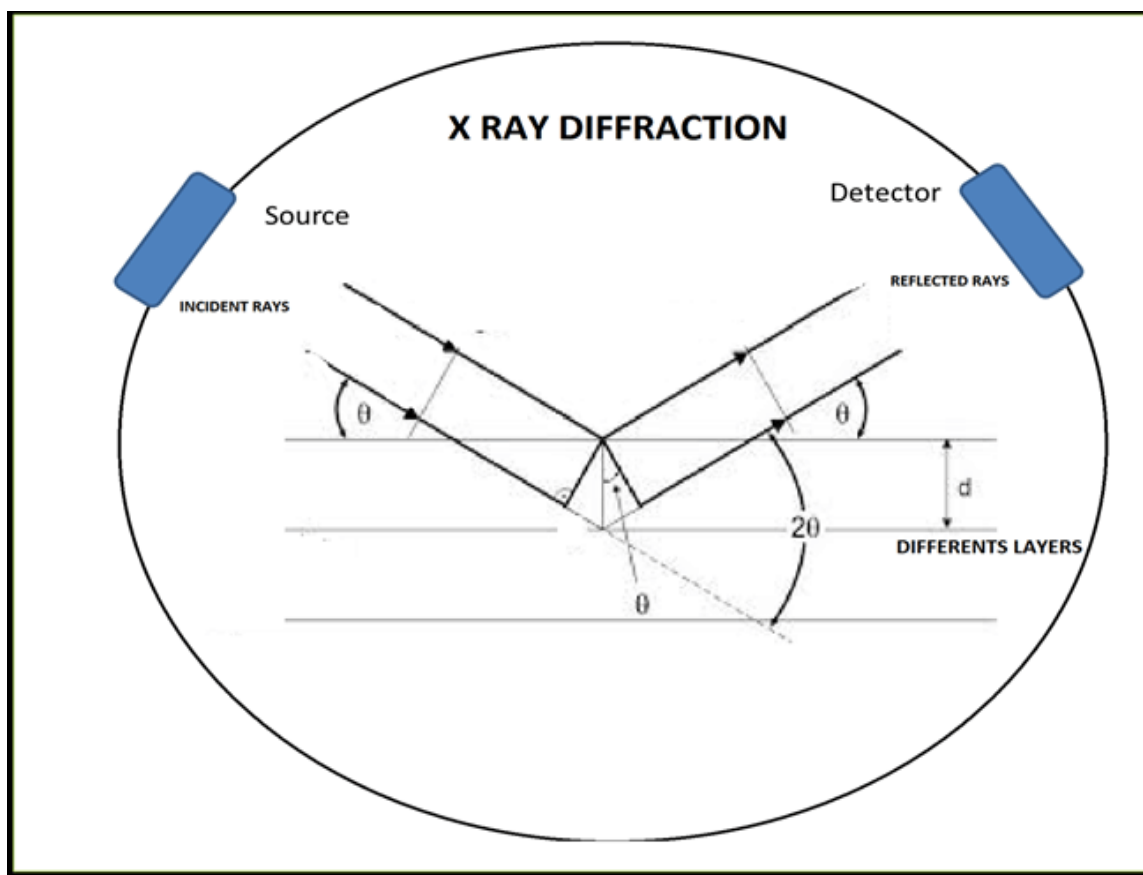


Fig.3.5 XRD analysis

### 3.5.2 Fourier Transform Infrared Spectroscopy:

Infrared (IR) spectroscopy is a most popular characterization technique in which a sample is placed in the path of an IR radiation source and its absorption of different IR frequencies is measured. Infrared absorption spectroscopy is the study of interaction of infrared radiation with matter as a function of photon frequency. Fourier Transform Infrared Spectroscopy (FTIR) provides specific information about the vibration and rotation of the chemical bonding and molecular structures, making it useful for analyzing organic materials and inorganic materials. An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms and making up the material. Because each material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum. Therefore, infrared spectroscopy can result in a



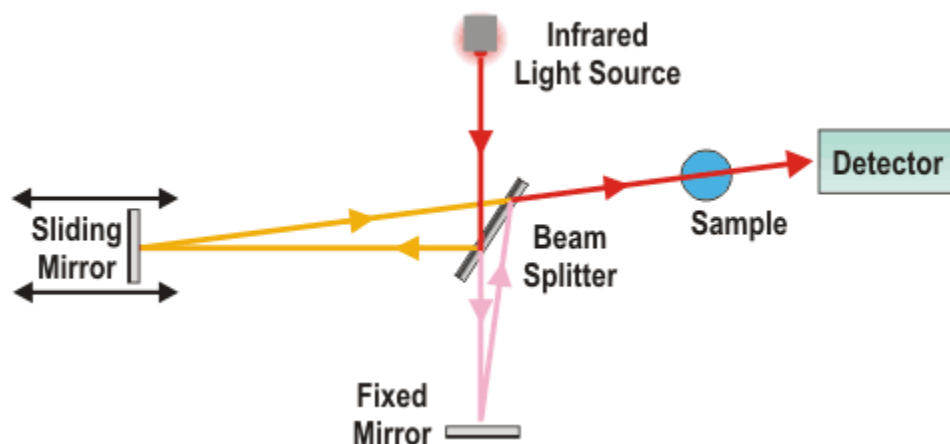
positive identification of every different kinds of material. The size of the peaks in the spectrum is a direct indication of the amount of material present.

The IR region is commonly divided into three smaller areas: IR ( $400\text{--}10\text{ cm}^{-1}$ ), mid-IR ( $4000\text{--}400\text{ cm}^{-1}$ ), and far – ( $14000\text{--}4000\text{ cm}^{-1}$ ). Infrared photons have high enough energy to cause group of atoms to vibrate with respect to the bonds that connect them. Like electronic transitions, these vibrational transitions correspond to distinct energies, and molecules absorb infrared radiation only at certain wavelengths and frequencies. Chemical bonds vibrate at frequencies, and when exposed to infrared radiation, they absorb the radiation at frequencies that match their vibration modes. Measuring the radiation absorption as a function of frequency produces a spectrum to identify functional groups and compounds. Some impurities produce their own characteristic band in infrared region. Spectral measurements of these bands are used to determine concentration of identification, the measured interferogram signal can not be interpreted directly.

Interferometer divides radiant beams, generates an optical path difference between the beams, and then recombines them in order to produce repetitive interference signals measured as a function of optical path difference by a detector. As its name implies the interferometer produces interference signals which contain infrared spectral information generated after passing through a sample. It consists of three active components: a moving mirror, a fixed mirror, and a beam splitter. The two mirrors are perpendicular to each other. The beam splitter device and is often made by depositing a thin film of germanium onto a flat KBr substrate.

IR spectra can be measured using liquids, solid or gaseous samples that are placed in the beam of infrared light. A drop of liquid can be placed as a thin film between two plates made of NaCl or KBr, which are transparent to infrared light at most important frequencies. A solid can be ground with KBr and pressed into a disk that is placed in the light beam. Alternatively, a solid sample can be ground into a pasty mull with paraffin oil. These gas cells often contain mirrors that reflect the beam through the cell several times for stronger absorption.

Infrared energy is emitted from a glowing black-body source. This beam passes through an aperture which controls the amount of energy presented to the sample. The beam enters the sample compartment where it is transmitted through or reflected off of the surface of the sample, depending on the type of analysis being accomplished. The beam finally passes to the detector for final measurement. The detectors are specially designed to measure the special interferogram signal.



**Fig.3.6 FTIR Spectroscopy**

### 3.5.3 UV-Visible Spectroscopy:

Ultraviolet and visible (UV-vis) absorption spectroscopy is the measurement of the attenuation of a beam of light after it passes through a sample or after reflection from a sample surface. Absorption measurements can be at a single wavelength or over an extended spectral range. Ultraviolet-visible (UV-vis) spectroscopy is widely utilized to quantitatively characterize organic and inorganic nanosized molecules. It deals with the study of electronic transitions between orbitals or bands of atoms, ions or molecules in gaseous, liquid and solid state. A sample is irradiated with electromagnetic waves in the ultraviolet and visible ranges and the absorbed light is analyzed through the resulting spectrum. It can be employed to identify the constituents of a substance, determine their concentrations, and to identify functional groups in molecules. Size dependent properties can be observed in a UV-vis spectrum, particularly in the nano and atomic scales. These include peak broadening and shifts in the absorption wavelength. The functioning of this instrument is relatively straight-forward. A beam of light from a visible and/or UV light source 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, passes through a small transparent container (cuvette) containing a solution of the compound being studied in a transparent solvent. The other beam, the reference beam, passes through an identical cuvette containing only the solvent. 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 10 • The intensity of the

sample beam is defined as  $I_0$ . 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 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. If no absorption has occurred,  $T = 1.0$  and  $A = 0$ . The wavelength of maximum absorbance is a characteristic value, designated as  $\lambda_{max}$ . Different compounds may have different absorption maxima and absorbance. 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. Since the absorbance of a sample will be proportional to its molar concentration in the sample cuvette, a corrected absorption value known as the molar absorptivity is used when comparing the spectra of different compounds.

UV spectroscopy obeys the Beer-Lambert law, which states that: when a beam of monochromatic light is passed through a solution of an absorbing substance, the rate of decrease of intensity of radiation with thickness of the absorbing solution is proportional to the incident radiation as well as the concentration of the solution.

The expression of Beer-Lambert law is

$$A = \log (I_0/I) = \epsilon cl$$

Where,  $A$  = absorbance

$I_0$  = intensity of light incident upon sample cell

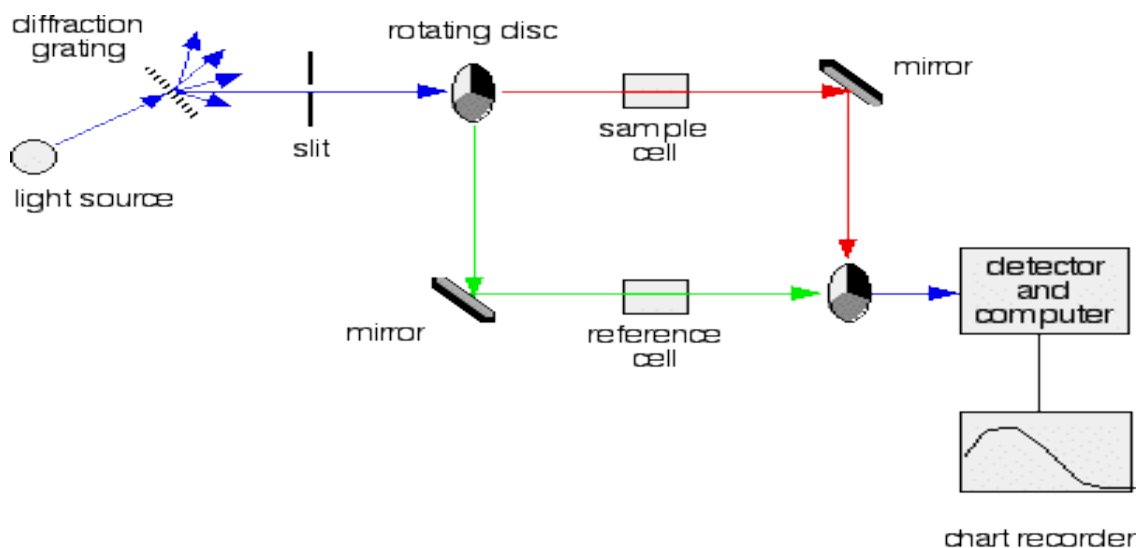
$I$  = intensity of light leaving sample cell

$C$  = molar concentration of solute

$L$  = length of sample cell (cm.)

$\epsilon$  = molar absorptivity

From the Beer-Lambert law it is clear that greater the number of molecules capable of absorbing light of a given wavelength, the greater the extent of light absorption. This is the basic principle of UV spectroscopy.



**Fig.3.7 UV-visible technique**

### 3.5.4 Photoluminescence Spectroscopy:

Photoluminescence spectroscopy is a contact less, nondestructive method of probing the electronic structure of materials. Photoluminescence (PL) is the spontaneous emission of light from a material under optical excitation. PL depends on the nature of the optical excitation. The excitation energy selects the initial photoexcited state and governs the penetration depth of the incident light. When light of sufficient energy is incident on a material, photons are absorbed and electronic excitations are created. Eventually, these excitations relax and the electrons return to the ground state. If radiative relaxation occurs, the emitted light is called PL. The energy of the emitted light (photoluminescence) relates to the difference in energy levels between the two electron states involved in the transition between the excited state and the equilibrium state. This light can be collected and analyzed to yield a wealth of information about the photoexcited material. The PL spectrum provides the transition energies, which can be used to determine electronic energy levels. The PL intensity gives a measure of the relative rates of radiative and nonradiative recombination. Electromagnetic radiation in the UV and visible ranges is utilized in PL spectroscopy. PL emission properties of the samples are characterized by intensity, emission wavelength, bandwidth of the emission peak and the emission stability. As the dimensions are reduced to the nanoscale, PL emission properties can change, in particular a size dependent shift in the emission wavelength can be observed. PL spectroscopy can be utilized to study material properties such as band gap, recombination mechanisms and impurity levels. This instrument uses a Xenon lamp as a source of

exciting light. The instrument shown is equipped with monochromators to select both the excitation and emission wavelengths. The excitation monochromator in this schematic diagram contains two gratings which decrease stray light, that is, light with wavelengths different from the chosen one. In addition, these monochromators use concave gratings, produced by holographic means to further decrease stray light. Both monochromators are motorized to allow automatic scanning of wavelength. The fluorescence is detected with photomultiplier tubes and quantified with the appropriate electronic devices. The output is usually presented in graphical form and stored digitally. The instrument also shows the components of the optical module that surrounds the sample holder. Shutters are provided to eliminate the exciting light or to close off the emission channel. A beam splitter is provided in the excitation light path. This splitter reflects part of the excitation light to a reference cell, which generally contains a stable reference fluorophore. The beam splitter consists of a thin piece of clear quartz, which reflects about 4% of the incident light. The intensity from the standard solution is typically isolated with a bandpass filter and is proportional to the intensity of the exciting light. Changes in the intensity of the arc lamp may be corrected for by division of the intensity from the sample by that of the reference fluorophore. Polarizers are present in both the excitation and emission light paths. The polarizers are removable and accurate measurement of fluorescence anisotropies requires accurate angular positioning of the polarizers. The polarizer mounts must be accurately indexed to determine the angular orientation. The PL emission intensities and wavelengths are dependent on particle size.

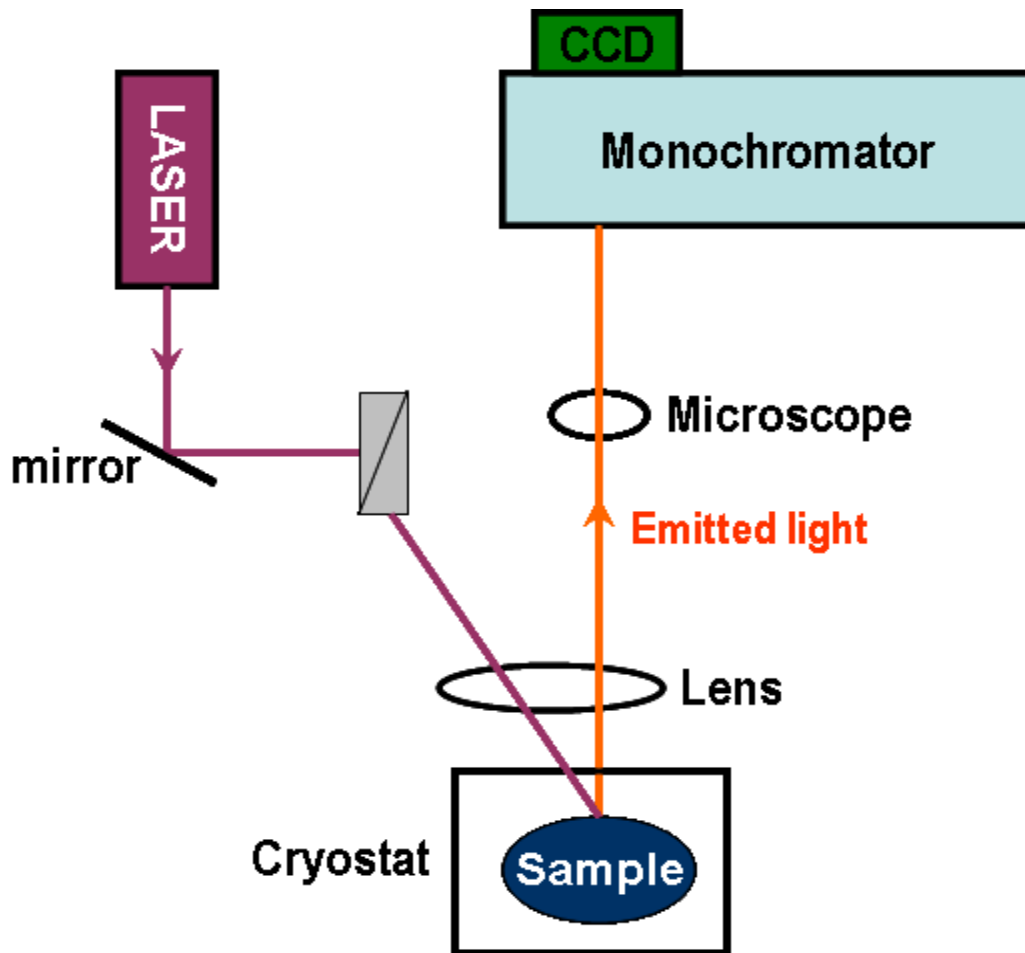
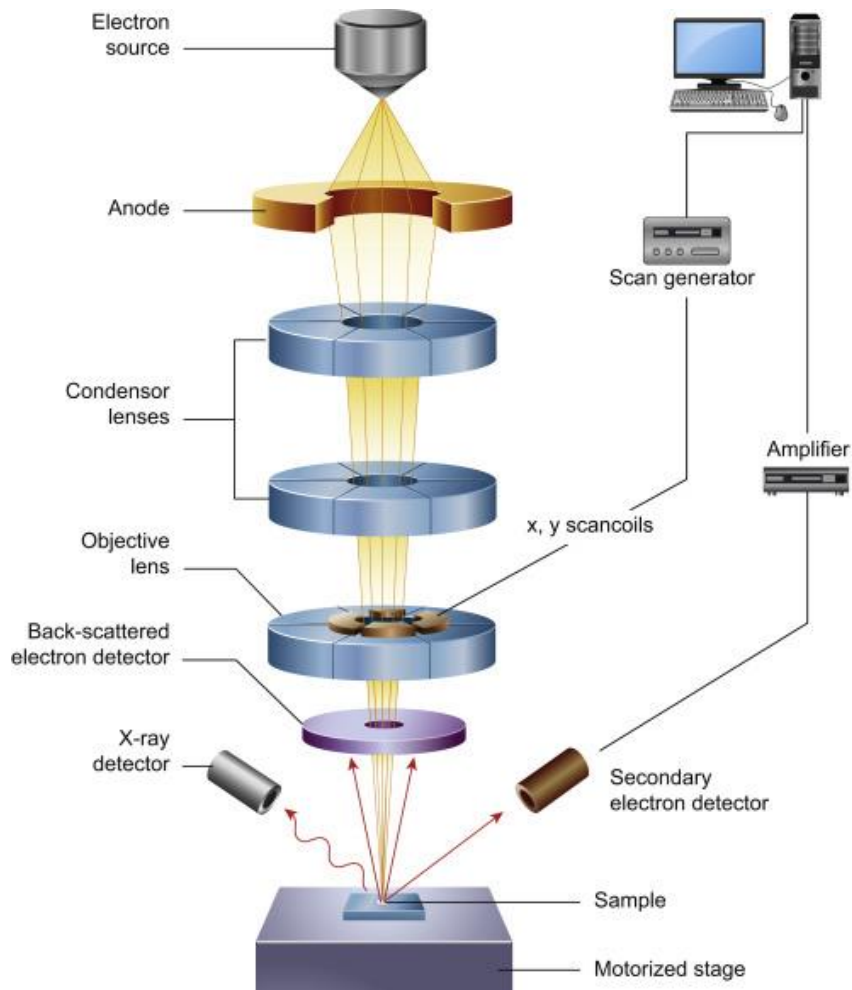


Fig.3.8 Photoluminescence Spectroscopy

### 3.5.5 Scanning Electron Microscope:

A Scanning Electron Microscope (SEM) is a type of electron microscope that produces images of a sample by scanning the surface with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that contain information about the surface topography and composition of the sample. The electron beam is scanned in a faster scan pattern, and the positions of the beam is combined with the intensity of the detected signal to produce an image. In the most common SEM mode, secondary electrons emitted by atoms excited by the electron beam are detected using an Everhart-Thornley detector. The number of secondary electrons that can be detected, and thus the signal intensity, depends among other things on specimen topography. SEM can achieve resolution better than 1 nanometer. Specimens are observed in high vacuum in conventional SEM.

The electron beam which typically has an energy ranging from 0.2 keV to 40 keV is focused by one or two condenser lenses to a spot about 0.4 nm to 5 nm in diameter. The beam passes through the pairs of scanning coils or a pairs of deflector plates in the electron column, typically in the final lens, which deflects the beam in the x and y direction so that it scans in a faster over a rectangular area of the sample surface.



**Fig.3.9 SEM analysis**

**CHAPTER-IV**  
**SYNTHESIS OF LEAD DOPED ZINC OXIDE NANOPARTICLES**



## CHAPTER – IV

### SYNTHESIS OF LEAD DOPED ZINC OXIDE NANOPARTICLES

#### 4.1 Experimental Procedure

##### *4.1.1 Introduction:*

Nanostructure ZnO nanoparticles can be synthesized by using many methods such as hydrothermal, sol-gel, solvothermal. Among all methods, I have chosen sol-gel method. It offers several advantages like better homogeneity, high purity, phase pure powder at low temperatures, controlled stoichiometry. It is the simplest method, consume less power and can be carried out in robust atmosphere. It has the ability to control the particle size and morphological through systematic monitoring of reaction parameters.

##### *4.1.2 Materials Required:*

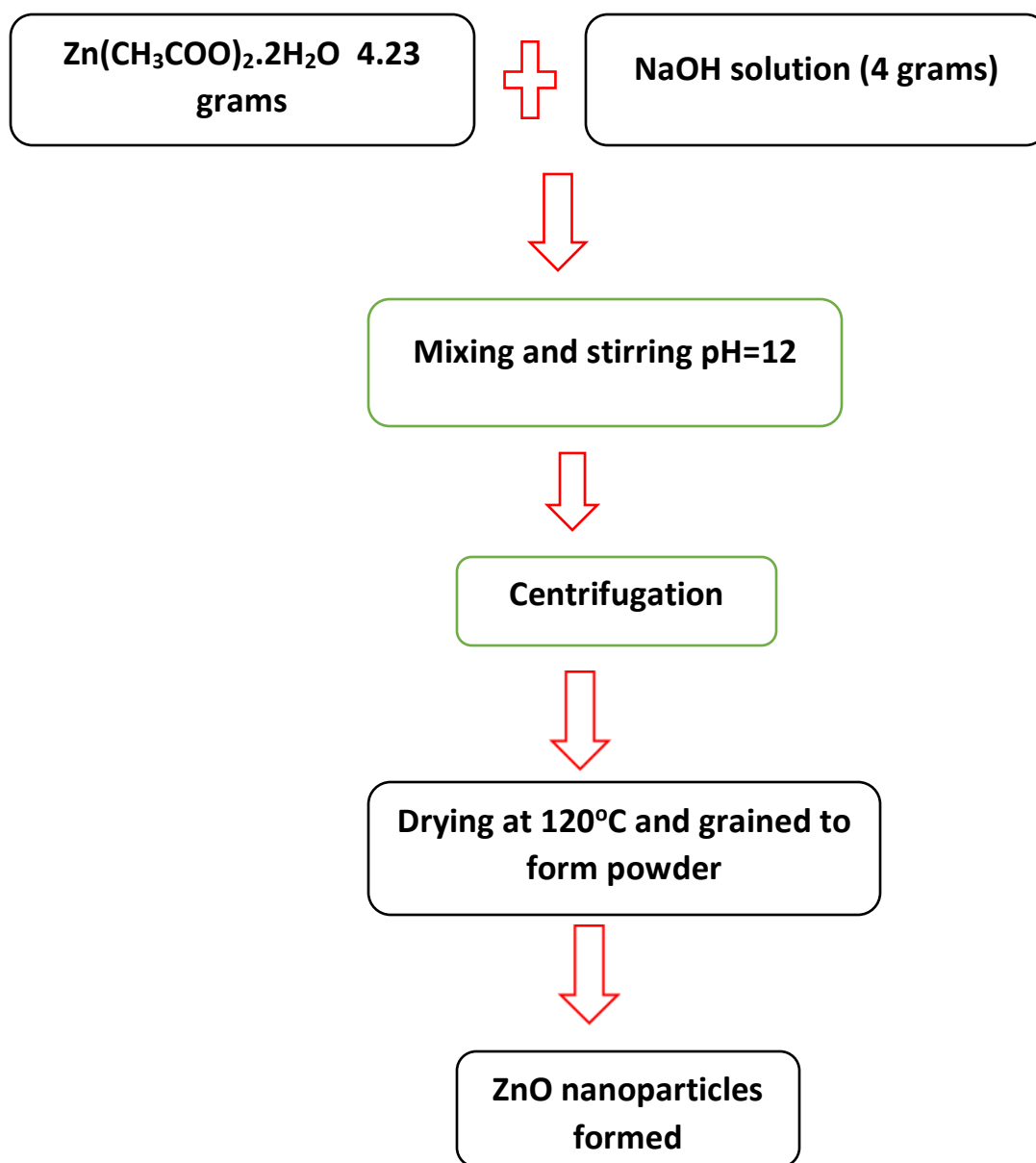
Zinc Acetate Dihydrate ( $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ), Sodium Hydroxide (NaOH), pH meter, distilled water are all analytical grades and used for synthesis without further purification.

##### *4.1.3 Synthesis of pure ZnO nanoparticles:*

Zinc oxide nanostructure was synthesized by using sol-gel method. In order to prepare a sol, 4.23 grams of Zinc acetate dihydrate was dissolved in 100ml of distilled water by constant stirred for half an hour. 4 grams of NaOH pellets were dissolved in 100ml of distilled water by vigorous stirred for 15 minutes. This solution was added drop by drop to above prepared solution to achieve the pH nearly 12. The pH test was carried out with the help of pH tester. The solution was further stirred for one hour and the precipitate was obtained. The entire process was carried out only at room temperature and ambient conditions. Collected precipitate was washed many times by distilled water and centrifuged. This was repeated for two or more times. After that the white solid product was collected and dried in hot air oven at  $120^\circ\text{C}$ . The fine powder was made by grinding the dried precipitate and was used for further characterization.

#### 4.1.4 Schematic Representation of Pure ZnO Nanoparticles:

##### Pure ZnO



## 4.2 Experimental Procedure

### 4.2.1 Introduction:

Nanostructure Pb doped ZnO can be synthesized by using Chemical co-precipitation method. It is a simple and inexpensive method. This method offers low cost, reliability, environmentally friendly synthetic route, large-scale production and this method provides the control of the particle size and shape of the nanoparticles. The structural, optical and electrical properties of the nanomaterials are sensitive to the preparation condition.

### 4.2.2 Materials Required:

Zinc Acetate Dihydrate ( $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ), Sodium Hydroxide (NaOH), distilled water, Lead Acetate Tetrahydrate  $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$

### 4.2.3 Molar Calculation:

$$\begin{aligned}\text{Mass of zinc acetate} &= \frac{\text{Molecular weight of zinc acetate} \times \text{Amount of solvent} \times \text{Mole}}{1000} \\ &= 219.50 \times 50 \times 0.99 / 1000 \\ &= 10.86 \text{ grams}\end{aligned}$$

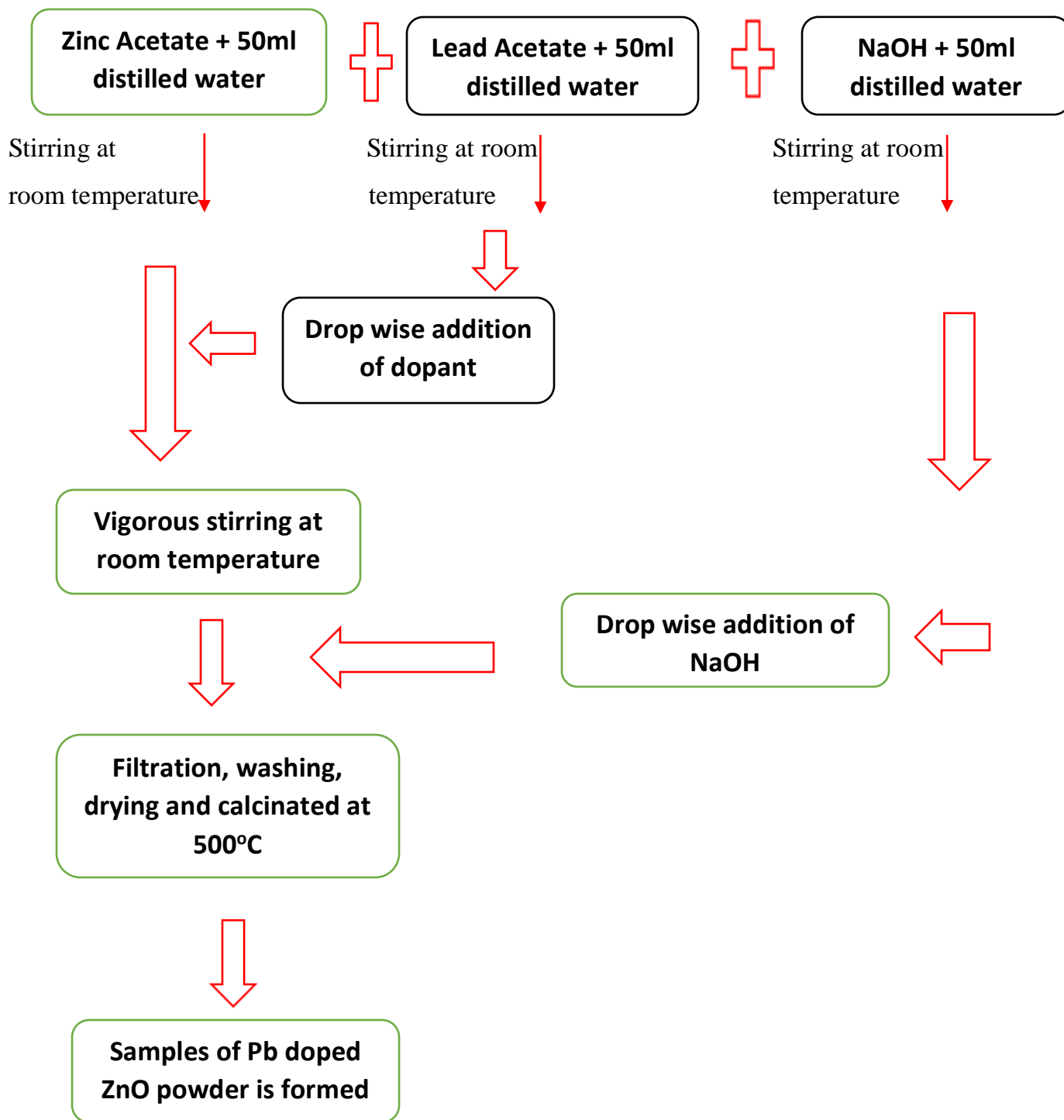
$$\begin{aligned}\text{Mass of NaOH} &= 40 \times 50 \times 1 / 1000 \\ &= 2 \text{ grams}\end{aligned}$$

$$\begin{aligned}\text{Mass of Pb acetate} &= 379.34 \times 50 \times 0.01 / 1000 \\ &= 0.1896 \text{ grams}\end{aligned}$$

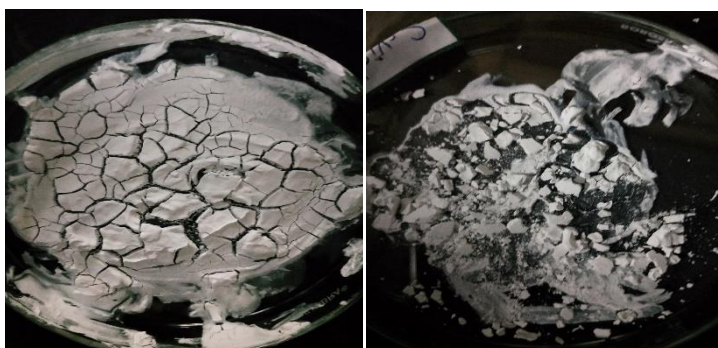
#### ***4.2.4 Synthesis of Pb doped ZnO Nanoparticles:***

Zinc oxide nanostructure was synthesized by using chemical co-precipitation method. In order to prepare a precipitate, 0.99M of Zinc Acetate Dihydrate, 1M of Sodium Hydroxide and 0.01M of Lead Acetate Tetrahydrate were dissolved in 50ml of distilled water separately each other by constant stirring for about 30 minutes each at room temperature and ambient conditions. Now lead acetate solution is added drop by drop to above zinc acetate solution and make vigorous stirred at room temperature for 30 minutes. Then NaOH solution is added drop by drop to above solution in order to make constant stirred for 2 hours. Collected precipitate was washed with distilled water and centrifuged by many times. This was repeated for two or more times. After that the white precipitate was collected and dried in hot air oven at 80°C to 90°C. Then the fine powder was made by grinding the dried white precipitate. After that the fine powder is taken in a crucible and calcinated at 500°C for 5 hours which turns white colour to yellowish colour. So the Pb doped ZnO powder is formed and used for further characterization.

#### 4.2.5 Schematic Representation of Pb doped ZnO Nanoparticle:



#### ***4.2.6 Pictorial Representation of Pb doped ZnO nanoparticles:***



Synthesis of ZnO Nanoparticle



Synthesis of Pb Doped ZnO Nanoparticles

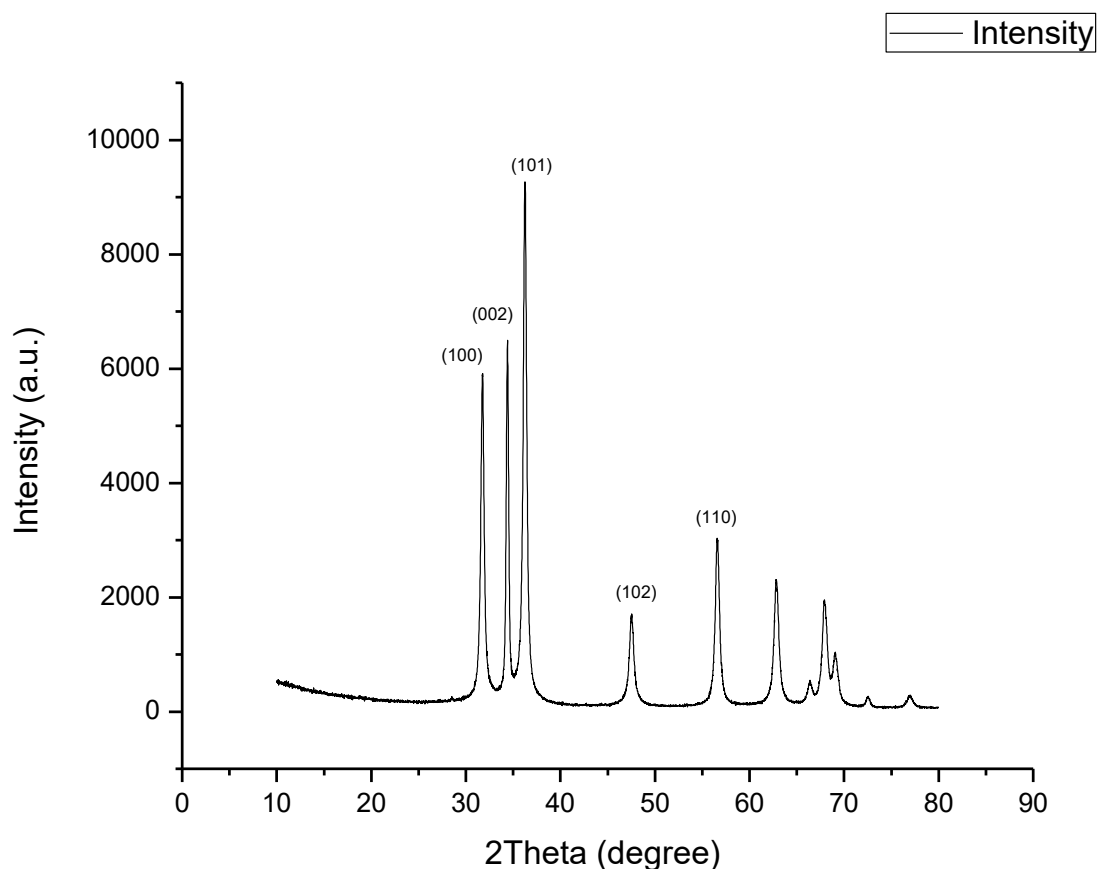
**CHAPTER-V**  
**RESULTS AND DISCUSSIONS**

## CHAPTER – V

### RESULTS AND DISCUSSIONS

#### XRD studies:

##### 5.1 XRD characterization of pure ZnO:

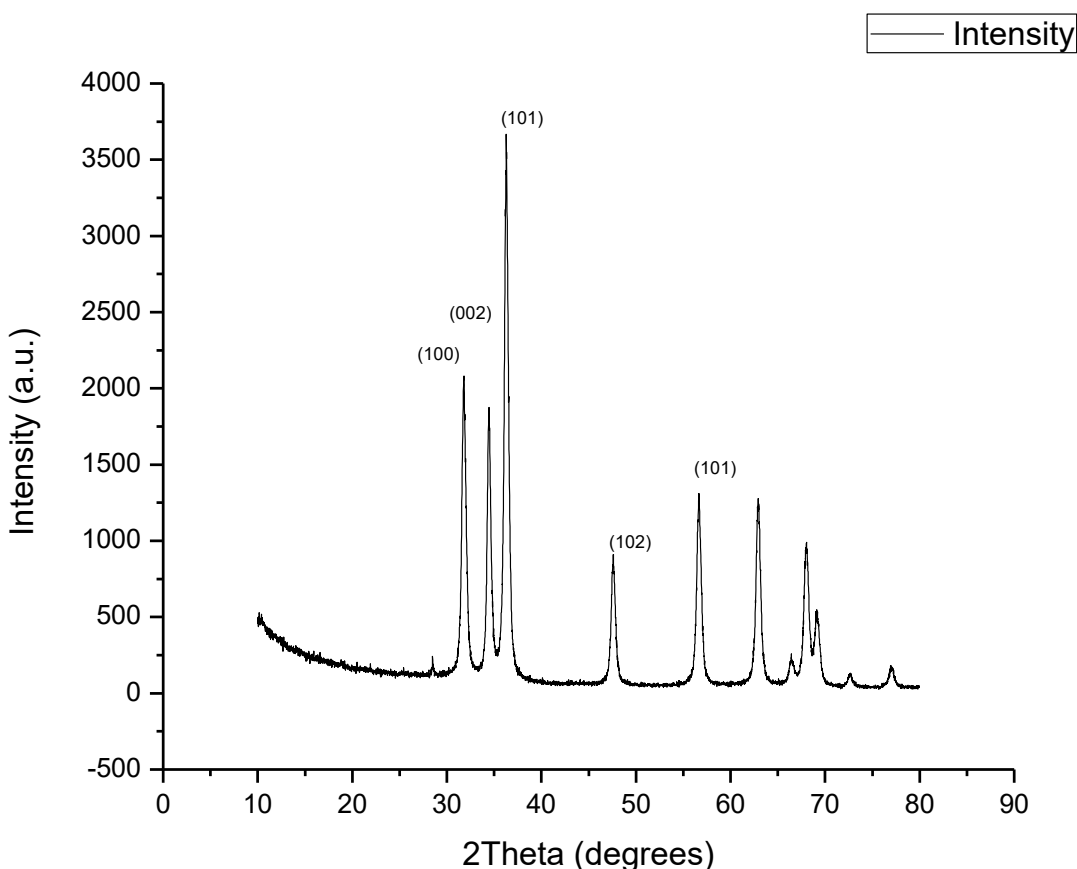


The structural composition of the samples was confirmed from XRD studies. The XRD pattern of ZnO nanoparticles synthesized which shows peaks at  $31.7339^\circ$ ,  $34.3741^\circ$ ,  $36.2232^\circ$ ,  $47.4903^\circ$ ,  $56.5502^\circ$  which corresponds to (100), (002), (101), (102) and (101) plane respectively. So the X-ray diffraction of synthesized ZnO nanoparticles Hexagonal wurtzite structure according to JCPDF data (card number PDF#800075ICSD#067849). The unit cell parameters are  $a=b=0.3253$  nm and  $c=0.5209$  nm. The full



width at half maximum was measured using Gaussian curve for the highest peak 101. The observed peak position are in good agreement with the hexagonal wurtzite structure. The average size of nanoparticles was found to be equal to 25.25 nm.

## 5.2 XRD characterization of Pb doped ZnO nanoparticle:



The structural composition of the samples was confirmed from XRD studies. The XRD pattern of Pb doped ZnO nanoparticles synthesized which shows peaks at  $31.7882^\circ$ ,  $34.4349^\circ$ ,  $36.2703^\circ$ ,  $47.5650^\circ$ ,  $56.6163^\circ$  which corresponds to (100), (002), (101), (102) and (101) plane respectively. So the X-ray diffraction of synthesized Pb doped ZnO nanoparticles Hexagonal wurtzite structure according to JCPDF data (card number PDF#800075ICSD#067849). The unit cell parameters are  $a=b=0.3253$  nm and

$c=0.5209$  nm. The full width at half maximum was measured using Gaussian curve for the highest peak 101. The observed peak position are in good agreement with the hexagonal wurtzite structure. The average size of nanoparticles was found to be equal to 18.39 nm.

Structural parameters such as lattice parameters and unit cell volumes for hexagonal ZnO nanoparticles are calculated from the lattice geometry equations.

$$\frac{1}{d^2} = \frac{4}{3} \left[ \frac{h^2+hk+k^2}{a^2} \right] + \frac{l^2}{c^2}$$

where  $a$  and  $c$  are the lattice parameters.  $h, k$  and  $l$  are the miller indices and  $d_{hkl}$  is the interplanar spacing.

The Debye Scherrer's formula was used to calculate the crystalline size ( $D$ ) from full width half maxima (FWHM) of major XRD peak.

$$D = \frac{K\lambda}{\beta \cos \theta}$$

Where

$D$  = crystalline size

$\lambda$  = X-ray wavelength

$\beta$  = Full Width Half Maxima

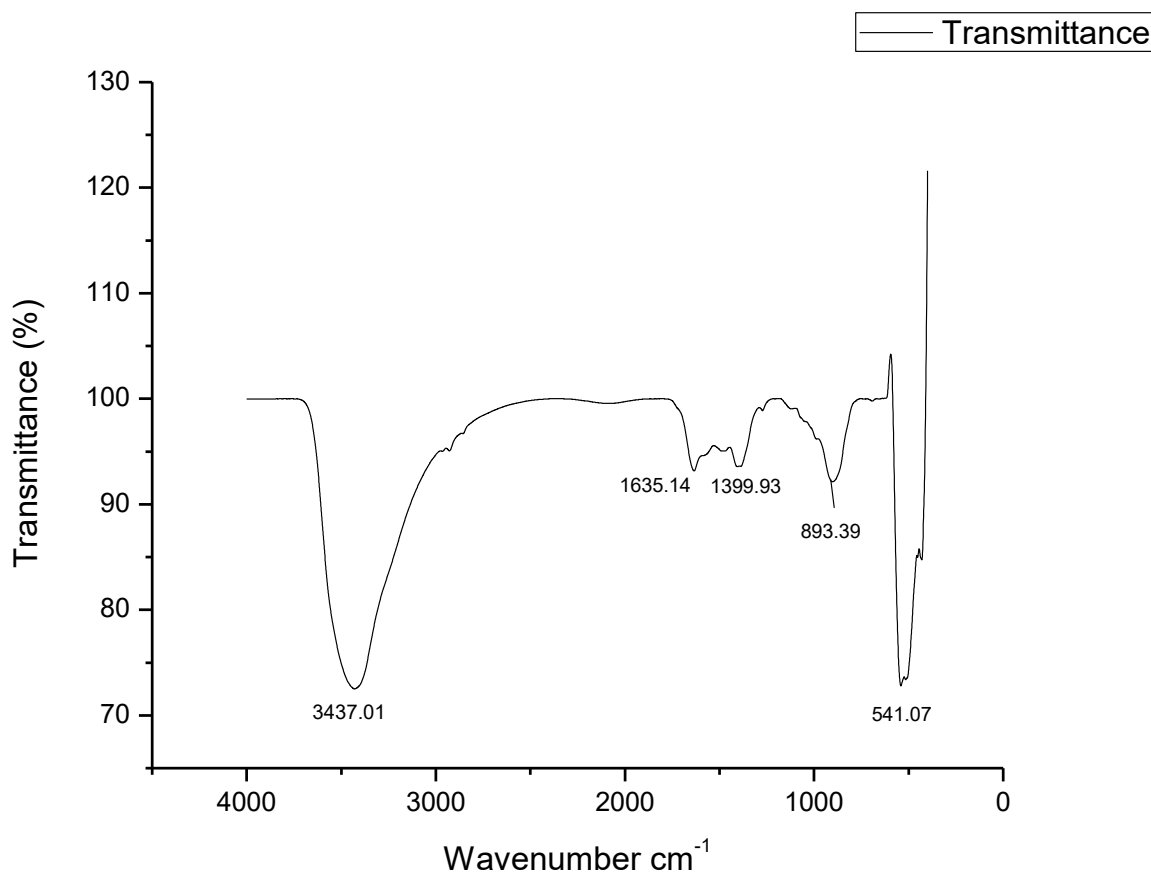
$\theta$  = Bragg diffraction angle

$K$  = shape factor whose value is 0.9

Hence from the above study shows that the Pb doped ZnO helps in controlling the size of nanoparticles.

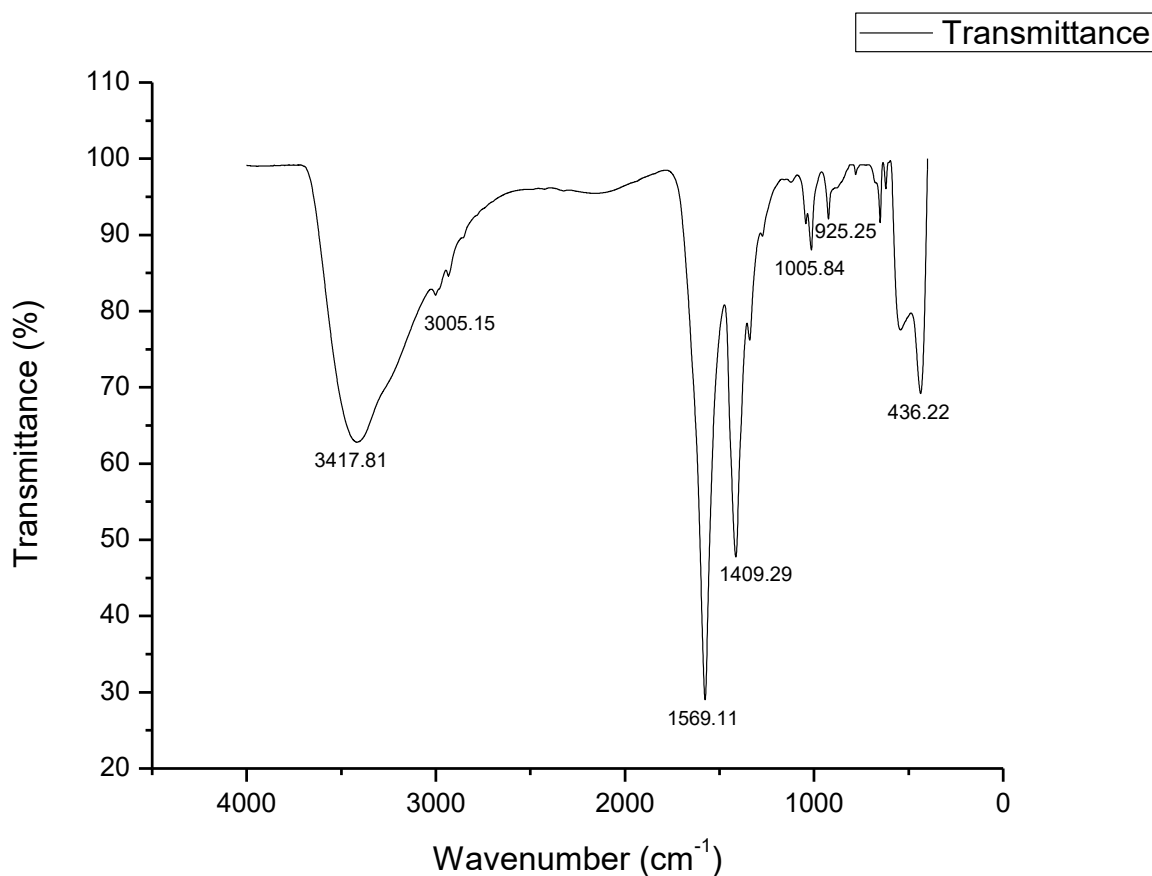
## FTIR studies:

### 5.3 FTIR characterization of pure ZnO nanoparticles:



- The broad envelope in the higher energy region about 3500 cm<sup>-1</sup> due to O-H group which represents the presence of water molecules on the surface of ZnO nanoparticles.
- Strong bands from 1500 cm<sup>-1</sup> to 1700 cm<sup>-1</sup> which corresponds to the functional group of C-O symmetric and antisymmetric stretching mode. Presence of water is also evident by its sharp peak about 1623 cm<sup>-1</sup>.
- The secondary vibrations of Zn-O bond are found to be lying at 541,07 cm<sup>-1</sup> and indicates the product is well crystallized.
- Hence the water might control the size of ZnO during the synthesis.

#### 5.4 FTIR characterization of Pb doped ZnO nanoparticles:



Recorded FTIR spectra of synthesized Pb doped ZnO nanoparticles. It depicts a sequence of absorption bands in a sort of 400 and 4000 cm<sup>-1</sup>.

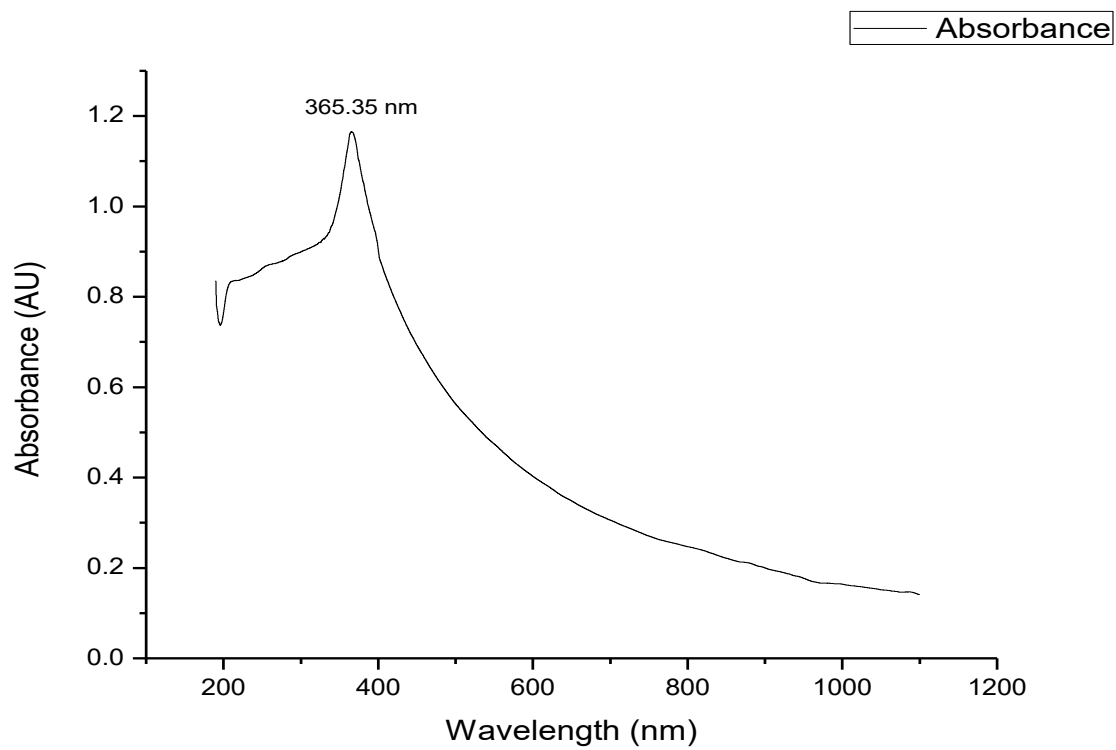
- The most intensive bands 3550-3200 cm<sup>-1</sup> strong bands corresponds to the O-H stretching mode of -COOH group in zinc acetate and water molecule.
- The peak ~2800 to 3000 cm<sup>-1</sup> corresponds to the asymmetric and symmetric (C-H) vibrations of acetate CH<sub>2</sub> groups.
- The bands appear 1593 to 1550 cm<sup>-1</sup> and 1440 to 1420 cm<sup>-1</sup> corresponds to the asymmetric and symmetric vibrations of COO<sup>-</sup> group.
- Absorption band observed around 850 to 950 cm<sup>-1</sup> might be from C-OH group.

- This sharp bands positioned at  $436\text{ cm}^{-1}$  is associated with the characteristic wurtzite lattice vibrations ZnO.

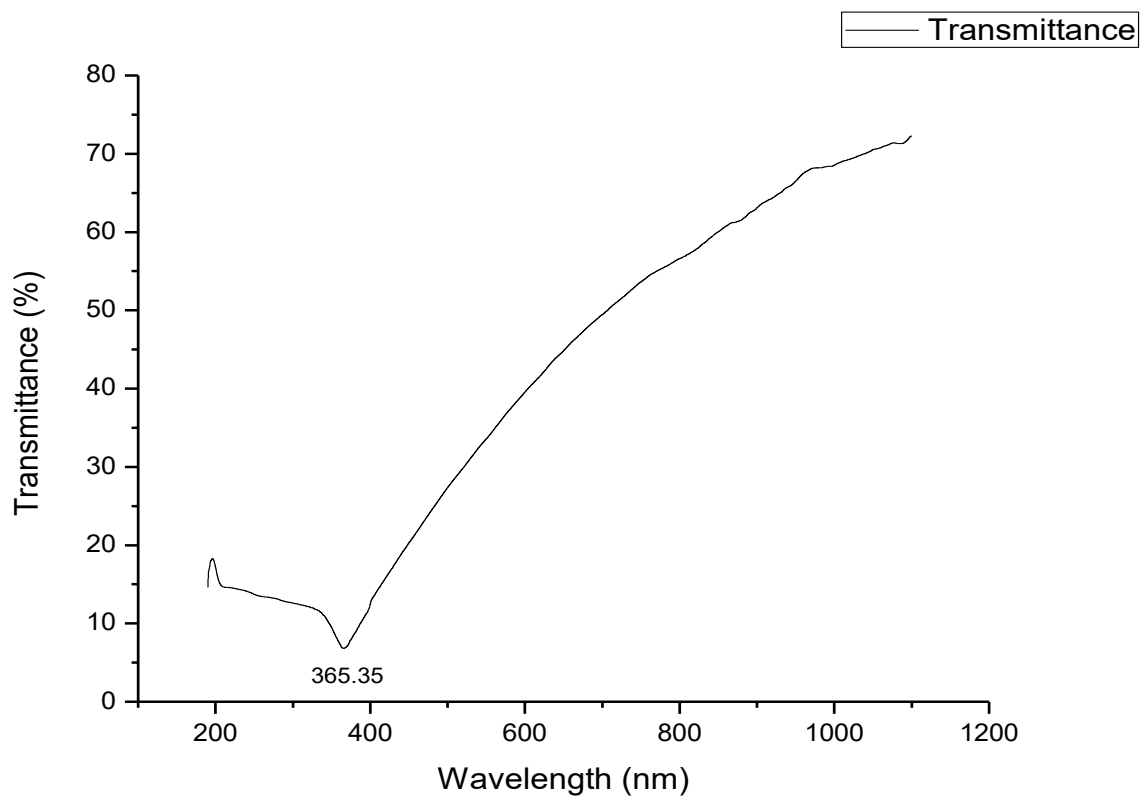
## UV-visible Spectroscopy analysis:

### 5.5 UV-visible characterization pure ZnO nanoparticle:

Absorbance vs Wavelength Graph:



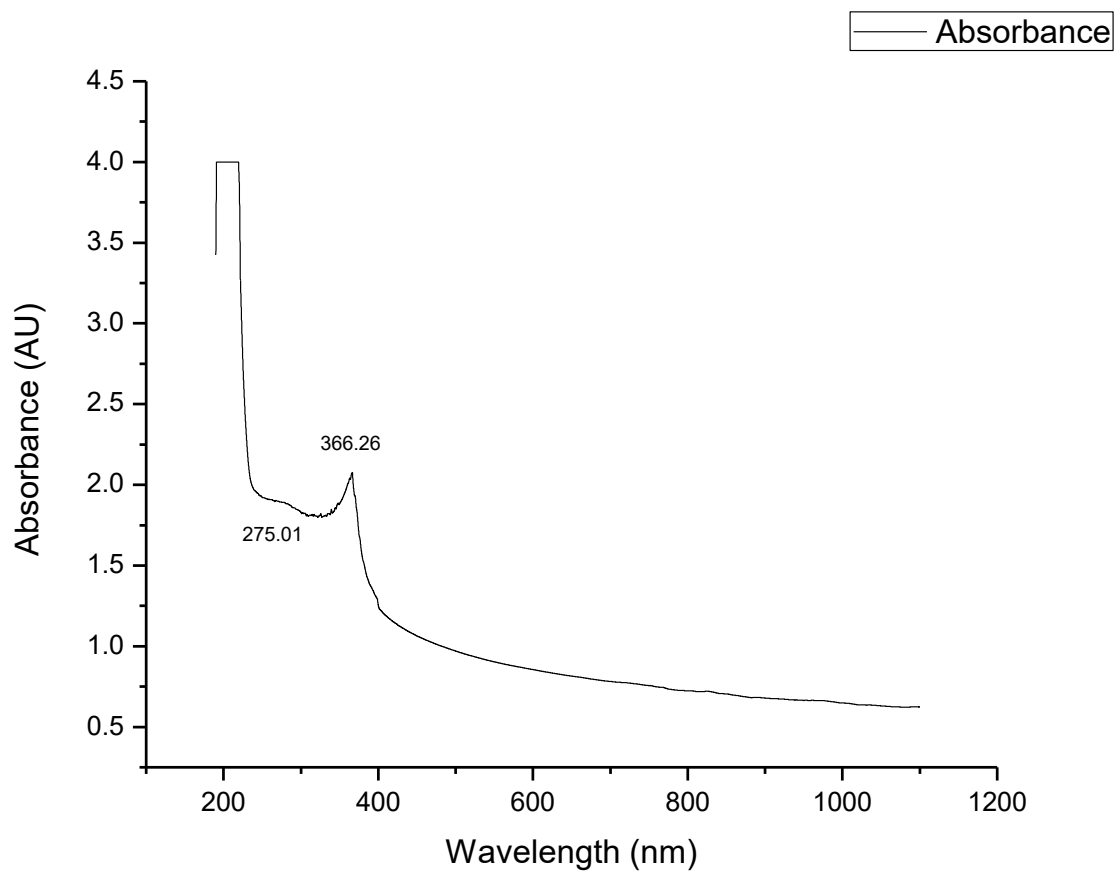
Transmittance vs Wavelength Graph:



The UV-visible transmission and absorption of ZnO nanopowder is presented above. The sample absorbs the radiations in the UV range upto 365.65 nm and almost all the visible spectrum radiations are transmitted by the ZnO nanoparticles.

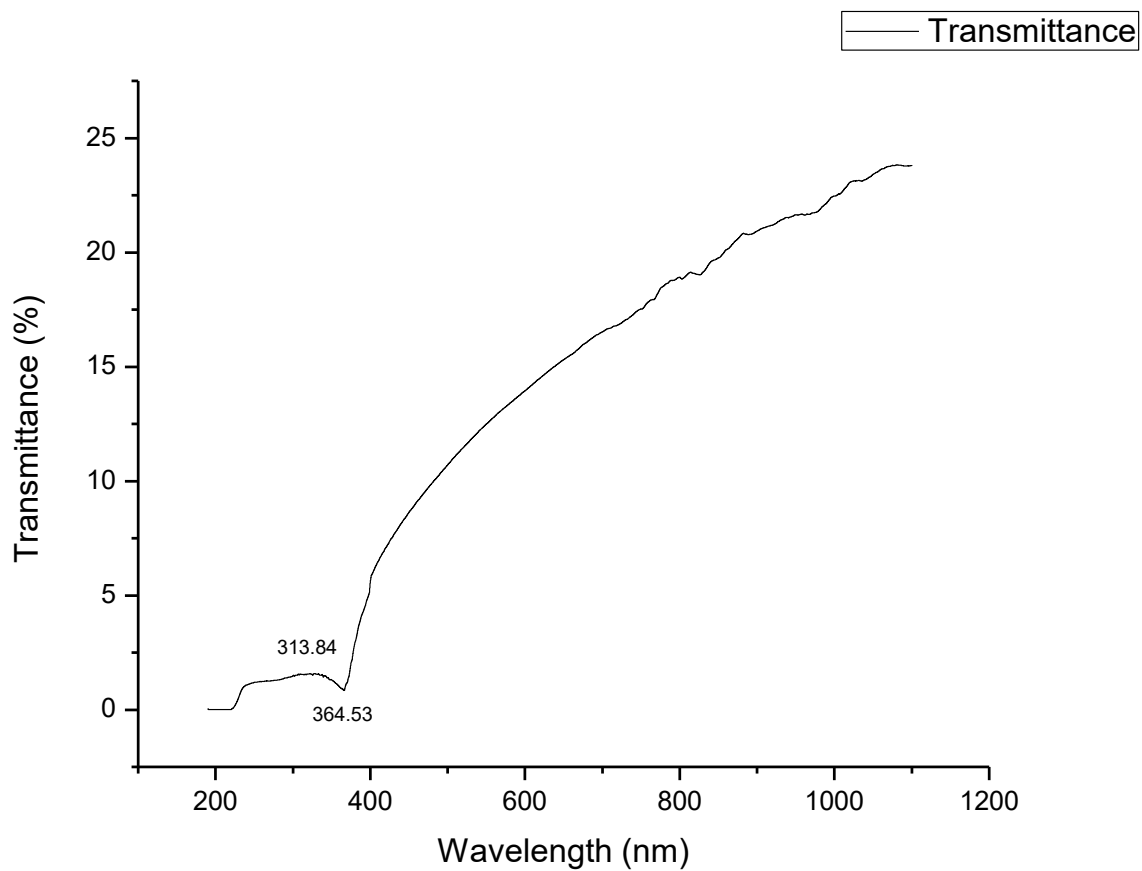
### 5.6 UV-visible characterization of Pb doped ZnO nanoparticle:

Absorption vs Wavelength Graph:





Transmittance vs Wavelength Graph:



The sample absorbs the radiations in the UV range upto 310.24 nm and almost all the visible spectrum radiations are transmitted by the Pb doped ZnO nanoparticle.

### 5.7 UV-visible Spectroscopy analysis:

UV-visible spectroscopy analysis has done for pure ZnO and Pb doped ZnO nanoparticles and the absorption peaks has found at 365.35 nm for pure ZnO nanoparticle and for Pb doped ZnO nanoparticle at 310.24 nm.

Optical bandgap has been calculated with bandgap calculation formula,

$$E = \frac{hc}{\lambda}$$

Where,

E is energy

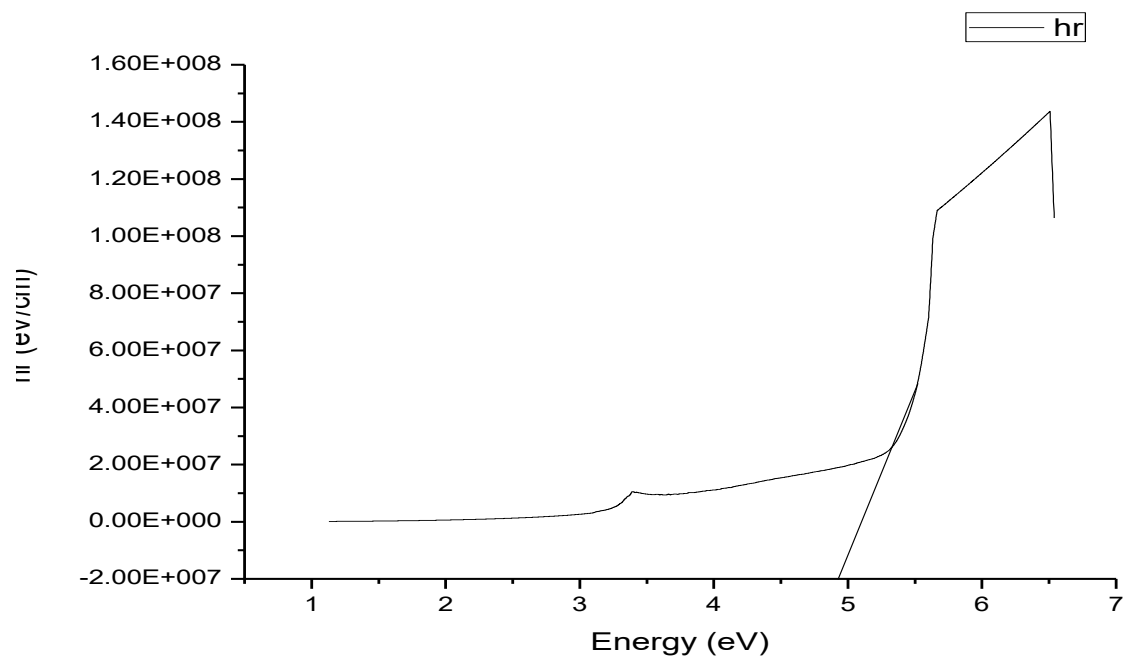
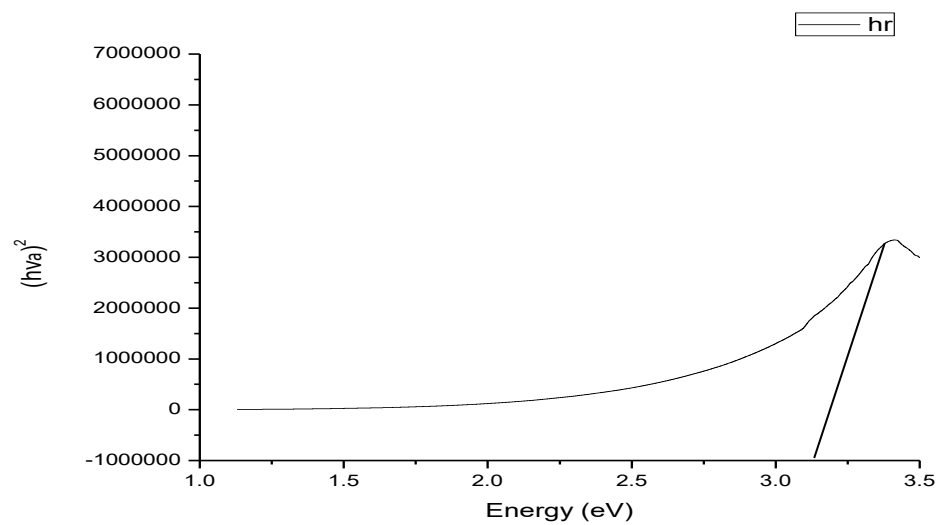
h is planck's constant =  $6.626 \times 10^{-34}$  Joules sec

c is velocity of light =  $2.99 \times 10^8$  m/s

$\lambda$  is wavelength = Absorption value,  $1\text{eV} = 1.6 \times 10^{-19}$  Joules

Using Tauc plots bandgap can be calculated via UV-visible spectroscopy by plotting graph. Thus Pb doped ZnO nanoparticle the energy bandgap is well optimized and increase in bandgap can be found.

By drawing graph between Energy vs  $(\alpha h\nu)^2$  and taking the tangent we found the energy bandgap of nanoparticles. In similar way pure ZnO and Pb doped ZnO nanoparticle bandgap has been found.



SAMPLES	ABSORPTION PEAK(nm)	BAND GAP (eV)
Pure ZnO	365.56	3.29
Pb doped ZnO	310.24	4.9

**CHAPTER-VI**  
**CONCLUSION**

## **CHAPTER – VI**

### **CONCLUSION**

In this project work, I have synthesized pure ZnO nanoparticle and Lead doped ZnO nanoparticle via sol-gel method and chemical coprecipitation method and I have done optical applications. Pb doped helps in controlling the size of the nanoparticle and enhance the optical properties. The pure ZnO shows the crystalline size of 25.25 nm whereas Pb doped ZnO shows the crystalline size of 18.39 nm. So the XRD examination verified the production of wurtzite shape nanoparticles. The secondary bond vibration pure ZnO was found to be at  $541\text{ cm}^{-1}$ , whereas the Pb doped ZnO at  $436\text{ cm}^{-1}$ . Bandgap of semiconductor depends on particle and as increase in grain size of the ZnO the bandgap energy is decreased. For the pure ZnO the absorption peak is at 365.35 nm whereas the Pb doped ZnO is at 310.24 nm of having the energy bandgap value of 3.29 eV and 4.9 eV is observed.

## **CHAPTER-VII**

## **REFERENCES**

## CHAPTER- VII

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