

## Structural And Optical Properties Of $\text{Cd}_{0.02}\text{Zn}_{0.98}\text{O}:\text{Re}$ Nanopowders By Sol-Gel Method For Led Applications



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### ABSTRACT:

In this study, we report on the improvement in the optoelectronic properties of n-ZnO. This was achieved by doping the ZnO with cadmium (Cd) and rare earth (Y,La). The  $\text{Cd}_{0.02}\text{Zn}_{0.98}\text{O}$  and  $\text{Cd}_{0.02}\text{Zn}_{0.98}\text{O}:\text{RE}$  nano powders synthesized by sol-gel method, can be used to fabricate the light emitting diodes (LEDs). Structural measurement revealed that nanopowders with wurtzite structure having a preferential

orientation along the (101) plane. The UV-vis spectra show that the optical band gap of  $\text{Cd}_{0.02}\text{Zn}_{0.98}\text{O}$  nanopowders is decreased in comparison to ZnO nanopowders. The effect of doping was to reduce the valence band offsets and consequently more hole injection has occurred leading to the observed enhancement of the broad band in the visible region.

**Keywords:** Cd<sub>0.02</sub>Zn<sub>0.98</sub>O, light emitting diodes (LEDs), nanopowders, UV–vis spectra

## INTRODUCTION

The term “nano” refers to the metric prefix 10<sup>-9</sup>. It means one billionth of something. “Nano” can be ascribed to any unit of measure. For example, you may report a very small mass in nanograms or the amount of liquid in one cell in terms of nanoliters.

**Nanoscience** is the study of structures and materials on the scale of nanometers. To give you an idea of how long a nanometer is, this printed page is about 75,000 nanometers thick. When structures are made small enough—in the nanometer size range—they can take on interesting and useful properties. Nanoscale structures have existed in nature long before scientists began studying them in laboratories. A single strand of DNA, the

building block of all living things, is about three nanometers wide. The scales on a morpho butterfly’s wings contain nanostructures that change the way light waves interact with each other, giving the wings brilliant metallic blue and green hues. Peacock feathers and soap bubbles also get their iridescent coloration from light interacting with structures just tens of nanometers thick. Scientists have even created nanostructures in the laboratory that mimic some of nature’s amazing nanostructures.

Because nanostructures are so small, specialized methods are needed to manufacture objects in this size range. Scientists use beams of electrons or ions to etch features as small as 25 nanometers into metal, silicon and carbon-based materials. In addition to being formed on these solid material surfaces, nanostructures can also be formed in liquids. Nanostructures can be created by reacting

chemicals in liquids and gases to generate nanofibers, nanocrystals and quantum dots, some as small as one nanometer wide. Scientists are even learning how to build three-dimensional structures at the nanoscale called nano-electro-mechanical systems, or NEMS, these devices might one day be used like microscopic robots to carry out tasks too small for humans to do themselves. For example, NEMS could carry out surgery on a single cell or act as mechanical actuators to move around individual molecules.

In order to observe and study nanostructures, specialized equipment must be used. If you wanted to magnify something ten times, you could use a magnifying glass that fits in your pocket. If you wanted to magnify something 200 times, you would need a microscope that may weigh several pounds and take up part of a desk. To magnify nanoscale structures, high-powered microscopes that fill an entire

room are needed! Nanoscience has already impacted our lives with innovations such as stain-resistant fabrics inspired by nanoscale features found on lotus plants and computer hard drives, which store information on magnetic strips that are just 20 nanometers thick. Scientists and engineers from several disciplines including physics, chemistry, biology and materials science use nanoscience principles for advanced applications in energy, medicine, information storage, computing and elsewhere. Although breakthroughs in any research field are difficult to predict, the future of nanoscience will likely involve scaling up from atomic assembly and individual nanodevices to macroscopic systems and structures with evolving properties and multiple functions.

**Nanotechnology is the engineering of functional systems at the molecular scale.** This covers both current work and concepts that are more advanced. In its original sense,

'nanotechnology' refers to the projected ability to construct items *from the bottom up*, using techniques and tools being developed today to make complete, high performance products.

**Nanomaterials** describe, in principle, materials of which a single unit is sized (in at least one dimension) between 1 and 1000 **nanometers** ( $10^{-9}$  meter) but is usually 1–100 nm (the usual definition of nanoscale).

Nanomaterials research takes a materials science-based approach to nanotechnology, leveraging advances in materials metrology and synthesis which have been developed in support of microfabrication research. Materials with structure at the nanoscale often have unique optical, electronic, or mechanical properties.

### Natural nanomaterials

Biological systems often feature natural, functional nanomaterials. The structure of foraminifera (mainly chalk) and viruses (protein, capsid), the wax crystals covering a lotus or nasturtium leaf, spider and spider-mite silk, the blue hue of tarantulas, the "spatulae" on the bottom of gecko feet, some butterfly wing scales, natural colloids (milk, blood), horny materials (skin, claws, beaks, feathers, horns, hair), paper, cotton, nacre, corals, and even our own bone matrix are all natural



*organic* nanomaterials. Natural *inorganic* nanomaterials occur through crystal growth in the diverse chemical conditions of the earth's crust. For example, clays display complex nanostructures due to anisotropy of

their underlying crystal structure, and volcanic activity can give rise to opals, which are an instance of naturally occurring photonic crystals due to their nanoscale structure. Fires represent particularly complex reactions and can produce pigments, cement, fumed silica etc.

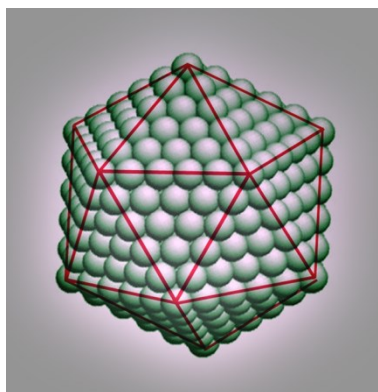


Figure 1: a) Viral capsid b) "Lotus effect", hydrophobic effect with self-cleaning ability

## SYNTHESIS METHODS

There are the several methods to prepare the nanoparticles, there are

- a) Co-precipitation method
- b) Hydro thermal method

- c) Solvo-thermal method.
- d) Sol- Gel method
- e) Chemical vapor deposition

### a) Co precipitation method:

Chemical precipitation is widely used in industry and research to synthesize nanometer sized oxide powders. The process starts from dissolving salts, which contain metal ions, in a liquid medium. The solution is then mixed with a solution of dissolved precipitating agent, such as oxalic acid or ammonium hydroxide, in order to precipitate the metal oxalates or hydroxides. The final crystalline oxide is then obtained by firing the precipitates at a higher temperature. A significant problem which has to be to overcome in chemical precipitation is the agglomeration of the particles in the solution. Thus, dispersants are often added in the reaction process to provide repulsive (electrostatic or steric) interactions between

the particles to prevent them from adhering to each other. To eliminate subsequent neck formation and aggregation in the calcinations and firing steps, organic solvents such as ethanol may be added in the final washing step to replace water adsorbed on the powder surface. The advantages of the precipitation method include technical simplicity, low manufacturing cost, high reproducibility and fine particle size. Disadvantages are the difficulty to control the final chemical composition of the products and up scaling issues. Also, the repeated washing and steps make precipitation a time-consuming method.

#### **b) Hydrothermal method:**

Hydrothermal processing is one of the promising processes in materials science and engineering. The definition of hydrothermal synthesis involves H<sub>2</sub>O as catalyst and occasionally as component of solid phases in the synthesis at elevated

temperatures and pressure (>few atmosphere). The hydrothermal process is one of (>100the promising methods for preparing fine ceramic powders). The term hydrothermally usually refers to any heterogeneous reaction in the presence of aqueous solvents mineralizes under high pressure and temperature conditions to dissolve and recrystallize (recover) materials that are relatively insoluble under ordinary conditions.

The powders synthesized by the hydrothermal method are well crystallized and easily dispersible in an aqueous medium. The hydrothermal process is also a good method to solve environmental and economic problems, because of its closed system and energy efficiency. This technique involves the synthesis of the materials at greatly reduced temperatures. For hydrothermal experiments the requirements for starting materials are



- ✓ accurately known composition
- ✓ as homogeneous as possible
- ✓ as pure as possible
- ✓ as fine as possible.

Nitrates or acetates in stoichiometric amounts are dissolved in deionized water.

The required pH is adjusted and solution sealed in a non-corrosive vessel called autoclave. The 00°C for varying periods under auto generated pressures, the container is then cooled to room temperature. Centrifuging temperature is maintained in between 100-200°C, then separates the solid and solution phases and the solids are washed free of dissolved salts.

The main advantage of this method is that the calcinations of compounds at higher salts. The main advantage of this method is that the calcinations of compounds at higher temperatures can be avoided and higher surface areas can be obtained.

### c) Solvothermal method:

Solvothermal synthesis is a method of producing chemical compounds. It is very similar to the hydrothermal route, the only difference being that the precursor solution is usually not aqueous. Thus Solvothermal synthesis allows for the precise control over the size, shape distribution, and crystallinity of metal oxide nanoparticles or Nano structures. These characteristics can be altered by changing certain experimental parameters, including reaction temperature, reaction time, solvent type, surfactant type, and precursor type. Solvothermal synthesis has been used in laboratory to make nanostructured titanium dioxide, graphene, carbon and other materials. The high photo catalytic capacity of titanium dioxide leads to the degradation of organic and biological molecules into smaller and less harmful compounds. Because of their small size, titanium dioxide nanostructures also provide increased surface area at which photo catalytic reactions may occur, increases their

activity. This photo catalytic activity may be applied to air purification, self-sterilization, water purification and molecular hydrogen production.

#### **d) Sol-Gel method:**

The sol-gel method was developed in the 1960s mainly due to the need of new synthesis methods in the nuclear industry.

A sol is a stable dispersion of colloidal particles or polymers in a solvent. The particles may be amorphous or crystalline. An aerosol is particles in a gas phase while a sol is particles in a liquid.

A gel consists of a three dimensional continuous network, which encloses a liquid phase, in a colloidal gel, the network is built from agglomeration of colloidal particles. In a polymer gel the particles have a polymeric sub-structure made by aggregates of sub-colloidal particles. Typical precursors are metal alkoxides and metal chlorides, which

undergo hydrolysis (Hydrolysis is a chemical reaction or process in which a chemical compound is broken down by reaction with water) and poly-condensation reactions (A chemical reaction in which two or more molecules combine upon the separation of water or some other simple substance) to form a colloid, a system composed of solid particles (size ranging from 1 nm to 1  $\mu$ m) dispersed in a solvent. The sol evolves then towards the formation of an inorganic network containing a liquid phase (gel). Formation of a metal oxide involves connecting the metal centers with Oxo (M-O-M) or hydroxide (M-OH-M) bridges, therefore generating metal-Oxo or metahydroxo polymers in solution. The drying process serves to remove the liquid phase from the gel thus forming a porous material, and then a thermal treatment (firing) may be performed in order to favor further polycondensation and enhance mechanical properties. The precursor sol can



be either deposited on a substrate to form a film (e.g. by dipcoating or spin-coating), cast into a suitable container with the desired shape. (E.g. to obtain a monolithic ceramics, glasses, fibers, membranes, aerogels), or used to synthesize powders (e.g. microspheres, Nano spheres).

**The sol-gel process usually consists of 4 steps:**

- (1) The desired colloidal particles once dispersed in a liquid to form a sol.
- (2) The deposition of sol solution produces the coatings on the substrates by spraying, dipping or spinning.
- (3) The particles in sol are polymerized through the removal of the stabilizing components and produce a gel in a state of a continuous network.

- (4) The final heat treatments pyrolysis the remaining organic or inorganic components and form an amorphous or crystalline coating.

The sol-gel approach is interesting in that it is a cheap and low-temperature technique that allows for the fine control on the product's chemical composition. As even small quantities of dyes, organic dyes and rare earth metals, can be introduced in the sol and end up in the final product finely dispersed.

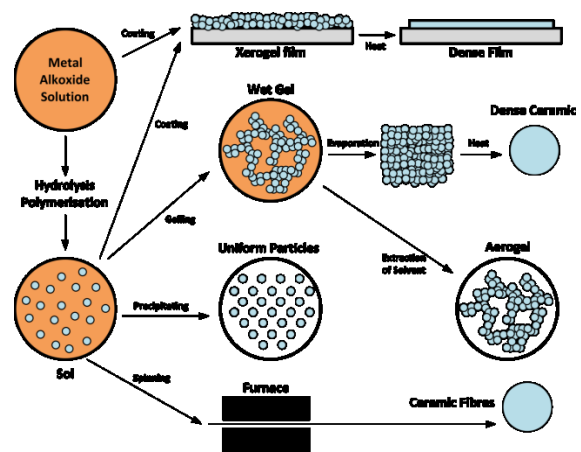


Figure 2: Schematic Overview showing two synthesis examples by the sol-gel method

**(e) Chemical Vapor Deposition (CVD)**

Chemical vapor deposition (CVD) is a chemical process used to produce high quality, high-performance, solid materials. The process is often used in the semiconductor industry to produce thin films. In typical CVD, the wafer (substrate) is exposed to one or more volatile precursors, which react and/or decompose on the substrate surface to produce the desired deposit. Frequently, volatile by-products are also produced, which are removed by gas flow through the reaction chamber.

Microfabrication processes widely use CVD to deposit materials in various forms, including: monocrystalline, polycrystalline, amorphous, and epitaxial. These materials include: silicon ( $\text{SiO}_2$ , germanium, carbide, nitride, oxynitride), carbon (fiber, nanofibers, nanotubes, diamond and graphene), fluorocarbons,

filaments, tungsten, titanium nitride and various high-k dielectrics. CVD is commonly used to deposit conformal films and augment substrate surfaces in ways that more traditional surface modification techniques are not capable of. CVD is extremely useful in the process of atomic layer deposition at depositing extremely thin layers of material. A variety of applications for such films exist. Gallium arsenide is used in some integrated circuits (ICs) and photovoltaic devices. Amorphous polysilicon is used in photovoltaic devices. Certain carbides and nitrides confer wear-resistance. Polymerization by CVD, perhaps the most versatile of all applications, allows for super-thin coatings which possess some very desirable qualities, such as lubricity, hydrophobicity and weather-resistance to name a few. CVD of metal-organic frameworks, a class of crystalline nanoporous materials, has recently been demonstrated. Applications for these films

are anticipated in gas sensing and low-k dielectrics

## SYNTHESIS PROCEDURE

### Instruments used

Magnetic stirrer, magnetic stirrer with hot plate, Glass beakers, Spatula, Digital Balance, watch Glasses, Butter Paper, Crucibles with lid, Bunsen Burner, droppers, pH paper, etc.

### Materials

Zinc nitrate, Cadmium Nitrate, Citric acid, Ammonia solution, Ethylene glycol, Double distilled water, etc.

### 3.2.1 Preparation of $Cd_{0.02}Zn_{0.98}O$ nanoparticles

#### Calculations

To prepare 5 grams of  $Cd_{0.02}Zn_{0.98}O$

Total Molecular Weight of Compound (TMWC)

= 0.02(Molecular Weight of Cadmium) + 0.98(Molecular Weight of Zinc) + 1(Molecular Weight of Oxygen).

$$= 0.02(112.411) + 0.98(65.389) + 1(15.999).$$

$$= 82.3284 \text{ gm/mol}$$

• Weight of  $Cd(NO_3)_2$  =

$$\frac{5 \times \text{ratio of Cd in Compound} \times \text{m.w. of } Cd(NO_3)_2}{TMWC}$$

$$= \frac{5 \times 0.02 \times 308.48}{82.3284}$$

$$= 0.3785 \text{ gm}$$

• Weight of  $Zn(NO_3)_2$  =

$$\frac{5 \times \text{ratio of Zn in Compound} \times \text{m.w. of } Zn(NO_3)_2}{TMWC}$$

$$= \frac{5 \times 0.98 \times 297.47}{82.3284}$$

$$= 17.8836 \text{ gm}$$

• Weight of Citric Acid = ratio \* total mole numbers of Metal ions \* m.w. of citric acid

• Weight of **Citric Acid** = 15.5472 gm.

## Procedure to prepare $Zn_{0.98}Cd_{0.02}O$ nanoparticles

- Washed the Beaker, watch glass, magnetic bead, dropper and spatulas for several times before the weighing and dissolving the chemicals using acetone and de-ionized water.
- Weighed the precursor nitrate chemicals according the calculations in watch glass using digital balance with 0.001 precision.
- Zinc nitrate (17.8836 gm), Cadmium Nitrate (0.3785 gm) A.R. grade chemical salts used without further purification and were dissolved in 100ml double distilled water using 500ml capacity beaker.
- Inserted a 1 inch magnetic bead into the beaker and stirred for homogeneous mixing using magnetic stirrer for 30 min.
- 15.5472 gm of citric acid salt was added to nitrate solution slowly with continuous stirring. This stirring process was continued for 1hr.
- Initially checked the pH value of the mixture solution using pH testing (litmus) paper.
- Then adequate ammonia solution was added to the solution drop by drop using dropper with long teat.
- After reaching the pH value 6.5–7, adding of ammonia solution was stopped and measured the quantity of the final solution. Started heating approximately at 100 °C using magnetic stirrer with hot plate.
- After reaching 1/3<sup>rd</sup> of the initial quantity of neutralized solution, 5ml of ethylene glycol was added. And stirred for 30 min for homogeneous mixing.

- Magnetic bead was extracted from the beaker and again started heating process approximately 250 °C to obtain gel and to be burned into ash like powder.
- These ashes like powders were taken into 50 ml capacity of crucibles and burned using Bunsen burner for 30 min.
- Then the final powder was ground for 30 min to get fine powder. The final powder samples were used to characterize and to study the further studies.

### Preparation of $Cd_{0.02}Zn_{0.96}O:La_{0.02}$ nanoparticles

#### Materials

Zinc nitrate, Cadmium Nitrate, Lanthanum nitrate, Citric acid, Ammonia solution, Ethylene glycol, Double distilled water, etc.

### Calculations to prepare $Cd_{0.02}Zn_{0.96}O:La_{0.02}$ nanoparticles

To prepare 5 grams of  $Cd_{0.02}Zn_{0.96}O:La_{0.02}$  (Metal Oxide) compound;

Total Molecular Weight of Compound (TMWC)

$$= 0.02(\text{Molecular Weight of Cadmium}) + 0.96(\text{Molecular Weight of Zinc}) + 0.02(\text{Molecular Weight of Lanthanum}) + 1(\text{Molecular Weight of Oxygen}).$$

$$= 0.02(112.411) + 0.96(65.389) + 0.02(138.905) + 1(15.999)$$

$$= 83.7987 \text{ gm/mol}$$

- Weight of  $Cd(NO_3)_2 = \frac{5 * \text{ratio of Cd in Compound} * m.w. \text{ of } Cd(NO_3)_2}{TMWC}$

$$= \frac{5 * 0.02 * 308.48}{83.7987} = 0.3718 \text{ gm}$$

- Weight of  $Zn(NO_3)_2 = \frac{5 * \text{ratio of Zn in Compound} * m.w. \text{ of } Zn(NO_3)_2}{TMWC}$

$$= \frac{5 * 0.94 * 297.47}{83.7987} = 17.2112 \text{ gm}$$

- Weight of  $\text{La}(\text{NO}_3)_3 =$

$$\frac{5 * \text{ratio of La in Compound} * \text{m.w. of } \text{La}(\text{NO}_3)_3}{\text{TMWC}}$$

$$= \frac{5 * 0.02 * 433.04}{83.7987} = 0.5220 \text{ gm}$$

- Weight of Citric Acid =  
15.1049 gr.

### Procedure to prepare $\text{Cd}_{0.02}\text{Zn}_{0.96}\text{O}:\text{La}_{0.02}$ nanoparticles

- Washed the Beaker, watch glass, magnetic bead, dropper and spatulas for several times before the weighing and dissolving the chemicals using acetone and de-ionized water.
- Weighed the precursor nitrate chemicals according the calculations in watch glass using digital balance with 0.001 precision.
- 17.211 gm of Zinc nitrate, 0.372 gm of Cadmium Nitrate and 0.522 gm of Lanthanum nitrate salts (A.R. grade

chemicals) were dissolved in 500ml capacity beaker with 100ml double distilled water.

- Inserted a 1 inch magnetic bead into the beaker and stirred for homogeneous mixing using magnetic stirrer for 30 min.
- 15.6025 gm of citric acid salt was added to nitrate solution slowly with continuous stirring. This stirring process was continued for 1hr.
- Initially checked the pH value of the mixture solution using pH testing (litmus) paper.
- Then adequate ammonia solution was added to the solution drop by drop using dropper with long teat.
- After reaching the pH value 6.5–7, adding of ammonia solution was stopped and measured the quantity of the final solution. Started heating

approximately at 100 °C using magnetic stirrer with hot plate.

- After reaching 1/3<sup>rd</sup> of the initial quantity of neutralized solution, 5ml of ethylene glycol was added. And stirred for 30 min for homogeneous mixing.
- Magnetic bead was extracted from the beaker and again started heating process approximately 250 °C to obtain gel and to be burned into ash like powder.
- These ashes like powders were taken into 50 ml capacity of crucibles and burned using Bunsen burner for 30 min.
- Then the final powder was ground for 30 min to get fine powder. The final powder samples were used to characterize and to study the further studies.

## Preparation of Cd<sub>0.02</sub>Zn<sub>0.96</sub>O:Y<sub>0.02</sub> nanoparticles

### Materials

Zinc nitrate, Cadmium Nitrate, Yttrium nitrate, Citric acid, Ammonia solution, Ethylene glycol, Double distilled water, etc.

### Calculations

To prepare 5 grams of Metal Oxide (MO) compound i.e., Cd<sub>0.02</sub>Zn<sub>0.96</sub>O:Y<sub>0.02</sub>

Total Molecular Weight of Compound (TMWC)

$$\begin{aligned}
 &= 0.02(\text{Molecular Weight of Cadmium}) + 0.96(\text{Molecular Weight of Zinc}) \\
 &+ 0.02(\text{Molecular Weight of Yttrium}) + 1(\text{Molecular Weight of Oxygen}). \\
 &= 0.02(112.411) + 0.96(65.389) \\
 &+ 0.02(88.906) + 1(15.999) \\
 &= 82.2691 \text{ gm/mol}
 \end{aligned}$$

- Weight of  $\text{Cd}(\text{NO}_3)_2 = \frac{5 * \text{ratio of Cd in Compound} * \text{m.w.of Cd}(\text{NO}_3)_2}{\text{TMWC}}$   

$$= \frac{5 * 0.02 * 308.48}{82.2691} = 0.3763 \text{ gm}$$

- Weight of  $\text{Zn}(\text{NO}_3)_2 = \frac{5 * \text{ratio of Zn in Compound} * \text{m.w.of Zn}(\text{NO}_3)_2}{\text{TMWC}}$   

$$= \frac{5 * 0.94 * 297.47}{82.2691} = 17.4191 \text{ gm}$$

- Weight of  $\text{Y}(\text{NO}_3)_3 = \frac{5 * \text{ratio of Y in Compound} * \text{m.w.of Y}(\text{NO}_3)_3}{\text{TMWC}}$   

$$= \frac{5 * 0.02 * 433.04}{82.2691} = 0.4673 \text{ gm}$$

- Weight of Citric Acid = 15.4589 gr.

### Procedure to prepare $\text{Cd}_{0.02}\text{Zn}_{0.96}\text{O}:\text{Y}_{0.02}$ nanoparticles

- Washed the Beaker, watch glass, magnetic bead, dropper and spatulas for several times before the weighing and dissolving the chemicals using acetone and deionized water.

- Weighed the precursor nitrate chemicals according the calculations in watch glass using digital balance with 0.001 precision.

- 17.4191 gm of Zinc nitrate, 0.3763gm of Cadmium Nitrate, and 0.4673 gm of Yttrium nitrate salts (A.R. grade chemicals) were dissolved in 500ml capacity beaker with 100ml double distilled water.

- Inserted a 1 inch magnetic bead into the beaker and stirred for homogeneous mixing using magnetic stirrer for 30 min.

- 15.459 gm of citric acid salt was added to nitrate solution slowly with continuous stirring. This stirring process was continued for 1hr.

- Initially checked the pH value of the mixture solution using pH testing (litmus) paper.



- Then adequate ammonia solution was added to the solution drop by drop using dropper with long teat.
- After reaching the pH value 6.5–7, adding of ammonia solution was stopped and measured the quantity of the final solution. Started heating approximately at 100 °C using magnetic stirrer with hot plate.
- After reaching 1/3<sup>rd</sup> of the initial quantity of neutralized solution, 5ml of ethylene glycol was added. And stirred for 30 min for homogeneous mixing.
- Magnetic bead was extracted from the beaker and again started heating process approximately 250 °C to obtain gel and to be burned into ash like powder.
- These ashes like powders were taken into 50 ml capacity of crucibles and

burned using Bunsen burner for 30 min.

- Then the final powder was ground for 30 min to get fine powder. The final powder samples were used to characterize and to study the further studies.



## RESULTS AND DISCUSSION

In this project, the following samples were prepared.

S.No.	Sample formula	Sample
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code		
1	Zn <sub>0.98</sub> Cd <sub>0.02</sub> O	Sample A
2	Zn <sub>0.96</sub> Cd <sub>0.02</sub> O:Y <sub>0.02</sub>	Sample B
3	Zn <sub>0.94</sub> Cd <sub>0.02</sub> O:Y <sub>0.04</sub>	Sample C
4	Zn <sub>0.96</sub> Cd <sub>0.02</sub> O:La <sub>0.02</sub>	Sample D
5	Zn <sub>0.94</sub> Cd <sub>0.02</sub> O:La <sub>0.04</sub>	Sample E

### XRD Analysis

All the prepared powders were characterized by powder X-ray diffraction (XRD) with Phillips, diffractometer (Germany make) using (40 kV, 30mA) CuK- $\alpha$  radiation ( $\lambda = 1.5406$  Å). XRD patterns were obtained in the range of 10.0100 to 79.9900 by step scanning mode with the step size of 0.0200°. Fig. 3.1 shows the XRD patterns of five Zn<sub>1-x</sub>Cd<sub>0.02</sub>O:RE<sub>x</sub> (RE=Y, La; x=0, 0.02, 0.04) samples prepared by sol-gel method. The XRD data analysis shows that all the five samples are single-phase of ZnO without any other secondary phase such as CdO. The preferential orientation of all the samples has been found to be along (1 0 1) plane. Other peaks were obtained along (1 0 0), (0 0 2), (1 0 2), (1 1 0), (1 0 3), (2 0 0), (1 1 2), and (0 0 4).

The analysis revealed that all the powders are of polycrystalline in nature having a hexagonal wurtzite type crystal structure according to the JCPDS files (PDF # 891397) and no peaks that correspond to either cadmium, zinc or their complex oxides could be detected. This suggests that the samples do not have any phase segregation. The crystalline size of the films was calculated by using Debye Scherer formula <sup>[89]</sup>, Crystallite size ( $D$ ) =  $\frac{0.9 \lambda}{\beta \cos \theta}$ . Where,  $\lambda$  is the wavelength of the X-Ray Source,  $\beta$  is the full width at half maximum (FWHM) in radians,  $\theta$  is the Diffraction angle i.e., Bragg's angle. The calculated crystallite sizes are found to be 36, 48, 28, 41 and 35 nm for samples A, B, C, D and E respectively.

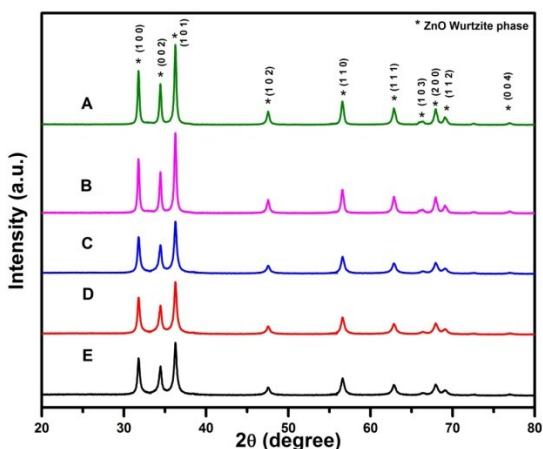


Figure 3: XRD pattern of prepared samples.

Compositional analysis (EDS)

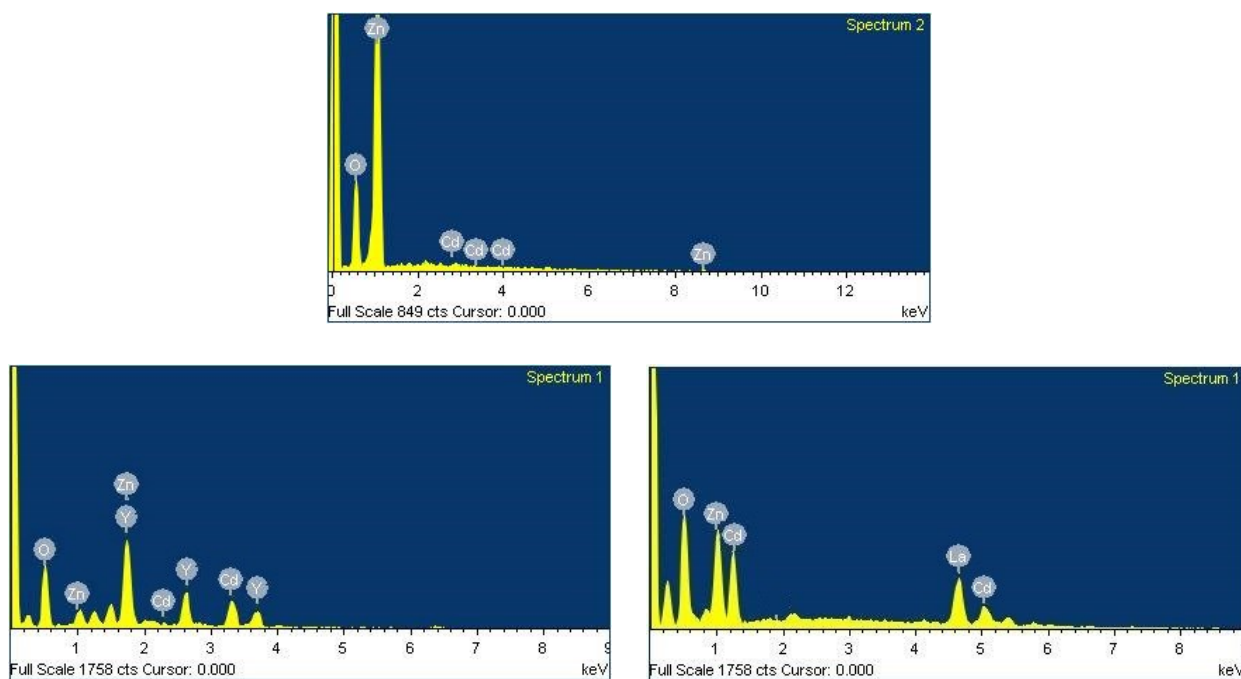


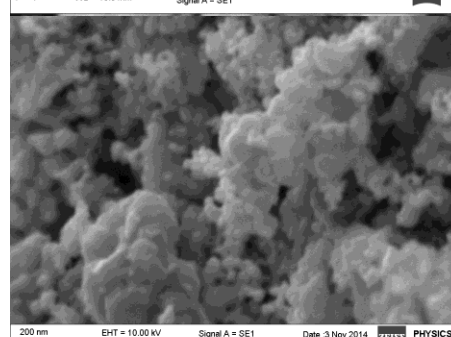
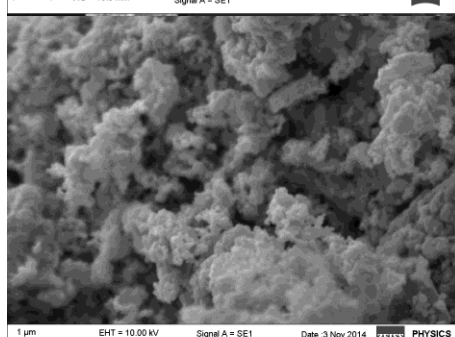
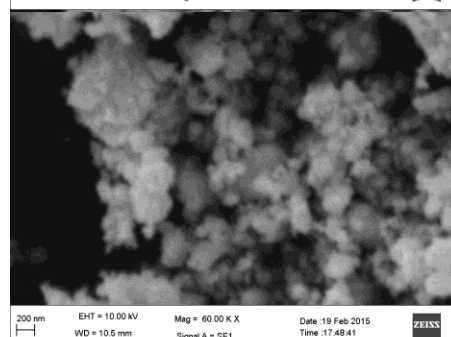
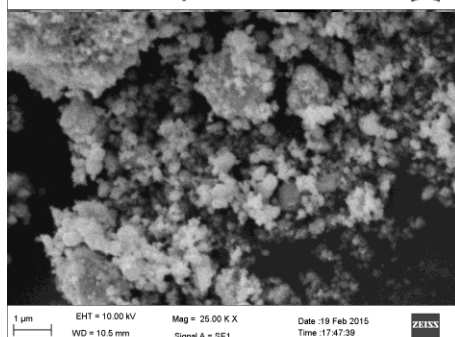
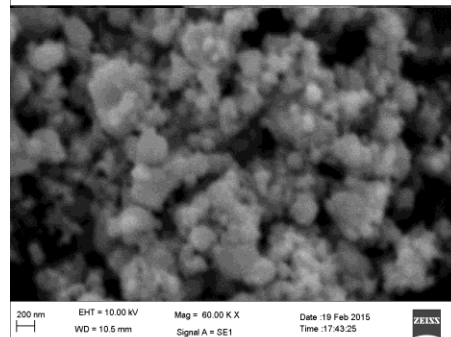
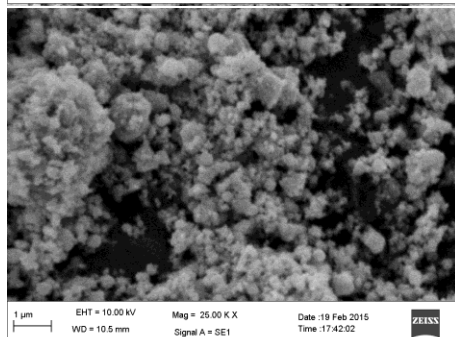
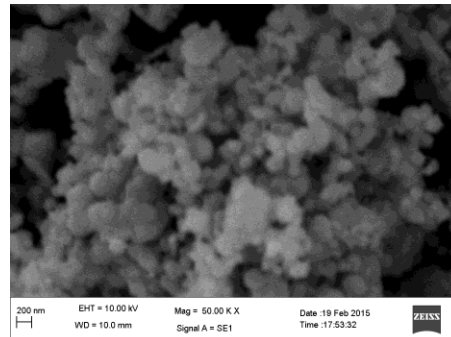
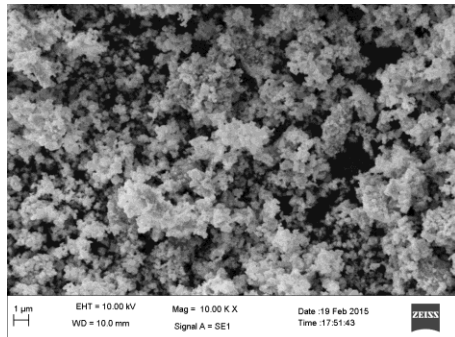
Figure 4: EDS Spectra of  $Zn_{0.98}Cd_{0.02}O$  (Top),  $Zn_{0.96}Cd_{0.02}O:Y_{0.04}$  (Left) and  $Zn_{0.96}Cd_{0.02}O:La_{0.02}$  (Right).

Sample	Weight percentages				
	Zn	Cd	O	RE (Y/La)	Total
Zn <sub>0.98</sub> Cd <sub>0.02</sub> O	77.84	2.73	19.43	--	100.00
Zn <sub>0.96</sub> Cd <sub>0.02</sub> O:Y <sub>0.02</sub>	75.81	2.72	19.32	2.15	100.00
Zn <sub>0.94</sub> Cd <sub>0.02</sub> O:Y <sub>0.04</sub>	73.82	2.70	19.21	4.27	100.00
Zn <sub>0.96</sub> Cd <sub>0.02</sub> O:La <sub>0.02</sub>	74.91	2.68	19.09	3.32	100.00
Zn <sub>0.94</sub> Cd <sub>0.02</sub> O:La <sub>0.04</sub>	72.08	2.64	18.76	6.52	100.00

Compositional analysis was performed by the EDS to further determine the doping of rare earths in host compound. The EDS analysis confirmed the presence of Zn, Cd, O and rare earth (Y, La) elements in the prepared samples. The carbon observed in the spectra may probably come from the carbon tape. The EDS spectrum taken on samples A, D and E is given in Fig. 3.2. The appearance of the Y, La peaks in the EDS spectrum of samples confirms the rare earth(s) incorporation in the powders. The weight percentages of samples are presented above table. From the table also we can confirm the composition of the prepared samples is in good agreement with the theoretical calculations.

### Microstructure analysis (SEM)

SEM is a promising technique for the topography study of samples, as it provides valuable information regarding the growth mechanism, shape and size of particles and/or grains. Fig. 3.3 shows the SEM images of prepared powders at different magnification to allow a review of the complete growth phenomenon of the samples. The growth of the samples was observed to be uniform and well covered. From SEM Fig. 3.3, it was observed that all the prepared powder samples are smooth, homogenous and densely packed with uniform growth of material. This image shows nature of the powders and the particles are spherical.



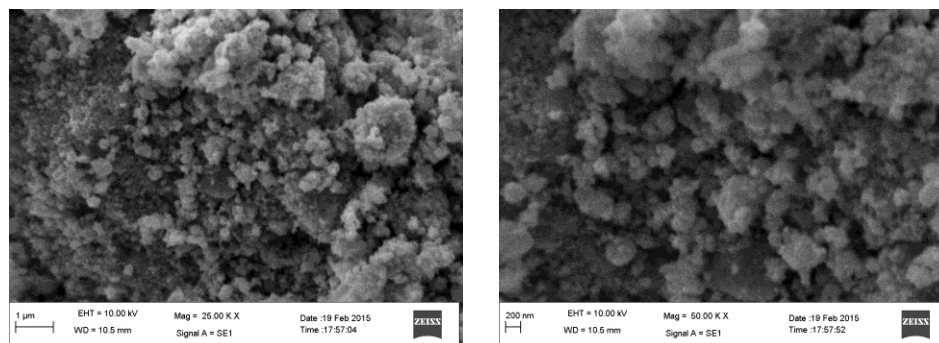


Figure 5: Microstructure (From Top to bottom) of  $Zn_{0.98}Cd_{0.02}O$ ,  $Zn_{0.96}Cd_{0.02}O:Y_{0.02}$ ,  $Zn_{0.96}Cd_{0.02}O:Y_{0.04}$ ,  $Zn_{0.96}Cd_{0.02}O:La_{0.02}$  and  $Zn_{0.96}Cd_{0.02}O:La_{0.04}$  samples respectively.

### Fourier Transform Infra Red Spectroscopy (FTIR)

The quality and composition of the prepared powders were characterized using the FTIR spectroscopy at room temperature in the range of 400– 4000  $cm^{-1}$  and shown in Fig. 3.4. The obtained spectrum show absorption bands around 498  $cm^{-1}$  and 441  $cm^{-1}$  which are the typical characteristic bands of the wurtzite hexagonal phase pure ZnO and CdO respectively [90]. Moreover, the band at around 3434  $cm^{-1}$  is related with the existence of hydroxyl group while the bands at 1360 and 1601  $cm^{-1}$  are due to the presence of C–O and C=O, respectively.

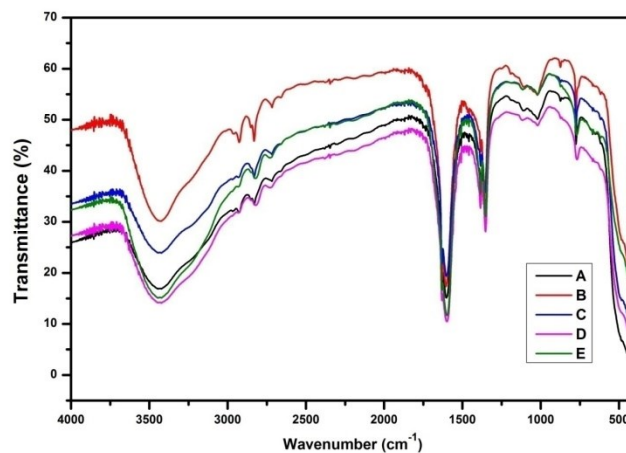


Figure 6: FTIR spectrum of  $Zn_{0.98}Cd_{0.02}O$ ,  $Zn_{0.96}Cd_{0.02}O:Y_{0.02}$ ,  $Zn_{0.96}Cd_{0.02}O:Y_{0.04}$ ,  $Zn_{0.96}Cd_{0.02}O:La_{0.02}$  and  $Zn_{0.96}Cd_{0.02}O:La_{0.04}$  samples respectively.

### UV-Visible Spectroscopy:-

The optical transmittance and absorbance spectra of the  $Zn_{0.98}Cd_{0.02}O$  and  $Zn_{0.98}Cd_{0.02}O:RE$  (RE=Y, La) samples in the wavelength range of 250–850 nm.

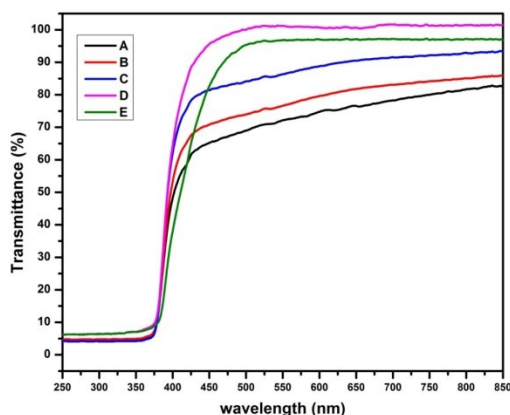


Figure 7: Optical Transmittance spectra of prepared  $Zn_{0.98}Cd_{0.02}O$ ,  $Zn_{0.96}Cd_{0.02}O:Y_{0.02}$ ,  $Zn_{0.96}Cd_{0.02}O:Y_{0.04}$ ,  $Zn_{0.96}Cd_{0.02}O:La_{0.02}$  and  $Zn_{0.96}Cd_{0.02}O:La_{0.04}$  nanopowder samples.

In order to determine the dependence of the band gap energy on the amount of cadmium in ZnO, the position of the transmittance's first derivative peak is measured. It is expected that the transmittance's first derivative diverges at

$\lambda_g = hc/E_g$ , where  $\lambda_g$  is the position of maximum peak for the samples. The position of the peak being a measurement of the band gap energy,  $E_g$ . The first derivative of transmittance with respect to wavelength ( $dT/d\lambda$ ), determines the band gap energy for the nanopowders [91,92]. According to our optical data analysis, the band gap energies were measured at 3.34, 3.30, 3.26, 3.21 and 3.25 eV for the  $Zn_{0.98}Cd_{0.02}O$ ,  $Zn_{0.96}Cd_{0.02}O:Y_{0.02}$ ,  $Zn_{0.96}Cd_{0.02}O:Y_{0.04}$ ,  $Zn_{0.96}Cd_{0.02}O:La_{0.02}$  and  $Zn_{0.96}Cd_{0.02}O:La_{0.04}$  nanopowders respectively. The observed peak position and energy gap values are tabulated in below table, which clearly shows the rare earths concentration effect on size and band gap of prepared samples.

Sample	$dT/d\lambda$ Peak position (nm)	$E_g$ (eV)
$Zn_{0.98}Cd_{0.02}O$	371	3.34
$Zn_{0.96}Cd_{0.02}O:Y_{0.02}$	375	3.30
$Zn_{0.94}Cd_{0.02}O:Y_{0.04}$	380	3.26
$Zn_{0.96}Cd_{0.02}O:La_{0.02}$	386	3.21
$Zn_{0.94}Cd_{0.02}O:La_{0.04}$	381	3.25

## Conclusions

In this work, I present the investigation of rare earth doping on  $Zn_{0.98}Cd_{0.02}O$  prepared by the sol-gel process. The structural, morphological and optical properties of the synthesized powders were analyzed by XRD, SEM, EDS, FTIR and UV-Vis spectroscopy techniques. The result obtained from the above characterization methods show the nano-metric size of the  $Zn_{0.98}Cd_{0.02}O$  crystallites and demonstrate that the introduction of yttrium, lanthanum in the host cation which is confirmed by EDS study. From XRD and SEM, the particle size, grain sizes are randomly varied due to the lattice distortions from host Zinc atom to the rare earths. While the all metal oxide bonds are observed from FTIR analysis. The optical band gap is reduced because of the rare earth doping. The band gap tuning useful in LED applications.

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