# Study of Structural, Morphological, Optical and Electrical Properties of Metal doped zinc oxide nanoparticles

M.Sc. thesis

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# DISCIPLINE OF PHYSICS INDIAN INSTITUTE OF TECHNOLOGY INDORE JUNE, 2018

# Study of Structural, Morphological, Optical and Electrical Properties of Metal doped zinc oxide nanoparticles

# **A THESIS**

Submitted in partial fulfillment of the requirements for the award of the degree of Master of Science

by

**RAMRAJ MEENA** 



# DISCIPLINE OF PHYSICS INDIAN INSTITUTE OF TECHNOLOGY INDORE

**JUNE, 2018** 



#### INDIAN INSTITUTE OF TECHNOLOGY INDORE

#### **CANDIDATE'S DECLARATION**

I hereby certify that the work which is being presented in the thesis entitled Study of Structural, Morphological, Optical and Electrical Properties of Metal doped zinc oxide nanoparticles in the partial fulfillment of the requirements for the award of the degree of MASTER OF SCIENCE and submitted in the DISCIPLINE OF PHYSICS, Indian Institute of Technology Indore, is an authentic record of my own work carried out during the time period from July 2016 to June 2018. Thesis submission under the supervision of Dr. Somaditya Sen, Associate Professor, Discipline of Physics.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

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This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.

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# Dedicated to Lord Krishna

# **ACKNOWLEDGEMENTS**

I am deeply grateful to my supervisor Dr. Somaditya Sen whose motivation and valuable ideas kept me on track during this journey. His constant support, valuable advices, constructive criticism and extensive discussion helped me in accomplishing my M.Sc. research project. Moreover, his principles, noble thoughts, fatherly care and simplicity always influenced me and will always help me in becoming a good person. It has been my privilege and honor to work with him and has been a great learning experience for me throughout my study at IIT Indore.

I take this opportunity to sincerely acknowledge Dr. Krushna R. Mavani and Dr. Rajesh Kumar (PSPC) for evaluating and giving their valuable comments for improving my research work. I want to thank whole science department for providing all resources and facilities for accomplishing my M.Sc. thesis. I thank SIC facilities of IIT Indore. Writing M.Sc. thesis without the help of colleagues is not possible. I sincerely thank my Ph. D Scholar Tulika Srivastava, Arun Kumar Yadav, Gaurav Bajpai, Anita Verma, Nashima Khatoon, Saurav, Prashant Mishra, Ruhul Amin and all the lab members for providing friendly and fulfilled environment in the lab. In particular, I want to special thank Ph.D. Scholar Tulika Srivastava Prashant Mishra and Ruhul amin for providing positive feeling to my work. I thank Dr. E.G. Rini for her advices and motivation. I sincerely thank Dr. Swasti Saxena also. Last but not the least, I express my sincere gratitude to my mother and my brother for all the sacrifices they made on my behalf. My mother is always being a source of encouragement and inspiration to me throughout my life. My brother always tries to bring smile on my face in every situation.

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# <u>Abstract</u>

A detailed study was carried out to investigate the effects of  $Ga^{3+}$  on structural, morphology, vibrational, optical and electrical properties of ZnO (x = 0, 0.01, 0.03, & 0.04) polycrystalline powders synthesis via a sol-gel method. Rietveld refinement of powder x-ray diffraction data showed that all samples are in hexagonal Wurtzite (with space group  $P6_{3}mc$ ) phase at ambient temperature. The lattice parameters increases, crystallite size increases from 50.90 nm to 89.28 nm, and strain decreases from 0.0026 to 0.0014 for x = 0, and 0.04 composition respectively. Vibrational study also revealed that all samples are in single phase. FESEM images show the hexagonal morphology for ZnO nanoparticles and become denser with increase in gallium doping. Ga doping increases optical band gap of ZnO from 3.18 eV to 3.28 eV for x = 0 & 0.04 respectively, due to decreasing defect level and stress. In addition, the I-V response indicates that the electrical conductivity is highly improved with Gallium doping. All samples are applicable as a TCO material.

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# Abbreviations

DMS	Dilute Magnetic Semi-conductor
RTFM	Room Temperature Ferromagnetism
XRD	X-ray Diffraction
DDIW	Distilled deionized water
TGA	Thermo-gravimetric Analysis
FESEM	Field Emission Scanning Electron Microscopy
LCD	Liquid-Crystal Display
LED	Light Emitting Diodes
TCO	Transparent conducive oxide

# **Chapter 1**

### Introduction

#### Introduction:

Zinc oxide (ZnO) is a II-VI semiconductor. It is a white powder which is insoluble in water, and it is widely used as an additive in numerous materials and products including rubbers, plastics, ceramics, glass, cement, lubricants, paints, ointments, adhesives, sealants, pigments, foods, batteries, ferrites, fire retardants and first-aid tapes. Although it occurs naturally as the mineral zincite, most zinc oxide is produced synthetically. It is a unique material with wide direct band gap of 3.37eV and large exciton binding energy of 60 meV. It is nontoxic material which is cheaply available in market. ZnO can be grown in varieties of morphological like nano rod, nano needles and Nano flower etc. Transition metal doped semiconductors have aroused huge research interest due to their robust magnetic properties which makes such materials of enormous technological importance. In dilute magnetic semi-conductor (DMS) a fraction of the host atoms is replaced by magnetic atoms resulting a magnetically active solid solution. The new class of semiconductor nanostructures having combine magnetic, optical and electronic properties have applications in the field of spintronic and nano electronics. A large number of research work has been published after the theoretical prediction on the room temperature ferromagnetism (RTFM) exhibited by transition metal doped zinc oxide (ZnO). Many synthesis routes like sol-gel, hydrothermal, co-precipitation, wet chemical method etc. has been used to obtain high quality nano/microstructure ZnO material [1]

#### **1.1 Crystal Structure:**

Zinc oxide crystalizes mainly in two forms: Hexagonal Wurtzite and cubic zinc blende. The Wurtzite structure is the most stable (thermodynamically) at ambient conditions and most common. The zinc

blend form can be stabilized by growing ZnO on substrates with cubic lattice structure. In both cases, the zinc and oxide centers are tetrahedral, the most characteristic geometry for Zn(II). ZnO converts to the rock salt structure at relatively high pressures about 10 GPa. The most stable Hexagonal Wurtzite structure belong to the space group  $P6_{3}mc$ . It has lattice parameters: a=b3.2501Å, c=5.2071Å and is characterized by two interconnecting sub lattices of Zn<sup>2+</sup> and O<sup>2-</sup> where each anion is surrounded by four cations at the corners of a tetrahedron with a typical  $sp^{3}$  covalent bonding. The number of alternating planes of tetrahedrally coordinated O<sup>2-</sup> and Zn<sup>2+</sup> ions which are pilled alternately along c-axis (Figure 1.1) describe the Wurtzite structure of ZnO.





ZnO is generally found to be n-type structure. This n-type is due to the structural point defect (vacancies and interstitials), notably the presence of oxygen vacancies in ZnO lattice gives it n-type conductivity.

Crystal Structure	Wurtzite	Cubic Zinc Blend
Space group	P6 <sub>3</sub> mc	F43m
Lattice constant	a=b=3.2501Å,	a=b=
	c=5.2071Å	c=5.4093Å
Coordination	Tetrahedral	Cubic
Geometry		

Table 1.1 Crystal Structure and Lattice parameters

#### **1.2 Properties**

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

ZnO (Pure) is white (in colour) and it change into yellow colour on heating. Its molecular weight is 81.38 g/mol. ZnO has density of 5.607 g/cm<sup>3</sup>. Under high pressure, the melting point of ZnO is 1900°C and its heat capacity is 9.62cal/deg /mole at 25°C. It is insoluble in water but soluble in nitric acid.

#### **1.2.2 Chemical Properties:**

ZnO occurs as a white powder. The mineral zincate usually contains manganese and other impurities that confer a yellow to red color. Crystalline zinc oxide is thermo-chromic, changing from white to yellow when heated and in air reverting to white on cooling. This colour change is caused by a small loss of oxygen to the environment at high temperatures. Zinc oxide is an amphoteric oxide. It is nearly insoluble in water, but it is soluble in (degraded by) most acids, such as hydrochloric acid,

 $ZnO + 2HCl \rightarrow ZnCl_2 + H_2O$ 

Bases also degrade the solid to give soluble zincates,

$$ZnO + 2NaOH + H_2O \rightarrow Na_2 [Zn (OH)_4]$$

ZnO reacts slowly with fatty acids in oils to produce the corresponding carboxylates, such as oleate or stearate. ZnO forms cement-like products when mixed with a strong aqueous solution of zinc chloride and these are best described as zinc hydroxyl chlorides, used in dentistry. ZnO also forms cement-like material when treated with phosphoric acid, related materials are used in dentistry. A major component of zinc phosphate cement produced by this reaction is hoplite, Zn<sub>3</sub>(PO4)<sub>2</sub>·4H<sub>2</sub>O. ZnO decomposes into zinc vapour and oxygen at around 1975 °C with a standard oxygen pressure. In a carbothermic reaction, heating with carbon converts the oxide into zinc vapour at a much lower temperature (around 950 °C).

$$ZnO + C \rightarrow Zn (Vapor) + CO$$

Zinc oxide can react violently with aluminum and magnesium powders, with chlorinated rubber and linseed oil on heating causing fire and explosion hazard. [2]. It reacts with hydrogen sulfide to give the sulfide. This reaction is used commercially:

$$ZnO + H_2S \rightarrow ZnS + H_2O$$

#### **1.2.3 Electrical Properties:**

ZnO has a relatively large direct band gap of  $\sim$ 3.3 eV at room temperature. Advantages associated with a large band gap include higher breakdown voltages, ability to sustain large electric fields, lower electronic noise, and high-temperature and high-power operation. The band-gap of ZnO can further be tuned to (3–4eV) by its alloying with other metal oxides. Mostly ZnO has n-type character, even in the absence of intentional doping. Non- stoichiometry is typically the origin of n-type character, but the subject remains controversial. An alternative explanation has been proposed, based on theoretical calculations, that

unintentional substitutional hydrogen impurities are responsible. Controllable n-type doping is easily achieved by substituting Zn with group-III elements such as Al, Ga, In or by substituting oxygen with group-VII elements chlorine or iodine. Reliable p-type doping of ZnO remains difficult. This problem originates from low solubility of p-type dopants and their compensation by abundant n-type impurities. This problem is observed with GaN and ZnSe. Measurement of p-type in "intrinsically" n-type material is complicated by the inhomogeneity of sample. [3].

Current limitation of doping does not limit electronic and optoelectronic applications of ZnO, which usually require junctions of n-type and p-type material. Known p-type dopants include group-I elements Li, Na, K; group-V elements N, P and As; as well as copper and silver. However, many of these form deep acceptors and do not produce significant p-type conduction at room temperature.

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

ZnO is a relatively soft material with approximate hardness ~5. Its elastic constants are smaller than other materials belonging to same group. The high heat conductivity, low thermal expansion and high melting temperature of ZnO are some of the basic characteristics of ZnO nanomaterial. High thermal conductivity makes it useful in rubber industry; ZnO is added in the rubber in order to increase the thermal conductivity of tyres. ZnO exhibits high radiation hardness property which makes it useful in space or at high altitude.

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

Various reports show that room temperature magnetism can be achieved by doping magnetic impurity in ZnO like Fe, Ni, Co etc. But preserving magnetism at room temperature in this material is still a challenge. Despite of many experimental results, the reason behind origin of magnetism in this material is not clear. In some cases, it is explained in

terms of segregation of metallic clusters while in other cases it is due to double exchange [4,5], Double exchange occurs between ions of different oxidation state which predicts the way by which electrons are transferred between two species.

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

According to reported literatures, the optical band gap of ZnO is 3.44eV at low temperature and 3.37eV at room temperature which corresponds to energy of 375.75Å photons. So, zinc oxide is transparent to visible light but strongly absorbs ultra violet light below 375.75Å. Due to this reason, ZnO is used in varieties of optoelectronic applications like Light Emitting Diode (LED's), Solar Cells, photo detectors etc. [6,7,8], The band gap of ZnO depends upon the carrier concentration; Band gap decreases with an increase in carrier concentration. Photoluminescence of ZnO represents a relatively sharp absorption peak at 380nm (due to band transitions) and a wider yellow-green emission band (due to presence of oxygen vacancies and other related defects.

#### **1.2.7 Opto-electronic properties:**

ZnO has a large exciton binding energy around 60 meV at room temperature due to excitonic recombination [8]. This large exciton binding energy makes efficient excitonic emission in ZnO which suggests ZnO a promising material for optical devices at room temperature and higher. The process of optical absorption and emission are very much influenced transition related to dopants or defects which are usually responsible for creating mid gap discrete electronic state [8]. Many reports show that the photoluminescence of ZnO shows green emission and the intensity of green emission increases with decrease particle size and reduced nanowire diameter which gives quantum size effect. The reduction in particle size increases the binding energy and which in turn enhances the Opto-electronic property of ZnO nanomaterial.

#### 1.3 Doping in ZnO:

Wide bandgap semiconductors such as GaN and metal oxides such as ZnO show doping asymmetry. Basically The materials occur naturally as n-type or p-type and it is quite difficult to achieve stable opposite conductivity by conventional extrinsic doping methods. Impurities and deliberate doping with differently charged ions have remarkable effects on the defect equilibria. Further Carriers in ZnO are introduced depending on whether the ions have a lower valence (e.g. Li<sup>1+</sup> introduces holes) or higher valence (e.g. Al3+ introduces electrons) than the Zn. Element doping offers a method to tailor electrical, optical, and magnetic properties of ZnO. For achieving n-type conductivity in ZnO, group III elements (B, Al, Ga and In), group IV elements (Si, Ge, Sn) on Zn- site and group VII elements (F, Cl) on O-site has been reported [9-13].

#### 1.4 Zinc oxide (ZnO) nanostructures:

ZnO nanostructures are of intense interest since they can be prepared by a variety of methods and in a range of different morphologies as shown in Figure 1.2. The variety of growth methods includes solution based methods which are low-temperature, scalable, simple and inexpensive. However, the primary motive of ZnO research is its great potential for a variety of practical applications, such as in optoelectronic devices, energy harvesting devices, electronic devices, sensors, catalysts, active compounds in sunscreens, etc.



Figure 1.2: Various morphologies of ZnO Nanostructures.

### **1.5 Applications:**

Because of its various chemical and physical properties, zinc oxide is widely used in many areas.



Figure 1.3: Worldwide consumption of zinc oxide



Figure 1.4: Schematic representation all the application of ZnO

It plays an important role in a very wide range of applications, ranging from tyres to ceramics, from pharmaceuticals to agriculture and from paints to chemicals. Figure 1.3 shows worldwide consumption of zinc oxide by region. In the figure below 1.4 summarized application paths of ZnO are presented.

#### 1.6.1 Rubber industries:

Between 50% and 60% of ZnO use is in the rubber industry. Zinc oxide along with stearic acid is used in the vulcanization of rubber. ZnO additive also protect rubber from fungi (medical applications) and UV light [14].

#### 1.6.2 The Pharmaceutical and Cosmetic Industries:

Due to its antibacterial, disinfecting and drying properties [15,16], zinc oxide is widely used in the production of various kinds of medicines. It was formerly used as an orally administered medicine for epilepsy, and later for diarrhea. At the present time it is applied locally, usually in the form of ointments and creams, and more rarely in the form of dusting powders and liquid powders. ZnO has properties which accelerate wound healing, and so it is used in dermatological substances against inflammation and itching. In higher concentrations it has a peeling

effect. It is also used in suppositories. In addition, it is used in dentistry, chiefly as a component of dental pastes, and also for temporary fillings. ZnO is also used in various types of nutritional products and diet supplements, where it serves to provide essential dietary zinc [17]. Due to their ability to absorb UV radiation, this material began to be used in creams.

#### **1.6.3 The Textile Industry:**

The textile industry offers a vast potential for the commercialization of nano-technological products. In particular, water repellent and selfcleaning textiles are very promising for military applications, where there is a lack of time for laundering in severe conditions. Also in the world of business, self-cleaning and water repellent textiles are very helpful for preventing unwanted stains on clothes. Protection of the body from the harmful UV portion of sunlight is another important area. Many scientists have been working on self-cleaning, water repellent and UV-blocking textiles [18-24].

For textile applications, not only is zinc oxide biologically compatible, but also nanostructured ZnO coatings are more air-permeable and efficient as UV-blockers compared with their bulk counterparts [25]. Therefore, ZnO nanostructures have become very attractive as UVprotective textile coatings. Different methods have been reported for the production of UV-protecting textiles utilizing ZnO nanostructures. For instance, hydrothermally grown ZnO nanoparticles in SiO<sub>2</sub>-coated cotton fabric showed excellent UV-blocking properties [26].

#### **1.6.4 The Electronics and Electro-Technology Industries:**

Zinc oxide is a new and important semiconductor which has a range of applications in electronics and electro-technology [27–29]. Its wide energy band (3.37 eV) and high bond energy (60 meV) [30,31] at room

temperature mean that zinc oxide can be used in photo-electronic [32] and electronic equipment [33], in devices emitting a surface acoustic wave [34], in field emitters [35], in sensors [36–41], in UV lasers [42], and in solar cells [43].

#### 1.6.5 Photo-catalysis:

Intensive scientific work has taken place in recent years on photocatalysis. In this process, an electron-hole pair is produced below the intensity of light by means of oxidation or reduction reactions taking place on the surface of the catalyst. In the presence of a photo-catalyst, an organic pollutant can be oxidized directly by means of a photogenerated hole or indirectly via a reaction with characteristic reactive groups (ROS), for example the hydroxyl radical OH $\cdot$ , produced in solution [44–46]. The photocatalytic properties of zinc oxide, titanium dioxide and ZnO-TiO2 composite were investigated by Guo et al. [47].

#### **1.6.6 Miscellaneous Applications:**

Apart from the applications mentioned above, zinc oxide can also be used in other branches of industry, including for example concrete production. The addition of zinc oxide improves the process time and the resistance of concrete to the action of water. Also, the addition of ZnO to Portland cement slows down hardening and quenching (it reduces the gradual evolution of heat), and also improves the whiteness and final strength of the cement.

Zinc oxide reacts with silicates (e.g., sodium silicate) to produce zinc silicates, which are water- and fire-resistant materials used as binders in paints. These fire-resistant and adhesive substances are used in the binding of cements used in the construction industry

ZnO is also used for the production of typographical and offset inks. It imparts good printing properties (high fluidity). The addition of ZnO means that the inks have better covering power, pure shade and high durability, and prevents darkening. Zinc oxide is also used in pigments to produce shine

It is added to many food products, including breakfast cereals. ZnO is used as a source of zinc, which is an essential nutrient. Thanks to their special chemical and antifungal properties, zinc oxide and its derivatives are also used in the process of producing and packing meat products (e.g., meat and fish) and vegetable products (e.g., sweetcorn and peas) [48].

#### **1.6 Selection of potential application:**

Zinc oxide is considered a special material, due to its chemical and physical properties. The wide range of properties offers to ZnO the possibility to be used in different technological domains, such as optoelectronics, solar cells and piezoelectric sensors. ZnO also attracted great interest as raw material in pharmaceutical and cosmetic industry, as pigment in paints, concrete and rubber industry, UV filter in products, textile industry and so on.

#### **1.7.1 Opto-electronic industry:**

ZnO is considered as a potentially attractive material for light-emitting devices in the ultraviolet (UV) region, because of its large exciton binding energy (60 meV). Due to its direct, wide bandgap of 3.37 eV, ZnO can be used as light-emitting diodes, photodetectors, in sensors, in solar cells and devices emitting a surface acoustic wave [49], [50]

#### 1.7.2 Cosmetic industry:

Due to its antibacterial and good antifungal activity, zinc oxide is widely used in production of various raw materials used in medicine such as disinfectant agents and for dermatological applications [51]. ZnO nanoparticles absorb UV radiation and can be used in sun protective creams [33].

#### **1.7.3** Concrete and rubber industry:

Zinc oxide is also used for concrete manufacturing, because by addition of ZnO powder, the processing time and resistance of concrete against water can be improved. Zinc oxide is known as additive in rubber industry, acting as activator for Sulphur vulcanization, by increasing the efficiency of the cross-linking system. Incorporation of zinc oxide filler in silicone rubber improves the mechanical and thermal properties.

Due to the high surface energy, ZnO nanoparticles have tendency to agglomerate and to form particles of large size in the polymer matrix of the coatings [52]. Thus, surface modification of ZnO is necessary to prevent the agglomeration of ZnO nanoparticles and also to ensure the perfect dispersion within rubber matrix [53].

#### **1.7.4 Textile industry:**

The applications of nanoparticles in textile industry become attractive because it provides high durability for treated fabrics due to large surface area and high surface energy that ensure better affinity for fabrics and leads to an increase of the desired textile functions [54].

The research work reported in present thesis has been accomplished systematically in following manner

(i) Synthesis of pure and doped ZnO samples

(ii) Analysis of structural properties of pure ZnO (strain. Lattic parameters etc) and its variation on increasing doping.

(iii) Analysis of Optical, Electrical and Morphological Properties of Pure ZnO and doped ZnO.

# **Chapter 2**

# **Experimental Techniques**

In this chapter we will know the basic information about the material synthesis procedure (sample preparation) and characterization techniques which is used in present research work. All presently studied samples have been prepared using sol-gel synthesis routes. In this present research, we have performed (i) X-ray diffraction (XRD) to confirm the formation of structural phase (ii) FESEM to study morphology and size of the material (iii) Raman spectroscopy to study the changes in vibrational modes in pure and Ga<sup>+3</sup>, doped ZnO (iv) UV-Vis spectroscopy to study the band gap affected by the defect states generated by doping.

#### 2.1 Material Synthesis Techniques:

Most of the present technological applications of ZnO, such as photodetectors, varistors, transparent conductive electrodes for solar cells, piezoelectric devices and gas sensors have made use of polycrystalline material that are synthesized by a variety of techniques like chemical vapour deposition [18–28], sol–gel synthesis [29–35], Hydrothermal [36–45], co-precipitation [46–50], mechano-chemical [51–56] etc. Although, range of solution based techniques have been emerged but among these sol-gel is the most versatile technique. This technique offers some advantage over other methods - It provides control over particle size and morphology, allows the use of low temperature during synthesis, reduces the cost and results in a homogenous and highly pure sample.

#### 2.2 Sol-gel synthesis techniques:

Sol-gel process is a known process since the late 1800s. The versatility of the technique has been rediscovered in the early 1970s when glass was produced without high temperature melting process [57]. Sol–gel

chemistry is the preparation of inorganic polymers or ceramics from solution through a transformation from liquid precursors to a sol and finally to a network structure called a 'gel' (figure 2.1). A "sol" is a colloidal suspension of solid particles of ions in a solvent. A "gel" is a semi-rigid mass that forms when sol begins to transform into a denser form in between solid and liquid by evaporation of the solvent. Particles or ions are left behind to join together in a continuous network.



Figure 2.1 Schematic diagram of sol-gel synthesis route

Formation of metal oxides involves connecting the metal centers with oxo (M-O-M) or hydroxo (M-OH-M) bridges, therefore generating metal-oxo or metal-hydroxo polymers in solution. After drying process, the liquid phase is removed from gel. In the sol–gel process, there are many different ways that a gel can be formed. Sometimes, the same precursors can result in very different structures with only small changes in conditions. Generally, gel state is simply defined as a non-fluid 3D network that extends through a fluid phase. In this route we use gelling agent "Citric acid". Citric acid is a small organic molecule which often used in sol–gel chemistry. Being a weak triprotic acid with three carboxylic acid moieties which are able to dissociate. It is readily

available and cheap making it an effective chelating agent. In a typical synthesis, aqueous metal salts (e.g. nitrates) are mixed with citric acid and the resulting solution heated to form a viscous solution or gel.

#### 2.2.1 Synthesis process:

ZnO nanoparticles were synthesized by sol-gel method [57], followed by solid state sintering. Schematic diagram and experimental steps evolved in nano powder synthesis using sol-gel technique (figure2.2).



*Figure 2.2: Schematic diagram of Sol-gel synthesis route of pure and doped ZnO.* 

ZnO powder (Alfa Aesar, purity 99.9%) was dissolved in HNO<sub>3</sub> [*ZnO* +2*HNO*<sub>3</sub>  $\rightarrow$  *Zn(NO*<sub>3</sub>)<sub>2</sub> + *H*<sub>2</sub>*O*] to form a Zn<sup>2+</sup> solution. A polymeric solution was formed by concentrated glycerol (Alfa Aesar, 99.9%) in de-ionized water at 70°C for 4hrs. The Zn solution was then added to the polymeric solution. This solution was stirred and heated on hot plates at ~60°C to obtain finally "gel-ready solution". The Zn ions get attached homogenously to the chains of the polymeric solution. The solution was gradually dehydrated to form gel in ~4hrs.

$$Zn(NO_3)_2 + C_6H_8O_7 + C_3H_8O_3 \longrightarrow$$
  
----[--(NO3)2--O--Zn--O--(NO3)2--]n---  
 $\longrightarrow$  ZnO + H\_2O + N\_2 + CO2

The gel was burnt on hot plates in ambient conditions to obtain yellowish white colored powders. These resultant powders were decarbonized and denitrified by heating in air at 450°C for 6 hours to form white powders of ZnO. The powders were further annealed at 600°C for 2 hours. For electrical characterization, the obtained white powders were pelletized under 3T pressure and sintered at 600°C for 2hr.

#### 2.2.2 Synthesis of Doped Sample:

For all doped samples the final "gel-ready solutions were prepared by obtaining a mixed solution of the constituent elements in the right proportions. The processes of obtaining these solutions are detailed in the following sections. For all doped samples the gels were burnt, decarbonized and denitrified similar to the process discussed in Section (a)

Ga<sup>+3</sup> doped ZnO synthesis:

 $Zn_{(1-x)}Ga_xO$  were synthesized for x=0, 0.0156, 0.0312, and 0.0468 named ZnG0, ZnG1, ZnG3, and ZnG4 respectively. Gallium nitrate [Ga(NO<sub>3</sub>)<sub>3</sub>] (Alfa Aesar (99%)) was used as a precursor for Ga<sup>+3</sup>. Appropriate amount of Ga precursor was dissolved in distilled deionized water (DDIW). These Ga solutions were then added to appropriate amount of Zn solution (prepared similarly as Section 2.2.1) to achieve ZnG1, ZnG3, and ZnG4.

 $Ga(NO_3)_3 + H_2O \rightarrow HO-(NO_3)_2-Ga + HNO_3$ 

The obtained homogenous mixtures containing Zn and Ga ions were constant stirred for several hours to obtain the "gel solutions".

$$Zn(NO_{3})_{2} + Ga(NO_{3})_{3} + HO-(NO_{3})_{2}-Ga + C_{6}H_{8}O_{7} + C_{3}H_{8}O_{3} \rightarrow$$

$$---[-(NO_{3})_{2}-O-Zn-O-(NO_{3})_{2}-Ga-(NO_{3})_{2}-]_{n}---$$

$$Zn_{(1-x)}Ga_{x}O + H_{2}O + CO_{2}\uparrow + N_{2}\uparrow$$

# 2.2.3 Denitrification and De-carbonization of synthesized pure ZnO:

Sol-gel processed pure ZnO powders need to be heated at a specific temperature in order to remove carbon, nitrates, moisture, and other undesirable material.

The denitrification and de-carbonization temperature also known as calcination temperature. Different materials have different calcination temperature which varies with synthesis condition and synthesis technique thermos-gravimetric analysis (TGA) has been done as shown in figure 2.3 The TGA curve for ZnO shows a weight loss in the temperature range of 0°C to 1000°C due to escape of adsorbed water molecules, nitrates, carbon and other undesirable materials. The first step is in the range of 80°C to about 350°C, demonstrating the loss of surface-adsorbed water. The second step, which is a major weightlessness step, occurs in the range of 350°C to about 420°C with no further weight loss up to 700°C temperature, indicating the loss of carbonates and nitrates [55,56].



Figure 2.3: Thermo-gravimetric analysis of pure ZnO in temperature range of  $0^{\circ}$ C to  $1000^{\circ}$ C showing loss of adsorbed water, nitrates and carbonates.

Considering the experimental evidence of removal of undesirable material from the sample above 420°C, all synthesized undoped and doped ZnO samples in this thesis work were calcined at 450°C 6h.

#### 2.3 Characterization Techniques:

We have synthesized all the samples (Metal doped ZnO samples) followed by sol-gel route and we have done following characterization techniques all these samples: (i) X-ray diffraction (XRD), (ii) Field emission scanning electron microscopy (FESEM) for Metal doped samples, (iii) Raman spectroscopy analysis and (iv) UV-Vis Absorption Spectroscopy.

#### 2.3.1 X-Ray Diffraction:

X–ray diffraction (XRD) is a basic characterization technique to assess the structure and hence the phase of a material. Using the fact that interatomic distances (d-spacing) of all matter are of the same order as X-rays wavelength,  $\lambda$  (Å), X-ray diffraction is a non-destructive method of assessing the d-spacing, and therefore the lattice constants. Strain and nano-crystalline size can also be estimated using XRD data. X-ray falls at an incidence angle,  $\theta$ , and gets diffracted by sets of atomic planes of the crystal lattice. When, d and  $\theta$  satisfy the condition that the path difference between diffracted rays generated by two parallel planes equals a multiple of  $\lambda$ , Bragg relation,  $2d\sin\theta = n\lambda$  (where, n is an integer), a constructive interference takes place. A schematic ray diagram explains the Bragg condition [figure 2.4]. By analyzing these constructive interference patterns, one can calculate the d-spacing and therefore the crystal structure. Geometrical path difference,  $\Delta$ , between two rays, PQR and P'Q'R',

$$\angle PQN' = 90^{\circ}$$
 So,  $\angle XQN' = \angle PQN' - \theta = 90^{\circ} - \theta$ 

Now 
$$\angle XQQ' = 90^\circ = \angle XQN' + U = 90^\circ - \theta + U$$

i.e.  $90^\circ = 90^\circ - \theta + U \Longrightarrow U = \theta$ 

Path difference =  $\Delta$ 

$$\Delta = N'Q' + Q'N = QQ'Sin\theta + QQ'Sin\theta = 2QQ'sin\theta = 2dSin\theta$$
(2.1)

For constructive interference, path difference must be an integer multiple of wavelength, i.e.,

$$\Delta = n\lambda \tag{2.2}$$

Thus, from equations 2.1 and 2.2, the Bragg's condition for constructive interference of diffracted X-rays is

$$n\lambda = 2dSin\theta$$
 (2.3)



Figure 2.4: Diffraction of X-rays through lattice/atomic planes of a crystal (indicating Bragg's law)

Where, n = integer.

The diffracted X-ray photons are detected and counted by a detector. Peaks arise whenever Bragg's condition is satisfied at specific  $\theta$  values corresponding to particular sets of planes. Conversion of diffraction peaks to d-spacing enables identification of the material under investigation. XRD patterns of each material are unique and are signatures of the materials' structural phase. This uniqueness of a set of d-values for a particular material identifies and validates the purity of a structural phase for given a material and provides information about the crystal structure, lattice parameters, bond angles, grain size, strain etc.

Instrumentation of XRD:

The main components of diffractometer are

- 1. X-ray Tube: the source of X Rays.
- 2. Incident-beam optics: to condition the X-ray beam before it hits the sample
- 3. Goniometer: the platform that holds and moves the sample, optics, detector, and/or tube



Figure 2.5: Schematic of XRD setup with different angles of rotation

- 4. Sample holder
- 5. Receiving-side optics: to condition the X-ray beam after it has encountered the sample
- 6. Detector: to count the number of X Rays scattered by the sample

Samples in powder, pellet or film forms can be probed for structural studies using XRD. Schematic of a typical x-ray diffractometer is shown in figure 2.5.  $\theta$  is the angle of incidence. Therefore,  $2\theta$  is the angle of diffraction, i.e. the angle between incident beam and diffracted beam.

#### 2.3.2 Field emission scanning electron microscopy(FE-SEM):

Morphological study of specimen has been carried out using FESEM [59]. In this work FESEM images were recorded using Supra TM 55; Carl Zeiss. In FESEM, electrons (negative ions) are incident on the surface atoms, very similar to visible light falling on matter. Due to a much smaller size of electron as compared to visible light it can resolute much better and can thereby see the sample's surface, topography,

morphology The energized electrons sometime while interacting with the atoms are capable of knocking x-ray from the same, by analyzing the x-ray spectrum, and thereby the composition of the materials.



Figure 2.6: Schematic Diagram of FESEM instrument

The interaction of electron (negative ions) and matter results in emission of secondary electrons (SEs), backscattered electrons (BSEs), Auger electrons, X-rays, etc. A FESEM instrument uses (i) SEs and (ii) BSEs for generation of images, x-rays for elemental analysis.

#### (a) Secondary electrons

Secondary electrons originate from the surface or near-surface region of the samples as a result of inelastic interaction between primary electron beam and the samples. They have lower energies ( $E \le 50eV$ ) and therefore electrons are ejected within few nanometers of the sample surface. In the work, the ejected electrons are detected by secondary electron detector.

#### (b) Backscattered electrons:

Backscattered electrons originate from broad region within the interaction volume. They generate due to elastic interaction between electrons (from electron gun) and atoms in the specimen which results in a change in electron trajectory. Backscattered electrons (BSE) consist of high-energy electrons (E>50eV), that are reflected by the specimen interaction volume by elastic scattering interactions with specimen atoms. Solid state detectors are used to detect backscattered electrons.

(c) Scanning Electron Microscopy (SEM) Imaging:

When the primary electron beam interacts with the sample, the electrons lose energy by repeated scattering and absorption. This interaction volume extends from less than 100 nm to approximately 5  $\mu$ m into the surface. The size of the interaction volume depends on the electron's energy, the atomic number of the specimen and the specimen's density. The energy exchange between electron beam and sample results in the reflection of high-energy electrons by elastic scattering, emission of secondary electrons by inelastic scattering and the emission of electromagnetic radiation, each of which can be detected by specialized detectors. The beam current absorbed by the specimen can also be detected and used to create images of the distribution of specimen current.

#### 2.3.2.1 Instrumentation:

The SEM requires an electron probe, a specimen stage to place the specimen, a secondary-electron detector to collect secondary electrons, a solid-state detector to collect backscattered electrons, an image display unit, and an operation system to perform various operations. Schematic diagram of FESEM instrument is shown in figure 2.6.

#### (a) Electron source

The illumination system of FESEM consists of an electron source/electron gun from which electrons are thermionically emitted. When electrons are ejected from electron guns, the temperature of the emitting metal becomes very high. Hence, due to its very high melting point and low vapor pressure amongst all metals, Tungsten is normally used in thermionic electron guns. The emitted electron beam, which typically has an energy ranging from a 100 eV to 30 kev, is passed through a magnetic lens system.

#### (b) Condenser lens and objective lens

The electron beam is further focused by a condenser lens to a spot  $\sim 0.4$  -5 nm in diameter. Two-stage lenses are located below the electron gun. The objective lens determines the final diameter of the electron probe up to 5 to 10 nm.

#### (c) Detector

A scintillator is coated on the tip of the detector and a high voltage of about 10 Kev is applied to it. The electrons hit the scintillator and generate light. Secondary electrons are detected by Everhart-Thornley detector. These electrons are accelerated towards a phosphor or scintillator positively biased to about +2,000 V. The accelerated secondary electrons are sufficiently energetic to emit flashes of light by the scintillator. A light pipe carries the photon signal from the scintillator inside the evacuated specimen chamber of the SEM to the photomultiplier outside the chamber. The amplified electrical signal output by the photomultiplier is displayed as a two-dimensional intensity distribution that can be viewed and photographed on an analogue video display, or subjected to analog-to-digital. The Everhart-Thornley detector (SEs Detector) is inefficient for the detection of backscattered electrons because it is positioned to one side of the specimen and also low positive charge cannot attract high energy

electrons. Therefore, solid state detectors are normally used having a pn junction. Electrons which escape the sample are absorbed by the detector in the depletion region and electron-hole pairs are generated. The number of these electron-hole pairs depends on the energy of backscattered electrons. One of the two electrodes of the p-n junction attract electrons while the other holes, thereby generating an electrical current. The value of the current is therefore proportional to number of backscattered electrons. The results are displayed on a liquid-crystal display (LCD).

#### 2.3.3 Raman Spectroscopy:

Raman spectroscopy is a spectroscopic technique used to observe vibrational, rotational and other low frequency phonon modes in a system [58]. It relies on inelastic scattering (Raman scattering) of monochromatic light (usually from a laser in the visible, near infrared or near ultraviolet range). The experimental set-up of Raman spectroscopy is shown in figure 2.7.





light interacts with phonons i.e. molecular vibrations in the system, resulting in modification of light. The modification gives information about the energy of the phonons of the system. The reflected light from the illuminated spot is collected with a lens and sent through a monochromator. Most of the reflected light is elastically scattered and is of the same wavelength as of the incident laser line (Rayleigh scattering). This is filtered out by either a notch filter or a band pass filter. Rest of the collected light is dispersed onto a detector. Spontaneous Raman scattering is typically very weak. Separating the weak inelastic Raman scattered light from the intense Rayleigh scattered laser light is a criticality. In this work Raman measurement was carried out on a RIR-M151 Research India micro-Raman system at room temperature, using 532 nm line of diode laser as an excitation source with 75 mW power.

#### (a) Laser:

Diode laser (Research Spectra) was used as an excitation source for Raman scattering experiments. Laser emission was accompanied by many spurious spontaneous emission lines which must be eliminated to avoid interference with the Raman emissions. Therefore, a laser-filter monochromator with a band pass of 1.0 nm (and transmission of 75 %) was used to eliminate the undesired plasma lines.

#### (b) Filter and microscope:

Standard microscope with three Plano chromatic objectives 10X, 50X and 100X, optically adapted to the aperture of the instrument. Other objectives with lower magnification can be used without a correct aperture adaptation which might introduce some vignetting effect. With the microscope, incident and scattered optical axis are identical i.e. back scattering geometry. Notch filters are used to remove Rayleigh scattering and pass Stokes and Anti-Stokes spectra. Normal mirrors and folding mirrors are used to focus the laser towards samples.

(c) CCD detector and recording system:

For this system, Peltier cooled CCD was used, working at  $\sim 215$ K is selected to offer highest performance to the system. Spectrometer is controlled by Research India software. The computer controlled scan range, integration time, scan speed and different scan units are available with the software.

#### 2.3.4 UV-Vis Absorption Spectroscopy:

When electromagnetic radiation (light) interacts with matter, various effects can be observed such as reflection, scattering, absorbance, transmittance and fluorescence phosphorescence. Total potential energy of a molecule can be represented as the sum of its electronic, rotational and vibrational energies. When energy of incident light is equal to the energy required to excite an electron from a lower energy level to higher level, the light is absorbed.

Basic working principal:

When light passes through a substance, the absorption of light takes place according to the *Beer-Lambert* law( $I = I_0 e^{-\alpha t}$ ). Amount of light absorbed is the difference between the incident radiation (Io) and the reflected or transmitted radiation (I). Quantitatively absorbance is described by equation (thickness t=1):

$$\alpha = -\ln\left(\frac{I}{Io}\right) \tag{2.4}$$

where,  $\alpha$  is absorbance, T is transmittance, Io and I are the intensities of incident and transmitted light respectively at a given wavelength. A UV-VIS spectrophotometer uses a tungsten-halogen or deuterium lamp as a source. A dispersion device like a monochromator is used to select the incident wavelength. A detector, which converts UV- visible light into electrical signal is the final component of the spectrophotometer. It is easy to calculate bandgap (Eg) from absorption spectra, in case of solid

films of known low thickness, due to low scattering properties. However, in colloidal samples, due to large surface area exposure scattering is enhanced. As dispersed light does not reach the detector it is counted as absorbed light. The technique (optical absorption) cannot distinguish between the two phenomena.

UV-Vis of powdered sample is carried out by dispersing it in the liquid medium like water, ethanol, methanol etc. For larger particle size, the particles precipitate. Thus, the spectrum is mostly due to the liquid. Diffuse reflectance spectroscopy (DRS) enables us to obtain Eg of powder samples, which scatter in perfectly diffuse manner. DRS works on Kubelka and Munk model, in which diffuse reflectance R is related to Kubelka–Munk function F(R) by

$$F(R) = \frac{(1-R)^2}{2R}$$
(2.5)

where, R denotes the percentage reflectance from the sample [60,61]. A graph between  $[F(R).hv]^2$  versus hv (in eV) can provide the Eg (band gap) values of a sample with direct bandgap. An indirect bandgap can be obtained from a plot of  $[F(R).hv]^{\frac{1}{2}}$  versus hv.

#### **Experimental Set-up:**

Spectrophotometers consist of a number of fundamental components: Light Sources (UV and VIS), monochromator (wavelength selector), sample holder, a detector, signal processor and readout.

The radiation source used is often a tungsten filament, a deuterium arc lamp which is continuous over the ultraviolet region, and more recently light emitting diodes (LED) and xenon arc lamps for the visible wavelengths. The detector is typically a photodiode or a CCD. Photodiodes are used with monochromators, which filter the light so that only light of a single wavelength reaches the detector. When measuring absorbance at the UV spectrum, the other lamp has to be turned off. The same goes when measuring visible light absorbance. Fig. 2.8 shows schematic diagram of UV–Vis Spectrophotometer.



Figure 2.8 experimental set-up of UV-Vis spectroscopy.

# **Chapter 3**

# **Results and discussion**

In this chapter we studied in detail about the effects of Metal ion (Ga<sup>+3</sup>) doping on ZnO. Structural, Morphological, Optical and Electrical behavior of ZnO and doped ZnO were discussed in this part. It also includes change in various parameters like: crystallite size, lattice strain, phonon vibration modes, optical band gap enhancement, and I-V conductance.

#### **3.1 Metal doped ZnO:**

#### **3.1.1 Structural Properties:**

Basically ZnO crystalizes mainly three forms:(i) hexagonal Wurtzite (ii) Cubic zinc blende (iii) Rock salt structure. According to the first principle periodic Hartree - Fock linear combination of atomic orbital theory, the hexagonal zinc oxide Wurtzite is found to be the most thermodynamically stable form [63]. Structural parameters like lattice parameters, strain, size etc. play an important role in determining its bandgap and other optical properties. Lattice parameters mainly depend upon the following factors [64].

- (i) Defect in lattice
- (ii) temperature
- (iv) strain
- (v) concentration of foreign substituted/doped atoms
- (vi) free electron concentration occupying conduction band minima
- (vii) difference in ionic radii of host and substituted atom.

So the metal ion doping or substitution generally generates distortion in the lattice introducing strain and thereby defects in the lattice.

#### 3.1.1.1 Doping effect of Ga<sup>3+</sup> on structural properties of ZnO:

Different concentrations of gallium were doped in ZnO lattice. When a  $Ga^{3+}$  ion (ionic radius ~ 0.61Å) is doped in ZnO lattice, Ga may go to an interstitial position due to its small size compared to both Zn<sup>2+</sup> and O<sup>2-</sup> ions (ionic radius ~ 0.74 and 1.24A respectively [65]). However, due to its +3 charge Ga<sup>3+</sup> will locally draw more oxygen than Zn<sup>2+</sup>. To compensate charge, a tendency of reduction of positive charge is natural. Thus, incorporation of Ga may be reason of decrease in oxygen vacancy. Hence, logically a substitution scenario is more probable, where lattice will arrange itself to accommodate Ga in the position of Zn, rather than an interstitial scenario. But this cannot continue for long as soon the oxygen dragged by increasing Ga<sup>3+</sup> concentration. The excess oxygen will drive the lattice to locally modify to other structures. However, all these changes must modify ZnO lattice parameters, strain, vibrational modes, electronic structure etc.

All the prepared samples were calcined and after that annealed at 600°C for 2h. 2h. The hexagonal Wurtzite ZnO structure was revealed from XRD studies as shown in Figure 3.1 (a). No secondary phases were found related to simple or complex oxides of Zn and Ga for x < 0.046, apart from some minor reflections of zinc blend. For x > 0.046, minor ZnGa<sub>2</sub>O<sub>4</sub> (zinc gallate) [61], like extra reflections appear. As discussed above x = 0.046 may be the solubility limit of gallium in ZnO where the Wurtzite structure does not get distorted enough to a rearrangement of a new structure. The ZnGa<sub>2</sub>O<sub>4</sub> structure is a result of bond arrangement.



Figure 3.1: (a) XRD reveals pure single phase of samples without the presence of any impure phases. (b) Crystallite size decreases as calculated from GSas software and also from Debye-Scherer formula.



Figure 3.2 SEM images showing morphology of the ZnG0, ZnG1, ZnG3 and ZnG4 samples.

 $Zn_{1-x}Ga_xO$  for x= 0, 0.0156, 0.0312 and 0.0468 (within solubility limit) have been named as ZnG0, ZnG1, ZnG3 and ZnG4, respectively, and will be discussed in this work. Field Emission Scanning Electron Microscopy (FESEM) [Supra 55 Zeiss] images show agglomerated particles for all samples [Figure 3.2]. From FESEM analysis it is observed that with increasing gallium doping in  $Zn_{1-x}G_xO$  material. it becomes denser.

The (002) peak shifts to lower angle with Ga<sup>3+</sup> incorporation [Table 3.1]. This indicates enhancement of c-axis from 5.144Å to 5.163Å with increasing gallium content. Such changes in lattice parameters may take place with possible substitution of Zn<sup>2+</sup> by Ga<sup>3+</sup> in ZnO lattice due to the excess oxygen in the Ga<sup>3+</sup> doped ZnO lattice which makes the lattice to enhancement. Average crystallite size was calculated from the XRD data using Scherer's formula. The crystallite size increases with substitution, from 80.9 to 66.67 nm [figure 3.1 (b)]. Size estimations using XRD is consistent with FESEM analysis. However, XRD values are smaller than the values obtained from SEM studies which reveal larger agglomerated particles composed of smaller crystals.

Table 3.1: (002) peak position and lattice parameter (c) in  $Ga^{3+}$ substituted ZnO

$Zn_{1-x}Ga_{x}O(X)$	Peak position (002)	c-axes parameter
	20 (°)	(Å)
0.00	34.366	5.207
0.0156	34.349	5.209
0.0312	34.304	5.21
0.0468	34.285	5.211



Figure 3.3: Rietveld refinement of ZnG0, ZnG1, ZnG3 and ZnG4 Rietveld refinement using GSAS software to changes in lattice parameters, crystallite size and strain with gallium substitution.



Figure 3.4 Rietveld refinement using GSAS software: lattice parameter

**Results and discussion** 



Figure 3.5 Rietveld refinement using GSAS software variation in (a) c/a ratio (b) Strain with Ga<sup>3+</sup> substitution.

X(concentration)	a=b	с	c/a ratio	Strain(S)
0	3.25	5.207	1.6021	0.0026
0.0156	3.251	5.209	1.6023	0.0024
0.0312	3.252	5.210	1.6021	0.0017
0.0468	3.253	5.211	1.6019	0.0014

Table 3.2: lattice parameter, c/a ratio and strain of Pure and doped ZnO

Variation of lattice parameters with doping is shown in figure 3.4. The ideal value of c/a strain-free single crystal ZnO is 1.63. From figure 3.5 (a), it is observed that c/a ratio of synthesized pure ZnO (ZnG0) is  $\sim$ 1.6021. With increasing substitution, the c/a ratio approaches to 1.6019 (in ZnG4), it indicates distortion and dis-orderness in the lattice with Ga doping. Strain is decreasing with increase in doping. Strain was calculated from using Eva software. Oxygen vacancies are

predominant defects found in ZnO due to which it shows n-type conductivity. The presence of Vo defect in ZnO at room temperature produce strain in that lattice. Substitution of  $Ga^{3+}$  at Zn<sup>2+</sup> site reduces this defect due to high charge of  $Ga^{3+}$  in comparison to Zn<sup>2+</sup>. Higher charge attracts more oxygen in the lattice and reduces oxygen vacancies, thereby reducing strain in ZnO lattice.

#### 3.1.2 Phonon vibration Modes (Raman spectroscopy):

Phonon vibrational modes were studied in detail [in Figure 3.6]. In hexagonal structures with  $C_{6v}^4$  symmetry, group theory predicts eight sets of phonon normal modes, namely, $2A_1+2E_1+2B_1+2E_2$ . Among them, one set of  $A_1$  and  $E_1$  mode are acoustic, while the remaining six modes, namely,  $A_1+E_1+2B_1+2E_2$ , are optical modes [63], The  $A_1$  and  $E_1$  branches are both Raman and infrared active, the two nonpolar  $E_2$ branches are Raman active only, and  $B_1$  branches are inactive.



Figure 3.6: Raman spectroscopy of Pure and doped ZnO (ZnG0, ZnG1, ZnG3 & ZnG4)

Raman phonon modes were also observed at 218.95cm<sup>-1</sup> 326.44 cm<sup>-1</sup>, ~378.70cm<sup>-1</sup>, 434.07 cm<sup>-1</sup> and 581 cm<sup>-1</sup> respectively. The non-polar  $E_2^{high}$  and  $E_2^{low}$  modes are due to relative vibrations of oxygen and zinc sub-lattices in two different orientations along c-axis. Intensity of  $E_2^{high}$  mode increases with substitution which reflects good crystallinity of Wurtzite ZnO. Thus, structural regularity improves with increasing doping. So there is a red and blue shift of  $E_2^{high}$  mode in the doped samples compared to pure ZnO (ZnG0).

For the single crystal the quantitative estimation of strain along a and b axes (exx and eyy) we can calculate using formula [71]:

$$\varepsilon_{xx} = \varepsilon_{yy} = -\frac{\Delta W.C33}{2(aC33 - bC13)} \qquad \dots \dots (3.1)$$

where,  $\Delta \omega = \omega - \omega_0$ , deformation potential constants, a = -774 cm-1 and b = -375 cm-1, elastic stiffness constants,  $C_{33} = 216$  GPa and  $C_{13} = 104$  GPa.

#### **3.1.3. Optical and electrical properties:**

**3.1.3.1.** Optical properties (Band gap investigation of pure and doped ZnO):

In order to understand the effect of Ga<sup>3+</sup> doping on optical properties of ZnO, bandgap modification has been investigated. The possible process behind this band gap modification has been discussed.

#### Bandgap Analysis:

Electrical bandgap was estimated using UV-Vis spectroscopy. Bandgap was calculated [Figure 3.6(a)] by plotting Tauc plot [69], using Tauc equation:

$$(\alpha h v)^2 = A(h v - E_g) \tag{3.2}$$

where,  $\alpha$  is absorption coefficient,  $\lambda$  is the wavelength, A is proportionality constant, v is the frequency of light and Eg is the

bandgap energy. The x-axis intercept of the extrapolated linear portion of this graph  $[(\alpha hv)^2$  versus hv] gives value of bandgap. Band gap was found to increase from 3.18 eV in ZnG0 steadily to 3.284 eV in ZnG4 [Figure 3.6(b)]. The band edges moved toward to closer wavelength side with increasing gallium doping levels partly shows enhancement in band gap energy. Similar result is reported in studies [65-66]



Figure 3.7: (a) Absorbance of ZnG0, ZnG1, ZnG3 and Zng4 [inset is x-intercept of the extrapolated lines to the linear portion of optical at the maximum slope of the  $(\alpha hv)^2$  versus hv] (b) Bandgap variation versus concentration.

#### 3.1.4 Electrical measurements (pure and Ga<sup>3+</sup> doped ZnO):

For electrical measurement, all the calcined powders annealed at 600°C were pressurized (3 tons) into pallets sintered at 600°C for 2hrs. Density of pellets were same for all samples. Sintering at 600°C was done to reduce porosity and remove moisture from the sample. The phase was

checked by XRD and Raman spectroscopy. There were no impurity peaks observed but the XRD peaks were sharper indicating increase crystallite size.

#### 3.1.4.1 Current-Voltage (I-V) Characteristics:

Pellets of uniform diameter (10mm) and thickness (1mm) were prepared. Silver paste was uniformly coated (as point contact with separation between them 1.3mm) on one sides of pellets and cured at the temperature of the silver paste ~150°C. I-V characteristics were measured in surface mode (two probe method ) [Figure 3.8] between - 10V to 10V. A rough estimation of conductivity could be measured by this method to analyze the effect of gallium doping on electrical properties of ZnO. Consistent and precise results were only obtainable for low voltages, most probably because Ohm's law is valid for low-voltage intrinsic regime of low-conductive materials.



Figure 3.8: Conductance behavior of ZnG0, ZnG1, ZnG3 & ZnG4.

Conductance was calculated from the I-V graph using relation:  $G = \frac{1}{R} = \frac{1}{V}$ , where R is resistance, I is the current, V is the voltage applied, [figure 3.9(a,b)]. The data reveals that Ga (gallium) incorporation increasing conductance of ZnO with increasing doping.

X G(K	$\Omega^{-1}$ ) 5V	10V
0.00	0.022	0.054
0.015	0.081	0.219
0.031	0.347	0.859
0.046	1.49	2.76

Table 3.3 Conductance at 5V and 10V



Figure 3.9 (a) Showing Conductance at 5V



Figure 3.9: (b) Showing conductance at 10V

# Chapter 4

# Conclusion

#### **Conclusion:**

We have prepared all the single phases samples of Ga<sup>3+</sup> doped using (Pechini) sol-gel synthesis route method with solubility limit. The solubility limit was ~4.68%. beyond the solubility limit secondary phase was observed. The characterizations study for all the prepared samples was carried out using XRD, FESEM, UV-Vis Spectroscopy, Raman Spectroscopy.

The XRD results shows the prepared samples are single phases with some minor peaks of Zinc blend and lattice parameters increase with increasing Ga<sup>3+</sup> doping. The UV-Vis spectroscopy results shows that the bandgap systematically increase with increasing doping. This could be due to higher bond energy of Ga-O (Ga-3d) states than Zn-O (Zn-3d) as Ga (gallium) more electronegative than Zn. As Ga is more electronegative than Zn.

Doping of Ga reduces strain in  $Zn_{(1-x)} Ga_x O$ . Hence we observe that by the doping strain decrease and crystallinity also become better drastically.

Also we observe that from surface morphology by FESEM analysis of all the prepared samples are denser and this material can be used to charge transportation.

Vibrational modes were studied using Raman spectroscopy. In  $Ga^{3+}$  doped ZnO, intensity of  $E^{2high}$  mode increases with  $Ga^{3+}$  substitution which reflects good crystallinity of Wurtzite ZnO.

Ga<sup>3+</sup> substitutions lead to increase in conductivity which was measured using I-V measurement system (Kethley Instrument 2401).

# Conclusion

#### **Future scope:**

Research work presented in this dissertation focuses on the effect of metal ion i.e.  $Ga^{3+}$  addition on defect structure, structural properties, and Opto-electronic properties of ZnO. All experimental characterization techniques which are required for analyzing properties of synthesized material has been carried out. Search of new functionalities utilizing these properties of modified ZnO like TCOs and UV/moisture sensors, etc. may lead to easier cheaper application in near future.

from above, possible future scope of work can be enlisted below:

- Modifying Ga-doped ZnO by co-doping K, Li etc.
- Synthesis of Ge-doped ZnO and performing a similar study to understand the difference between the two dopants
- Investigations of the role of ionic radii difference on structural and Opto-electronic properties.
- Investigating effect of defect modifications by selective doping to introduce magnetic properties of ZnO.

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