Photoluminescence investigation of hydrothermally grown ZnO and 3d transition metal (Mn/Co/Ni/Cu) doped ZnO nanostructures

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Photoluminescence investigation of hydrothermally grown ZnO and 3d transition metal (Mn/Co/Ni/Cu) doped ZnO nanostructures

Ph.D. thesis in the field of Physics

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Front cover: SEM images of hydrothermally grown ZnO nanoflowers

April 2016

Dedicated to my mother

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 25^{th} April 2016

Certificate

Certified that the work presented in this thesis entitled "Photoluminescence investigation of hydrothermally grown ZnO and 3d transition metal (Mn/Co/Ni/Cu) doped ZnO nanostructures" is based on the authentic record of research carried out by Vinod. R under my guidance and supervision at the Department of Physics, Cochin University of Science and Technology, Cochin-22, India and has not been included in any other thesis submitted previously for the award of any degree. I declare that all suggestions made by the audience during Pre-synopsis seminar and recommended by the Doctoral committee have been incorporated in the thesis.

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Declaration

Certified that the work presented in this thesis entitled "Photoluminescence investigation of hydrothermally grown ZnO and 3d transition metal (Mn/Co/Ni/Cu) doped ZnO nanostructures" is based on the original research work done by me under the supervision and guidance of Prof. M. Junaid Bushiri, Professor, Department of Physics, Cochin University of Science and Technology, Cochin-682 022 and has not been included in any other thesis submitted previously for the award of any degree.

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Preface

Nanoscience is one of the important branches of modern science which has potential applications in various areas of technology. Nanoscience is basically related to the study of materials at molecular and macromolecular levels, where its properties are mostly size and shape dependent. Optoelectronic as well as magnetic properties of the materials can be tuned by changing the size and shape to nanometer scale. Research on II-VI group wide band gap (WBG) semiconductors received great attention due to its interesting luminescence properties in the UV and visible region. Among these, ZnO is an important II-VI group wide direct band gap (3.37 eV) semiconducting material with a large exciton binding energy (60 meV) at room temperature. ZnO based nanostructures are identified to be good material for the fabrication of optoelectronic devices such as UV light-emitting diodes, LEDs, laser diodes, solar cells, gas sensors, and photo detectors etc. Further, investigation on transition metal doped ZnO (ZnO:TM) nanostructures can boost the existing fundamental knowledge and fabrication of optoelectronic as well as magnetic devices based on it.

Hydrothermal method is cost effective method for the growth of nanostructures compared with other high temperature physical or chemical vapor deposition methods. The optical properties of ZnO nanostructures depend on its morphology and size of the crystallites as well as influenced by the growth technique and transition metal dopants. The pressure dependent photoluminescence and Raman studies of ZnO nanostructures are interesting one since it possess different crystalline structures like wurtzite (B_4), rocksalt (B_1), and zinc blend (B_3). The present work is mainly focussed on the structural and optical properties of ZnO nanoflowers. Structural phase transition of ZnO nanoflowers under hydrostatic pressure is also presented in the thesis. This thesis has been classified in to seven chapters.

Chapter 1 consists of the general introduction of nanoscience and nanotechnology. This chapter gives an overview description about quantum confinement effect observed in nanostructures. Different synthesis methods, properties and applications of nanomaterials are also discussed. Importance of dilute magnetic semiconductors and transition metals doped semiconductors are elaborated. A detailed literature review of ZnO and 3d transition metal doped ZnO (ZnO:TM) nanostructures are also presented.

Chapter 2 describes the experimental set up for the low temperature hydrothermal growth of ZnO and ZnO:TM (3d) nanostructures. The different measurements and analysis techniques employed to characterize the materials are also included in this chapter. The schematic diagrams and working principles of the experimental set up and characterization tools are also included.

Chapter 3 deals with the low temperature hydrothermal growth of ZnO nanoflowers at an optimized temperature of 200 $^{\circ}$ C. The growth mechanism of ZnO nanoflowers under hydrothermal process is discussed. The structural, morphological and optical properties of the hydrothermally grown ZnO nanoflowers are analyzed in detail. ZnO nanoflowers are highly crystalline with a hexagonal wurtzite phase preferentially oriented along the (1 0 1) plane. The average length and diameter of the nanorods constituting the flower-like struc-

ture are 234-347 and 77-106 nm respectively. The band gap of ZnO nanoflowers is estimated as 3.23 eV. The Rietveld refinement analysis of the X-ray diffraction data reveal that stress relaxes elastically in ZnO nanoflowers grown using the hydrothermal process. The room temperature PL spectrum of ZnO nanoflowers shows a strong UV emission peak at 392 nm with a negligible visible emission related to the defect states as compared with the UV emission. Weak Raman bands at 541 and 583 cm⁻¹ are associated with the defect states in ZnO which confirms the significant reduction of the optical active defects. ZnO nanoflowers grown using the hydrothermal process at an optimized growth temperature and growth time can be used as a good UV emitting source in light emitting devices.

Chapter 4 reports the pressure-dependent photoluminescence and Raman spectral investigation of ZnO nanoflowers grown by hydrothermal method. Intrinsic near-band-edge UV emission from ZnO nanoflowers is monotonously blue shifted under pressures up to 13.8 GPa with a pressure coefficient of 26 meV/GPa, and this pressure value is nearly 5 GPa above the transition pressure from the wurtzite to the rock salt phase for bulk ZnO. The Raman band corresponds to the wurtzite phase, the $E_2(high)$ and $E_2(low)$ modes are observed up to about 11 GPa from the spectra. The progressive decrease of the PL and Raman signal suggests that the W-to-RS transition pressure is inversely correlated to the nanocrystal size. The smallest nanocrystals remain in the W phase up to 14 GPa, which is understood from the grain size calculated from the experimental Raman data.

Chapter 5 discusses the low temperature hydrothermal growth of ZnO:Mn nanorods under autogenous pressure. The influences of Mn ions on the structural, morphological, optical and magnetic properties of ZnO are explained. The ZnO:Mn nanorods (Mn - 3, 4 and 5 wt%) displayed variation in optical band gap with respect to dopants in ZnO nanoflowers. The blue shift of UV

emission peak (PL) from 392 (ZnO) to slightly lower wavelength region and quenching of photoluminescence emission in ZnO:Mn is due to the Mn incorporation in ZnO lattice. The presence of E_2 (high) mode at 437 cm⁻¹ in the Raman spectra with slight reduction in intensity in Mn alloyed ZnO nanorods reveals that wurtzite structure is retained in ZnO:Mn. The Raman and PL analysis confirms the good crystalline quality of ZnO which is slightly reduces as the Mn concentration increases in ZnO:Mn systems. The quenching of PL emission intensity in the UV region at around 392 nm as a result of nominal doping of Mn (Mn - 3, 4 and 5 wt%) in ZnO is attributed to the increase of non-radiative recombination process, reduced size of ZnO:Mn nanorods as well as comparatively lower quality of crystallites caused by Mn²⁺ incorporation into ZnO lattice.

The magnetic properties of Mn-doped ZnO (ZnO:Mn) nanorods have been studied using SQUID magnetometer. The magnetic behavior of ZnO:Mn nanorods depends on the doping percentage of Mn into the ZnO lattice. Hydrothermally grown ZnO nanorods exhibit a diamagnetic nature at 10 and 300 K. At room temperature (300 K), ferromagnetism is observed in ZnO:Mn (5 wt%) nanorods, while ZnO:Mn (3 wt%) nanorods show paramagnetism. The ZnO:Mn (3 wt%) and ZnO:Mn (5 wt%) nanorods exhibit spin-glass behavior below 150 and 140 K, respectively. The variation of magnetic behavior with respect to the level of Mn doping can be attributed to the population of Mn^{2+} ions in the ZnO crystalline lattice. The interaction between doped Mn^{2+} ions and the substitution of Mn^{2+} ions into Zn^{2+} sites and the increase in specific area of the grain boundaries are contributing factor for the origin of the magnetic behavior. ZnO:Mn nanorods with low radiative defects density synthesized by hydrothermal method at a reduced reaction time (3 h.) and low growth temperature (200 $^{\circ}$ C) can be a potential material for fabricating short-wave magneto-optical and spintronic devices.

Chapter 6 describe the hydrothermal growth of Co, Ni and Cu (3, 4 and 5) wt%) doped ZnO nanostructures under autogenous pressure and its characterization. The XRD analysis confirms the substitution of Co²⁺, Ni²⁺, and Cu²⁺ ions into ZnO lattice which is evident from the variation of lattice parameters 'a' and 'c' in the TMs (Co, Ni and Cu) doped ZnO samples. The $E_2(high)$ mode in the Raman spectra around 438 cm^{-1} further confirms wurtzite structure of the ZnO: Co/Ni/Cu samples. The presence of defect related Raman bands at 574 and 666 $\rm cm^{-1}$ that exhibited a shift and enhancement of intensity is contributed to the incorporation of Co²⁺, Ni²⁺, and Cu²⁺ ions into ZnO lattice. The DRS measurements shows the optical band gap of ZnO:Co (3, 4, and 5 wt%) nanostructures decreases with increase of the doping concentration. ZnO:Ni and ZnO:Cu (3, 4, and 5 wt%) samples, band gap is also decreased with increasing concentration of respective dopants. The PL studies reveal that intensity of the strong violet emission (400 to 420 nm) in almost all the samples decreases with increasing the doping concentration of the impurity ions. Room temperature ferromagnetism is observed in ZnO:Co (5 wt%) and ZnO:Ni (5 wt%) while ZnO:Cu (5 wt%) sample shows diamagnetic nature.

Chapter 7 presents major results, summary and conclusions. The scope of future studies is also highlighted in this chapter.

Journal Publications

- Enhanced UV emission from ZnO nanoflowers synthesized by hydothermal process, R. Vinod, P. Sajan, R. A. Sreekumar, M. T. Carmen, M. S. Vicente and M. J. Bushiri, J. Phys. D: Appl. Phys. 45, (2012) 425103.
- 2. Mn²⁺-induced room temperature ferromagnetism and spin-glass behavior in hydrothermally grown Mn-doped ZnO nanorods, **R. Vinod**, M. J.

Bushiri, P. Sajan, R. A. Sreekumar and M. S. Vicente , Phys. Status Solidi A. 211, (2014) 1155.

- Quenching and blue shift of UV emission intensity of hydrothermally grown ZnO:Mn nanorods, R. Vinod, M. J. Bushiri, R. A. Sreekumar and M. S. Vicente, Mater. Sci. Eng. B-Adv 191, (2015) 1.
- Pressure induced phase transition in hydrothermally grown ZnO nanoflowers investigated by Raman and Photoluminescence spectroscopy, M. J. Bushiri, R. Vinod, A. Segura and J. A. Sans, J. Phys.: Condens. Matter. 27, (2015) 385401.
- Boosted UV emission at 349 nm from mesoporous ZnS, P. Sajan, M. J. Bushiri and R. Vinod, Appl. Phys. A. 113, (2013) 321.
- High luminescent yield from Mn doped ZnS at yelloworange region and 367 nm, P. Sajan, R. Vinod and M. J. Bushiri, J. Lumin. 158, (2015) 110.

Conference publications

- Synthesis of flower like ZnO nanorods, R. Vinod, P. Sajan and M. Junaid Bushiri, National Symposium on Advances in Material Science and Technology (AMST-2012) at Gujarat University, Ahmedabad, Gujarat, India on 03-04 February, 2012.
- Hydrothermal growth of Manganese Oxide nanostructures, P. Sajan, R. Vinod and M Junaid Bushiri, National Symposium on Advances in Material Science and Technology (AMST-2012) at Gujarat University, Ahmedabad, Gujarat. India on 03-04 February, 2012.

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Chapter 1

Introduction to Nanoscience and Nanotechnology

1.1 Introduction

Nanotechnology is one of the important technologies of the modern era which is based on nanoscience. 'Nano' is a Greek word which means 'dwarf'. Nanoscience deals with phenomena of materials at atomic, molecular and macromolecular scales and its characteristics are different from that of the bulk scale materials [1]. In other words, nanoscience is the study of materials at nanometer regime, roughly 1 to 100 nanometers (nm) (1 nm = 10^{-9} m). But 'Nanotechnology' defines the design, synthesis/production, characterization, and application of nanostructures, devices and systems, basically changing the shape and size to nanometer scale [1]. Expressed in a different way, the science and technology of ultra fine particles are termed as Nanoscience and Nanotechnology. Science of materials at nanoscale is entirely different from that of the bulk and all the physical laws related to the behavior of bulk materials are changed. The more loosely bound surface atoms present in nanomaterials constitute a significant fraction of the sample, which will influence their properties and behavior. Nanostructures are termed as low dimensional materials and can be used for the fabrication of functional materials and devices. Nanomaterials exhibits unpredicted visual properties because these materials are too small to scatter visible light rather than absorb it. For example, gold is seems to be deep red to black when the size approaches nanoscale. The manipulation and control of individual atoms of the nanomaterials in a constructive manner which is the ultimate objective of the nanotechnology and these definition may be extended to the organization of objects having nano dimensions [2].

1.2 Materials at Nanoscale

Materials at nanoscale give dramatic change of its properties compared to the same mass of material synthesized in the large scale. The high surface areato-volume ratio is very important characteristic of nanoparticles. The surface area of nanomaterials are very large as compared to that of its volume. Because of this physical property, materials exhibit higher reactivity contributed to the presence of more electrons at the surface of the material [3]. In the case of conventional materials, most of the atoms are not on the surface. Physical and optical properties of nanomaterials are size depended, consequently its band gap, melting point, specific heat etc. are entirely different from that of the bulk material. These properties of nanostructures opens numerous chances for synthesizing new functional materials and facilitating chemical process [3, 4].

Another important property of nanomaterials is its quantum confinement effect. Quantum effect begin to dominate the properties of materials at the nanoscale, which contribute to novel optoelectronic and magnetic characteristics of materials. Size-dependent, quantum confinement is mostly seen in semiconductor particle. The surface plasmon resonance observed in some metal-

Quantum confinement

lic nanoparticles and superparamagnetism in magnetic materials are due to reduction of size of particles to nanoscale. Similar to magnetic and optical properties, the mechanical properties like flexibility of strength and electrical conductivity of the material are entirely different at nanometer regime. Normally, the optical energy band gap is shifted for nanomaterials which gives the possibility of tremendous applications in the semiconductor industry [3, 4].

Nanomaterials provided a stimulus to new applications of the nanotechnology since they exhibit novel optical, electrical, magnetic properties etc. The first generation of nanotechnology envisaged on performance improvement to existing micromaterials. Nanomaterials started to engage much more significant and comprehensive manner in second generation. The structural characteristics of materials at nanoscale can be obtained in the form of clusters, thin films, multilayers, and nanocrystalline materials. Generally, materials represented based on the dimensionality are 0D, 1D, 2D and 3D which include metals, amorphous, crystalline alloys, semiconductors, oxides, nitride and carbide ceramics in the form of clusters, thin films, multilayers, and nanoparticles, nanowires, nanodots etc.

1.3 Quantum confinement

The term quantum confinement, describes the confinement of the electron-hole pair within the physical boundaries of the semiconductor materials [5]. The electronic and optical properties of materials may change when its size is sufficiently small enough is termed as quantum confinement. And it is generally observed when the size of nanostructures are 10 nm or less. Quantum confinement effect is analogous to the quantum mechanical concept of particle in a box [5]. When the electron-hole pair (exciton) dimension approaches a critical quantum measurement, known as the exciton Bohr radius. The electronic excitation in a semiconductor crystal usually consists of a loosely bounded electron-hole pair (Mott-Wannier exciton), which is delocalized over a length much longer than the lattice constant [6, 7]. When the dimension of semiconductor nanocrystalline materials approaches this exciton Bohr diameter, its electronic properties will change. As a result, blue shift in the band gap or change in exciton energy may occur because of quantum confinement effect [8, 9]. The band structure and optical properties of materials may modified due to quantum size effect especially in ultra fine materials [4]. The optical energy band gap of the materials can vary as the size of the nanostructure decreases.

1.3.1 One dimensional Confinement: Quantum wells

A potential well structure which confines carriers to two dimensions and forcing them to occupy a planar region, is known as quantum well. These charge carriers may be electrons or holes. Quantum confinement effect can take place in the quantum well nanostructures when the quantum well diameter is comparable to that of the De Broglie wavelength of the carriers. This effect leads to formation of "energy sub bands" means the carriers can only have discrete energy values [3]. Recombination of electrons and holes takes place in a narrow line width or fixed wavelength in quantum well nanostructures. The confinement of charge carriers sometimes leads to the formation of electronhole pair, known as exciton, created by the strong Coulomb attraction. The confinement of excitons in a layer in which its thickness is less than excitonic Bohr diameter, the binding energy and the oscillator strength of the exciton increases [4]. This will leads to the stability of excitons at room temperature. The structures made of different materials in the form of layers is termed as heterostructures. The width of such layered materials join directly sometimes at the atomic level. In the case of two semiconductors which are joined two
Quantum confinement

different bands in the two materials will line up in energy with one another. Because of their quasi-two dimensional structure, the electrons in quantum wells have a sharper density of states than that of the bulk materials. This property of quantum wells are useful for the fabrication of diode lasers, high electron mobility transistors (HETMs) and low-noise electronic devices [10]. Quantum well infrared photo detectors are also used in low noise electronics and infrared imaging [11].

1.3.2 Two dimensional Confinement: Quantum wires

One dimensional nanostructures have a specific axial direction in which other two direction are spatially confined and is called quantum wires. It is like an electrical conducting wire, and the quantum confinement effects dominates its charge transport. It can simply defines as two dimensional confinement of electrons and holes [12]. This means the free carriers move only in one dimension. But in the case of bulk material, charge carries are free to move in all the three directions. One dimensional nanostructures exhibit different morphological varieties such as whiskers, nanowires, nanorods, nanofibers, nanocables, and nanotubes. Quantum wires have several merit over conventional nanostructures because of its high electrical conductivity attributed to the high mobility, light weight, low chemical reactivity and high tensile strength [13].

According to the existing literature about quantum wires, there are many reports on the metallic nanowires which are used as the gas sensors [14]. Apart from that, the quantum wired structures are used in dye sensitized solar cells for photovoltaic applications [15]. Nanowires of metallic elements are one of the best candidates for the substitution of metallic carbon nanotubes because of its high electrical conductivity, small diameter, low chemical reactivity and high tensile strength [13].

1.3.3 Three dimensional Confinement: Quantum dots

In quantum dots, charge carriers are confined in all the three dimensions in which the electrons exhibit a discrete atomic-like energy spectrum. Quantum dots made of semiconductors can confine the motion of conduction band electrons, valence band holes and excitons in three spatial directions [3]. The electrons are dimensionally confined just like an electrons confined near the nucleus. Quantum dots posses discrete energy levels so that it is termed as artificial atom. The electrons in a quantum dot represent a zero-dimensional electron-hole gas [16].

Variation in colour with respect to quantum dots size is one of the important optical properties of hyperfine quantum dots. Larger the size of the quantum dots, fluorescence bands may shift towards the the red end of the spectrum, which can be observed in the fluorescence spectrum. In the case smaller dot, blue shift is observed in fluorescence spectrum. The energy levels of the quantum dot especially its size is directly related to its coloration. The band gap energy of the quantum dot that determines the energy (and hence colour) of the fluorescent light is inversely proportional to the square of the size of the quantum dot. Quantum dots that are larger in size can have more closely packed energy levels [17]. This permits the quantum dot to absorb photons containing less energy, i.e., those closer to the red end of the spectrum [3]. Shape of the quantum dot is also a factor related to coloration, based on some of the recent research reports [3].

1.3.4 Confinement regimes

In bulk materials, the carriers can exist in nearly continues bands. The carriers are restricted to a specific set of completely quantized energy states in quantum dots due to the confinement of charges in all the three directions. The effect of

Quantum confinement

confinement on the resulting energy state can be represented with Schrodinger wave equation, for the carriers in a confined space.

Depending upon the confinement regimes energy state equations are different. Based on ratio between the nanocrystal radius 'a', and the bulk exciton radius 'a_x', there exists three different confinement regimes viz. strong confinement regime, weak confinement regime and intermediate stage. The strong and weak states are determined by the degree of coupling between the electron and hole in the exciton.

Strong confinement regime:- Strong confinement state occurs when the quantum dot radius a_0 is smaller than the excitonic Bohr radius a_B ,

i.e;
$$a_0 << a_B$$

which means as the degree of confinement is increased in a smaller dot, the exciton can no longer exist and therefore an electron and hole can be treated as an independent particle [18]. Interestingly, in this case, Coulomb forces are small compared with the quantization of the kinetic energy of the carriers (confinement regimes). When these conditions occur in a material the carriers are said to be strongly confined and the corresponding electron and hole wave function are uncorrelated. Therefore, the approach of solving the energy states in a strong confinement regime is similar to that of weak confinement regime with the electron and hole have independent Bessel function in strong confinement [19]. The resulting energy shift expression can be written as [20]

$$E = E_g + \frac{\hbar^2 \pi^2}{2eR^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - \frac{1.786e}{4\pi\epsilon_0\epsilon_r}R - 0.248E_{ex}$$

Where E is the band gap energy of the dots, E_g is the bulk band gap, R is the dot size. m_e^* and m_h^* are the effective masses of electron and hole respectively. The last term $0.248E_{ex}$, represents the correlation energy, which can be expressed in terms of the excitonic binding energy E_{ex} [21, 22].

Weak confinement regime:- When the quantum dot radius, a_0 is few times greater than the excitonic Bohr radius a_B , this corresponds to the weak confinement regime.

i.e.,
$$a_0 >> a_B$$

In this case Coulomb interaction energy is on the order of the electron and hole sublevel separations and it has to be taken into account. Here the electron and hole motion are strongly correlated via Coulomb interaction. And the energy spectra of the nanocrystal is determined by the quantization of the exciton center of mass. Expression for energy quantization in a spherical 0D structure is

$$E = E_g + \frac{\hbar^2 \pi^2}{2eMR^2} - E_{ex}$$

Where M is the translational mass of the exciton, which is the algebraic sum of the electron and hole effective masses, R is the mean dot size. This equation gives the shift in energy that occurs when a bulk solid exciton is confined into 3D in the range of 3 - 10 times the exciton Bohr radius. i.e, a blue shift in energy results as the size of the crystal decreases [21].

Intermediate stage:- There occurs a complex interplay between quantum confinement and Coulomb electron-hole interaction in the case of intermediate state energy structures. II-IV nanocrystals posses relatively large exciton Bohr radius which are convenient systems for the studies of the these three confinement conditions viz. strong, weak and intermediate regimes. The Coulomb interaction scale with the nano radius as a^{-1} where as the confinement energies proportional to a^{-2} . Therefore in the strong confinement regime, the Coulomb term in the Hamiltonian can be ignored which leads to a problem of independent quantization of electron and hole energies [21, 22]. Density of states

1.4 Density of states

The density of states is defined as the number of energy states present in a unit energy interval per unit volume of the material structure [23]. The density of states gives an idea of the energies when we combine the effect of confinement in one direction and unconfined in the remaining directions [24]. From analytical expressions of density of states, we can see the effect on the electronic structure for bulk semiconductor (unconfined in all direction) and semiconductor having confined in one direction, two and three directions [25].

The density of states for a three dimensional material (bulk) can be defined as [23],

$$N_{3D} = \frac{1}{2\pi^2} [\frac{2m}{\hbar^2}]^{3/2} \sqrt{E}$$

Now let us consider the density of states in a material structure having confinement in one direction (say z) such as a quantum well.

The comprehensive density of states can be written as

$$N_{2D}' = \frac{m}{\hbar^2 \pi} \sum_{n=1,2,\dots} \Theta(E - En_z)$$

Where Θ is a step function and

When
$$E = En_z$$
; $\Theta = 1$ and for $E \neq En_z$; $\Theta = 0$

But in one dimensional materials, two dimensions are confined i.e, in z and y directions and along x direction is unconfined.

The density of states for one dimensional system is as follows.

$$N_{1D}' = \frac{1}{\pi} \sqrt{\frac{2m}{\hbar^2}} \sum_{n_z, n_y} \frac{1}{\sqrt{E - En_z, n_y}} \Theta(E - En_z, n_y)$$

When $E = En_z, n_y; \Theta = 1$ and for $E \neq E_z, n_y; \Theta = 0$

In a zero dimensional material all three dimensions are confined (say z, y and x). In this case, there is no other dimension for the free motion of charge carriers. It is not having any allowed values of wave vector along x, y and z directions.

The density of states for zero dimensional system is shown below.

$$N_{0D}' = \delta(E - En_z, n_y, n_x)$$

Figure 1.1 shows the schematic representation of density of states of material.



Figure 1.1: Schematic representation of density of states

[23]

1.4.1 Concept of quasi particle: electron, hole and exciton

A conduction band electron in a crystal can be represented as particle with charge -e, spin $\frac{1}{2}$, effective mass m_e^* with quasi momentum $\hbar k$, based on conservation law. Charge and the spin of the electron will be same in vacuum and in a crystal.

Quasi particle are described as the elementary excitons of the system consisting of a number of real particle [23]. Based on this concept, an electron in the conduction band is the primary elementary excitation of the electron subsystem of a crystal. If elementary excitation is a hole, which is considered to be quasi a particle formed as a result of removal of an electron from an ensemble in the valance band. The holes are having positive charge, spin $\frac{1}{2}$, effective mass m_h^* and a proper quasi momentum [23].

Energy of a photon falling on a semiconductor material whose band gap energy is comparable to the energy of that photon. This photon may be absorbed by the electrons and form atomic bonds between neighbors and provide enough energy to break free electrons and move around in the body of the crystal [26]. This is a process in which exciting an electron from the valance band across the band gap into the conduction band. If the photon energy is larger than that of the band gap energy, a free electron may be formed consequently an empty state is left with in the valance band [26]. This empty state is known as holes which behaves as though it positively charged and hence forms a bond with the electrons in the conduction band. This bound electron-hole pair is known as exciton and attractive potential leads to the potential energy of the electron and hole [26].

1.5 Nanomaterials - synthesis and processing

There are wide variety of techniques which can be used for the synthesis of nanostructures with various degrees of quality, speed and cost. These manufacturing approaches generally belongs to two categories "top-down" and "bottom-up" [1, 27]. Figure 1.2 shows the schematic diagram of "top-down" and "bottom-up" approaches of nanomaterial synthesis.



Figure 1.2: Schematic illustration of Top-down and Bottom up approaches [27]

1.5.1 Top-down approach

A bulk material is physically or chemically reduced to nanometer size or successive cutting off, it is termed as top down approach. It is a versatile method for the bulk production of nanomaterials. In top-down synthesis method, a larger piece of material is made to small scale by different manufacturing techniques [26]. Ball milling, chemical etching and lithography etc. are the important top-down approaches used for the synthesis of nanostructures.

The product of lithographic technique is not smooth and can have the possibility of more impurities and structural defects on its surface. These defects may affect the surface behavior of nanomaterials. It may also cause the reduction of conductivity and excessive formation of heat. Top-down synthesis method instigate internal stress in materials in addition to surface defects and contaminations with respect to bottom-up methods. Crystalline imperfection especially on surface structure is one of the major issues of top-down approach which produce crystallographic damage to the materials. These damages are undesirable especially for the functionalization of these materials, design and fabrication of device based on it. Top-down approach is a reliable one and is not so complex even though it often requires higher usage of energy [27].

1.5.2 Bottom-up approach

The synthesis of nanostructures, atom by atom or molecule by molecule is termed as bottom-up approach [27]. In this approach, molecular components are arrange themselves into some useful conformation with the concept of molecular self-assembly. The bottom-up approach often produces nanostructures with less defects, homogeneous chemical composition as compared to that of nanostructures produced by the top-down approach [26]. Physical and chemical methods are used for synthesis of nanostructures which includes chemical synthesis, self-assembly, and positional assembly. Physical vapor deposition (PVD), Atomic layer deposition (ALD), Chemical vapor deposition (CVD), Pulsed laser deposition (PLD), sputtering etc. and chemical methods such as sol-gel method, hydrothermal method, spin coating, spray pyrolysis etc., are the major methods of preparation materials by bottom-up approach.

1.6 Characteristics of nanomaterials

Structural behavior of nanomaterials is in the midway between the atomic states and the bulk state. Majority of the microstructured materials shows identical behavior as that of its bulk counterpart. But in the case of nanoscale materials, the properties are entirely different from those of atomic state and bulk state materials. The major reason for deviation of behavior of nanometer sized materials are due to higher fraction of surface atoms, greater surface energy, spatial confinement, lower imperfections etc [3, 4, 28]. Surface area to volume ratio of nanomaterials are higher due to its small dimensions resulting more surface dependent material properties. Particularly when the sizes of nanomaterials are comparable to area, the entire material will be influenced by the surface properties of nanomaterials.

1.6.1 Mechanical properties

The mechanical properties of nanomaterials is quite interesting, since it is problematic to create macroscopic bodies with a large density and a grain size in the range of less than 100 nm [28]. Mechanical properties such as hardness, elastic modulus, fracture toughness, scratch resistance and fatigue strength etc., of the nanomaterials are different from that of the bulk materials due to the size reduction in nanometer scale [29, 30]. These enhanced mechanical properties of the nanomaterials could have many potential applications in mechanical nanoresonators, sensors, microscope probe tips and nanotweezers for nanoscale object manipulation, light weight high strength materials, flexible conductive coatings, wear resistance coatings, tougher and harder cutting tools [29] etc.

Variation in mechanical properties will modify structural characteristics of materials like, increased surface tension, and enhancement in diffusion properties etc. Thermodynamic notation efficiency of nanoscaled device will differ from its microscopic counterpart due to the thermal fluctuations, quantum noise [31] and changes in the efficiency of nanoscaled devices [32].

1.6.2 Physical properties

Majority of the physical properties of the material at nanoscale are quite different from that of the bulk. The material size is one of the important parameter at nanoscale and the size reduction alone often create qualitatively new behavior. Whenever the size of a nanostructure are less than the characteristic length scale for scattering of electrons or phonons (mean free path) new modes of transport will occur for electrical current or heat. This effect explains the discovery of persistent normal (non-superconducting) currents in mesoscale metallic rings and ballistic transport current in carbon nanotubes [33, 34]. Devices with sizes ranging nanometers lie at the soft boundary between the quantum and classical domains in which thermal energy fluctuations and Brownian motion can have remarkable effects.

In nanostructured materials, the reduction in thermal transport are expected, because of the phonon mean free path reduction due to grain boundary scattering. Reduced thermal conductivities in nanostructured Yttria stabilized zirconia (YSZ) is observed which is useful for applications such as thermal barrier coatings [35].

1.6.3 Chemical properties

The change in structure as a function of particle size is related to its electronic properties. The energy required to remove an electron (ionization potential) is generally larger for small atomic clusters with respect to bulk material. The ionization potential sometimes show fluctuations as a function of the cluster size which may effects the chemical reactivity of the materials [36].

Higher surface area to volume ratios of the nanostructures produce alteration in chemical reactivity. Nanostructured catalyst can increase the rate of efficiency of the chemical reaction and reduce the waste and pollution. The solubility of nanostructured materials in water are higher than the bulk material due to its high reactivity. Further, the ionization potential exhibits fluctuations with respect to its cluster size and this effects appear to be linked to chemical reactivity of the materials. Thermodynamic behaviors, some collective phenomena and phase transitions conditions, ferromagnetism, ferroelectricity, and superconductivity of the materials changes when chemical structures contain a small particles [36].

1.6.4 Biological properties

Nanomaterials are promising tools for diagnostic biosensors, drug and gene delivery systems, and imaging for tissues etc. Nanomaterials have distinct physicochemical and biological properties [37]. Size tunable light emission from nanomaterials have been employed to get images of tumor sites. Nanomaterials also employed for treatment of microbes because of its antimicrobial properties.

1.6.5 Structural properties

There are numerous applications of nanostructures have been proposed in the areas of photonics and photocatalysis [38, 39]. Recently, a rapid improvement is observed in the development of alternative approaches to fabricate photonic crystals by using self-assembled systems of the order of nanoscale dimensions [40]. Moreover, the development in self-assembly method should allow assembling these photonic structures into integrated device systems at low cost

[41]. The important advantages are expected from these photonic structures, including the control of radiative behavior and lifetimes that in turn can control chemical reactions and catalysis. One of the important phenomenon is the localization of light in a disordered photonic crystal, in analogy to the localization of electrons in disordered systems [42]. Such optoelectronic-crystal structures have huge potential for the fabrication of large variety of photonic devices.

1.6.6 Optical properties

Optical properties of nanomaterials is one of the interesting and useful feature as far as fundamental science and technology is concerned. The low dimensional nanostructured materials has received great attention on its optical behavior especially due to the quantum confinement effect. The major parameters that depend on the optical behavior of nanomaterials are its size, shape, surface area, and dopants interaction with the surrounding environment. The shape of the nanomaterial are also play important role on optical behavior of metal nanostructures.

The quantum size effect, especially in the case of semiconductor nanostructures give interesting optical properties. In which the band gap increases with a decreasing size of the nanostructures, resulting in the inter band transition shifting to higher frequencies [43, 7]. Blue shift in the energy band gap is observed in semiconductor nanostructures attributed to energy sub bands corresponding to quantization along the direction of confinement. By tuning the size of the nanoparticles, the luminescent emission from the semiconductor nanostructures can be modified. In the case of nanoscale materials, the colour may be different from its bulk, which is reported in nanostructured Au and CdSe [44]. Several devices such as optical detector, laser, sensors, display, solar cell etc. are fabricated based on optical properties nanostructured materials. Apart from that, these materials are important for imaging, photocatalysis, phosphor, photo-electrochemistry and biomedical applications.

1.6.7 Electrical properties

There exists systematic transformations in the density of electronic energy levels as a function of the size in nanomaterials, as a result electronic configurations of nanomaterials are significantly different from that of its bulk counterpart. These variations in electronic energy levels results differences in the optical and electrical properties with size. The nanostructures, especially nanowires are considered as electrically conducting wires due to higher order conductivity compared with that of the bulk material [33, 34]. Metal or semiconductor nanocrystals of a few nanometers in diameter gives discrete charging of the metal particles due to quantum effects. Such a discrete electronic configuration allows one to pick up the electric charge from one electron at a time, at specific voltage values. This Coulomb seige behavior (Coulombic staircase) of nanoparticles with diameters below 2-3 nm may be helpfull to use as basic components of single electron transistors (SETs). Electrical transporting carbon nanotubes are used for the fabrications of single electron transistors.

1.6.8 Magnetic properties

A non-ferromagnetic bulk materials may exhibit ferromagnetic-like behavior when it is in the nano range. Considerable quantization and other physical phenomenon are expected to occur in nanomaterials which will generate magnetism at the nanometer scale materials. Theoretical constrains proposed that a near doubling of the energy outcome of hard magnets may be feasible with an optimum nanoscale configuration [45, 46]. Epitaxial and hetero-epitaxial structures of magnetic nanostructures, including metallic oxide and semiconducting phases shows magnetic properties which are useful for the device applications [47, 48].

Surface atoms of nanostructures can be modified by interaction with other chemical species, that is, by capping the nanoparticles. This phenomenon opens the possibility to modify the physical properties of the nanoparticles by capping it with appropriate molecules and is useful for several magnetic applications of nanoparticles including drug delivery.

1.7 Wide band gap semiconductors

The semiconductor materials having comparatively wide energy band gap with respect to silicon is termed as wide band gap (WBG). Relatively higher energy band gap is the important characteristics that make WBG materials superior to silicon as a semiconductor [49]. The term electronic band gap in semiconductor materials is the energy gap between the top of the valence band and the bottom of the conduction band. The electrons from the valence band can be excited to the conduction band with thermal or optical excitation. WBG materials based devices tolerate larger operating temperatures in a smaller size than the equivalent silicon based devices, which is one of the important advantages of these materials. Silicon possesses a band gap of 1.1 eV and SiC, ZnO, and GaN have a band gap of 3.3 eV, 3.37 eV and 3.4 eV, respectively and these are the popular WBG materials used in devices and other applications [49].

1.7.1 Wide band gap II-VI semiconductors

Wide band gap II-VI semiconductors are one of the most crucial materials for high performance optoelectronic devices such as light emitting diodes (LEDs) and laser diodes (LDs) which can give visible or ultraviolet source. Moreover, the ionicity of these materials are higher because of that these materials are good candidates for high electro-optical and electro-mechanical coupling applications. The basic characteristics of important wide band gap II-VI compounds semiconductors are shown in the table 1.1 [49].

The II-VI semiconductors received great attention due to its important applications on photonic, luminescent, optoelectronics and lasing materials. [50]. These materials are suitable for variety of mechanical and optoelectronic applications and intensive research on these materials are continuing for the last several years. The wide band gap II-VI semiconductors are important candidates for blue to UV spectral range emitters and may replace materials like GaN in light emitting laser applications [51].

Wide band gap II-VI compound semiconductors				
Material properties	ZnS	ZnO	ZnSe	ZnTe
Energy gap E_g (direct) at 300 K (eV)	3.67	3.37	2.71	2.39
Exciton binding energy (meV)	36	60	21	10
Melting point (K)	2038	2248	1715	1513
Lattice constant at	a = 3.811,	a = 3.2498,	a = 3.98,	a = 4.27,
300 K (Å)	c = 6.234	c = 5.2066	c = 6.53	c = 6.99
Thermal conductivity (Wcm ⁻¹ K^{-1})	0.27	0.6	0.19	0.18
Electron Hall mobility $(300 \text{ K}) \text{ (cm}^2/\text{Vs})$	165	125	500	340

Table 1.1: Characteristics of wide band gap II-VI compounds semiconductors [49]

ZnO: An overview

1.7.2 Dilute magnetic semiconductors (DMS)

Semiconducting materials in which random substitution/replacement of a fraction of the original atoms by magnetic atoms are generally called as diluted magnetic semiconductors (DMS). The diluted magnetic semiconductors, which combine ferromagnetism with semiconductivity, are identified to be potential building blocks for spintronic devices [52]. These DMS alloys may be considered as containing two interacting subsystems. First one is the effect of delocalized conduction and valence band electrons of the mixed system and the other one is the random, diluted system of localized magnetic moments of the magnetic atoms. The crystalline structure and the electronic properties of the host crystals should be well suited for magnetic interactions, coupling the spins of the band carriers and the localized spins of the dopant ions. These coupling between the localized magnetic moments introduce change in magnetic phases of the materials such as paramagnets, spin glasses and antiferromagnets etc. Lattice constants and optical energy band gap of DMS can be varied by varying the composition of the dopant and host material because of its ternary nature [52]. Magnitude of magnetic properties and magneto-optical effects of the material can be changed altering the concentration of the magnetic ions in it. The important DMS belongs to II-VI group compound semiconductors are CdTe, ZnSe, CdSe, CdS, ZnO etc., doped with transition metal ions like Mn, Fe, Co, Ni etc. substituting its original cations. ZnO based DMS received great attention due to its wide direct band gap and large exciton binding energy [53].

1.8 ZnO: An overview

Among the II-VI semiconductors, Zinc oxide (ZnO) is a unique and versatile material that shows semiconducting, piezoelectric, and pyroelectric multiple properties [54]. It has a wide direct band gap (3.37 eV) and large exciton binding energy (60 meV) at 300 K as compared to that of other wide band gap II-VI semiconductors (Table 1.1). Zinc oxide is one of the important transparent conducting oxide (TCO) semiconductor material. ZnO is an important compound for the fabrication of modern solid state devices due to its wide direct optical energy band gap, high transmission coefficient (> 80%) in the visible and near infrared spectral range, high electrical conductivity, piezoelectric and photoelectric properties. This material is identified as an excellent candidate for a dye sensitized oxide semiconductor solar cell, gas sensors, or field emitters [55]. ZnO is used for the fabrication of transparent field effect transistors, light emitting diodes, gas sensors, solar cells, transparent conducting electrodes, optoelectronic devices in ultraviolet and visible spectral ranges, etc. [56]. Because of the multifaced properties, ZnO is recognized as a promising photonic material in the ultraviolet (UV) and visible region. It has good photocatalytic, electrical, optical and photochemical properties suitable for applications relevant with respect to these properties. ZnO is also a promising material for short wavelength optoelectronic devices, like UV light-emitting diodes, LEDs and laser diodes due to its large exciton binding energy [57].

1.8.1 Characteristics of ZnO

ZnO is a versatile semiconducting material because of its unique nature which give excellent structural morphological variations consequently electronic and optical properties. Generally, ZnO crystallize in either cubic zinc blende or hexagonal wurtzite structure. In these structures, each anion is surrounded by four cations at the corners of a tetrahedron, and vice versa. This tetrahedral coordination is typical of sp^3 covalent bonding and its posses considerable ionic character [58]. The ionicity ZnO resides at the borderline between covalent and ionic semiconductor. The crystalline forms of ZnO are wurtzite (B₄), zinc blende (B₃), and rocksalt (B₁). The schematic representation of the different

ZnO: An overview

crystal structures of ZnO such as wurtzite (B₄), zinc blende (B₃), and rocksalt (B₁) are shown in figure 1.3. At ambient conditions, wurtzite structure is the thermodynamically stable crystal structure of ZnO, the zinc blende structure is stabilized in most cases growing it on cubic substrates. The rocksalt (NaCl) structure may be obtained at relatively high pressures [58]. The hexagonal wurtzite structure with lattice parameters, 'a' and 'c', in the ratio of $c/a = \sqrt{8/3} = 1.633$ belongs to the space group of $C_{6\nu}^4$ or $P6_3mc$ [58]. This structure consist of two interpenetrating hexagonal close packed (hcp) sublattices and each of them having four atoms per unit cell and every atom of one kind (group-II) atom is surrounded by four atoms of the other kind (group VI), or vice versa, which are coordinated at the edges of a tetrahedron [58].



Figure 1.3: Schematic representation of the different crystal structures of ZnO [58]

Each hcp sublattices of the wurtzite structure consist of one type of atom displaced with respect to each other along the threefold c-axis by the amount of u = 3/8 = 0.375 (in an ideal wurtzite structure) in fractional coordinates (the u parameter is defined as the length of the bond parallel to the c-axis, in units of c) [58]. In the case of ZnO crystal, the wurtzite structure deviates from the ideal arrangement, by changing the c/a ratio or the u value [58]. It is note

that a strong correlation exists between the c/a ratio and the u parameter. When the c/a ratio decreases, the u parameter increases in such a way that those four tetrahedral distances remain nearly constant through a distortion of tetrahedral angles due to long range polar interactions [58].

In the case of wurtzite ZnO, the lattice constants mostly range from 3.2475 to 3.2501 Å for the 'a' parameter and from 5.2042 to 5.2075 Å for the 'c' parameter at room temperature. Various experimental measurements and theoretical calculations are in good agreement with these values [59]. The c/a ratio and u parameter vary in a slightly wider range, from 1.593 to 1.6035 and from 0.383 to 0.3856, respectively. The deviation from that of the ideal wurtzite crystal is probably due to lattice stability and ionicity. It has been reported that free charge is the dominant factor responsible for expanding the lattice proportional to the deformation potential of the conduction-band minimum and inversely proportional to the carrier density and bulk modulus. The point defects such as zinc antisites, oxygen vacancies, and extended defects, such as threading dislocations, also contribute to the increase of lattice constant [58]. Figure 1.4 shows the schematic representation of hexagonal wurtzite structure of ZnO.

The potential utility of a semiconductor can be mainly determined by the band structure of that material. A number of theoretical approaches are employed to calculate the band structure of wurzite, zinc-blende, and rock salt ZnO structure. Several research publication arises regarding the band structure of the electronic states of wurzite ZnO. X-ray or UV-Vis absorption techniques have been conventionally used to measure the electronic core levels. These methods basically measure the energy difference by inducing transitions between different electronic levels. The wurtzite structure is the natural structure of ZnO, because of low symmetry, resulting in the existence of spontaneous polarization along the c-direction. As a direct and wide band gap





Figure 1.4: Schematic representation of hexagonal wurtzite structure of ZnO

material, ZnO is attracting a lot of attention for a variety of electronic and optoelectronic applications. The major advantages of large band gap semiconductor include higher breakdown voltages, ability to sustain large electric fields, lower noise generation, high temperature and high power operation [58].

1.8.2 Properties of wurtzite ZnO under high pressure

Wurtzite ZnO can be transformed to rocksalt (NaCl) phase structure with the application of external hydrostatic pressures. This phase transition is due to the reduction of the lattice dimensions [60]. This reduction in lattice dimension under hydrostatic pressure contributes to the interionic Coulomb interaction which favor the ionicity more over the covalent nature. The spacegroup symmetry of the rocksalt type of structure is Fm3m, and the structure is sixfold coordinated. The pressure induced phase transition from wurtzite

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ZnO (B_4) to the rocksalt (B_1) phase occurs at approximately 10 GPa and a large volume decrease of about 17% from the wurtzite structure reported [60].

1.8.3 Other applications of ZnO

About a million tonnes of ZnO are utilized through out the world annually. Among the rubber products, tyres are the major products which use zinc oxide due to the pigmentary properties of ZnO. It enhance the ability to absorb frictional heat which is an important property with regards to tyre performance. The proficiency of the incorporation of zinc oxide into rubber compound can be improved by coating the particles with propionic acid which binds the zinc oxide surface and the resulting hydrocarbon chain in a more compatible manner [61]. Latex rubber products are often formulated with very fine zinc oxide known as active grades which have low levels of opacity [61]. ZnO is one of the components of ceramic glazes which is used in tiles and is also used in frit formulation. ZnO can contribute to reduction of melt temperature of the glaze. ZnO is also used for the manufacture of heat resistant glass and cook wears and photochromic lenses.

Zinc based compounds are the major nutrients of living body metabolism and is required for proper functioning of organs of living animals. Bulk form of zinc oxides could not flow smoothly inside the organs, sometimes it may stick to surfaces, hence ZnO made of kiln operations are used for making animal feeds. ZnO is a good catalyst especially for organic reactions such as dehydrogenation. Zinc oxides synthesized with zinc hydroxide or carbonate are used in these applications [62]. ZnO is used for the manufacture of variable resistors or varistors and these varistors consists of ceramic blocks of ZnO that have been sintered along with other metals with well defined grain boundaries between crystals [61]. Even though the zinc oxide is a nonmagnetic material, it is widely used to make iron oxide/nickel oxide ferrite compositions. A wide range of ferrite materials for multiple applications can be made, depending on the formulation. Paint was one of the important products made of ZnO which has a larger opacity [61]. Zinc oxide and carbonate compositions are made into absorbent pellets which are used to desulphurize liquid and gas streams [62].

ZnO can protect human skin from infections without side effect and is a mild antiseptic. It is used in baby powder and barrier creams to treat diaper rashes, calamine cream, anti-dandruff shampoos, and antiseptic ointments [63]. ZnO strongly absorb ultra violet light and is a material of choice for making sunscreens [63].

1.9 ZnO nanostructures: A literature review

Zinc oxide nanostructures are one of the important II-VI semiconductor materials which possess direct wide band gap (3.37 eV). It is an excellent transparent conducting oxide (TCO), having comparatively high electron mobility (> 100 cm²/Vs), photoconductivity, and strong room temperature luminescence with large exciton energies of 60 meV [49, 64, 65]. Apart from that ZnO has relatively high refractive index (2 at $\lambda = 632.8$ nm), high thermal conductivity etc. ZnO is a good photocatalytic material and also have antibacterial and UV-protection properties [66, 67]. Because of its good thermal stability, irradiation resistance and flexibility, nanosized ZnO has various applications for making solar cells, electronic devices, ultraviolet light detectors and photo diodes etc [67]. ZnO nanostructures are good candidate for dye sensitized solar cells [68], piezoelectric devices [69], gas sensors [70], and UV laser diodes [71].

One dimensional (1-D) ZnO nanostructures has considerable interest especially for use in nanoscale optoelectronic devices. Synthesis procedure of 1D ZnO nanostructures, such as nanowires [72], nanorods [73], nanotubes [74], nanobelts [75], nanoneedles [76], nanorings [77] and nanowhiskers [78] etc., are reported in the literature. The growth of two and three dimensional (2D, 3D) ZnO structures like nanodisk [79], urchin-like nanospheres [80], nanoflowers [81], nanonails [82], nanobridge [83] etc., are also reported by researchers in the literature. 3D ZnO architectures may have novel properties compared to 1D and 2D nanostructures which can be used as the building blocks to fabricate photonic devices. There are different physical and chemical methods used for the preparation of ZnO nanostructures.

Thermal evaporation [84], chemical vapor deposition (CVD) and metalorganic chemical vapor deposition (MOCVD) [85, 86], vapor liquid solid (VLS) assisted [87] etc., are widely used by researchers for the synthesis of ZnO nanostructures. The advent of new laser sources leads to the development of laser based technique like Pulsed laser deposition (PLD) for the fabrication of ZnO layers [88]. Further, radio-frequency magnetron sputtering [89], molecular beam epitaxy (MBE) [90] are also used to synthesize ZnO nanostructures. For above mentioned techniques, high temperatures and vacuum conditions are required which limit the choice of substrate and the economic viability. Interestingly, MOCVD and MBE can give high quality 1D ZnO nanostructures, but it gives poor sample uniformity and low yield with high production cost. The pulsed laser deposition, sputtering etc., have less controllability and reproducibility with respect to other techniques. These synthesis methods need either high temperature or vacuum. Therefore, the above mentioned synthesizing methods are incompatible for the growth of 1D ZnO nanostructures. Solution based technologies are more eco-friendly and cost effective than that of vacuum techniques for the synthesis of 1D ZnO. Solution based non vacuum techniques such as chemical method [91], wet chemical method [92], hydrothermal process [93], solvothermal process [94], sol-gel method [95], spray pyrolysis [96], chemical bath deposition [97] etc., are commonly used for the synthesis of ZnO nanomaterials.

Among the solution based synthesis methods, hydrothermal technique is a best strategic non vacuum and cost effective technique to synthesize 1D ZnO and ZnO based DMS nanostructures. In this method, simultaneous application of heat and pressure is involved. The growth medium is usually made of solution of precursor salt. Hydrothermal method is identified as the most attractive technique for obtaining well aligned ZnO nanowires as well as hierarchical or branched nanowires. The complex 3D nano-architectures like nanoflowers, nanospheres, nanonails, nanobridge etc., are easily synthesized by controlling the growth parameters in hydrothermal process.

1.10 Hydrothermal growth of ZnO nanostructures: A review of recent reports

Rajeswari *et al.* [98] tuned the aspect ratio (length/diameter) of ZnO nanorods grown by hydrothermal process with various precursors and determined the optical energy band gaps which is in the range of 2.93 - 3.00 eV. The optical band gap of ZnO nanostructures were 3.3, 3.22, and 3.3 eV grown with hydrothermal method reported by Li *et al.* [99]. ZnO nanorods grown in a disturbed hydrothermal growth solution exhibited enhancement in the field emission properties of emitters based on it [100]. Zhang *et al.* [101] reported that different ZnO nanostructures are synthesized by a two-step hydrothermal method which shows variation energy band gap values (3.32, 3.24, 3.23, and 3.25 eV), with respect to different concentration (M = 0.005, 0.01, 0.1, 0.2) precursor solution.

The disk like and flower like ZnO nanostructures have been grown by citric acid (CA) assisted hydrothermal process by Zhang *et al.* [102]. The pH value,

temperature and the molar ratio of Zn^{2+} and the amount of citric acid plays significant influence on the morphology of ZnO nanostructures [102]. Among the different growth parameters, pH value is believed to be a key factor because it can appreciably change the quantity of ZnO nucleation center and of growth units. By adjusting different growth parameters, the disk-like and flower-like ZnO nanostructures, which are all hexagonal crystalline nature, have been achieved. Amin *et al.* [103] varied pH of the starting solution from 1.8 to 12.5., the final pH reaches at an inherent value of 6.6 independently of the initial pH solution in hydrothermal method. ZnO structures with different morphology like nanotetrapod-like, flower-like, and urchin-like were obtained at alkaline pH in the range 8 to 12.5. Amin *et al.* [103] reported that when the pH of the growth solution lower than 8 gives rod-like nanostructures.

Some non-hydrothermal technique are also recently reported for the synthesis of ZnO nanoflowers. Oxygen vacancies are observed in the ZnO nanoflowers synthesized by reactive vapor deposition which is understood from its PL studies [104]. In order to tune the optical properties of ZnO nanoflowers, Ai *et al.* [104] deposited ZnO thin films with varying thicknesses on the nanoflowers by atomic layer deposition, which can distinctly improve the band edge photoluminescence properties without changing their morphologies. Ultraviolet emission at 375 nm and broad green emission at 526 nm respectively are reported in ZnO nanoflowers synthesized on AlN films by solution method Yong *et al.* [81].

Hydrothermal process have been employed for the synthesis of different types of ZnO nanostructure such as nanowires and nanobelts [105], whiskers [106], nanoflowers [107, 108, 109], nanorods [110, 64, 111], Urchin-like structures [112], nanobridges and nanonails [113] etc. In an intermediate growth condition especially in hydrothermal process, novel nanostructure, namely flower-like bundle of ZnO nanosheets was formed, which is different from known ZnO nanostructures [114]. Tong *et al.* [115] grown ZnO nanostructures such as nanotowers, nanovolcanoes, nanorods, nanotubes, and nanoflowers by using the hydrothermal technique. Wang *et al.* [116] reported the flowerlike, spindle like, sword like, and umbrella-like ZnO architectures of the hexagonal phase. ZnO microrods, hexagonal pyramid-like rods and flower-like rod aggregates, have been synthesized on glass substrates by controlling precursor concentration, reaction time and pH of the growth solution in hydrothermal method [117].

1.10.1 ZnO nanostructures under hydrostatic pressure

ZnO exists in a hexagonal wurtzite structure (B_4) at normal conditions of temperature and pressure. ZnO occurs in nature as a mineral, its high-pressure phase is geologically important which is a component of the lower mantle [118]. For lowering the energy through more efficient volume packing, bulk ZnO transforms to the cubic rocksalt structure (B_1) at a pressure about 9 GPa [60]. At a relatively modest external hydrostatic pressures wurtzite (B_4) ZnO can be transformed to the rocksalt (NaCl) (B_1) phase attributed to the reduction of the lattice dimensions. The space-group symmetry of the rocksalt type of structure is $Fm\Im m$, and the structure is sixfold coordinated.

Recio *et al.* [119] reported the results of a combined experimental and theoretical investigation on the stability and the volume behavior under hydrostatic pressure of the rocksalt (B₁) phase of ZnO based on X-ray diffraction data with synchrotron radiation. Desgreniers *et al.* [120] reported the dense ZnO phases, obtained by static compression at room temperature, studied by X-ray diffraction using synchrotron radiation. The initial wurtzite structure of ZnO is observed to transform to the rocksalt structure at 9.1 \pm 0.2 GPa with a large volume collapse of 16.7% on increasing pressure.

1.11 Transition metal (TM) doped ZnO nanostructures (Mn/Co/Ni/Cu): An overview

Among the II-VI semiconductors, ZnO-based DMS have attracted a great deal of research attention due to intrinsic properties of ZnO such as its wide band gap and large exciton binding energy. Researchers investigated the effect of doping especially 3d transition metals (Mn, Fe, Co, Ni, Cu etc.) ions on nonmagnetic semiconductor extensively expecting to get diluted magnetic semiconductor (DMS). Room temperature ferromagnetism in Mn doped ZnO was predicted and suggested the introduction of small amounts of magnetic ions such as Mn, Co, Ni, or Fe into non magnetic ZnO [121].

The synthesis of ZnO and TM-doped ZnO nanostructures via the low temperature hydrothermal method is considered as a promising technique due to low cost, environmental friendly and simple solution process. Diverse 1-D ZnO nanostructures can be achieved, and large scale production of nanostructures on any type of substrate, and their properties can be controlled by the growth parameters with hydrothermal method. Synthesis condition of 1-D ZnO and TM-doped ZnO nanostructures with controlled shape, structure and uniform size distribution on large area substrates with desirable properties, low cost and simple processes are of great interest and it is a big challenge at present [121]. Some of the important recent research reviews on the 3d transition metals such as Mn, Co, Ni and Cu doped ZnO nanostructures synthesized by various technique are given below.

i. Mn doped ZnO nanostructures

Manganese doped ZnO nanoparticles were synthesized using the co precipitation technique and tuned the band gap energy of ZnO and observed better UV as well as visible light-response [122]. The diffusion doping of Mn on ZnO tetrapod nanostructures prepared by evaporating Zn metal under humid argon flow resulted an increase of the size of tetrapods and it shows ferromagnetic behavior [123].

Intermediary energy levels within the band gap were observed in the Mndoped ZnO samples grown by the microwave assisted hydrothermal method with respect to increasing doping concentration [124]. The optical band gap of Mn doped ZnO nanoparticles with different doping concentration (1, 2, 3, 4, 5 at.%) varies between 3.34 eV and 3.22 eV [125]. Chang *et al.* [126] synthesized large-scale flower-shaped Mn doped ZnO nanostructures on silicon substrates by thermal evaporation at atmospheric pressure and observed the presence of oxygen vacancies in the photoluminescence spectra.

ii. Co doped ZnO nanostructures

Gandhi *et al.* [127] reported the effect of Cobalt doping on structural, optical, and magnetic properties of ZnO nanoparticles synthesized by Coprecipitation method. They also observed that the pure and Co doped ZnO nanoparticles showed significant changes in the M-H loop. Majeed *et al.* [128] reported that the increasing Co content leads to a decrease of the optical band gap and increases the width of localized states in Co doped ZnO nanostructures. Enhanced photocatalytic activity was observed from the Co doped ZnO nanodisks and nanorods prepared by a facile wet chemical method [129]. Excitonic emission was found to be suppressed at higher Co dopant concentration in ZnO due to increase in the distortion of host lattice and defects in Co doped ZnO thin films deposited on c-sapphire substrates by dual-beam pulsed laser deposition [130]. Monodispersed spherical nanoparticles are obtained in cluster assembled cobalt doped ZnO nanostructured film prepared by low energy cluster beam deposition [131].

iii. Ni doped ZnO nanostructures

Cong *et al.* [132] synthesized nanosized Ni doped ZnO with phase reactionprecursor method and the Ni doped ZnO nanoparticles show ferromagnetic behaviors at room temperature. The origin of ferromagnetism was explained by the Ruderman-Kittel-Kasuya-Yosida (RKKY) theory [132]. Kant *et al.* [133] synthesized Ni doped ZnO nanospheres by sol-gel method and studied structural, optical and photocatalytic properties of ZnO and Ni doped ZnO nanospheres.

Huang *et al.* [134] reported the synthesis, structure, and room-temperature ferromagnetism of Ni doped ZnO nanoparticles and observed that the wurtzite structures degrade gradually with increasing Ni concentration. Room temperature PL spectra of Ni doped ZnO nanoparticles shows near band edge related emission and emission due to intrinsic defects [135]. Srinet *et al.* [136] investigated the structural, optical, vibrational, and magnetic properties of sol-gel derived Ni doped ZnO nanoparticles and observed enhancement in optical band gap with Ni doping from 3.29 to 3.32 eV through UV-visible spectroscopic analysis.

iv. Cu doped ZnO nanostructures

Cu doped ZnO nanorods with different Cu concentrations were synthesized through the vapor transport method [137]. Red shift in band edge absorption peak is observed in the UV-Vis absorbance spectrum of Cu doped ZnO nanorods with increasing Cu content and it shows photocatalytic activity [137]. Diffuse reflectance spectroscopic investigation of Copper doped ZnO nanorods prepared by hydrothermal method show red shifts with increase of Cu content. Orange-red photoluminescent emission originates from the oxygen vacancy or ZnO interstitial related defects and it shows strong ferromagnetic behavior [138]

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The morphological properties of the Cu-doped ZnO nanorods arrays were influenced significantly by the presence of Cu impurities [139]. Nanocrystalline Cu doped ZnO particles synthesised by co-precipitation method have a hexagonal wurtzite structure with a high degree of crystallization and a crystallite size of 10-16 nm. Mukhtar *et al.* [140]. Chow *et al.* [141] reported the synthesis and characterization of Cu-doped ZnO one-dimensional structures for miniaturized sensor applications with faster response.

1.11.1 Magnetic studies on ZnO based nanostructures

Hao *et al.* [142] investigated the magnetization of $Zn_{0.93}Mn_{0.07O}O$ hierarchical microspheres (HMSs) as a function of temperature at the zero-field-cooled [ZFC] and field-cooled [FC] processes with an applied magnetic field of 1,000 Oe. Interestingly, the $Zn_{0.93}Mn_{0.07}O$ HMSs are ferromagnetic with T_c higher than 400 K. Cui *et al.* [143] shows the room temperature magnetization behavior of as-grown ZnO:Co and those sample annealed at 400, 700, and 900 °C. The as-grown sample showed a coercivity field, H_C of 120 Oe and a saturation magnetization, M_S of 9.5 memu.

Cheng *et al.* [144] presents the M-H curves (field dependence of magnetization) of the ZnO_{0.95}Ni_{0.05}O nanorods measured at 300 K. Hysteresis loops with a coercive field, $H_C \sim 72$ Oe can be observed at 300 K, shows ferromagnetic characteristic behavior. Li *et al.* [145] observed hysteresis behavior in Zn_{0.99}Cu_{0.01}O, Zn_{0.98}Cu_{0.02}O, and Zn_{0.95}Cu_{0.05}O indicates that Cu-doped ZnO films exhibit room temperature ferromagnetism (RTF). Saturation magnetization of as synthesized Zn_{0.99}Cu_{0.01}O, Zn_{0.98}Cu_{0.02}O, and Zn_{0.95}Cu_{0.05}O are 1.02, 2.75, and 0.26 emu cm⁻³, respectively and confirmed that the ferromagnetism is originated from Cu doping but not due to strain [145].

1.11.2 Photoluminescence studies on ZnO based nanostructures

Room temperature photoluminescence spectrum recorded from hydrothermally grown ZnO nanowires and nanobelts showed a weak UV band emission at 379 nm (near-band emission) and a strong broad yellow emission around 564 nm [105]. The deep-level yellow luminescence was attributed to interstitial oxygen. The PL spectrum of the hollow flower-like ZnO structures shows strong UV emission corresponds to the near band edge emission of the wide band gap of ZnO, due to the recombination of excitonic centers(quantum confinement effect) [146].

A weak peak at ~396 nm and a broad peak at ~469 nm were observed in the photoluminescence (PL) spectra of the ZnO and the UV emission is attributed to near band-edge emission of the wide band gap of ZnO reported by Jiang *et al.* [147]. Flower-like ZnO microstructures with an average diameter of 1 μ m assembled from nanorods synthesized hydrothermal method shows PL emission peak located at about 465 nm, a broad emission peak in the range of 510-560 nm may be attributed to the recombination of an electron and a photogenerated hole caused by surface defects and oxygen vacancies [148]. Hao *et al.* [142] reported that ZnO microsphere exhibit a UV emission peak at 395 nm and defect level associated emissions located at 425, 475 nm and one at 490 nm in the PL spectra. They also observed that the increase in Mn concentration leads to the intensity reduction of both UV and blue emissions, due to the increase of defect concentration induced by Mn doping.

ZnO nanowires exhibit an emission peak at 379 nm due to the near bandedge emission and a weak visible emission around 550 nm associated with the defects in ZnO and the visible emission intensity increases significantly at higher Co doping concentration [143]. Hydrothermally grown ZnO:Ni shows the free exciton peak at 377 nm and is red shifted from 379 to 380.3 nm, then to 381.4 nm with the increase of Ni doping content [149]. Interestingly, the band gap of the ZnNiO nanorod array shrinks with Ni doping concentration due to the coupling effects between Ni ions substituting by Zn ions in ZnO lattice and electrons from 2p layer of oxygen [149]. Lupan *et al.* [150] observed two visible PL bands in the spectrum of Zno:Cu at low temperature around 1.85 eV and 2.4 - 2.5 eV.

1.11.3 Raman studies on ZnO based nanostructures

Room-temperature Raman spectrum ZnO samples with different morphology shows bands in the range of 200-800 cm⁻¹. The observed peaks at 383, 413, and 438 cm⁻¹ can be assigned to $A_1(TO)$, $E_1(TO)$, and $E_2(high)$ modes, respectively [116]. The relatively weak peaks at 540 and 575 cm⁻¹ are attributed to $A_1(LO)$ and $E_1(LO)$ modes. It is generally accepted that the $E_2(high)$ mode originates from the lattice vibration of ZnO, while the $E_1(LO)$ mode is associated with defects in ZnO such as oxygen vacancy or other defect states [116]. Hernndez *et al.* [151] presents the Raman spectrum of the ZnO sample and no additional Raman peaks associated to chemical reactants or possible sub-products were detected.

Polsongkram *et al.* [152] carried out Raman analysis on ZnO nanorods synthesized via hydrothermal method. The dominant peaks at 100 and 438 cm⁻¹, are assigned to the low- and high- E_2 mode of non-polar optical phonons, respectively. ZnO:Mn microspheres shows decreased intensity of the peak at about 437 cm⁻¹ with Mn doping indicates that the crystallization of the Hierarchical microspheres (HMSs) becomes worse [142]. Mn incorporation into the ZnO matrix leads to the appearance of anomalous broad Raman bands in the 500 to 600 cm⁻¹ region. Lupan *et al.* [150] presents room temperature micro-Raman spectrum of the Cu:ZnO/GaN heterostructure, indexed with GaN and ZnO emission modes. The appearance of Raman band at 439 cm⁻¹ with a FWHM

of 8 cm⁻¹ corroborates the high quality of hydrothermally grown Cu:ZnO. Cui *et al.* [143] reported the improvement of ZnO:Co crystalline quality as a result of annealing is demonstrated with Raman spectroscopy. Yanmei *et al.* [149] shows that pure ZnO and ZnO:Ni nanorod arrays have similar Raman spectra in which $E_2(low) - 98cm^{-1}$ and $E_2(high) - 437 cm^{-1}$ appear on their spectra indicating that the ZnO and ZnNiO nanorods all grow preferentially along [0 0 1] direction vertical to the substrate.

Chapter 2

Experimental techniques: Hydrothermal synthesis and characterization tools

2.1 Introduction

This chapter describes the experimental set up for the low temperature hydrothermal growth of nanostructures. The different measurements and analysis techniques employed to characterize the as synthesized materials are also included in this chapter. The schematic diagrams, photographs and working principles of the experimental set up and characterization tools are also presented.

2.2 Synthesis of nanostructures

There are a variety of synthesis techniques used for the synthesize of nanostructures. These methods are basically based on top-down and bottom-up approaches. Bottom-up approaches is mainly used for synthesizing nanostructures/microstructures [1, 27]. Some of the bottom-up approaches such as thermal evaporation, chemical vapor deposition, pulsed laser deposition, atomic layer deposition and sputtering etc., require vacuum for the synthesis process which add up with the cost. The chemical method, sol-gel method, spin coating, spray pyrolysis technique and hydrothermal method are low cost bottom up approaches for the synthesize of nanostructures and these techniques do not require vacuum. Among the non vacuum technologies, hydrothermal process is a very useful cost effective technique to synthesize high quality one dimensional nanostructures.

2.2.1 Hydrothermal technique

Hydrothermal synthesis method is one of the important tools used for the advanced level material processing of nanostructured materials which has applications in the field of electronics, optoelectronics, catalysis, ceramics, magnetic data storage, biomedical, biophotonics, etc [99]. Hydrothermal processing helps to synthesis monodispersed homogeneous nanoparticles as well nano-composite materials. The term 'hydrothermal' is derived from the Greek words 'hydros' means water and 'thermos' means heat [153]. The word 'hydrothermal' was first put forward by the British geologist, Sir Roderick Murchison to describe the reaction of water at higher temperature and pressure [154]. Hydrothermal synthesis method can be defined as the heterogeneous chemical reaction in the presence of water, which is aqueous or non-aqueous above the room temperature and at pressure greater than 1 atm in a closed container [154].

Now a days, any chemical reaction in the presence of water or mineralizes under pressure and temperature conditions are generally called as hydrothermal reaction process. Hydrothermal method give numerous advantages over

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Hydrothermal technique

other conventional methods for the synthesis of nanomaterials. It offers the synthesis of different dimensional nanomaterials with respect to the low costs for instrumentation, energy and precursors salt used. It is an eco-friendly process than many other methods, since the reactions occur inside a sealed container. The stoichiometric control is less for the materials synthesized at high temperature reaction processes due to volatilization of components and stress-induced defects caused by phase transformations. But, relatively low temperature hydrothermal process can avoid such undesirable problems and the capability to precipitate the powders directly from solution regulates the rate and uniformity of nucleation, growth and aging, which influence the size, morphology and aggregation control etc. Hydrothermal method have the capability of synthesizing materials with various morphologies and particle sizes, that can be achieved by changing different growth parameters.

Pressure-temperature interaction is one of the important physical process in hydrothermal solution because of that it is very difficult to synthesize different phases of the materials. Materials synthesized under hydrothermal method often shows variation in population of point defects when compared to materials synthesized by high temperature synthesis [155]. The main consideration of researchers about hydrothermal experiment is that, the system should operate reliably under extreme pressure-temperature conditions [153]. Temperature fluctuations of the oven causes the rise in temperature of the growth medium which leads to a higher dissolution rate. This method is also beneficial to industrial production of morphologically controlled materials with desired size and shape.

2.2.2 Hydrothermal technique:-Instrumentation

A vessel/container which withstand highly corrosive solvent at high temperature and pressure is the main part of a hydrothermal set up which is known as autoclave. Some researchers used to call hydrothermal autoclave as hydrothermal bomb since there occur high pressure inside the reaction system during experiments. Nevertheless, an ideal hydrothermal autoclave should have the following features [153] such as,

- Inertness to acids, bases and oxidizing agents other reactants used for the experiment.
- Apart from that it is easy to handle especially during assembling and disassembling.
- The autoclave should have sufficient length to obtain a desired temperature gradient.
- It should be a perfect leak-proof mechanism to maintain temperature and pressure range during reaction process.
- It should bear high pressure and temperature experiments for longer periods without any damage. Further, it should not need any treatment after each experimental run.

The autoclaves can be fabricated with any of the following materials a thick glass cylinder or a thick quartz cylinder with high strength alloys, such as stainless steel, iron, nickel, cobalt-based super alloys, etc. The experimental temperature, pressure conditions and its corrosion resistance of a given solvent or chemicals is the primary concern related to selection of materials for the synthesis of autoclave. Teflon lining or beakers, platinum, gold, silver tubes or lining etc., are used to protect the autoclave main part from highly corrosive media and extreme pH conditions. In the present, study we used sealed stainless steel autoclaves and Teflon beaker as the reaction container. The Teflon

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X-ray diffraction technique

beaker, autoclave and hydrothermal oven which are used for the present work is shown in figure 2.1.



Figure 2.1: 1)Teflon beaker, 2) Autoclave, and 3) Hydrothermal oven

The precursor solution mainly made of water is transferred into the Teflon beaker. The Teflon beaker containing precursor solution was kept inside the stainless steel autoclave. This system is sealed well in order to avoid any solvent leakage during heating of the system. The sealed autoclave is kept into the electrically heated oven for providing desired temperature. On application of the desired hydrothermal synthesis temperature, an autogenous pressure is generated within the autoclave. The hydrothermal growth advances by the presence of applied temperature and the autogenous pressure developed in the autoclave.

2.3 Characterization tools

2.3.1 X-ray diffraction technique

X-ray diffraction technique is a widely used non destructive characterization tool in materials science. It is a qualitative and quantitative phase identification technique. X-ray diffraction technique give crystalline structure of the materials at the atomic level. It is a fingerprint characterization method for the determination of structure of crystalline materials. Every solid crystalline materials can have a unique characteristic X-ray diffraction pattern which can be used for the identification of that material. The major information obtained from the diffraction technique are crystal structure, packing of atoms together in the crystalline state, interatomic distance and angle between the atomic bonding [156, 157]. X-diffraction analysis is useful to know the state of chemical combination of the elements in a particular phase. The information obtained from the material is basically related to its crystalline structure rather than other factors. X-ray diffraction studies gives a whole range of information about the crystal structure, orientation, average crystalline size and stress in the material.

When a beam of X-rays hit on a crystalline material, the electrons around the atoms in the material oscillate with the same frequency of the incoming X-ray beam. In a crystal lattice, the atoms are arranged in a in a regular pattern, constructive interference occur along a few directions. A well defined X-ray beams leaving from the sample to various directions and the waves are in the same phase. A diffracted beam which composed of scattered rays are mutually reinforcing one another [157]. Scattering from the periodic arrays of atoms that leads to the diffraction effect. Scattering represented in term of simple expression which is known as Bragg's law. It is the basic law involved in the diffraction method of structural analysis between the scattering angle, the wavelength of the radiation and the spacings between the planes of atoms [157]. Since the distances between the atomic planes are dependent on the size and distribution of atoms, the structure of the material [156, 157].

In the present study, Powder X-ray diffraction (XRD) characterization were carried out to study the crystallographic structure of the hydrothermally grown ZnO and transition metal doped ZnO (ZnO:TM). The structural characteriX-ray diffraction technique



Figure 2.2: Rigaku D-max C X-ray diffractometer

zation of as synthesized samples were done by Rigaku D-max C X-ray diffractometer with CuK α radiation ($\lambda = 1.5414$ Å) varying 2θ from 20° to 80° at scanning rate $5^{\circ}/\text{min}$ (Figure 2.2). X-ray tube voltage and current were set at 30 kV and 20 mA respectively.

In crystalline material, atoms are arranged regularly in three-dimensional ways called crystal lattices. A crystal can be assumed to be made up of a number of crystal planes [158]. When X-ray beam is incident on a crystal surface, the atoms of the crystal occupying definite positions in the crystal lattices act as scattering centers of X-rays. X-rays getting scattered from different atoms reinforce each other under certain conditions and scattered X-rays come out in certain directions. These scattered waves can be considered as reflected waves or diffracted waves. Certain crystal planes will be rich in atoms and from these crystal planes we get scattered waves of large intensities [158].

Consider a crystal in which the crystal planes are at a distance 'd' apart as shown in the figure 2.3. Parallel beam of X-rays are incident on the crystal surface at an angle ' θ '. We get scattered wave BC corresponding to the incident wave AB. Where ' λ ' is the wavelength of X-ray and 'd' is the interplanar distance.



Figure 2.3: Illustration of Bragg's diffraction
[159]

Another wave along A'B' is incident on the next layer of atoms and scattered along B'C'. The two reflected waves BC and B'C' will reinforce each other to produce a strong reflected X-ray if the path difference between them is equal to the product of wavelength of X-ray and an integer 'n' $(n\lambda)$. To find the path difference draw the normal BM and BN. Therefore path difference between BC and B'C' is MB' + B'N [159].

For triangle BB'M,

$$\frac{MB'}{BB'} = \sin \theta$$

i.e., $MB' = BB' \sin \theta$

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Scanning electron microscope (SEM)

 $MB' = d\sin\theta$ (since BB' = d, the inter planar distance)

Similarly from triangle BB'N,

 $B'N=d\sin\theta$

Therefore for reinforcement or to produce a reflected X-ray beam,

$$d\sin\theta + d\sin\theta = n\lambda$$
, or
 $2d\sin\theta = n\lambda$

This is known as Braggs Law.

Experimentally obtained diffraction patterns of the sample are compared with the standard powder diffraction files (JCPDS). The XRD data of present samples were processed with the Rietveld refinement analysis in order to extract the lattice parameters using the FullProf program [160].

2.3.2 Scanning electron microscope (SEM)

Scanning electron microscope (SEM) is one of the sophisticated devices for the morphological analysis of the nano or microstructures, mainly morphological imaging of the sample surfaces. When the sample is irradiated with an electron beam, secondary electrons are emitted from the specimen surface. These secondary electrons will create the image of the material surface [161]. The major components of SEM are electron system to produce an electron probe, a sample stage for placing the sample, a secondary-electron detector to collect secondary electrons, an image display unit, and an operation system to perform various operations.

The electron optical system is made of an electron gun, a condenser lens and an objective lens, a scanning coil to scan the electron probe [161]. The electron optical system (inside of the microscope column) and a space surrounding the specimen are kept at vacuum. Electron beam generation system is usually fixed at the top of the microscope column. This system generates the illuminating beam of electrons known as the primary electron beam for imaging purpose. The electron gun is made of tungsten filament by heating the filament at high temperature about 2800 K which produces electron beam. These thermoelectrons are focussed as an electron beam, flowing into the metal plate (anode) by applying a positive voltage to the anode. The electron beam is finely focused by the action of the Wehnelt electrode. Generally, Field-emission electron gun (FE gun) or the Schottky-emission electron gun (SE gun) are also used for the generation of electron beam in order to get better resolution of images [161].

If we apply an electric current passing through a coil wound over electric wire, a rotationally-symmetric magnetic field is formed and it will act as a magnetic lens [161]. Detection system usually consist of different types of detectors, each sensitive to different energy per particle emissions that occur on the sample. A fluorescent material is coated on the tip of the detector. A high voltage of about 10 kV is applied to it and the secondary electrons from the sample are attracted by this high voltage. These secondary electrons generate photon by hitting the scintillator. These photons are transmitted to a photo-multiplier tube (PMT) through a light guide and these light is converted to electrons and amplified as an electrical signal. A supplementary electrode, called the collector, is also placed before the scintillator in order to help the scintillator to acquire secondary electrons and number of secondary electrons which is collected by it can be controlled by changing this applied voltage [161].

Electrons have the tendency to disperse or scatter due to collisions with other molecules. Therefore, SEM instrument required a good vacuum system. The electron optical system and the sample chamber should be kept at high

Transmission electron microscope (TEM)

vacuum which is of the order 10^{-3} to 10^{-4} Pa and is achieved by means of a diffusion pump, a turbo molecular pump or with a sputter ion pump. A specimen stage, which stably supports the specimen and moves smoothly, is required for keeping the specimen inside the sample chamber. The specimen stage for a SEM can perform horizontal movement (X, Y), vertical movement (Z), sample tilting (T), and rotation (R) movements. The X and Y movements for selection of a field of view, while the Z movement for better resolution and the depth of focus [161, 162]. The SEM characterization of the present study were carried out using a Hitachi S-4800 scanning electron microscope which is shown in figure 2.4.



Figure 2.4: Hitachi S-4800 scanning electron microscope [163]

2.3.3 Transmission electron microscope (TEM)

Transmission electron microscope (TEM) is used for the imaging of ultra fine particles with high magnification. Transmission electron microscope have three major components which are electron gun, image producing system and image recording system. The electron gun is the source of electrons similar to that of electron gun in SEM described previously. V-shaped tungsten filament (cathode) is used for the production of electrons, and these beams are focused by the condenser system onto the sample. Lanthanum hexaboride nanowires are also used for the production of electron beams in high resolution TEM instrument. The filament is surrounded by a control grid (Wehnelt cylinder) and negative potential is applied to the cathode and the control grid which is equal to the accelerating voltage of electrons. A disk shaped structure with an axial hole is used as anode. The electrons ejected from the cathode is accelerated toward the anode [164].

The image producing system constitute an objective lens, movable specimen stage, and intermediate and projector lenses. This system helps to focus the electrons passing through the sample to form a real and magnified image. The condenser lens controls the beam intensity [164]. The objective lens is having short focal length of the order of 1-5 nm which produces a real intermediate image. Image recording system is used to convert the electron image into visual image which is achieved by means of a fluorescent screen, gauges, etc.

The quality of the final image in the transmission electron microscope depends largely upon the accuracy of electromagnetic lenses. These lenses are aligned to one another to the illuminating system. The lenses need power supplies with high accuracy in order to get highest standard of resolution as well as electronic stabilization. Transmission electron microscope also need high vacuum system which is maintained by diffusion, turbo pumps similar to that in scanning electron microscope [164]. The operational control of transmission electron microscope is done by means of computer controlled system with software. The TEM characterization of the samples used in the present study Energy dispersive X-ray analysis (EDX)

were carried out using a JEOL JEM-2100 transmission electron microscope which is shown in figure 2.5.



Figure 2.5: JEOL JEM-2100 transmission electron microscope [165]

2.3.4 Energy dispersive X-ray analysis (EDX)

Energy dispersive X-ray (EDX) is an analytical method for identifying the elemental composition of the materials. The interaction between the electron beam with a sample target leads to the emission of X-rays with various range of energy [166]. The characteristic X-rays of different elements in the energy spectrum can be known by analyzing the energy of the emitted X-rays [167]. In EDX measurements, the sample is bombarded with an electron beam, these electron beam collide with the electrons of the sample atoms resulted the X-ray emission. Every element releases X-rays with unique nature which is characteristic of that particular element. By measuring the amounts of energy present in the X-rays being emitted by a sample during electron beam bombardment,

Experimental techniques



Figure 2.6: Elements in an EDX spectrum are identified based on the energy
[169]

the identity of the atom from which the X-ray was emitted can be established [168].

An EDX spectrum identifies the element corresponding to each of its peaks and also the type of X-ray. A peak corresponding to the amount of energy possessed by X-rays emitted by an electron in the L-shell going down to the K-shell is identified as a K_{α} peak [169]. The peak corresponding to X-rays emitted by M-shell electrons going to the K-shell is identified as a K_{β} peak shown in the figure 2.6. The EDX measuring arrangement is usually housed inside the scanning electron microscope or transmission electron microscope.

2.3.5 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy is a quantitative spectroscopic surface chemical analysis method used to estimate the chemical composition and electronic state of elements on the surface of materials or ultra thin layers of materials [170, 171]. XPS usually collect quantitative information from the top most atomic layer of the solid surface [170]. Further more, XPS can be used to determine the thickness of materials made one or more thin layers (1-8 nm) with different materials. X-ray photoelectron spectroscopy operates on the principle of photoelectric effect postulated by Albert Eientein. It operates under ultra vacuum conditions. XPS can give information about the empirical formula of the sample and the chemical state of elements present in a material [171]. When a photon (X-rays) of suitable energy is incident on a material, it will emit photoelectrons. If we know the quantity i.e, energy of the particular X-ray wavelength used to excite an electron from a core orbital of an atom, we can determine the electron binding energy of each of the emitted electrons by using the following equation.

$$E_{binding} = E_{photon}$$
 - $E_{kinetic}$ - ϕ

Where $E_{binding}$ is the energy of electron emitted from one electron configuration within the atom, E_{photon} is the energy of the X-ray photons being emitted, $E_{kinetic}$ is the kinetic energy of the emitted electron as measured by the instrument and ϕ is the work function of the spectrometer and not of the material. Measuring the kinetic energy and the binding energy of the electron gives an idea about the oxidation state of the elements present on the materials. The number of electron reflects the proportion of the specific elements on the surface [171].

The major limitation of XPS is that it could not detect light elements like Hydrogen or Heleum because these elements have only valance orbitals. The elemental composition of the samples used in the present study were carried out using a Kratos AXIS Ultra spectrometer which is shown in figure 2.7.

Experimental techniques



Figure 2.7: Kratos AXIS Ultra spectrometer [172]

2.3.6 UV-Vis diffuse reflectance spectra (DRS)

Diffuse reflectance is an important tool for the optical characterization of powdered sample in the UV-Vis-NIR spectral ranges [173]. The DRS measures the spectral change between incident and back scattered light intensity related to absorption and scattering processes. DRS technique is used mostly in the case of samples with poor optical transmission. The reflectance from the sample at particular wavelength consist of the sum of two components: regular or specular (mirror) reflectance and diffuse (volume or nondirectional) reflectance.

DRS basically depend on the projection focus of the spectrometer beam into the sample where it is reflected, scattered and transmitted through the sample material. The diffusely scattered light and the back reflected light is then collected by the accessory and directed to the detector of the spectrometer. Sometimes the sample may absorb a portion of the incident light [173]. A portion of the incident beam undergoes scattering within the sample and returned to the surface of the sample and is called diffuse reflection. The



Figure 2.8: JASCO V 570 spectrophotometer

specular reflectance component in diffused reflectance light may contribute to changes in band shapes and its relative intensity These process follows laws of geometric optics. When a light beam is absorbed by a sample it follows Lambert absorption law [173].

$$I = I_0 e^{-\alpha t}$$

In which 'I' is the radiation flux transmitted from an initial flux 'I₀' following passage through a layer of thickness 't' of a sample with an absorption (or extinction) coefficient ' α ' measured in transmission [173].

If the size of the sample is small with respect to beam cross section but large relative to the wavelength of light, there is probability of optical diffraction. Randomly distributed particles with such a small size are seen in powdered sample. As a result, a portion of the incident radiation goes back at all angles into the hemisphere of origin of the radiation. This reflection process contributed to reflection, refraction, diffraction, and absorption by particles oriented in all directions is called diffuse reflection [167, 173]. When light falls on a powder sample, it is reflected in all directions because of variation in shape of the sample. A part of the light is refracted as it enters the powder, and is scattered due to internal reflection, reflection from the surfaces of other grains, or repeated refraction. Some of this scattered light is return back into the air medium. As the diffuse reflected light is reflected or passes through the powder, it becomes weaker if it is absorbed by the powder [173]. This results in a diffuse reflected spectrum, similar to the transmission spectrum. K-M function $(F(R_{\infty}))$ derived by Kubelka-Munk is used for comparison to transmission spectra or quantitative analysis [174].

$$F(R_{\infty}) = \frac{(1-R_{\infty})^2}{2R_{\infty}} = \frac{K}{S}$$

Where $F(R_{\infty})$ is usually termed the remission function or Kubelka-Munk (KM) function. R_{∞} is the absolute reflectance, 'K' is the absorption coefficient, and 'S' is the scattering coefficient. However, due to the difficulty in measuring the absolute reflectance R_{∞} , in practice, the comparative reflectance r_{∞} with respect to a standard BaSO₄, of which 'K' is nearly zero in the actual measurement range.

The comparative reflectance r_{∞} is calculated from the equation,

$$\mathbf{r}_{\infty} = rac{R_{\infty}(Sample)}{R_{\infty}(Standard)}$$

In the present study, we are used Jasco V 570 spectrophotometer for DRS measurement and BaSO₄ as standard (Figure 2.8). $R_{\infty}(Standard)$ is taken as unity and is taken as unity and $R_{\infty}(Sample)$ is the diffuse reflectance of the sample. Therefore $F(r_{\infty})$ become,

$$F(r_{\infty}) = \frac{(1-r_{\infty})^2}{2r_{\infty}} = \frac{K}{S}$$

The band gap of the material is estimated from the plot of $[(k/s)h\nu]^2$ versus $h\nu$ (where $h\nu$ is the photon energy) by extrapolating the graph to the x-axis.

2.3.7 Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared (FTIR) spectroscopy is a versatile analytical method used to analyze organic or inorganic solid, liquid or gas samples which gives both qualitative and quantitative information from the sample. It is a relatively cost effective method for the analysis of crystalline or amorphous samples [175, 176]. When an electromagnetic radiation in the IR region passes through a material, molecules in the material will vibrate which result in absorption of IR radiation corresponds to the vibration of the molecule. Each molecule has its own characteristic vibrational frequency which gives unique information about the molecular structure and functional groups present in the material. In FTIR spectrometers, the interference of radiation between two rays gives an interferogram [177]. The interferogram is measured for all frequencies in the corresponding frequency range simultaneously and a time domain spectrum is obtained from the sample. The time domain spectrum is converted to frequency domain spectrum with Fourier transformation. A spectrum consist of intensity vs individual frequency and this makes the interpretation of data much more easier. The Fourier transformation operation is carried out with a computer program [178]. The FTIR instrument consists of a moving mirror, fixed mirror, beam splitter, IR radiation source and detector. Michelson interferometer like optical arrangement is used to generate interferogram from the sample.

The resolution for an FTIR instrument is limited by the maximum path difference between the two beams. The limiting resolution in wave numbers (cm^{-1}) is the reciprocal of the path length difference (cm) and it is usually gives high resolution [177]. Optical slits and other restricting devices are not using in FTIR spectrometer so the total source output can be passed through the sample continuously. This results in a substantial gain in energy at the detector [177]. The optical components of the IR spectrometer are made of

hygroscopic alkali halide materials like KBr which limits the efficiency of this machine in highly humid environment. Further, the sample will be damaged, because it requires to make pellet with IR transmitting material like KBr for the measurement. Majority of the FTIR spectrometer operates in the mid IR frequency region which is from 400-4000 cm⁻¹. In the present study we have used Shimadzu Prestige spectrometer for FTIR measurements (Figure 2.9).



Figure 2.9: Shimadzu Prestige FTIR spectrometer

2.3.8 Raman Spectra

The Raman spectroscopy is complimentary method to infrared spectroscopy which measures the molecular vibrations, rotations, lattice vibrations etc., of a molecule. Raman spectroscopic technique can be used to study solid, liquid and gaseous samples [179]. The physical phenomenon involved in Raman spectroscopy is different from the infrared spectroscopy. Raman spectroscopy is based on the scattering of light while the infrared spectroscopy is based on absorption of photons. The basic phenomenon Raman effect was experimentally observed by C.V. Raman in the year 1928 and is popularly known as Raman effect [180]. Raman scattering measurement technique is based on

Raman Spectra

the phenomenon of Raman Effect. Raman spectra occurs due to the inelastic scattering of incident radiation through its interaction with molecules of the sample [181].

The Raman effect is based on molecular deformations in the electric field 'E' determined by molecular polarizability ' α '. An electromagnetic radiation especially laser beam can be considered as an oscillating electromagnetic wave with electrical vector 'E'. The interaction of this radiation with the sample induces electric dipole moment $P = \alpha E$ which deforms molecules. Because of periodical deformation, molecules start vibrating with its characteristic frequency of the molecules present in a material ' ν_m '. A change in polarizability during molecular vibration is an essential requirement to obtain Raman spectrum of the sample [181, 182].

When a monochromatic light beam strikes on the sample, it scatters and the scattered radiation split up into three components. Among these, one has a frequency equal to frequency of incident radiation called the Rayleigh scattering [181]. Only a small fraction of scattered radiation have frequency less than that of incident radiation gives stokes lines in the Raman spectrum. But when the frequency of scattered radiation is higher than frequency of incident radiation, anti-stokes lines originate in the Raman spectrum [182]. Stokes Raman bands involve the transitions from lower to higher virtual energy vibrational levels which are more intense than anti-stokes bands. Stokes Raman bands are measured in conventional Raman spectrometer and anti-stokes bands are measured especially from the fluorescing samples [181, 182]. The magnitude of Raman shifts does not depend on wavelength of incident radiation, but it depends on frequencies of vibration of molecules.

The most important advantages of Raman spectroscopy over other analytical techniques are the easiness of sample handling and the rich information gathering in the frequency range 50-4000 cm⁻¹ [183]. Moreover, no two



Figure 2.10: Horiba Jobin Yvon LabRam HR spectrometer [184]

molecules give exactly the same Raman spectrum, so the Raman spectrum of each sample gives unique information. The intensity of the scattered light is related to the amount of material present in the sample. Raman spectra gives both qualitative and quantitative information about the sample.

Raman spectroscopy is an important non-destructive technique, extensively for analysis of crystallinity of materials, phase transitions and polymorphs [183]. In the present study, Raman spectrum of the sample was recorded with a Horiba Jobin Yvon LabRam HR system with Ar-ion laser (514.5 nm) as the excitation source (Figure 2.10).

2.3.9 Photoluminescence

Photoluminescence (PL) is a physical process in which spontaneous emission of light from a material will occur under optical excitation. Photoluminescence spectroscopy is a nondestructive sensitive analytic method for probing

Photoluminescence

the discrete electronic structure of materials without any electrical contact [185]. PL investigations of a material will provide a lot of information related to material parameters. The PL emission spectrum can be used to identify surface, interface, and impurity levels in a material. The intensity of the PL signal provides information on the quality of surfaces and interfaces. By using pulsed excitation sources, the transient PL intensity gives knowledge about lifetime of non-equilibrium interface and bulk states. Thermally activated physical phenomenons in a material will also leads to variation in PL intensity with respect to the temperature [185]. When light incident on a sample, it is absorbed by the sample and the excess energy is used for photo-excitation. The sample will dissipate this excess energy through the emission of light, or luminescence [186]. Photo-excitation leads to the lifting of electrons within a material to move into permissible excited states and these excited electrons return to their equilibrium states, by giving out the excess energy in the form of photons. The relaxation process of electrons from excited state to normal state are either radiative process or a non-radiative process (Figure 2.11). In a radiative process, the energy of the emitted light relates to the difference in energy levels between the two electronic states. The quantity of the emitted light is related to the relative contribution of the radiative process. Resonant radiation, fluorescence and phosphorescence are the major photoluminescence process, the phenomina of each emission process is different [186].

A photon of a particular wavelength is absorbed and an equivalent photon is immediately emitted in resonant radiation process which occur within a time of 10 nanoseconds. When a material undergoes internal energy transitions before relaxing to its ground state by emitting photons, some of the absorbed energy is dissipated so that the emitted light photons are of lower energy than those absorbed is fluorescence, which has a short lifetime $(10^{-8} \text{ to } 10^{-4} \text{ s})$ [186].

If the energy of a photon is greater than the band gap energy, then it



Figure 2.11: Schematic diagram of PL emission
[187]

can be absorbed and thereby raise an electron from the valence band to the conduction band across the forbidden energy gap in a semiconductor material [187]. After this photo-excitation process, the electron may falls down, the energy it loses is converted back into a luminescent photon which is emitted from the material. This the energy of the emitted photon is a direct measure of the band gap energy (E_g) [187].

PL technique can be provide a detailed information on discrete electronic states involving both intrinsic optical processes and the wide variety of defect present in material. In practical semiconductor materials, an extrinsic optical processes by applying an external light with energy $h\nu \geq E_g$; where E_g denotes the energy band gap, and observing the re-emitted photons. The major features of photoluminescence measurements are given below [185],

Photoluminescence

- Study the recombination mechanisms and identification of surface, interface, and impurity levels.
- Common radiative transitions in semiconductors occur between states in the conduction and valence bands, which has an energy difference equivalent to its band gap, E_g . As a result the band gap of the semiconducting materials can be easily determine with PL technique.
- Further, material quality can be measured by quantifying the amount radiative recombination. Since most of the non-radiative recombination is associated to localized defect levels that are detrimental to material quality and subsequently to device performance.
- Sometimes, radiative transitions also contributes to the involvement of localized defects, the photoluminescence energy associated to these levels can be used to identify specific defects.
- It gives information about deep energy states in a material, because radiative transitions give very broad spectra due to strong phonon coupling.

In the present work, room temperature photoluminescence (PL) of the samples was measured on a Horiba Jobin Yvon LabRam HR system with the He-Cd laser (325 nm) as excitation source (Figure 2.10).

2.3.10 Diamond anvil cell (DAC) technique

The diamond anvil cell (DAC) can be used to create very high pressures of the order of 100 GPa for high-pressure physical measurements. The major feature of DAC is its adaptability for different experimental setups due to its smaller size [188]. The experimental sample is kept between flat parallel faces of two diamond anvils which are termed as called cutlet faces of the diamond. A modest force applied across the wide face of the diamond (table face) which can generate high pressure on the small 'cutlet face' [188]. The applied force pushes one anvil diamond against the other. The diamond anvils should be perfectly aligned axially and set parallel to each other which is required for pressure generation [188]. Solid and liquid samples can be put in between the cutlet faces of the diamonds because diamond is very hard and inert [188]. Especially, powder samples can be easily investigated with DAC because powder sample will be trapped between the two anvils smoothly. Once compressed, it will become a circular film approximately 30 μ m thick. There pressure gradient within the sample since the center of the sample will be at high pressure and the edges it is about 1 atmosphere [188]. Pressures within the diamond anvil cell can be made about 100 GPa (1 GPa = ~ 9869.23 atmospheres). Figure 2.12 shows the typical schematic representation of diamond anvil cell.

The major parts of the diamond anvil cell are given below [188],

• Diamond anvil

Two diamonds having $\frac{1}{2}$ - 1 carat in size can cut like small 'cutlet face' which helps the diamond anvils sit on 'seats'. The seats are usually made of strong material so that they can transmit the load from rest of the cell to the diamonds [188].

• Gasket

The gasket which used to contain the sample is a thin sheet which has a small hole about $\frac{1}{2}$ diameter of the cutlet face of the diamond - typically <500 μ m. The steep pressure gradient is contained in the gasket which spares with the sample. Rhenium, Kapton Cu, Be etc. are commonly used material for making gasket [188].



Figure 2.12: Schematic representation of diamond anvil cell [188]

• Pressure media

Gases such as Ne, Ar, or N_2 etc. are used to transmit pressure (Pressure transmitting medium) on the sample. The pressure inside the DAC can be adjusted by simply changing distance between the diamonds and keeping them in that position. Pressure transmitting medium in the liquid form due to compression provide hydrostatic environment inside the DAC [188].

• Pressure Measurement

Ruby crystal exhibit fluorescent emission consists of two well defined peaks at wavelengths of 6942 Å (R_1 line) and 6927 Å (R_2 line). The position of these fluorescent emission will change with respect to pressure and can be used to

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monitor the pressure inside a DAC [188]. The ruby scale shows almost linear behavior up to 300 kbar [189]. The pressures dependence of ruby fluorescence lines shows the following relationship [190].

$$\mathbf{P} = \left[\frac{1094}{B} \left(1 + \frac{\Delta\lambda}{694.24}\right)^B - 1\right]$$

Where 'P' is the pressure in GPa, ' $\Delta\lambda$ ' is the ruby R₁ line shift in nm, and parameter 'B' is 7.665 for quasi-hydrostatic conditions and is 5 for nonhydrostatic conditions.

2.3.11 Superconducting quantum interference device magnetometer (SQUID)

Superconducting quantum interference device (SQUID) consists of ring of superconductor worked on the principle of Josephson effect [191]. It can be used to detects very small variations in magnetic flux. The SQUID is used to study the magnetic properties of materials especially materials showing weak magnetic properties because of its size. It is also used to detect small quantities of paramagnetic ions, and quantitative determination of the number of unpaired electrons in samples [192]. Apart from that it can be used to measure the small magnetic field, current, magnetic susceptibility, etc. of materials [193]. In the present study, the magnetic properties of the samples were studied with a SQUID magnetometer (QUANTUM DESIGN).

The Magnetic property measurement system (MPMS) in the SQUID device is the source of the instrument sensitivity, which does not measure the magnetic field from the sample directly. The experimental specimen is allowed to move through a superconducting coils. The current from the detection coils are inductively coupled to the SQUID sensor [191]. The change in magnetic flux leads to the variations in the current in the detection coils which produce

66

corresponding variation in the SQUID output voltage which are proportional to the magnetic moment of the sample [191]. These systems are extremely sensitive to magnetic properties of materials and it can be measured in different temperatures especially in the low temperature up to liquid He temperature.

2.3.12 Vibrating sample magnetometer (VSM)

Vibrating sample magnetometer (VSM) systems are usually used to study the magnetic properties of materials and its sensitivity less with respect to that of SQUID. It can used to measure the magnetic properties of materials as a function of magnetic field, temperature, and time. Samples in different forms such as powders, solids, and thin films can be used in the sample holder set-up [193]. It can measure magnetic properties of materials such as hysteresis, saturation, coercivity, and anisotropy [194].

Based on Faradays law of induction, the VSM relies on the detection of the emf induced in a coil of wire which is given by [194],

 $e = -N\frac{d}{dt} (BA \cos \theta)$

where 'N' is the number of wire turns in the coil, 'A' is the coil turn area, and ' θ ' is the angle between the field B and the direction normal to the coil surface. In VSM, the magnetic sample is placed on a long rod which is driven by a mechanical vibrator. This rod is placed between the pole pieces of an electromagnet which is attached with detection coils. The motion of the magnetized sample will induce a voltage in the detection coils which is proportional to the magnetization of the sample [194, 195]. The room temperature magnetic properties of the present samples were studied by using a Lakeshore VSM-7410 vibrating sample magnetometer.

Experimental techniques

Chapter 3

Hydrothermal growth and PL investigation of ZnO nanoflowers

3.1 Introduction

ZnO is a wide band gap (3.37 eV) transparent semiconductor with attractive technological applications [196]. ZnO is a promising material for short wavelength optoelectronic devices, especially UV light-emitting diodes, LEDs and laser diodes due to its large exciton binding energy (60 meV) [57]. ZnO is a potential photocatalyst, has the advantage of lower cost, absorbing more light quanta and higher photocatalytic efficiencies for the degradation of several organic pollutants in both acidic and basic medium [197]. The preparation of crystalline ZnO with specific structures is crucial to explore its potential applications in depth [198]. ZnO nanostructures with different morphologies, such as flowerlike [199], nanorods [200], nanowires [201], nanobridges, nanonails [202], nano/micro-sized particles [203] and micro-tubes [204] can be synthesized by different methods. These nanostructures can be used as efficient gas sensors and also for the fabrication of photodiodes, photodetectors, solar cells

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and next generation UV sources [64]. ZnO nanostructures usually exhibit UV near band-edge (NBE) emission as well as defect level emission in the visible region [205]. Light-emitting properties and photocatalytic activity of ZnO nanostructures can be modified by changing its structural and morphological features [206]. It is a technologically important and challenging task to synthesize ZnO nanostructures at low cost to be used as UV generating sources. In this context, hydrothermal synthesis is a promising eco-friendly solution based method to grow different types of ZnO nanostructures. It is worth noting that Haiyong *et al.* have demonstrated the ability of a direct growth of ZnO nanoflowers on substrates using the hydrothermal method: GaN-based LED epiwafer and AlN that are grown on c-sapphire [207, 81].

Recently, flower-like ZnO nanostructures were identified to be a material of choice for fabricating low power consumption sensors because of its respond time (about 30 s) longer than that for sensors working at high temperatures [208]. Flower-like ZnO nanostructures (ZnO nanoflowers) proved their potential use as photoanode for dye-sensitized solar cells that enhanced the solar cell efficiency about 90% due to improved dye-loading and light harvesting [209]. On the other hand, Kim *et al.* [210] studied the field emission characteristics of the flower-like ZnO arrays for cold cathode emitter applications. ZnO nanoflowers exhibited excellent electron emission characteristics with a low turn-on field of 0.13 V μ m⁻¹ which was several orders of magnitude lower than that of 7.6 V μ m⁻¹ for the vertically aligned high density ZnO nanoneedles [210]. Furthermore, the light-emitting devices fabricated using these nanoflowers arrays as electron emitter demonstrated strong light emission, indicating that the luminescence originates from the electron emission from the ZnO nanoflower arrays. There are many studies reported on the growth of ZnO nanoflowers with a growth temperature ranging from 90 to 200 °C and reaction/growth time of 30 minute to 13 hours [207, 81, 211, 212, 213]. The re-

Experimental

duction in reaction time is an important consideration with respect to a large scale production of nanomaterials for technological applications. However, in all the above mentioned studies the ZnO nanoflowers exhibited un-desirable green/visible emission related to the defect states in the ZnO nanostructures. Taking this into account, we have performed several experiments in order to optimize the growth condition of ZnO nanoflowers by a hydrothermal synthesis process with a short reaction time and low growth temperature in order to obtain flower-like ZnO nanostructures with minimum defect related emission. In this work, we report the synthesis and characterization of ZnO nanoflowers with enhanced UV emitting nature (with suppressed visible emission related to defect states in ZnO), grown by the hydrothermal method at an optimized growth temperature of 200 °C and a growth time of 3 hours.

3.2 Experimental

ZnO nanoflowers were synthesized by the reaction of $\text{Zn}(\text{CH}_3\text{COO})_2.2\text{H}_2\text{O}$ (0.1 M) and NaOH (1 M) under autogenous pressure, at a temperature of 200 °C for a growth time of 3 hours. The pH of the reaction solution was about 8. The entire reaction was carried out in a teflon lined sealed stainless steel autoclave. After the heating process, the autoclave was allowed to cool naturally to room temperature. As-collected resulting white precipitate was washed with distilled water, filtered and dried in air atmosphere at room temperature. The structural characterization of synthesized samples were carried out by a Rigaku (D.Max.C) X-ray diffractometer using Cu K α radiation ($\lambda = 1.5414$ Å). X-ray photoelectron spectroscopy (XPS) measurement was carried out by using a Kratos AXIS Ultra spectrometer. The scanning electron microscope (SEM) images and energy-dispersive X-ray analysis (EDX) of the samples were taken using a Hitachi S-4800 SEM. The transmission electron microscopy (TEM),

high resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) images of the sample was obtained with a JEOL JEM-2100 transmission electron microscope. Raman spectrum of the sample was recorded with a Horiba Jobin Yvon LabRam HR system with Ar-ion laser (514.5 nm) as the excitation source with a resolution better than 3 cm⁻¹. The UV-visible spectrum was recorded within the wavelength range 200-800 nm with a Jasco V-570 spectrometer. Room temperature photoluminescence (PL) of the samples were measured on a Horiba Jobin Yvon LabRam HR system with the He-Cd laser (325 nm) as excitation source.

3.3 Results and discussion

Figure 3.1 depicts the SEM images of the ZnO nanoflowers synthesized at an optimized growth temperature of 200 °C and a growth time 3 hours. The morphology of the ZnO nanoflowers here obtained are closely matched with that obtained by Zhang *et al.* [107] using the hydrothermal process and Chu *et al.* using the solution growth process [213]. The morphology of as-grown crystals is flowerlike and the petal-like parts constitute prismatic needle-shaped elongated crystallites. These petal-like elongated prismatic structures are closely packed around the center of the flower-like structure and have slightly reduced dimensions towards the unattached end. Each petal-shaped part has dimensions of about 234-347 nm in length and 77-106 nm in width. SEM images recorded from various regions of the sample exhibited the uniform morphology.

The TEM, HRTEM and SAED of the hydrothermally grown ZnO is shown in the figure 3.2. The TEM image shows that the average diameter of the individual nanorods constituting the ZnO nanoflower structures varies in the range \sim 90-280 nm and the corresponding aspect aspect ratio is about \sim 5-13 respectively. The HRTEM and SAED data of ZnO indicate the crystalline

Results and discussion



Figure 3.1: SEM images of (a) ZnO nanoflowers synthesized by the hydrothermal method and (b) is a magnified image of the same sample

nature of the sample. The HRTEM image also shows that the interplanar distance (d) is 0.25 nm for hydrothermally grown ZnO nanoflowers which is in good agreement with previously reported value.

The X-ray diffraction patterns/peaks recorded from the ZnO nanoflowers are indexed according to the typical hexagonal wurtzite structure of ZnO with space group P6₃mc (JCPDS: 36-1451) (Figure 3.3). The sample exhibited preferential orientation along the $(1 \ 0 \ 0)$ plane. However, we can observe sharp diffraction peaks from the $(1 \ 0 \ 1)$ and $(0 \ 0 \ 2)$ plane indicating the good crystallinity and purity of the prepared sample. The X-ray diffraction peak along the $(0 \ 0 \ 2)$ plane is indicative that growth of ZnO nanorods constituting the ZnO nanoflowers is in the c-axis orientation. The powder XRD patterns of samples were processed with the Rietveld refinement analysis in order to extract the lattice parameters using the FullProf program [214]. The Rietveld refinement profile of XRD patterns is shown in figure 3.4.

The values so obtained from the Rietveld analysis are a = 3.2499 Å and

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Figure 3.2: TEM image of hydrothermally grown (a) ZnO, (b) HRTEM and SAED (inset) of ZnO



Figure 3.3: X-ray diffraction pattern of ZnO nanoflowers

Results and discussion



Figure 3.4: The Rietveld refinement profile of XRD data of ZnO nanoflowers

c = 5.2151 Å. These values are slightly different from the standard values of hexagonal ZnO: a = 3.2498 Å and c = 5.2066 Å (JCPDS: 36 -1451). The differences in lattice parameter observed from ZnO nanoflowers can be due to the surface stress on the nanostructures. This stress induces a lattice strain, leading to a lattice expansion, mainly in the c-direction, in order to relieve the strain [215, 216]. We can consider this as evidence that in ZnO nanoflowers grown by using the hydrothermal process, the stress relaxes elastically.

The elemental composition of the as synthesized sample is confirmed with EDX and XPS measurements. Figure 3.5 shows EDX and high-resolution XPS spectra of hydrothermally grown ZnO nanoflowers. The peaks at 531.1, 1021.9 and 1044.8 eV in the XPS spectra corresponding to the singlet of O1S and the doublet of $Zn2P_{3/2}$ and $Zn2P_{1/2}$, respectively, can be attributed to the formation of hexagonal ZnO nanorods [217]. The atomic and weight percentage of elements of the sample obtained from EDX and XPS measurements are



Figure 3.5: a) EDX and b) XPS of spectra of hydrothermally grown ZnO nanoflowers

shown in the table 3.1. The values which are obtained from EDX and XPS measurements are closely match to each other.

Table 3.1: The atomic and weight percentage of elements of the sample obtainedfrom EDX and XPS measurements

Elemental composition				
Elements	EDX		XPS	
	Atomic	Weight	Atomic	Weight
	percentage	percentage	percentage	percentage
Zn	42.70	76.23	49.52	80.04
0	43.19	18.86	50.48	19.96

The catalyst free growth of ZnO nanoflowers at low temperature depends on the other growth conditions. The physical and chemical nature of the sol-
vents is the key factor which influences the nucleation and the oriented growth process of ZnO materials [108]. The reaction between $Zn(CH_3COO)_2.2H_2O$ and NaOH will give $Zn(OH)_2$ which is not stable with a heat treatment under autogenous pressure. Therefore, $Zn(OH)_2$ dissociates to Zn^{2+} ions and $OH^$ ions, and the detachment of OH^- radical may activate the nucleation centres. ZnO nuclei can be preferentially formed on the coalescent sites by the Coulomb interactions between Zn^{2+} ions and O^- ions within the solution [107]. As the time of growth increases more ZnO molecules will be attached to the initially formed nucleation centres. On these individually formed nucleation centres, bundles of ZnO nanorods are aggregated in three dimensional array and flower-like morphology is developed.

Figure 3.6 depicts the Raman spectrum recorded from the ZnO nanoflowers at room temperature. In the Raman spectrum of the sample, a strong Raman active phonon band located at 437 cm⁻¹ corresponds to E_2 (high) mode, whereas the suppressed bands of ZnO observed at 583 and 541 $\rm cm^{-1}$ are attributed to the $E_1(LO)$ mode and second order $2B_1$ low; 2LA overtones, respectively [218, 219]. The weak bands are also seen in the Raman spectrum of hydrothermally grown ZnO nanorods at 330, 382, 541, and 583 $\rm cm^{-1}$ which are assigned in detail (Table 3.2). The Raman bands at 583 and 660 $\rm cm^{-1}$ are associated with structural disorders, such as oxygen vacancy, Zn interstitial etc. [220]. The presence of an intense $E_2(high)$ mode and a suppressed $E_1(LO)$ mode in the Raman spectrum indicates that the as synthesized ZnO nanoflowers are highly crystalline with a hexagonal wurtzite phase which is in agreement with X-ray diffraction results. Another three prominent Raman bands are observed at 99, 330 and 382 cm^{-1} . Raman bands recorded from the ZnO nanoflowers are compared with the reported values of single crystal ZnO which are presented in table 3.2 [218].

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Figure 3.6: Raman spectrum of ZnO nanoflowers synthesized by the hydrothermal method

The strong band observed $E_2(high)$ at 437 cm⁻¹ is the intrinsic characteristic Raman active mode of wurtzite hexagonal ZnO [221]. The Raman bands at 99, 330 and 382 cm⁻¹ [218] corresponds to multiple phonon scattering processes of $E_2(low)$, $E_2(high)-E_2(low)$ and $A_1(TO)$ modes, respectively. Raman bands observed in between 541 and 583 cm⁻¹ are associated with crystal structural disorders, such as oxygen vacancy, Zn interstitial and their combination [222, 223, 224]. It is to be noted that the Raman modes correspond to defect states (541 and 583 cm⁻¹) are very weak, pointing to the fact that the ZnO nanostructure obtained here, using the hydrothermal process are comparatively less number of optical active defects, which will demonstrate in the following section using the PL study.

Figure 3.7(a) depicts the reflectance spectrum recorded from ZnO nanoflow-

Frequency (cm-1)						
This work (ZnO	Single crystal	Assignments				
nanoflowers)	ZnO [218]					
99 (s)	99	$E_2(low)$				
205 (w)	203	$2TA; 2E_2(low)$				
330 (w)	333	$E_2(high)-E_2(low)$				
382 (w)	378	$A_1(TO)$				
437 (vs)	438	$E_2(high)$				
541 (vw)	536	$2B_1(low); 2LA$				
583 (vw)	590	$E_1(LO)$				
660 (w)	657	$A_1 (TA + LO)$				

Table 3.2: Raman spectral data (cm⁻¹). (Note: w-weak; vw-very weak; s-strong; vs-very strong)

ers. The optical absorption edge of ZnO nanoflowers appears at 384 nm which is red shifted by 11 nm relative to the bulk exciton absorption (373 nm) [225]. Correspondingly, the ZnO nanoflowers exhibited a lower optical energy gap of 3.23 eV with respect to bulk ZnO. The band gap of the flower-like ZnO nanostructure is estimated from $[(k/s)h\nu]^2$ versus $h\nu$ plot (Figure 3.7(b)), where 'k' and 's' denote the absorption and scattering coefficients, and ' $h\nu$ ' is the photon energy [226]. The ratio of (k/s) is calculated from the reflectance via the Kubelka Munk equation [227]. The reason for red shift in absorption edge/optical energy gap can be well explained as due to the oriented attachment of the nanorods and it has been specifically observed in ZnO with flowerlike morphology [198]. From the X-ray diffraction analysis, we have seen that ZnO nanoflowers obtained using the hydrothermal process are strain relaxed, as evident from the enhanced lattice parameters 'a' and 'c'. This in turn could



Figure 3.7: (a) Reflectance spectrum and (b) $[(k/s)h\nu]^2$ versus $h\nu$ plot of ZnO nanoflowers synthesized by the hydrothermal method

incur a slight decrease in the band gap of the ZnO nanoflowers [228].

The room temperature PL spectrum under the excited wavelength of 325 nm of the as-prepared ZnO nanoflowers is shown in figure 3.8. The PL spectrum of the ZnO nanoflowers generally shows two emission bands, one is in the UV region at 392 nm, and an almost negligible blue band at 510 - 580 nm. The UV emission band at 392 nm pertains to the recombination of free excitons between the conduction and valence bands and is called the NBE emission (NBE), while the longer wavelength band can be attributed to the radial recombination of a photo-generated hole with electron, which belongs to the singly ionized oxygen vacancy [229]. The strong UV emission located at about 392 nm in the PL spectrum of the present sample indicates that, the ZnO nanoflowers have good crystal quality with few oxygen vacancies which corresponds to the self-activated luminescence [219]. The improvement in the crystal quality such as low structural defects, oxygen vacancies, zinc interstitials and decrease in the impurities. This may cause the appearance of sharper



Figure 3.8: PL spectrum of ZnO nanoflowers at room temperature

and stronger UV emission with a suppressed and weakened green-red emission [230]. Moreover, the optical properties are also directly influenced by the morphologies and size of the final products [231]. The structure of flower-like ZnO has small size and large surface area which in turn contributes to intensity enhancement.

Chu et al. [213], in a study conducted on ZnO nanoflowers grown using the solution growth technique, observed an enhanced visible emission centred around ~ 550 nm over the UV emission with an increase in the random distribution of ZnO nanoflowers. The dominant visible emission observed (with respect to the UV emission) was explained due to the enhanced adsorbed oxygen, as a result of increased surface area of the random distributed ZnO nanoflowers. Similarly they observed a gradual decrease in the X-ray diffraction peak along the (0 0 2) plane with increase in the random distribution of ZnO nanoflowers, which is evidence of degradation of the c-axis orientation of the ZnO nanorods constituting the flowers [213]. In the present case, we obtained randomly distributed ZnO nanoflowers morphology similar to that obtained by Chu *et al.* [213]. However, as synthesized ZnO nanoflowers exhibited negligible visible emission related to the defect states as compared with the UV emission centered at 392 nm. The X-ray diffraction pattern recorded from ZnO nanoflowers exhibited strong and sharp peak of ZnO along the (0 0 2) plane (Figure 3.3). This indicates that even though the ZnO nanoflowers are randomly distributed, the ZnO nanorods constituting the nanoflowers structure are oriented along the c-axis, which favours the growth of ZnO nanoflowers with minimal defects (adsorbed oxygen, oxygen vacancy, Zn interstitial). Similarly Raman analysis supported that the ZnO nanoflowers have minimum defect states, as observed from the suppressed Raman active modes at 541 and 583 cm^{-1} respectively.

3.4 Conclusions

In summary, good crystalline ZnO nanoflowers with less optical active defects can be synthesized by a low-temperature hydrothermal method at a relatively low reaction time of 3 hours. The X-ray diffraction and Raman analysis confirmed the crystalline quality of the ZnO nanoflowers. The Rietveld refinement analysis of the X-ray diffraction data reveal that, stress relaxes elastically in ZnO nanoflowers grown using the hydrothermal process. This behavior is determined from the calculation of lattice parameters which indicate an expansion, mainly in the c-direction, of the ZnO nanoflowers. As synthesized ZnO nanoflowers exhibited an optical energy gap of 3.23 eV. The lower value of the observed band gap (with respect to the bulk ZnO) is attributed to the flower-like surface morphology and the expansion of lattice in order to relieve the lattice strain. The room temperature PL spectrum of ZnO nanoflowers

shows a strong UV emission peak at 392 nm with a negligible visible emission related to the defect states as compared with the UV emission. The very weak Raman active modes at 541 and 583 cm⁻¹ associated with the defect states in ZnO confirm the significant reduction of the optical active defects. Therefore, the ZnO nanoflowers grown using the hydrothermal process at an optimized growth temperature and growth time can be used as a good UV emitting source in light-emitting devices.

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Chapter 4

Pressure dependent Photoluminescence and Raman investigation of hydrothermally grown ZnO nanoflowers

4.1 Introduction

ZnO possess different crystalline structures depending on its growth/pressure conditions. The stable crystal structure of ZnO is wurtzite (W) (B₄), but it can also exist in metastable rocksalt (RS) (B₁) [232], zinc-blende (ZB) (B₃) phases [58]. Theoretical calculations also propose the metastability of graphitic ZnO nanoparticles [233]. High pressure investigations are an excellent tool to investigate the effect of morphology on the pressure-induced phase transition of ZnO. The available literature on bulk ZnO under high pressure includes optical studies [234, 235], Raman [223] and structural [236] investigations, which reported W-to-RS phase transition at around 9 GPa. The RS phase of ZnO has an inversion center, there are no Raman-active phonon modes, and its band gap has an indirect character [235]. Consequently, one should expect an intensity reduction of Raman bands as well as PL peaks as a signature of the W-to-RS transition. Chen et al. [237, 238] reported the pressure-dependent PL of ZnO nanotubes and nanosheets, and observed a W-to-RS transition at about 15 GPa and 11 GPa, respectively, which is a higher transition pressure than the one observed in bulk ZnO (9 GPa). The elastic properties of ZnO crystals and nanopowder with a grain size of about 65 nm were also reported by Duzynska etal., and the W-to-RS transition is seen at 11 GPa [239]. Previous investigation on the pressure dependence of the band-to-band PL of ZnO nanowires up to 15 GPa revealed that the phase transition occurs in the 12-14 GPa range [240]. Xiaoqin et al. [241] reported that Raman peaks corresponding to the W structure in ZnO nanowires reversibly disappear at about 10.3 GPa. These studies indicate that pressure-dependent PL emission properties as well as the W-to-RS phase transition pressure of ZnO nanostructures are related to their size and morphology. Enhanced UV emission at 392 nm from hydrothermally grown wurtzite ZnO nanoflowers was observed and the details were explained in chapter 3. In the present chapter, we report the results of PL emission and Raman scattering measurements on W-ZnO nanoflowers under high pressure up to 14 GPa.

4.2 Experimental

The ZnO nanoflowers used in the present study were grown by a hydrothermal process by the reaction of zinc acetate and NaOH at a temperature of 200 o C for a reaction time of 3 h; the details are given in chapter 3. For PL and Raman scattering measurements under high pressure, ZnO nanoflower sample was placed together with a 10 μ m ruby microsphere into a 200 μ m

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diameter hole drilled into a 50 μ m thick steel gasket placed in a membrane diamond anvil cell (MDAC) [242]. A combination of methanol-ethanol-water (16 : 3 : 1) was used as a pressure transmitting medium, and the pressure was monitored by measuring the luminescence of ruby [243]. A 266 nm pulsed UV laser was employed for PL excitation and a box-car synchronized to the laser frequency was used for the detection of signals. The Raman spectra of the sample were recorded using a confocal HORIBA Jobin-Yvon LabRam spectrometer supported by a diffraction grating (1200 grooves mm⁻¹). The slit width of the spectrometer was adjusted to 100 μ m and the Raman intensity was collected with a thermoelectric cooled multichannel CCD detector (resolution better than 2 cm⁻¹). An Ar⁺ laser source with a wavelength of 514 nm and a laser power of 10 mW was used as an excitation source. The data acquisition time for each spectrum was 500 s and the occurrences of spikes were eliminated by taking the average of two spectra for each measurement. The laser-induced damage did not occur in the sample during the spectral measurement.

4.3 Results and discussion

The PL spectrum of ZnO at room temperature show a near band edge (NBE) emission in the UV region and a defect-related emission in the visible region usually above 500 nm. As shown in chapter 3, the present nanoflower sample shows only an intense NBE band at 3.23 eV [244]. As the pressure increases, the NBE PL peak monotonously shifts to higher photon energies (Figure 4.1)

The PL peak intensity is virtually constant up to 5.2 GPa and then gradually decreases with the increasing pressure and the intensity become negligible at 13.8 GPa. The pressure evolution of the PL peaks does not strictly reflect the pressure dependence of the band gap. The stokes shift associated with all processes involving photo excited carrier thermalization and changes



Figure 4.1: PL spectra of ZnO nanoflowers under hydrostatic pressures at room temperature

in the line width can modify the pressure dependence of the PL peak maximum. The derivative of the PL spectra will give further information about pressure-dependent behavior. Two energies are chosen as representative of the pressure dependence spectra; one of them corresponds to the PL maximum and the other one to the derivative minimum, i.e. the inflexion point on the high energy side of the PL peak. Figure 4.2 shows the pressure dependence of the two photon energies obtained from the PL peaks and its derivative, as well as the pressure dependence of the PL peak intensity.

The experimental pressure dependence of each PL energy can be fitted to a quadratic equation, $E_{PL}(P) = E_{PL}(0) + aP + bP^2$, as shown in figure 4.2

 Table 4.1: Pressure coefficients extracted from the pressure dependence of the photon energies corresponding to the PL peak maximum and the PL peak derivative minimum

	Eg (P=0) (eV)	$\mathbf{a} (\mathrm{meV/GPa})$	$\mathbf{b} \; (\mathrm{meV/GPa^2})$
This work (300 K)	3.204 ± 0.006	27 ± 2	-0.6 ± 0.2
This work (300 K)	3.270 ± 0.004	26 ± 1.6	-0.3 ± 0.1
Mang $et al.[234]$ (6	3.4553 ± 0.0002	25.6 ± 0.2	-0.28 ± 0.02
K)			

[234]. The obtained parameters of the quadratic fit are given in table 4.1, together with results from the previous report done by Mang *et al.* [234] for comparison.

At the Brillouin zone center, group theory predicts the existence of the following optical modes for W-ZnO [223], $\Gamma = A_1 + 2B_1 + E_1 + 2E_2$, of which B_1 modes are silent and the rest are Raman active. Polar modes (A_1 and E_1) are also infrared (IR) active and their pressure dependent behavior is investigated by means of FTIR spectroscopy [245]. A detailed analysis of Raman spectrum of ZnO nanoflowers at room temperature was previously reported [244]. Figure 4.3 shows the Raman spectra of the present sample in the pressure range from 0.35 to 12 GPa at ambient temperature. The observed Raman bands at 0.35 GPa are tentatively assigned to $E_2(high)$ -437, $E_2(low)$ -98, $A_1(TO)$ -388, $E_1(TO)$ -420 and $E_1(LO)$ -568 cm⁻¹ and these correspond to the hexagonal W-ZnO phase [218].

In addition to the above bands, a Raman band is seen at 340 cm⁻¹ and its frequency and pressure dependence nature suggest that it may be assigned as a second order mode $E_2(high)-E_2(low)$. However, its pressure-dependent behaviour is complex as it becomes wider and asymmetric until around 3 GPa,



Figure 4.2: (a) The variations of the energy position for the PL NBE emission as a function of pressure, and (b) the intensity of the PL NBE emission as a function of pressure

where this Raman feature splits into two peaks. One of these peaks follows a positive linear trend with pressure and the other shows a slightly negative quadratic tendency. The former can be associated with the $E_2(high)-E_2(low)$ second-order Raman mode due to the similar behavior to the $E_2(high)$ Raman mode under pressure [246]. Whereas the latter was assigned by Serrano *et al.* [247] to the $B_1(high)-B_1(low)$ second-order Raman mode, as discussed by Manjon *et al.* [248]. The discrepancy of the $B_1(high)-B_1(low)$ frequency measured at ambient pressure and the corresponding value directly obtained from the subtraction of the frequencies of these silent modes can be explained

by the fact that these modes are not active in the zone center (Γ -point). But their difference gives a second-order contribution owing to the narrow energy range occupied by the dispersion branches of the B₁(high) phonon along the Γ -A-L-M high-symmetry directions of the Brillouin zone (BZ).

The Raman frequency of the $E_2(high)$, $A_1(TO)$, and $E_1(TO)$ modes increases with increasing pressure while the $E_2(low)$ mode frequency slightly decreases (Figure 4.4). The lines shown in figure 4.4 correspond to the linear fits to the experimental data. The Gruneisen parameter of each Raman active phonon mode was determined from the expression [223].

$$\gamma_i = \frac{d[ln\omega_i]}{d[lnV]} = \frac{B_0}{\omega_i} \frac{d\omega_i}{dP}$$

Where ω_i is the mode frequency, V is the pressure dependent unit cell volume, B₀ is the bulk modulus, and P is the applied pressure. For the present calculation, a value of B₀ = 142.6 is taken from Desgrenier *et al.* [120]. Table 4.2 gives the frequencies at ambient pressure, the pressure coefficients, and the Gruneisen parameters of the different phonon modes.

The $E_2(high)$ and $E_2(low)$ modes remained relatively intense up to the W-to-RS phase transition and it was possible to determine the pressure dependence of their FWHM (full width at half maximum). Figure 4.5(a) shows the $E_2(high)$ Raman peak at four different pressures and the Lorentzian fits that reproduce quite accurately the peak line-shape. Figure 4.5(b) shows the pressure dependence of the Lorentzian FWHM for both modes. The symmetry of the $E_2(high)$ line-shape confirms the hydrostatic measurement condition along with the pressure range used in the present investigation.

Above 10.9 GPa, an abrupt decrease in the intensity of the $E_2(high)$ mode is observed. The disappearance of the characteristic Raman peaks belonging to wurtzite ZnO indicates the occurrence of a W-to-RS phase transition. At higher pressures the Raman spectrum only shows broad bands (especially



Figure 4.3: Raman spectra of ZnO nanoflowers under different hydrostatic pressures



Figure 4.4: Pressure-dependent Raman shift of ZnO nanoflowers

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in the range between 520 and 620 cm^{-1}) which corresponds to the disorderinduced Raman response of RS-ZnO, reflecting the phonon mode density in that frequency range [223].

Raman	ω_0	$d\omega/dP$	$\mathrm{d}\omega^2/\mathrm{d}\mathbf{P}^2$	γ_i	γ_i
modes	(cm^{-1})	$(\mathrm{cm}^{-1}/\mathrm{GPa}^{-1})$	$(\mathrm{cm}^{-2}/\mathrm{GPa}^{-2})$		
$E_2(high)$	98.07	-0.79 (1)		-1.14	-1.6
	(5)				
$E_2(high)$ -	329(2)	5.8(3)		2.51	
$E_2(low)$					
B ₁ (high)-	329(3)	-0.30 (16)	2.6(1.8)		
$B_1(low)$					
A ₁ TO	382.7	4.0(3)		1.49	2.1
	(15)				
E ₁ TO	401(3)	6.0(6)		2.13	1.8
$E_2(high)$	438.1	4.94 (4)		1.60	2.0
	(2)				
E ₁ LO	569(14)	2(2)		0.50	1.4

Table 4.2: Pressure coefficients and frequencies at P = 0 GPa and the corresponding Gruneisen parameters

When compared to values found in the literature on the pressure dependence of the ZnO band gap [234], as given in table 4.1, one can see that besides the energy shift due to the different temperatures and the PL stokes shift, the parameters obtained from the pressure dependence of the PL derivative minimum perfectly agrees with the pressure coefficients reported by Mang *et al.* for ZnO single crystals [234]. It is important to note that a better agreement with

the single crystal bandgap coefficient is found for the PL derivative minimum. This is most likely due to the fact that the high energy tail of the PL peak is mainly determined by PL reabsorption by the sample and, consequently, it should reflect the behavior of the ZnO intrinsic absorption edge much better than the PL peak or the low-energy side, which are more affected by the Stokes shift. The slight disagreement of the PL maximum pressure parameters (with respect to the derivative minimum) can be contributed to the observed PL peak widening for pressures higher than 8 GPa. This observation confirms the high crystalline quality of hydrothermally grown W-ZnO nanoflowers is in agreement with our previous result and the details are given in chapter 3.

In spite of the intensity decrease above 5-7 GPa, the nanoflower's PL signal is observed up to nearly 14 GPa, which is in agreement with the observations of other ZnO nanostructures reported in the literature [237]-[240], indicating that the W phase remains metastable. The metastability of the low-pressure phase in nanostructures (beyond the bulk phase transition pressure) are attributed to the surface energy difference between the crystal phases involved in the transition, which depends on the nanostructure morphology [249, 250]. The observed progressive decrease in the PL intensity with respect to increasing pressure may be attributed to a gradual W-to-RS transition in which the larger nanocrystals undergo a transition at lower pressure. Similarly, Chen *et al.* [237, 238] also reported the UV emission above 9 GPa, which is generated by the smallest W-ZnO nanostructures.

One can see from the Raman spectra that the W-to RS phase transition is completed at around 10.9 GPa. The discrepancy in the transition pressure is due to the relative intensity of the Raman scattering signal with respect to the PL. While the PL intensity can even be enhanced by quantum confinement in nanostructures, the Raman signal from the remaining nanostructures may be too weak to be detected. This is confirmed by the pressure dependence of the $E_2(low)$ and $E_2(high)$ modes FWHM.

At low pressure, there is a decrease in the FWHM of the $E_2(high)$ mode. This behavior was predicted by Serrano *et al.* [251], who calculated the anharmonic contributions of the $E_2(high)$ mode lifetime. They showed that the frequency of the acoustic phonon mode density peak (responsible for one of the main $E_2(high)$ decay channels) decreases under pressure, while the $E_2(high)$ frequency increases; as a result the anharmonic decay rate decreases and consequently so does the $E_2(high)$ FWHM. The observation of this effect, with the FWHM of the same order of those calculated is also a confirmation of the crystal quality of the samples [249]. It is interesting to note that at pressures above 6 GPa, the FWHM quickly increases. Its values in the metastability range increase by a factor 2 with respect to the minimum, confirming that the Raman signal in this pressure range is originated from small nanocrystals. For the case of the $E_2(low)$ mode its natural width is very low due to the scarcity of anharmonic decay channels for this low energy mode [120]. The FWHM value of $E_2(low)$ mode is found to be about 0.4 cm⁻¹ at 300 K [251]. In our experiment, up to about 6 GPa the measured $E_2(low)$ FWHM practically corresponds to the instrumental width (2 cm^{-1}) , but it increases to about 3 cm^{-1} at 10 GPa. By comparing with the previous results on the FWHM of the $E_2(low)$ and $E_2(high)$ modes as a function of the nanocrystal size [252, 253], we can estimate the size of the largest nanocrystals remaining in the W-phase at a given pressure. According to this estimation, the W-ZnO nanocrystal size decreases from about 15 nm at 8 GPa to below 5 nm at 10.3 GPa.

The pressure behavior of the phonon modes is analyzed with respect to the Gruneisen parameter. The Gruneisen parameter is positive for all Raman modes except the $E_2(low)$ mode and the second-order $E_2(high)-E_2(low)$ phonon mode. The negative pressure coefficient of the $E_2(low)$ mode indicates the

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Figure 4.5: (a) Line-shape and Lorentzian fits of the $E_2(high)$ phonon mode of ZnO nanoflowers at different pressure conditions, (b) pressure dependence of the FWHM of the $E_2(low)$ and $E_2(high)$ phonon modes.

softening of this mode under the application of hydrostatic pressure, which is seen in II-VI compounds like ZnO, which is in agreement with the $E_2(low)$ mode reported by Klotz *et al.* [254]. The Gruneisen parameters for TO modes are significantly larger than those corresponding to LO phonons.

4.4 Conclusions

The good crystalline quality of the ZnO nanoflowers is confirmed by the observation of intrinsic behaviors such as the pressure coefficient of the NBE PL energy (26 meV/GPa) and the narrowing of the E_2 (high) Raman band under pressure. A broad range of wurtzite phase metastability, above the bulk ZnO W-to-RS transition pressure is observed, and the NBE PL signal is detected up to 14 GPa. The progressive decrease of the PL and Raman signal suggests that the W-to-RS transition pressure is inversely correlated to the nanocrystal size. The above result is further confirmed by the large increase in the FWHM of E_2 (high) mode. The smallest nanocrystals remain in the W phase up to 14 GPa, which is understood from the grain size calculated from the experimental Raman data.

Chapter 5

Optical and magnetic studies of Mn doped ZnO (ZnO:Mn) nanorods synthesized by hydrothermal method

5.1 Introduction

Manganese doped ZnO (ZnO:Mn) nanostructures in the form of nanowires and nanorods are of great interest owing to their unique and fascinating properties, which made it a potential candidate for nano-devices and spintronic applications [255, 256]. ZnO exhibit strong UV emission at room temperature whereas, nanostructured ZnO:Mn exhibit ferromagnetism at room temperature [257, 244, 258]. A single material that exhibits UV emission property as well as ferromagnetism at room temperature is of particular interest for fabricating spintronic devices. Solution-based hydrothermal synthesis is an efficient way to prepare ZnO:Mn nanorods and nanowires [259, 260, 261]. The research reports on transition metal alloyed ZnO nanostructures, especially ZnO:Mn nanorods are comparatively less. Among them, most of the works are related to the magnetic properties of Mn doped ZnO; nevertheless, there are few papers dealing with the optical properties of this material. It has been previously reported that the concentration of Mn has a significant influence on the optical properties of ZnO [262, 263]. Bhat et al. observed an initial red shift in the band gap of ZnO:Mn for Mn concentration less than 3% mol followed by increase with Mn concentration [262]. Investigations on UV and blue light emission properties of Mn doped ZnO nanocrystals reveals that the optical properties of ZnO can be tuned by using manganese as a dopant [264]. There is a decrease of optical transmittance, optical band gap and the particle size of ZnO:Mn nanopowder on increasing the Mn concentration [265]. The optical band gap of ZnO:Mn decreased to values 3.06, 2.90 and 2.78 eV with Mn concentration 1, 2 and 3 mol%, respectively, as compared to that of ZnO (3.37 eV) [265]. Bhat *et al.* also reported a non-monotonic variation of band gap in Mn doped ZnO nanocrystals [262].

Further, Diluted magnetic semiconductors (DMS), which combine ferromagnetism with semiconductivity, are identified to be potential building blocks for spintronic devices [52, 266, 267]. Nonmagnetic materials like TiO₂, SnO₂, HfO₂ showed room-temperature ferromagnetism while doping it with a suitable quantity of transition metal elements [268, 269, 270, 271]. Prellier *et al.* [272] reported ferromagnetism in transition metals (TM) doped DMSs with a Curie point above room temperature and are useful for advanced spintronic applications. In semiconductor materials, ferromagnetism occurs at doping levels far below the percolation threshold and the average magnetic moment per dopant cation progressively increases with decreasing dopant concentration [273]. Room-temperature ferromagnetism is theoretically predicted in Mn doped ZnO (ZnO:Mn) [121]. Following to the theoretical prediction, ZnO

Experimental

would become ferromagnetic at room temperature by doping with 3d transition elements, intensive experimental work has been carried out to understand the DMS behavior [274, 275, 276]. Manganese is a good transition metal candidate to be used as dopant because of its better thermal solubility (10 mol%) [275]. High-temperature and vapor phase methods are mostly employed for the fabrication of 1D nanostructures of ZnO:Mn [277]. Mn doped ZnO nanowires are also obtained by doping Mn into ZnO by using various techniques, such as ion implantation, thermal evaporation, and wet chemical method [58]. Solution based synthesis like solvothermal and hydrothermal methods are the efficient strategies to synthesize Mn-doped ZnO 1D semiconductor nanostructures [278, 244, 260, 261, 279, 280]. As stated previously, there are several reports on the magnetic characteristics of ZnO:Mn and inconsistencies exist in these reports [281, 282, 283, 284, 285]. A recent first-principles based study could open new ways to the understanding of the ferromagnetic interactions in this material [286].

In this context, it requires more experimental and theoretical support to understand the origin of luminescence and ferromagnetism in ZnO:Mn with different nanostructures. In the present chapter, the structure, morphology, and optical behavior of ZnO:Mn (3 wt%), ZnO:Mn (4 wt%) and ZnO:Mn (5 wt%) nanorods have been studied. Magnetic properties of ZnO:Mn (3 wt%) and ZnO:Mn (5 wt%) were investigated.

5.2 Experimental

For the synthesis of ZnO and ZnO:Mn nanorods, an aqueous solution made of $Zn(CH_3COO)_2 2H_2O (0.1 \text{ M})$, $Mn(CH_3COO)_2 2H_2O (0.1 \text{ M})$ and NaOH (1 M) were placed in a sealed teffon reaction vessel. The sealed reaction vessel is subjected to hydrothermal reaction under autogenous pressure at a growth temperature of 200 °C for a time of 3 hours. The detailed synthesis procedure is given in chapter 3. The samples were examined by using a Hitachi S-4800 scanning electron microscope (SEM). The transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) images of the samples were obtained with a JEOL JEM-2100 transmission electron microscope. The X-ray diffraction (XRD) pattern of the synthesized samples were recorded by employing a Rigaku (D.Max.C) X-ray diffractometer with CuK α radiation ($\lambda = 1.5414$ Å). The X-ray diffraction data of as synthesized samples were processed with the Rietveld refinement analysis in order to extract unit cell parameters of the hydrothermally grown ZnO and ZnO:Mn using FullProf program [258, 214]. Fourier transform infrared (FTIR) spectroscopy measurements of the samples were performed in the wave number range $400 - 4000 \text{ cm}^{-1}$ using the Shimadzu Prestige spectrometer by KBr pellet method. The experimental conditions for recording the Raman spectra, UV-Vis spectra and room temperature photoluminescence spectra of the samples are presented in chapter 3. X-ray photoelectron spectroscopy (XPS) measurement was carried out by using a Kratos AXIS Ultra spectrometer. Magnetic properties of the samples were studied with a SQUID magnetometer (QUANTUM DESIGN).

5.3 Results and discussion

SEM images of hydrothermally grown ZnO:Mn nanorods (Mn - 0, 3, 4, and 5 wt%) are shown in figure 5.1. The ZnO sample exhibits flower like morphology as described in chapter 3 whereas, ZnO:Mn (Mn - 3 - 5 wt%) samples have nanorod morphology. The observed change in morphology, from nanoflower-like to nanorod shape on Mn doping may be due to the change in growth dynamics of ZnO:Mn attributed to the presence of Mn^{2+} ions. Interestingly,

a decrease in the size (length and diameter) of the nanorods were observed on increasing Mn doping concentration from 3 to 5 wt%, which is an indication of low growth rate of ZnO:Mn (Figure 5.1). The TEM, HRTEM and SAED of the as synthesized ZnO and ZnO:Mn(5 wt%) are shown in figure 5.2 for comparison. The size of the nanorods decreased on increasing the Mn doping concentration which is similar to that of previously mentioned observation with SEM. The diameter of the nanorods varies in the range $\sim 90 - 280$ nm for ZnO (Chapter 3) and $\sim 80 - 120$ nm for ZnO:Mn (5 wt%). Its aspect ratios are determined as $\sim 5 - 13$ for ZnO and $\sim 3 - 12$ for ZnO:Mn (5 wt%). HRTEM and SAED data of both ZnO and ZnO:Mn (5 wt%) indicate the crystalline nature of the samples. HRTEM images also shows that the interplanar distance corresponds to 'd' value are 0.25 nm for ZnO and 0.26 nm for ZnO:Mn (5 wt%) respectively.

The elemental composition of as synthesized samples are confirmed with EDX and XPS analysis. The EDX spectra of the hydrothermally grown ZnO:Mn (3, 4 and 5 wt%) are shown in figure 5.3 and the corresponding atomic and weight percentage of each elements are presented in table 5.1 which indicates the incorporation of Mn into the ZnO crystalline system. Further, we carried out the XPS measurements on ZnO:Mn (3 wt%) and ZnO:Mn (5 wt%) for comparison purpose. Figure 5.4 shows the high resolution XPS Mn-2p spectra of ZnO:Mn nanorods (Mn - 3 and 5 wt% doped samples). The Mn-2p peak of ZnO:Mn nanorods is observed at 642.29 eV. This result is in agreement with previously reported binding energy values of the Mn²⁺ ionic state (Mn $2P_{3/2}$) [287]. This indicates the presence of the Mn²⁺ ions in the samples as well as incorporation of Mn²⁺ ions into the ZnO lattice. This observation also confirms the XRD of the present sample, in which there is no additional phase or Mn clusters or crystalline Mn oxides detected.



Figure 5.1: SEM images of hydrothermally grown (a) ZnO, (b) ZnO:Mn (3 wt%),
(c) ZnO:Mn (4 wt%) and (d) ZnO:Mn (5 wt%) (inset is the magnified image of ZnO:Mn (5 wt%))



Figure 5.2: TEM image of hydrothermally grown (a) ZnO, (b) HRTEM and SAED (inset) of ZnO, (c) ZnO:Mn (5 wt%), (d) HRTEM and SAED (inset) of ZnO:Mn (5 wt%)

The XRD pattern shows that ZnO:Mn nanorods are preferentially oriented along (1 0 1) plane and having good crystallinity (Figure 5.5). All the X-ray diffraction peaks of ZnO:Mn (Mn - 0, 3, 4 and 5 wt%) nanorods can be indexed according to the hexagonal wurtzite structure of ZnO (JCPDS: 36-1451). Further, we carried out Rietveld refinement analysis on XRD data of hydrothermally grown ZnO:Mn in order to extract the lattice parameters (figure 5.6). The lattice parameters of the as synthesized ZnO:Mn samples enhanced on increasing the doping percentage of Mn^{2+} ions (Figure 5.7). Further, the observed increase of the lattice parameters of Mn-doped ZnO indicates the Mn incorporation into the ZnO lattice/replacement of Mn^{2+} ions in the sites of Zn^{2+} ions. The lattice parameters 'a' and 'c' of the as synthesized samples were found to be slightly increased with respect to the doping percentage of Mn^{2+} ions (Table 5.2). The slight variation in calculated lattice constants can be understood if we consider the larger radius of Mn^{2+} ions (0.66 Å) with respect to that of the Zn^{2+} ions (0.60 Å) [288]. This incorporation of Mn into the ZnO lattice alters the lattice parameters, and induces lattice strain that generates a stress on the host lattice. Nevertheless, the wurtzite structure remains unchanged by the substitution of Mn^{2+} ions instead of Zn^{2+} ions into the ZnO crystal system.

The replacement of Zn^{2+} with less ionic radius (0.60 Å) by Mn^{2+} ions of larger ionic radius (0.66 Å) is likely to generate a lattice stress on the ZnO host lattice that in turn modify the lattice parameters which is consistent with present observation [288]. The wurtzite structure is retained by the ZnO:Mn samples, even though Zn^{2+} ions are substituted by Mn^{2+} ions as observed in XRD (Figure 5.5) [265]. It is interesting to note that on increasing the Mn concentration, all the diffraction peaks were shifted towards lower 2θ values and intensity of the XRD peaks also decreases. The shifting of the peak position to lower 2θ values with increase in Mn doping concentration shows the expansion of the lattice parameters of ZnO:Mn [289]. The decrease in intensity of Xray diffraction peaks of ZnO:Mn on increasing Mn concentration is probably associated to the lattice disorder and strain induced in the crystalline lattice due to the substitution of Zn^{2+} by Mn^{2+} having comparatively higher ionic radius [288].



Figure 5.3: EDX spectra of hydrothermally grown (a) ZnO:Mn (3 wt%), (b) ZnO:Mn (4 wt%), and (c) ZnO:Mn (5 wt%) nanorods



Figure 5.4: XPS spectra of hydrothermally grown ZnO:Mn (3 wt%) and ZnO:Mn (5 wt%) nanorods

Table 5.1: EDX data of hydrothermally grown ZnO:Mn (3, 4, 5 wt%) nanostructures

Elemental composition									
Flomenta	ZnO:Mn (3 wt%)		ZnO:Mn (4 wt\%)		ZnO:Mn (5 wt\%)				
Elements	Zn	0	Mn	Zn	0	Mn	Zn	0	Mn
wt%	72.33	21.20	2.12	67.03	23.15	3.13	67.58	21.07	3.46
at%	39.31	47.09	1.37	34.55	48.77	1.92	35.00	44.59	2.13

The absence of vibrational bands above 1000 cm^{-1} in hydrothermally grown ZnO nanorods in the FTIR spectra suggest that there is no organic impurities are present in the sample (Figure 5.8). A weak FTIR band at 1430 cm⁻¹ in ZnO:Mn indicate the presence of organic impurity like acetate (COO⁻) probably contributed to acetate salts used for the synthesis of present materials [290]. The FTIR band at 545 cm⁻¹ is assigned to the stretching mode of ZnO [291] which is present in all the samples indicates that the incorporation of Mn is not affected the crystalline structure of ZnO:Mn nanorods consistent with X-ray observation. This band is shifted to lower frequency side while increasing the Mn concentration and appeared at 541, 538 and 534 cm⁻¹ in 3, 4 and 5 wt% Mn doped ZnO. This shift in the band position of the ZnO absorption bands by Mn incorporation shows that the Zn-O-Zn network is perturbed by the presence of Mn [142].



Figure 5.5: X-ray diffraction pattern of hydrothermally grown ZnO, ZnO:Mn (3 wt%), ZnO:Mn (4 wt%) and ZnO:Mn (5 wt%)



Figure 5.6: Rietveld refined XRD pattern of hydrothermally grown (a) ZnO:Mn (5 wt%), (b) ZnO:Mn (4 wt%), and (c) ZnO:Mn (3 wt%) nanorods

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Lattice	standard JCPDS	Unit cell parameters obtained					
constants	values [36-1451]	with Rietveld refinement anal-					
	in Å	ysis (Å)					
		ZnO	ZnO:Mn	ZnO:Mn	ZnO:Mn		
			(3 m wt%)	(4 wt%)	(5 wt%)		
a	3.2498	3.2455	3.2567	3.2641	3.2948		
с	5.2066	5.1982	5.1997	5.2066	5.2569		

Table 5.2: Lattice parameters of hydrothermally grown ZnO and ZnO:Mn with the doping concentration of Mn

Raman spectra recorded from ZnO:Mn (Mn 0, 3, 4 and 5 wt%) nanorods are shown in figure 5.9. The intense Raman band observed at 437 cm⁻¹ corresponds to E_2 (high) mode [244, 292]. The weak bands are also seen in the Raman spectra of hydrothermally grown ZnO nanorods at 330, 382, 541, 583 cm⁻¹ which are assigned in detail (Table 5.3) [244, 218]. The Raman bands at 583 and 660 cm⁻¹ are associated with structural disorders, such as oxygen vacancy, Zn interstitial, impurity atoms like Mn and their combination [244, 293, 220, 294]. The broad, intense peak at 1150 cm⁻¹ contains contributions of 2A₁ (LO) and 2E₁ (LO) modes at the point of the Brillouin zone [218].

The slight shift of Raman bands at 437 cm^{-1} toward lower frequencies with Mn incorporation shows that the Mn²⁺ is substituted at Zn²⁺ sites in the ZnO lattice. Raman band at 330 cm⁻¹ of ZnO:Mn shifted toward lower frequency region of the order of 3, 4 and 7 cm⁻¹ on increasing Mn concentration to 3, 4, and 5 wt% respectively. The defect related Raman band at 583 are shifted toward lower wave number side with increasing Mn concentration (Table 5.3). Previous studies showed that Mn incorporation leads to the shifting of Raman



Figure 5.7: Variation of lattice parameters 'a' and 'c' of ZnO:Mn nanorods with nominal Mn doping concentration)

bands toward lower frequencies [295]. In the present study, Raman band at 660 cm^{-1} become stronger with respect to Mn doping concentration which is similar to that observed by Wang *et al.* [296]. The shift of Raman band at 660 cm⁻¹ toward higher frequency side (3 cm⁻¹ in 3 wt%, 5 cm⁻¹ in 4 wt%, 8 cm⁻¹ in 5 wt%) is observed in Mn doped ZnO nanorods. The presence of E₂ (high) mode in the Raman spectra with slight reduction in intensity even with 5 wt% Mn doping indicated that the Mn doped ZnO nanorods retained the wurtzite structure in agreement with XRD data FTIR spectral information discussed previously.

The intensity of Raman band at 437 cm^{-1} decreased with Mn doping concentration into ZnO that may be attributed to the degradation of crystalline



Figure 5.8: FTIR spectra of hydrothermally grown ZnO, ZnO:Mn (3 wt%), ZnO:Mn (4 wt%) and ZnO:Mn (5 wt%) nanostructures

quality similar to that of reported in Mn doped hierarchical microspheres [142]. This could arise due the substitution of Mn into the Zn site that introduced defects and lattice distortions, due to larger ionic radius of Mn^{2+} ions. The Raman profile of ZnO:Mn sample shows intensity enhancement with respect to increase in concentration of Mn in the region 585 - 665 cm⁻¹ which is in agreement with previous report by Phan *et al.* [297, 298]. The Raman modes associated with the defect states at 541 and 583 cm⁻¹ are very weak in both-ZnO:Mn and ZnO samples indicating comparatively low population of defects.

The diffuse reflection spectra (DRS) of hydrothermally grown ZnO and ZnO:Mn nanorods measured at room temperature is shown in figure 5.10. The optical absorption edge of hydrothermally grown ZnO:Mn was red shifted by 10, 9, 8 and 4 nm for 0, 3, 4 and 5 wt% of Mn respectively as compared


Figure 5.9: Raman spectra of hydrothermally grown ZnO, ZnO:Mn (3 wt%), ZnO:Mn(4 wt%) and ZnO:Mn (5 wt%)

to the bulk ZnO exciton absorption (372 nm) [225]. The observed red shift in absorption edge/optical energy gap can be due to the oriented attachment of the nanorods [244, 198]. The band gap of ZnO and ZnO:Mn are estimated from $[(k/s)h\nu]^2$ versus $h\nu$ plot in which 'k' and 's' denotes the absorption and scattering coefficients respectively and ' $h\nu$ ' is the photon energy [226]. The ratio of (k/s) is calculated from the reflectance via the Kubelka-Munk equation [226] as mentioned in chapter 3. The band gap of ZnO:Mn is slightly increased from 3.23 to 3.28 eV on increasing the Mn concentration from 0 to 5 wt% (Figure 5.11). The Burstein-Moss effect in which the Fermi level merges into the conduction band with increasing carrier concentration resulting in lower energy transitions, will also contribute to increase in band gap [299].

Table 5.3: Raman spectral data (cm⁻¹) (Note: w, weak; vw, very weak; vs, very strong; s, strong. Δ S, change in wave number position with respect to ZnO nanoflowers (cm⁻¹))

Single		Raman bands of ZnO and ZnO:Mn								
crystal ZnO	ZnO nano- flowers	ZnO:Mn (3 wt%)		ZnO:Mn (4 wt%)		ZnO:M (5 wt)	/In %)	ments		
	Raman	Raman	ΔS	Raman	ΔS	Raman	ΔS			
99	99 s	98 w		98 vw		97 vw		$E_2(low)$		
203	205 w	202 vw	-3	201 vw	-4	119 vw	-6	2TA; $2E_2(low)$		
333	330 w	327 w	-3	326 w	-4	323 w	-7	$\begin{array}{c} E_2(high)-\\ E_2(low) \end{array}$		
378	382 w	379 w	-3	377 w	-5	376 wv	-6	$A_1(TO)$		
438	437 vs	436 s		433 s	-4	430 s	-7	$E_2(high)$		
536	541 w	535 vw	-6	532 vw	-9	530 vw	-11	$2B_1(low);$ $2LA$		
590	$583 \mathrm{w}$	580 vw	-3	577 vw	-6	575 vw	-8	$E_1(LO)$		
657	660 w	$663 \mathrm{\ s}$	+3	$665 \mathrm{~s}$	+5	$668 \mathrm{\ s}$	+8	$A_1(TA+LO)$		
1158	1150 s	1127 w	-23	1129 w	-21	1123 w	-27	$2A_1(LO),$ $2E_1(LO),$ 2LO		

Figure 5.12 shows the photoluminescence (PL) spectra recorded from ZnO:Mn (Mn - 0, 3, 4 and 5 wt%) at room temperature. ZnO sample shows UV emission centered at 392 nm, which could pertain to the recombination of free exciton between the conduction and valance bands through an exciton-exciton collision process as described in chapter 3.



Figure 5.10: Diffuse reflectance spectra of hydrothermally grown ZnO, ZnO:Mn (3 wt%), ZnO:Mn(4 wt%) and ZnO:Mn (5 wt%).



Figure 5.11: $[(k/s)h\nu]^2$ versus $h\nu$ plot of hydrothermally grown ZnO, ZnO:Mn (3 wt%), ZnO:Mn(4 wt%) and ZnO:Mn (5 wt%) (Inset: Variation of band gap with doping concentration of Mn)

One could observe that with increase in concentration of Mn on ZnO:Mn, the PL emission intensity decreases (Figure 5.12). This observation indicates that Mn incorporation into ZnO lattice quenches PL emission of ZnO [300] and is similar to that of reported in Mn doped ZnO nanorods grown by thermal diffusion and ZnO:Mn nanowires by CVD [297, 298]. Quenching of photoluminescence emission in the present samples may be attributed to the loss of photogenerated carries through non-radiative transitions to the defect states that are generated due to Mn incorporation into ZnO crystalline lattice. The reduction in intensity of NBE PL band as well as Raman band at 438 cm⁻¹ (E₂ (high)) suggest an intrinsic relation between the E₂ (high) mode of Raman and NBE emission of PL. In addition, Mn incorporation into the ZnO host lattice resulted in shifting of UV emission towards shorter wavelength region and the ZnO:Mn nanorods grown by thermal diffusion also exhibit similar phenomena [297]. The blue shift of the order of ~57meV is observed in the case of ZnO:Mn (5 wt%) with respect to ZnO.

The HRTEM and SAED results confirms that the hydrothermally grown ZnO and ZnO:Mn (5 wt%) having crystalline nature. The observed quenching of PL emission intensity in ZnO:Mn (5 wt%) is probably due to the increase of non-radiative recombination processes with increasing Mn concentration. It is worthwhile to note that ZnO:Mn even at 5 wt% doping shows only NBE emission and this indicate that the nominal doping of Mn in the ZnO crystal grown by hydrothermal method have less number of defects. This asserts the fact that ZnO:Mn grown using hydrothermal method under optimized growth condition favour the formation of ZnO:Mn nanorods with low density of radiative defects, which is of interest when we consider these nanorods for device application. SEM images of the sample indicate that the diameter of the ZnO nanorods decreases with increase in Mn concentration. This size reduction in ZnO:Mn nanorods may be one of the reasons for the reduction of

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Figure 5.12: PL spectra of hydrothermally grown ZnO, ZnO:Mn (3 wt%), ZnO:Mn(4 wt%) and ZnO:Mn (5 wt%) (Inset: Variation of PL intensity with doping concentration of Mn)

UV emission intensity.

Note that the luminescence of manganese in the ZnO host latiice is not observed in the PL spectrum, which indicates Zn^{2+} ions are substituted by Mn^{2+} ions in the ZnO host lattice [301]. This is further confirmed with the red shift of Raman band at 660 cm⁻¹ with respect to increase in Mn concentration. The substitution of Mn^{2+} into the Zn^{2+} site introduces more defects and lattice distortions, because the ionic radius of Mn^{2+} is larger than that of Zn^{2+} . The strong UV emission located at 392 nm in the PL spectrum of ZnO nanorods indicate that it have good crystal quality with few oxygen vacancies which corresponds to the self-activated luminescence [244]. The improvement in the crystal quality such as low structural defects, oxygen vacancies, zinc interstitials and decrease in the impurities may cause the appearance of sharper and stronger UV emission and a suppressed and weakened green - red emission from the as prepared samples [302]. Previous studies on Mn doped ZnO shows that the defect related emission in the range 400-650 nm. But, the absence of defect related emission in our sample clearly indicates that Mn^{2+} ions are incorporated in Zn^{2+} site in the wurtzite ZnO [303, 304].

M-H characteristics of hydrothermally grown ZnO nanorods at 10 and 300 K are shown in figure 5.13. These samples exhibit diamagnetic nature at both temperatures (10 and 300 K), which is the expected result from the ZnO nanorods. On the other hand, the M-H curve at 300 K is almost a straight line without any hysteresis loop for ZnO:Mn (3 wt%) sample (Figure 5.14). In the ZnO:Mn (3 wt%) sample, the magnetization reaches a maximum value at an applied field strength of about 69.56 kOe, and showing a magnetic moment of 0.067 emu/g, and being not saturated.

The magnetic susceptibility shows a positive value that indicates the paramagnetic behavior of the material. Interestingly, the ZnO:Mn (5 wt%) sample shows an increase in its magnetic moment as compared to ZnO:Mn (3 wt%) samples at 300 K. The M-H curve at 300 K of ZnO:Mn (5 wt%) shows a hysteresis loop with coercivity (H_c) of the order of 0.017 kOe, remanence (M_r) ~ 1.611 x 10⁻⁴ emu/g (Figure 5.15). This result indicates that the ZnO:Mn (5 wt%) nanorods exhibit room temperature weak ferromagnetic behavior.



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Figure 5.13: M-H curve of hydrothermally grown ZnO nanorods at 10 and 300 K



Figure 5.14: M-H curve of hydrothermally grown ZnO:Mn (3 wt%) nanorods at 300 K



Figure 5.15: M-H curve of hydrothermally grown ZnO:Mn (5 wt%) nanorods at 300 K

On the other hand, at low temperature (10 K) (Figure 5.16), hysteresis loops with relatively low coercivity were observed from all the samples under investigation. ZnO:Mn (3 wt%) samples show coercivity (H_c) ~ 0.3129 kOe and a remanence value of (M_r) ~ 0.0123 emu/g. In the ZnO:Mn (5 wt%) sample, coercivity (H_c) ~ 0.4256 kOe and remanence (M_r) ~ 0.0205 emu/g, respectively. Even at this temperature, magnetization is not saturated for all the samples. The hysteresis loop has a nonlinear behavior which shows that the crystalline system is a mixture of paramagnetic and ferromagnetic states.



Figure 5.16: M-H curve of hydrothermally grown ZnO:Mn (3 wt%) and ZnO:Mn (5 wt%) nanorods at 10 K.

The temperature dependence of magnetization, under field cooling (FC) with an applied magnetic field of 50 Oe and zero field cooling (ZFC) of ZnO:Mn (3 wt%) nanorods is shown in figure 5.17. The FC and ZFC curves overlap above 47 K and separate from each other below this temperature. Under FC conditions, the magnetization increases slowly with decreasing temperature from 300 to 95 K, and then followed by a rapid increase up to 10 K. ZFC is also gradually increased with respect to the decrease of the sample temperature.

The FC and ZFC curves overlap in the measuring range of temperatures from 15 to 300 K. The magnitude of the ZFC and FC condition continues to increase without saturation while lowering the temperature, which indicates the presence of diamagnetic ordering in the sample. The magnetization increases slowly with decreasing temperature from 300 to 100 K, followed by a



Figure 5.17: M-T plot (FC and ZFC) of hydrothermally grown ZnO:Mn (3 wt%) nanorods at an applied field of 50 Oe. The inset shows the enlarged portion in the low temperature region

steep increase up to 10 K in the plot of ZnO:Mn (5 wt%) sample (Figure 5.18). The figure shows the bifurcation of FC and ZFC at 34 K.

There are different possibilities for the occurrence of ferromagnetism in transition-metal-doped ZnO. Dietl *et al.* [121] theoretically explained that the room-temperature ferromagnetism in transition-metal-doped ZnO is on the basis of hole doping contributed to the substitution of transition metal in Zn^{2+} sites. The above theoretical explanation is not vivid, because the substitution of the equal valence ions (Mn^{2+} instead of Zn^{2+}) will not create holes. Another model suggests the formation of nanosized Mn_3O_4 with a Curie temperature of 44 K could be a reason for the origin of ferromagnetism in ZnO:Mn [277].

As described previously, there is no MnO, Mn₃O₄, etc. detected in the



Figure 5.18: M-T plot (FC and ZFC) of hydrothermally grown ZnO:Mn (5 wt%) nanorods at an applied field of 50 Oe. The inset shows the enlarged portion in the low-temperature region

ZnO:Mn nanorods synthesized by the hydrothermal process. The observed increase in lattice constants suggest that the substitution of Mn^{2+} ions instead of Zn²⁺ sites rather than the formation of oxide phase of Mn. There will be the possibility to have different types of defects in hydrothermally grown ZnO:Mn nanorods. The native crystal defects like vacancies of O₂ and Zn interstitials on the ZnO host lattice may also generate ferromagnetism in the ZnO nanorods. However, our studies on photoluminescence specta of ZnO nanorods even with Mn doping reveal the absence of defect level emission. So there is no possibility for defect-level-activated ferromagnetism to occur in hydrothermally grown ZnO:Mn nanorods (Figure 5.15). ZnO and transition-metal-doped ZnO samples exhibit ferromagnetic behavior only when the specific area of grain boundaries exceeds a certain threshold value [305]. Straumal *et al.* [305] reported that a threshold value of specific area of grain boundaries in ZnO is 5.3 x 10^7 and that for ZnO:Mn is $2.4 \ge 10^5 \text{ m}^2/\text{m}^3$. In the case of the present sample, these values are found to be 6.7 x 10^6 , 1.7 x 10^6 , and 10 x 10^6 m²/m³ in ZnO and ZnO:Mn 3 and 5wt%, respectively. The Mn dopant promotes formation of grain boundaries and the ferromagnetic transition [306]. Further, the solubility of Mn increases with the size of grains and ferromagnetic properties of doped structures are nonmonotonic [305]. The observance of room-temperature ferromagnetism in ZnO:Mn (5 wt%) is attributed to the presence of the increased specific area of grain boundaries and higher solubility of Mn ions in its grains as evidenced by the reduction in diameter of ZnO:Mn (5 wt%) (Figure 5.1). From these results, it is inferred that the paramagnetic behavior observed from ZnO:Mn (3 wt%) at 300 K probably due to the reduction of the specific area of grain boundaries as compared to that of ZnO:Mn (5 wt%). Also, an increase in band gap is observed with the increase in content of Mn into ZnO, the origin of ferromagnetism is also due to Mn doping in the ZnO lattice, which is closely related to the change in band gap energy of nanorods by the substitution of Mn^{2+} in Zn^{2+} sites [307].

A nonzero difference between the FC and ZFC curves of ZnO:Mn (3 wt%) and ZnO:Mn (5 wt%) indicates the short-range ferromagnetic ordering while decreasing the temperature of the sample, as usually observed in spin glass systems [308]. This ferromagnetic ordering is further confirmed by the presence of the hysteresis loop at 10 K. The FC and ZFC curves bifurcate each other from a temperature below T_c , indicating the influence of the aging on the spin-glass state, as was previously reported in La_{0.95}Sr_{0.05}CoO₃ and Ag(Mn) spin-glass systems [309, 310].

In the FC - ZFC curve of the ZnO:Mn (5 wt%) sample, the magnetization increases with the decrease in temperature in the range of 300 - 100 K and a rapid increase occurs below 100 K. This behavior is similar to the paramagnetic

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one. However, this sample shows remanent magnetization and coercivity at room temperature as well. The rapid increase of magnetization at low temperature in ZnO:Mn (5 wt%) can be related to the ferromagnetic properties. Our ZnO sample (Figure 5.13) exhibits only diamagnetic behavior at room temperature as well as at 10 K. So, the magnetic properties detected in ZnO:Mn nanorods are due to the interaction between the manganese ions in the ZnO host lattice. The detected magnetism point to a superexchange interaction between Mn^{2+} ions and Zn^{2+} ions as well as an increase in specific area of the grain boundaries [311, 305].

One can clearly observe that the ZFC magnetization of both samples does not saturate in the entire measurement range. This is due to the glassy state; the magnetic moments are randomly frozen such that it will take a longer time for the field to turn those spins along the field direction [312]. In addition, the FC magnetization is not saturating at low temperature, which indicates the short-range spin ordering in the material [313]. In order to understand the spinglass ordering, the magnetization irreversibility (M_{irr}) vs. T, the temperature is plotted. The irreversible magnetization, $M_{irr} = M_{FC} - M_{ZFC}$ as a function of temperature for ZnO:Mn (3 wt%) and ZnO:Mn (5 wt%) nanorods is shown in figure 5.19.

From the graph, one can see that M_{irr} become non-zero at a temperature of 150 K (T_g-1) for Mn (3 wt%) doped ZnO and that of Mn (5 wt%) doped ZnO is at 140 K (T_g-2). This temperature is termed as the spin-glass transition temperature (T_g). The spin-glass transition temperature T_g-1 and T_g-2 corresponds to Mn 3 and 5 wt% doped ZnO, respectively. The M_{irr} is found to rapidly increase and shows a linear behavior from a temperature of about 88 K (T_{cro}-1) in Mn (3 wt%) doped ZnO and 82 K (T_{cro}-2) in Mn (5wt%) doped ZnO. This temperature is termed as the crossover temperature, as reported by Svedberg *et al.* [314]. The temperature dependence of M_{irr} in Mn



Figure 5.19: Temperature-dependent irreversibility magnetization $M_{irr} = M_{FC} - M_{ZFC}$ of ZnO:Mn (3 wt%) and ZnO:Mn (5 wt%) nanorods.

3 and 5 wt% doped ZnO is an indication of spin glass ordering attributed to the competing interaction of frozen disorders and magnetic frustrations [315]. However, there are two regimes that can be observed in the graph representing the temperature-dependent irreversibility of magnetization for the spin-glass ordering of the present sample (Figure 5.19). The first one is between the T_g and T_{cro} of each sample for which the rate of variation remains small. But below T_{cro} , a rapid, roughly linear increase is determined in both the samples. The linear upward curve seen in the low temperature region suggests that the spin-glass transition observed in the present sample is similar to that of the Ising model predicted by De Almeida-Thouless [316, 317].

5.4 Conclusions

We successfully demonstrated the capability of hydrothermal method to grow ZnO:Mn (Mn - 3, 4 and 5 wt%.) nanorods having reduced optical radiative defects. Hydrothermally grown ZnO retains the rod-like morphology with low percentage of Mn doping. The presence of E_2 (high) mode at 437 cm⁻¹ in the Raman spectra with slight reduction in intensity in Mn doped ZnO nanorods reveals that wurtzite structure is retained in ZnO:Mn. The intensity enhancement of Raman bands at 660 $\rm cm^{-1}$ in ZnO:Mn confirms the increase in structural defects with respect to the Mn concentration in ZnO:Mn as compared to ZnO nanoflower. The Raman and PL analysis confirms the good crystalline quality of ZnO which slightly reduces as the Mn concentration increases in ZnO:Mn systems. The quenching of PL emission intensity in the UV region around 392 nm as a result of nominal doping of Mn (Mn - 3 - 5 wt%) in ZnO is attributed to the increase of non-radiative recombination process, reduced size of ZnO:Mn nanorods as well as comparatively lower quality of crystallites caused by Mn^{2+} incorporation into ZnO lattice. The absence of radiative defect bands around 450 - 550 nm range in PL spectra of hydrothermally grown ZnO:Mn (Mn - 3 - 5 wt%) indicates that there exist less number of defects. The blue shift of PL emission from ZnO:Mn is attributed to the band gap broadening due to the nominal incorporation of Mn. Hydrothermally grown ZnO nanorods exhibit a diamagnetic nature at 10 and 300 K. At room temperature (300 K), weak ferromagnetism is observed in ZnO:Mn (5 wt%) nanorods, while ZnO:Mn (3 wt%) nanorods show paramagnetism. The ZnO:Mn (3 wt%) and ZnO:Mn (5 wt%) nanorods exhibit spin-glass behavior below 150 and 140 K, respectively. The variation of magnetic behavior with respect to the level of Mn doping can be attributed to the population of Mn^{2+} ions in the ZnO crystalline lattice. The exchange interaction between doped Mn^{2+} ions, the substitution of Mn^{2+} ions into Zn^{2+} sites and the increase in specific area of the grain boundaries are the contributing factors in the origin of magnetic behaviour.

Chapter 6

Optical and magnetic properties of hydrothermally grown ZnO:TM (Co/Ni/Cu) nanostructures

6.1 Introduction

Zinc Oxide (ZnO) is a wide band gap (3.37 eV) semiconductor material and has a high exciton binding energy (60 meV), which resulted low trapping capacity of carriers and higher luminescence efficiencies [130, 244, 318]. ZnO based dilute magnetic semiconductors (DMSs), particularly one dimensional (1D) nanostructures attracted considerable attention for the fabrication of spintronic and magneto-optic devices [319, 258, 320]. Interestingly, doping of 3d transition metal (TM) ions into ZnO lattice leads to the modification of optoelectronic and magnetic properties [321]. Hydrothermal process is one of the non-vacuum and cost effective techniques used to synthesize one dimensional (1D) transition metal doped ZnO nanostructures [244, 318]. It has been previously reported that hydrothermally grown ZnO:Co nanorods show a group of ultraviolet narrow photoluminescence (PL) lines in the near-band-edge region of 3.0-3.4 eV and a very broad band at 3.20 eV at low temperatures [322]. And hydrothermally grown ZnO:Ni hexagonal nanodiscs exhibits a blue shift and a weak ultraviolet (UV) emission peak, compared with ZnO [323]. Near-band edge (NBE) and a broad blue-green PL emission bands at around 378 and 545 nm respectively, are observed from hydrothermally grown ZnO:Cu nanorods [139].

Synthesis of ZnO based DMSs with relatively low growth time and temperature is a challenging task [324]. Mustaqima *et al.* reported a list of experimental result of ZnO:Mn and ZnO:Cu in which they demonstrated the synthesis method and magnetic characterization [325]. We have studied the optical and magnetic properties of ZnO:Mn nanorods and the enhanced UV emission at 392 nm from ZnO nanoflowers grown by using hydrothermal method in chapters 3 and 5. In the present chapter, we report the optical and magnetic properties of ZnO:Co, ZnO:Ni and ZnO:Cu nanostructures grown by using hydrothermal method at a relatively low growth temperature of 200 °C and growth time of 3 hours.

6.2 Experimental

The low temperature hydrothermal experiments were performed for the synthesis of ZnO:(Co/Ni/Cu) (3, 4, and 5 wt%) nanostructures at an optimised growth temperature of 200 °C and a growth time of 3 hours. The $\text{Zn}(\text{CH}_3\text{COO})_2$ 2H₂O (0.1 M), Co(CH₃COO)₂ 4H₂O (0.1 M), Ni(CH₃COO)₂ 4H₂O (0.1 M), Cu(CH₃COO)₂ H₂O (0.1 M) and NaOH (1 M) were used as precursor for

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the hydrothermal synthesis of ZnO:(Co/Ni/Cu) nanostructures. The detailed hydrothermal synthesis procedure is explained in chapter 3.

The SEM images of the hydrothermally grown samples were recorded by using a Hitachi S-4800 scanning electron microscope (SEM). The transmission electron microscopy (TEM) and selected area electron diffraction (SAED) images of the samples were obtained with a JEOL JEM-2100 transmission electron microscope. The X-ray diffraction (XRD) pattern of the as synthesized samples were recorded with a Rigaku (D. Max. C) X-ray diffractometer with Cu K α radiation ($\lambda = 1.5414$ Å). The XRD data of the samples were processed with the Rietveld refinement analysis in order to extract unit cell parameters using FullProf program as described in chapter 3. A Horiba Jobin Yvon Lab Ram HR system with Ar-ion laser (514.5 nm) as the excitation source (resolution 3 cm^{-1}) was used for the Raman measurements. The UV-visible spectra of the samples were recorded with a Jasco V-570 spectrometer (200-800 nm). The room temperature photoluminescence (PL) from the samples were measured using a Horiba Jobin Yvon LabRam HR system using He-Cd laser (325 nm) as excitation source. The room temperature magnetic properties of the samples were studied by using a Lakeshore VSM-7410 vibrating sample magnetometer.

6.3 Result and discussion

Figure 6.1 shows the SEM images of ZnO:Co, ZnO:Ni and ZnO:Cu (3, 4, and 5 wt%) samples synthesized using hydrothermal process at a temperature of 200 °C. The ZnO:Co (3 and 4 wt%) samples exhibited nanorod morphology, whereas ZnO:Co (5 wt%) showed nanodisk morphology. In the case of ZnO:Ni (3, 4, and 5 wt%), all the samples exhibited the flower like morphology. ZnO:Cu (3 wt%) sample also shows flower like morphology. But on increasing the doping concentration of Cu to 4 wt%, shows the nanoflower morphology

with wider arrangements of individual nanorods and these nanorods are not concentrated towards the nucleation centre. Further, Cu (5 wt%) doped ZnO looks like tetrapod morphology.



Figure 6.1: SEM images of hydrothermally grown ZnO:Co, ZnO:Ni and ZnO:Cu (3, 4, and 5 wt%) nanostructures

But, the exact quantity of initial dopants used in the precursor reactants are not incorporated in the sample as expected. The difference in morphology exhibited by ZnO:(Co/Ni/Cu) (3, 4, and 5 wt%) is attributed to the hydrothermal growth condition contributed to the dopant and basicity of the respective precursor solution. The TEM and SAED of hydrothermally grown ZnO:Co, ZnO:Ni and ZnO:Cu (3, 4, and 5 wt%) nanostructures are shown in figure

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6.2.



Figure 6.2: TEM and SAED images of hydrothermally grown ZnO:Co, ZnO:Ni and ZnO:Cu (3, 4, and 5 wt%) nanostructures

The SAED pattern of the hydrothermally grown ZnO:Co, ZnO:Ni and ZnO:Cu (3, 4, and 5 wt%) indicate the crystalline nature. The nanodisk morphology of ZnO:Co (5 wt%) sample were further confirmed with TEM measurements. The difference in morphology exhibited by ZnO:(Co/Ni/Cu)



Figure 6.3: EDX spectra of hydrothermally grown ZnO:Co, ZnO:Ni and ZnO:Cu (3, 4, and 5 wt%) nanostructures

(3, 4, and 5 wt%), can be probably attributed to the hydrothermal growth condition contributed to the dopant in respective precursor solution. The EDX analysis of the samples confirms the incorporation of Co/Ni/Cu ions into the ZnO lattice (Figure 6.3) (Table 6.1, 6.2, 6.3).

During the initial stage of nucleation process, the continuous nucleation of ZnO from $Zn(OH)_4^{2-}$ leads to the formation of multiple nuclei aggregation (Jiang *et al* [326]). These aggregations may act as the nucleation center for 1D ZnO nanostructures growth. Depending upon temperature and pressure of the growth medium, 1D ZnO nanostructures may oriented randomly or oriented along the nucleation center while advancing the growth process [326]. The random orientation of 1D ZnO nanostructures results in the growth of ZnO nanorods/nanowires and the growth oriented along the nucleation center give rise to the development of flower like morphology.

Elemental composition										
Elements	ZnO:Co (3 wt%)			ZnO:Co (4 wt%)			ZnO:Co (5 wt%)			
	Zn	0	Со	Zn	0	Со	Zn	0	Co	
$\mathrm{wt}\%$	80.77	15.28	3.95	80.47	15.15	4.38	79.77	15.49	4.74	
at%	54.72	42.31	2.97	54.65	42.05	3.30	53.78	42.68	3.54	

Table 6.1: EDX analysis result of ZnO:Co (3, 4, 5 wt%) nanostructures

Table 6.2: EDX analysis result of ZnO:Ni (3, 4, 5 wt%) nanostructures

Elemental composition									
Elements	ZnO:Ni (3 wt\%)			ZnO:Ni $(4 \text{ wt}\%)$			ZnO:Ni $(5 \text{ wt}\%)$		
	Zn	0	Ni	Zn	0	Ni	Zn	0	Ni
wt%	93.11	2.05	4.83	92.59	2.27	5.14	89.93	2.19	7.88
at%	87.11	7.85	5.04	86.07	8.61	5.32	83.54	8.31	8.15

Table 6.3: EDX analysis result of ZnO:Cu (3, 4, 5 wt%) nanostructures

Elemental composition									
Elements	ZnO:Cu (3 wt%)			ZnO:Cu (4 wt\%)			ZnO:Cu (5 wt\%)		
	Zn	0	Cu	Zn	0	Cu	Zn	0	Cu
wt%	95.19	1.93	2.88	92.44	1.98	5.58	92.16	1.70	6.14
at%	89.76	7.45	2.79	86.99	7.61	5.41	87.43	6.57	5.99

Optical and magnetic studies of ZnO:TM(Co/Ni/Cu) nanorods

Figure 6.4 shows the XRD pattern recorded from ZnO:(Co/Ni/Cu) (3, 4 and 5 wt%) samples synthesized by low temperature hydrothermal process. The diffraction peaks of all the samples were indexed with hexagonal wurtzite phase of ZnO (JCPDS: 36-1451). The lattice parameters 'a' and 'c' and corresponding unit cell volume of ZnO:(Co/Ni/Cu) (3, 4 and 5 wt%) are obtained from the XRD data with Rietveld refinement analysis (Table 6.4). The slight shifts in lattice parameters observed with respect to ZnO indicate that the Co^{2+} , Ni^{2+} or Cu^{2+} ions are substituted at Zn^{2+} ionic site of ZnO host lattice without changing the wurtzite structure. This change in lattice constants are contributed to the compatibility of the effective ionic radii of Co (0.58 A), Ni (0.55 Å) and Cu (0.57 Å) which are slightly smaller that of Zn (0.60 Å)[322, 288, 132, 327]. The ideal wurtzite structure has the hexagonal unit cell with c/a ratio is 1.633 [58]. In ZnO:(Co/Ni/Cu) (3, 4 and 5 wt%) nanorods, the wurtzite structure is deviated from the ideal arrangement by adjusting the c/a ratio (Table 6.4) [328]. The unit cell volume of the TM doped samples are slightly different from the ideal wurtzite structure (V = 47.625 Å³) reported in the literature. The basicity of the dopants probably plays a key role for the deviation of c/a and V (unit cell volume) from the ideal wurtzite crystalline structure of ZnO [58]. The crystal defects such as zinc antisites, oxygen vacancies, atomic dislocation can also influence the change of these parameters. The slight shifts in lattice parameters of doped crystallites with respect to ZnO indicate that Co^{2+} , Ni^{2+} or Cu^{2+} are substituted in the Zn^{2+} ionic site of ZnO host lattice without changing the wurtzite structure.

The preferential growth direction of polar ZnO nanostructure is along [0001] direction, plane having lowest surface energy and the growth velocity along $\langle 10\overline{1}0 \rangle$ is slower than that along [0001] direction, which results the growth of nanorod morphology [129]. The precursor salt source may give variation in anions initially affect the final structure by influencing the crystal nucleation

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Figure 6.4: XRD pattern of hydrothermally grown ZnO:Co, ZnO:Ni and ZnO:Cu (3, 4, and 5 wt%) nanostructures

ZnO:TM		Lattice	Lattice		Unit cell	
		constant	constant constant		volume	
		a Å c Å			Å	
	(3 wt%)	3.2441	5.1965	1.6018	47.3630	
ZnO:Co	(4 wt%)	3.2489	5.2037	1.6016	47.5699	
	(5 wt%)	3.2439	5.1961	1.6017	47.3538	
	(3 wt%)	3.2434	5.1961	1.6020	47.3392	
ZnO:Ni	(4 wt%)	3.2453	5.1992	1.6020	47.4208	
	(5 wt%)	3.2445	5.1979	1.6024	47.3869	
ZnO:Cu	(3 wt%)	3.2403	5.1923	1.6024	47.2122	
	(4 wt%)	3.2424	5.1943	1.6019	47.2936	
	(5 wt%)	3.2424	5.1943	1.6019	47.2943	

Table 6.4: Lattice constants, c/a ratio and volume of the unit cell

rate of different facets [329]. The observed nanodisk morphology of ZnO:Co (5 wt%) is probably contributed to the precursor salt source (Cobalt acetate).

Raman spectra recorded from ZnO:Co, ZnO:Ni and ZnO:Cu (3, 4, and 5 wt%) are shown in figure 6.5. The Raman bands of ZnO hexagonal wurtzite structure is reported at 438 cm⁻¹ due to E_2 (high) mode [218]. Raman spectra of ZnO:Co - 3, 4, and 5 wt% exhibits E_2 (high) bands at 431, 434 and 422 cm⁻¹ respectively. There is no considerable shift is observed in E_2 (high) Raman bands of both ZnO:Ni (3, 4, and 5 wt%) and ZnO:Cu (3, 4, and 5 wt%) (Table 6.5). In ZnO:Co (3, 4, and 5 wt%) nanorods, strong Raman band corresponding to A₁ (LO) at 574 cm⁻¹ is shifted to 522 cm⁻¹. The A₁ (LO) mode of ZnO:Ni - 3, and 4 wt% is seen at 581 cm⁻¹ is shifted to 569 cm⁻¹ in ZnO:Ni (5 wt%). In Cu doped ZnO the bands corresponds to A₁ (LO) is observed as weak band at 584, 575 and 570 cm⁻¹ with respect to Cu 3, 4, and

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$5~{\rm wt}\%$ dopants.

Raman bands attributed to 2TA, 2E₂ (low), E₂ (high)-E₂ (low), 2LA, A₁ (TA + LO) and 2A₁ (LO) are also slightly shifted with respect to ZnO and the detailed assignments are given in table 6.5. The broad, intense band at 1158 cm⁻¹ of ZnO is shifted to lower wave number and is observed in all samples (Table 6.5). The observed shift in wave number position of A₁ (LO) mode with respect to ZnO (574 cm⁻¹) is attributed to the incorporation of dopants in crystalline lattice of ZnO which is in good agreement with powder XRD result.

The appearance of $E_2(high)$ in all the sample under investigation indicate the formation of wurtzite phase of ZnO even with doping with different TM metals such as Co, Ni or Cu. The Raman bands at 574 and 666 cm⁻¹ are associated with structural disorders such as oxygen vacancy, Zn interstitial, substitution of impurity atoms like Co, Ni and Cu and their corresponding individual combination to Zn and oxygen [330, 295, 331, 296, 220]. The broad intense Raman band at 1158 cm⁻¹ in ZnO and shifting of this band in ZnO:Co/Ni/Cu further suggest the incorporation of Co²⁺, Ni²⁺ and Cu²⁺ ions in ZnO crystalline lattice [332].

Figure 6.6 shows the diffuse reflectance spectra of the hydrothermally grown ZnO:Co, ZnO:Ni and ZnO:Cu (3, 4, and 5 wt%) nanostructures recorded at room temperature. The slight shift in optical absorption edge is observed from almost all samples with respect to ZnO exciton absorption edge at 372 nm (Table 6.6) [318, 225].



Figure 6.5: Raman spectra of hydrothermally grown ZnO:Co, ZnO:Ni and ZnO:Cu (3, 4, and 5 wt%) nanostructures

		Aggingen								
		ZnO:Co			ZnO:Ni Z		ZnO:Cu		monts	
ZnO										menus
[218]	0	Co (wt%	()	l I	Ni (wt%))	Cu (wt%)			
	3	4	5	3	4	5	3	4	5	
203	200	195	193	207	205	203	204	204	199	2 TA; $2 \text{E}_2 \text{ (low)}$
	w	W	W	W	VW	vw	W	W	W	
333	319	315	315	333	332	338	332	328	326	E_2 (high)-
	w	w	s	vw	vw	vw	s	w	s	\mathbb{E}_2 (low)
438	431	434	422	438	438	437	438	438	437	E_2 (high)
	vw	s	vw	s	s	s	vs	vs	vs	
483	475	482	480	489	485	480	473	496	496	2 LA
	vw	s	vw	vw	vw	vw	vw	vw	vw	
574	522	522	522	581	581	569	584	575	570	A_1 (LO)
	vs	s	vs	vw	vw	vw	W	W	W	
666	691	704	655	666	660	670	655	659	634	$A_1(TA+LO)$
	vw	s	vw	vw	vw	vw	vw	vw	vw	
										$2A_1$ (LO),
1158	1112	1119	1101	1146	1150	1128	1141	1137	1128	$2E_1$ (LO),
	s	s	s	w	w	w	s	s	s	2LO

Table 6.5: Raman spectral data (Note:- w: weak, vw: very weak, vs: very strong,s: strong)



Figure 6.6: Diffuse reflectance spectra of hydrothermally grown ZnO:Co, ZnO:Ni and ZnO:Cu (3, 4, and 5 wt%) nanostructures

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The observed shift of optical absorption edges are contributed to the oriented attachment of TMs (Co, Ni and Cu) doped ZnO nanostructures [333]. The optical band gap (E_g) of the hydrothermally grown ZnO:Co, ZnO:Ni and ZnO:Cu (3, 4, and 5 wt%) nanostructures are determined by using Tauc plot based on Kubulka-Munk relation [226, 334, 335]. Figure 6.7 exhibits the variation of optical band gap with respect to the increase in doping concentration of Co^{2+} , Ni²⁺ and Cu²⁺ ions into ZnO. The optical band gap of ZnO:Co/Ni/Cu (3, 4, and 5 wt%), of the samples decreases with increasing the doping concentration of corresponding transition metal ions into ZnO (Table 6.6), in comparison with ZnO nanoflowers (3.23 eV) [244].



Figure 6.7: Variation of band gap in ZnO with respect to the doping concentration of TM ions



Figure 6.8: Photoluminescence spectra of hydrothermally grown ZnO:Co, ZnO:Ni and ZnO:Cu (3, 4, and 5 wt%) nanostructures

ZnO·TM	Absorption	Band gap	$PL,(DLE_1)$	$PL,(DLE_2)$	
	edge (nm)	(eV)	(nm)	(nm)	
ZnO:Co (3 wt%)	389	3.19	405	470-650	
ZnO:Co $(4 \text{ wt}\%)$	391	3.17	403		
ZnO:Co (5 wt%)	399	3.11	400		
ZnO:Ni (3 wt%)	407	3.05	417	500-650	
ZnO:Ni (4 wt%)	414	3	412	550-650	
ZnO:Ni (5 wt%)	421	2.95	407	500-650	
ZnO:Cu (3 wt%)	398	3.12	420	585-650	
ZnO:Cu (4 wt%)	399	3.11	418	580-650	
ZnO:Cu (5 wt%)	403	3.08	415	480-650	

Table 6.6: Optical band gap and PL emission wavelength of the samples

The red shift of band gap in all the samples may be attributed to the sp-d exchange interactions between the band electrons and localized 'd' electron of transition metal ions substituted at Zn^{2+} site and the difference in morphologies of the samples [335, 299].

Figure 6.8 depicts the photoluminescence (PL) spectra recorded from hydrothermally grown ZnO:Co, ZnO:Ni and ZnO:Cu (3, 4, and 5 wt%) nanostructures at room temperature. In the case of ZnO:Co nanostructures, the strong emission peak is seen at 405 nm, 403 nm and 400 nm for 3, 4 and 5 wt% Co doped ZnO respectively. Whereas, in the case of ZnO:Ni nanostructures, the emission is at 417, 412 and 407 nm for 3, 4 and 5 wt% Ni doped ZnO and the emission is located at 420, 418 and 415 nm for 3, 4 and 5 wt% Cu doped ZnO respectively. The hydrothermally grown ZnO nanoflowers exhibits enhanced near band edge UV emission at 392 nm [244] (Chapter 3). Present results indicates that the NBE emission is suppressed while incorporating Co, 146 Optical and magnetic studies of ZnO:TM(Co/Ni/Cu) nanorods Ni and Cu ions into the ZnO lattice. Further, weak PL bands corresponding to defect related deep level emission (DLE) is also observed above 470-650 nm (Table 6.6).

The observed strong PL emission peaks around visible region (400-420 nm) for almost all the samples is attributed to the presence of defects like i) oxygen vacancy (V_O) , ii) zinc vacancy (V_{Zn}) , iii) zinc interstitial (Zn_i) , iv) oxygen interstitial (O_i) , antisite defect-like v) Zn at an oxygen site (Zn_O) , vi) oxygen at a Zn site (O_{Zn}) , or the presence of impurity ions [336, 337]. The violet emission located at 400 to 420 nm is probably due to the radiative defects Zn_i and V_{Zn} related to the interface traps existing at the grain boundaries and emitted radiative transition between this level and the valence band or the conduction band [338]. The reduction of relative intensity of violet emission with increasing the doping concentration of TMs (Co, Ni and Cu) can be probably due to the decrease in population of radiative defects like Zn_i and V_{Zn} with the incorporation extrinsic impurities (Co²⁺, Ni²⁺ and Cu²⁺ ions) in the ZnO host lattice (Figure 6.9). The intensity of deep level emission is reduced significantly with increasing the Co^{2+} , Ni^{2+} or Cu^{2+} ions similar to that of quenching of PL emission intensity in Co and Mn doped ZnO nanostructures [339, 340, 341]. These TM ions have the tendency to form cluster around oxygen, which results the non-radiative recombination process as well as passivation of surface nanostructures [339, 340].



Figure 6.9: Variation of PL emission wavelength with difference in doping concentration of ZnO:Co, ZnO:Ni and ZnO:Cu (3, 4, and 5 wt%) nanostructures

The passivated layer of the oxides of Co, Ni and Cu on the surface of the ZnO:(Co/Ni/Cu) nanocrystallites have the potential energy large enough to prevent surface states from trapping photo-generated electrons or holes and may lead to the quenching of the visible emission by increasing concentration of Co, Ni and Cu into ZnO [342].

Figure 6.10 shows the magnetization versus magnetic (M-H) characterization curve of hydrothermally grown ZnO:Co (5 wt%), ZnO:Ni (5 wt%) and ZnO:Cu (5 wt%) nanostructures measured at room temperature. The magnetic susceptibility exhibits positive value for both ZnO:Co (5 wt%) and ZnO:Ni (5 wt%) samples while ZnO:Cu (5 wt%) shows negative value. The ZnO:Cu (5 wt%) nanostructure sample shows diamagnetic nature even at the relatively higher doping concentration (5 wt%) at room temperature. The magnetization is not saturated even at 15 kOe for both ZnO:Co (5 wt%) and



Figure 6.10: M-H curve of hydrothermally grown ZnO:Co, ZnO:Ni and ZnO:Cu (3, 4, and 5 wt%) nanostructures
Conclusions

ZnO:Ni (5 wt%) samples and shows clear hysteresis loop at room temperature. The coercivity (H_c) and remanence (M_r) of ZnO:Co (5 wt%) is around 0.44 kOe and 1.85 x 10^{-3} emu/g, and that for ZnO:Ni (5 wt%) is about 0.51 kOe and 8.06 x 10^{-4} emu/g respectively. These results indicate that both ZnO:Co (5 wt%) and ZnO:Ni (5 wt%) exhibits ferromagnetic behavior at room temperature and ZnO:Cu (5 wt%) shows diamagnetic nature at 300 K.

The origin of room temperature ferromagnetism (RTFM) in DMS oxides are still under debate and are explained on theories such as Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction, super-exchange, double-exchange between the 'd' states of TMs, free-carrier mediated exchange, and sp-d exchange mechanism, etc. [343, 344]. The magnetic cations, carriers, and defects may become bound magnetic polarons (BMPs) consequently responsible for the RTFM in TM doped ZnO [343]. These BMPs include electrons locally trapped by oxygen vacancy; with the trapped electron occupying an orbital overlapping with the d shells of TM neighbours thereby developing FM in TM doped ZnO [343]. Moreover, crystalline defects such as oxygen vacancy, cation vacancy, interstitials and strain also leads to RTFM in TMs doped ZnO [345]. In the present case, the origin of RTFM may be due to the sp-d exchange interactions between the band electrons and locolized 'd' electron of transition metal ions substituted at Zn^{2+} site as well as the presence of different types of defects in these materials which is evident from the previously described XRD and PL studies.

6.4 Conclusions

ZnO:Co, ZnO:Ni and ZnO:Cu (3, 4, and 5 wt%) nanostructures are grown by low temperature hydrothermal process. The XRD analysis confirms the substitution of Co^{2+} , Ni^{2+} , and Cu^{2+} ions into ZnO lattice which is evident from the variation of lattice parameters 'a' and 'c' in the TMs (Co, Ni and Cu) doped ZnO samples. The presence of E_2 (high) mode in the Raman spectra located around 438 cm^{-1} confirms wurtzite structure of the ZnO:(Co/Ni/Cu) samples. The defect related Raman bands located at 574 and 666 $\rm cm^{-1}$ with Raman shift and enhancement of intensity also confirms the incorporation of Co^{2+} , Ni^{2+} , and Cu^{2+} ions into ZnO lattice. The DRS measurements shows the optical band gap of ZnO:Co (3, 4, and 5 wt%) crystallite decreases with increasing the doping concentration, whereas in the case of ZnO:Ni and ZnO:Cu (3, 4, and 5 wt%) samples, the band gap increased with increasing the corresponding doping concentration. The photoluminescence spectra of the samples exhibits the presence of strong deep level emission (DLE) peak at the violet region instead of the usual near band edge emission (NBE) at UV region. The intensity of the strong violet emission (400 to 420 nm) from almost all the samples decreased with increasing the doping concentration of the dopant ions. The present study shows the tunability of photoluminescence emission wavelength of ZnO nanostructures from UV region to visible region and vice versa while doping with suitable transition metals. The room temperature ferromagnetism is observed in ZnO:Co (5 wt%) and ZnO:Ni (5 wt%) while ZnO:Cu (5 wt%) exhibited diamagnetic nature. Material showing visible emission with novel magnetism is very important for the fabrication of magneto-optic as well as spintronic devices. Therefore, the violet emission with ferromagnetism of the hydrothermally grown ZnO:Co and ZnO:Ni (3, 4, and 5 wt%) doped nanostructures can be used as the potential building block of functional spintronic devices.

Chapter 7

Summary and future scope of the work

7.1 Summary of the present study

ZnO nanoflowers were synthesized by the hydrothermal process at an optimized growth temperature of 200 °C and a growth/reaction time of 3 h. Various characteristion studies reveal that the as-synthesized flower-like ZnO nanostructures are crystalline with a hexagonal wurtzite phase preferentially oriented along the (1 0 1) plane. The flower like structures are constituted by nanorods which having the average length 234-347 nm and diameter 77-106 nm respectively. The band gap of ZnO nanoflowers were estimated as 3.23 eV, the lowering of band gap with respect to bulk ZnO is attributed to the flower-like surface morphology. Room temperature photoluminescence spectrum shows strong UV emission peak at 392 nm, with a suppressed visible emission related to the defect states, indicating the defect free formation of ZnO nanoflowers. The suppressed Raman bands at 541 and 583 cm⁻¹ related to defect states in ZnO also confirms that the ZnO nanoflowers having reduced number of optical active defects.

Intrinsic near-band-edge UV emission from hydrothermally grown ZnO nanoflowers is monotonously blue-shifted under hydrostatic pressure up to 13.8 GPa with a pressure coefficient of 26 meV/GPa. This transition pressure value is nearly 5 GPa above the transition pressure from the wurtzite to the rock salt phase reported from the bulk ZnO. The $E_2(high)$ and $E_2(low)$ Raman bands corresponds to the wurtzite phase ZnO are observed up to about 11 GPa from the spectra. The transition pressures determined from photoluminescence and Raman studies suggests that there is a gradual phase transition, in which the smallest nanoparticles are expected to remain in the wurtzite phase up to 13-15 GPa.

The XRD, SEM and Raman, FTIR investigations reveal that ZnO:Mn (Mn -3-5 wt%) synthesized by using hydrothermal process at an optimized growth temperature of 200 °C and a growth time of 3 hours retained hexagonal wurtzite crystal structure with nanorod morphology. The HRTEM and SAED analysis confirm the crystalline nature of hydrothermally grown ZnO and ZnO:Mn (5 wt%) nanorods. The ZnO:Mn nanorods (Mn -3-5 wt%) displayed optical band gap in the range 3.23-3.28 eV. The blue shift of UV emission peak (PL) from 392 (ZnO) to 386 nm and quenching of photoluminescence emission in ZnO:Mn is due to the Mn incorporation in ZnO lattice. Relative increase in intensity of Raman band at 660 cm⁻¹ with nominal doping of Mn -3-5 wt% in ZnO indicate that defects are introduced in ZnO:Mn system as a result of doping that leads to the quenching of photoluminescence emission at 392 nm.

Mn (3 wt%) and (5 wt%)-doped ZnO samples exhibit paramagnetic and ferromagnetic behavior, respectively, at room temperature. The spin-glass behavior is observed from the samples with respect to the decrease of temperature. At 10 K, both samples exhibit a hysteresis loop with relatively low

Future scope of the work

coercivity. The room-temperature ferromagnetism in 5 wt% Mn-doped ZnO nanorods is attributed to the increase in the specific area of grain boundaries and the interaction between substituted Mn^{2+} ions and Zn^{2+} ions from the ZnO host lattice.

The transition metal (Co/Ni/Cu) doped ZnO nanostructures that exhibited strong violet photoluminescence emission with novel magnetism can be grown by hydrothermal technique at an optimized growth temperature of 200 °C and a growth time of 3 hours. The scanning electron micrographs recorded from the as synthesized samples (ZnO:Co, ZnO:Ni and ZnO:Cu) displayed nanorods, nanosheet and nanoflower mophology depending up on the dopant/doping percentage. X-ray diffraction, EDX and Raman analysis confirmed the incorporation of Co, Ni and Cu ions into ZnO lattice, retained the hexagonal wurtzite structure even after doping with these dopant ions. The optical energy band gap of ZnO:Co, ZnO:Ni and ZnO:Cu decreased with increasing the doping concentration TM ions. The room temperature violet emission is observed instead of near band edge emission from almost all the Co, Ni and Cu doped ZnO nanostuctures. However, the emission intensity of violet luminescence quenched with increasing the doping concentration of Co^{2+} , Ni^{2+} and Cu^{2+} ions into ZnO. The present study shows the tunability of photoluminescence emission wavelength of ZnO nanostructures from UV region to visible region and vice versa while doping with suitable transition metals such as Co, Ni and Cu. The ZnO:Co and ZnO:Ni shows ferromagnetism while ZnO:Cu exhibited diamagnetic behavior at room temperature.

In conclusion, hydrothermally grown ZnO nanoflowers shows an optical band gap of 3.23 eV and enhanced UV emission located at 392 nm. As synthesized ZnO nanoflowers exhibits diamagnetism at room temperature. While doping of transition metal (TM) into ZnO, the optical as well as magnetic properties of these materials changed with respect to the doping concentration of TM ions.

7.2 Future scope of the work

The hydrothermally grown ZnO nanoflowers have greater porous nature due to its flower like morphology. This material can be used as dye absorbing material in dye sensitized solar cells (DSSCs) instead of TiO₂. Hydrothermally grown ZnO and ZnO:Mn nanostructures can be used for the fabrication of UV light emitting devices. ZnO:Co/Ni/Cu nanostructures can be grown by hydrothermal process with different morphology as well as defects. As synthesized ZnO:Co/Ni/Cu nanostructures may be a material of choice for the fabrication of violet light emitting devices. These material is expected to show efficient photo catalytic activity, so that it is an important candidate for the treatment of industrial waste containing dyes especially from textile industry. It may be possible to synthesis blue light emitting material by adjusting the doping concentration of Co, Ni or Cu into ZnO lattice which may replace GaN in Blue LEDs.

Appendix A

Abbreviations used in the thesis

Abbreviation	Expansion
ALD	Atomic Layer Deposition
BMP	Bound Magnetic Polaron
CCD	Charge coupled Device
CRT	Cathode Ray Tube
CVD	Chemical Vapor Deposition
DAC	Diamond Anvil Cell
DLE	Deep Level Emission
DMS	Diluted Magnetic Semiconductor
DRS	Diffuse Reflectance Spectroscopy
EDX	Energy Dispersive X-ray
\mathbf{FC}	Field Cooling
FE	Field Emission
FM	Ferromagnetism

Abbreviation Expansion

FTIR	Fourier Transform Infrared
FWHM	Full Width Half Maximum
HETM	High Electron Mobility Transistors
HMS	Hierarchical Microspheres
HRTEM	High Resolution transmission Electron Microscope
IR	Infrared
JCPDS	Joint Committee on Powder Diffraction Standards
LD	Laser Diode
LED	Light emitting Diode
MBE	Molecular Beam Epitaxy
MOCVD	Metal Organic Chemical Vapor Deposition
MPMS	Magnetic Property Measurement System
NBE	Near Band Edge
PL	Photoluminescence
PLD	Pulsed Laser Deposition
PMT	Photomultiplier Tube
PVD	Physical Vapor Deposition
RKKY	Ruderman-Kittel-Kasuya-Yosida
RS	Rocksalt
RTFM	Room temperature Ferromagnetism
SAED	Selected Area Electron Diffraction
SE	Schottky Emission

Appendix

Abbreviation Expansion

SEM	Scanning Electron Microscope
SET	Single Electron Transistor
SQUID	Superconducting Quantum Interference Device
TCO	Transparent Conducting Oxide
TE	Thermionic Emission
TEM	Transmission Electron Microscope
TM	Transition Metal
UV	Ultraviolet
VLS	Vapor Liquid Solid
VSM	Vibrating Sample Magnetometer
W	Wurtzite
WBG	Wide Band gap Semiconductor
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray diffraction
YSZ	Yttria Stebilized Zirconia
ZFC	Zero Field Cooling
ZnO	Zinc Oxide
ZnO:Co	Cobalt doped Zinc Oxide
ZnO:Cu	Copper doped Zinc Oxide
ZnO:Mn	Manganese doped Zinc Oxide
ZnO:Ni	Nickel doped Zinc Oxide

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