PREFACE

The unique and fascinating properties of II-VI compound semiconductors have triggered tremendous motivation among the scientists to explore the possibilities of using them in industrial applications. Out of these II-VI compound semiconductors, we have selected zinc oxide (ZnO) whose ionicity resides at the borderline between the covalent and ionic semiconductors. It is a piezoelectric, dielectric, transparent semiconducting oxide. ZnO crystallizes in three different forms i.e. hexagonal wurtzite, cubic zinc blende and rarely observed cubic rocksalt. It is the most common material used in the commercial manufacture of devices and research due to its low cost and wide availability. The renewed interest in ZnO is fuelled and fanned by prospects of its applications in optoelectronics owing to its direct wide bandgap ($E_g = 3.3 \text{ eV at } 300 \text{ K}$), large exciton binding energy (60 meV), and efficient radiative recombination. The large exciton binding energy paves the way for an intense near band-edge excitonic emission at room and even higher temperatures, because this value is 2.4 times the room-temperature (RT) thermal energy ($k_B T = 25 \text{ meV}$). Therefore, laser operation based on excitonic transitions, as opposed to electron–hole plasma, is expected. In this respect, there have also been a number of reports on laser emission from ZnO-based structures at room temperature and beyond. During the past few years, the research area on nanostructures of semiconductors has become very active because of their unique properties and wide potential in nanodevices. In recent years, ZnO nanostructures are currently being widely investigated because of their great potential for electronic, photonic and spintronics applications. It is well known that both the shape and size of inorganic materials have a strong influence on electrical and optical properties. Extensive efforts have been focused on many different morphological zinc oxide nanostructures, including nanowires, nanorods, nanocables and nanobelts. It has various applications in blue and ultraviolet optical devices such as light-emitting diodes, UV detectors, field emission, high sensitivity gas sensors, biosensors, dye-sensitized solar cells, photoluminescent materials, photocatalytic degradation of pollutants and antibacterial treatment and laser diodes. Therefore, ZnO has several fundamental advantages over its chief competitor GaN and SiC.
Recently, focus on modifying ZnO by doping with transition metals such as Ag, Ni, Mn, Cu, Co, Cr, Ti has become a point of interest for researchers. Transition metal impurities are interesting from two points of view. One deals with acceptor-like doping in the context of electronic properties. The other deals with magnetic properties when the transition element concentrations is relatively high but still within the dilute limit so as not to change the main structural nature of the ZnO matrix. These studies demonstrated that the metals can change $E_g$ of ZnO and grain size. ZnO is also considered for spintronics applications with magnetic ion (Co, Ni, V, Fe and Mn) doping. For this reason, Mn doping has valuable spin off in structural, morphological, electrical, optical and magnetic properties of ZnO. Among all the magnetic transition ion-doped ZnO systems, Mn doping is usually the single most concerned mainly because of the fact that the thermal solubility of metallic Mn is larger than 10 mol% in ZnO, and the ‘electron effective mass’ is as large as approximately 0.3 $m_e$, where ‘$m_e$’ is the free-electron mass. Therefore, injected spins and carriers in the nanostructures can be large, thus making Mn-doped ZnO ideal for the fabrication of spintronic nanodevices, a proposed technology that uses the electron spin rather than the electron charge for reading and writing informations.

ZnO has probably the richest variety of different nanostructures. It includes highly ordered nanowire arrays, tower-like structures, nanorods, nanobelts, nanosprings, nanocombs, nanoparticles and nanorings. There are different ways in Bottom-up and Top-down approaches to synthesize these varieties of ZnO nanostructures. Looking to this aspect, we here have selected hydrothermal and microwave irradiation methods i.e. Bottom-up approach for synthesizing ZnO nanostructures.

Hydrothermal technique is a promising alternative synthetic method to synthesize ZnO nanostructures because of the low process temperature and ease to control the particle size. The hydrothermal process have several advantage over other growth processes such as use of simple equipment, catalyst-free growth, low cost, environmental friendliness and less hazardous.

Compared to the conventional methods, the microwave synthesis has the advantages of producing small particle size metal oxide with high purity owing to
short reaction time. It is found that this method is fast, mild, energy efficient and environment friendly route to produce ZnO nanoparticles.

The entire thesis has been divided into seven chapters :-

**Chapter 1** deals with the complete literature survey on the existing information of zinc oxide material, its structure and various properties of zinc oxide along with its applications. This chapter also describes the present status of the research work going on in the field of synthesis of zinc oxide / Mn doped zinc oxide nanostructures across the globe.

**Chapter 2** provides the basic principle and instrumental details of EDAX (Energy Dispersive Analysis of X-rays), XRD (X-ray powder Diffraction), TEM (Transmission Electron Microscopy), Raman spectroscopy, UV-Vis-NIR spectrophotometer, Spectrofluorometer-PL (Photoluminescence), FTIR (Fourier Transform Infrared Spectroscopy), XPS (X-ray Photoelectron Spectroscopy) and TGA (Thermogravimetric Analysis) techniques used for characterization of ZnO nanostructures prepared in the present work.

**Chapter 3** provides the details of the methods used for synthesizing ZnO nanorods by hydrothermal method and undoped and Mn doped (with Mn content: 5 mol%, 10 mol% and 15 mol%) ZnO nanoparticles by microwave irradiation at 720 watt.

**Chapter 4** consists of results and discussion of ZnO nanorods prepared by hydrothermal method. EDAX provided information about chemical composition of the material and showed the purity of the sample with no foreign contaminants in it. The XRD and Selected area electron diffraction (SAED) patterns clearly showed the formation of a single-phase compound with wurtzite structure having reported lattice parameter. Size and morphology of the ZnO nanorods were analyzed by TEM. Raman spectroscopy has been used to examine crystal quality of ZnO nanorods. The optical
properties of the samples were investigated by UV-Vis–NIR spectroscopy, photoluminescence (PL) and Fourier Transform Infrared Spectroscopy (FTIR). The optical energy band gap was determined from the absorption spectra. The photoluminescence spectra of ZnO nanorods exhibits UV emission and strong blue emission. FTIR spectra indicate the existence of distinct characteristic absorption peak corresponding to ZnO stretching mode. Thermogravimetric analysis (TGA) measurements showed the thermal stability of ZnO materials up to 100°C and after that it starts decomposing.

**Chapter 5** consists of results and discussion of characterization of undoped and Mn doped (with Mn content: 5 mol%, 10 mol% and 15 mol%) ZnO nanoparticles prepared by microwave irradiation. EDAX provided the information of presence of Zn, O and Mn elements without any other impurities in these samples. X-ray diffractogram of all these samples has been indexed based on hexagonal wurtzite structure and lattice parameters calculated showed good resemblance with the reported values. It is found that Mn doping in ZnO, slightly increases the lattice parameter. The particle size, shape and morphology were examined by TEM. Raman spectroscopy has been used to examine crystal quality for ZnO nanoparticles or to find possible secondary oxide phase in magnetic transition ion-doped ZnO. The optical properties of the samples were investigated by means of using UV-Vis–NIR spectroscopy, PL and FTIR. The optical energy band gap was determined from the absorption spectra. The room-temperature photoluminescence shows that the intensity of near band energy (NBE) emission depends strongly on the content of Mn in ZnO. The chemical groups of the samples were confirmed by FTIR spectra. To analyze the chemical states of the constituent elements, XPS measurements were performed. XPS spectra for ZnO and Mn doped ZnO nanoparticles shows peaks for Zn 2p, Zn 3d, O 1s and Mn 2p. TGA measurements carried out only for undoped ZnO nanoparticles showed the stability of the material up to 100°C.

**Chapter 6** describes the study on antibacterial behavior of ZnO nanorods and undoped and Mn doped (with Mn content: 5 mol%, 10 mol% and 15 mol%) ZnO
nanoparticles. We investigated the antibacterial activity of ZnO nanorods/nanoparticles against *Escherichia coli*, *Bacillus subtilis*, *Pseudomonas aeruginosa*, *Serratia marcescens*, *Proteus vulgaris* and *Staphylococcus aureus* and the results of these studies are given in detailed in this chapter.

**Chapter 7** deals with the summary drawn from the entire thesis and scope for the future work.