

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 °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 $E_2(\text{high})$ and $E_2(\text{low})$ 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 $E_2(\text{high})$ 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 Mn^{2+} 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 °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 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 $E_2(\text{high})$ 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 cm^{-1} that exhibited a shift and enhancement of intensity is contributed to 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%) 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

1. Enhanced UV emission from ZnO nanoflowers synthesized by hydrothermal 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. Mn^{2+} -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.**
3. 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.**
 4. 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.**
 5. Boosted UV emission at 349 nm from mesoporous ZnS, P. Sajan, M. J. Bushiri and **R. Vinod**, **Appl. Phys. A. 113, (2013) 321.**
 6. 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

1. 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.
2. 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.

3. Photoluminescence and Raman studies of Mn doped ZnO nanorods, **R. Vinod**, P. Sajan and M. Junaid Bushiri, Second International Conference on Materials and Thin Films for Advanced Technology (OMTAT-2013) at Department of Physics, Cochin University of Science and Technology, Kochi, Kerala, India on 2-5 January, 2013.
4. Optical studies of nanocrystalline ZnS grown by hydrothermal method, P. Sajan, **R. Vinod** and M Junaid Bushiri, Second International conference on Materials and Thin Films for Advanced Technology (OMTAT-2013) at Department of Physics, Cochin University of Science and Technology, Kochi, Kerala, India on 2-5 January, 2013.
5. Grain size engineering of ZnS Quantum dots prepared via molarity variation by chemical method, P. Sajan, **R. Vinod** and M Junaid Bushiri, National conference on Nano India 2013 at National Institute for Interdisciplinary Science and Technology (CSIR-NIIST), Thiruvananthapuram, Kerala, India on February 19-20, 2013.
6. Optical studies of Ni doped ZnO nanoflowers. **R. Vinod**, P. Sajan and M. Junaid Bushiri, National Conference on Innovative trends in - Material Science (ITMS-2013), at Department of Physics, Arignar Anna College, Nagarcoil, Tamil Nadu, India on August 23-24, 2013.
7. Magnetic studies of ZnO:Mn (4 wt%) nanorods, **R. Vinod** and M. Junaid Bushiri, National Conference on Nanophotonics (NCNP-2014), School of Physics, Bharathidasan University, Tiruchirappally, Tamil Nadu, India on March 6-7, 2014.
8. Optical properties of ZnO:Pb nanoparticle, **R. Vinod**, S. Agouram and M. Junaid Bushiri, International Conference on Energy Harvesting, Storage and Conversion (IC-EEE-2015), Department of Physics, Cochin Uni-

versity of Science and Technology, Kochi, Kerala, India on 4-7 February, 2015.

9. Optical and magnetic studies of ZnO:Mn (4 wt%) nanorods, **R. Vinod** and M. Junaid Bushiri, Fourth International Conference on Frontiers in Nanoscience and Technology (COCHIN NANO-2016), Department of Physics, Cochin University of Science and Technology, Kochi, Kerala, India on 20-23 February, 2016.