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 ^{o}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 ^{o}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

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 ^{o}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 TiO_2. 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.