CHAPTER 9

CONCLUSION AND FUTURE SCOPE

Conclusion :

An inexpensive microwave assisted solvothermal method is used for preparing pure SnO_2 powders and transition metal ions (Ni, Mn, Co and Cu) doped SnO_2 powders with nanosized particles. The samples are annealed at 500^oC temperature for 1 hour to get the crystalline nature. Our study is mainly focused on the structural, morphological, photoluminescence and room temperature ferromagnetism of diluted magnetic semiconductor SnO_2 at nano scale. The significant modification in the above properties of SnO_2 nanoparticles is observed by adding the transition metal ions as dopants on parent system. The structural and morphology analysis of NPs are done by XRD, SEM, EDAX, TEM and FT-IR. Besides the structural and morphological analysis, the optical and magnetic behaviours of transition metal ions doped SnO_2 NPs are examined by UV-Vis, photoluminescence spectroscopy and vibrating sample magnetometer.

The chapter under the heading of Introduction explains the nanotechnology, nanoscience, metal oxide semiconducting nanomaterials and the physical properties of tin oxide. A brief review related to the present investigation is included in this chapter. The second chapter describes the various work related to our research done by other researchers through literature review. The different synthesis methods for the preparation of nanoparticles, the spectral characterization techniques and VSM analysis used to study the magnetic nature of synthesized NPs have been summarized in the third chapter. The results and discussions of the present work are

reported in the consecutive chapters. At the end, selective and relevant references are included.

The present investigation leads to the following conclusions,

1) Synthesis :

SnO_2 nanoparticles and transition metal Ni, Mn, Co and Cu doped SnO_2 nanoparticles (0.01, 0.02, 0.03 and 0.04 molar ratios) have been successfully synthesized by microwave assisted solvothermal method using the following precursors

i. tin II chloride ($SnCl_4 \cdot 2H_2O$) to prepare SnO_2 nano powder.

ii. tin(II) chloride ($SnCl_4 \cdot 2H_2O$) and nickel acetate ($Ni(CH_3COO)_2 \cdot 4H_2O$) to form $Sn_{1-x}Ni_xO_2$ series.

iii. tin(II) chloride ($SnCl_4 \cdot 2H_2O$) and manganese chloride ($MnCl_2 \cdot 4H_2O$) to synthesis $Sn_{1-x}Mn_xO_2$ series

iv. tin(II) chloride ($SnCl_4 \cdot 2H_2O$) and cobalt (II) chloride ($CoCl_2 \cdot 6H_2O$) to produce $Sn_{1-x}Co_xO_2$ series.

v. tin (II) chloride ($SnCl_4 \cdot 2H_2O$) and copper (II) acetate monohydrate $Cu(CH_3COO)_2 \cdot H_2O$) to make $Sn_{1-x}Cu_xO_2$ series.

2) Structural and Morphological Studies :

i. At room temperature, the prepared sample illustrates the amorphous nature. The material becomes crystalline nature under increasing annealing temperature and it is indicated by the decrease in the broadening of diffraction peaks in XRD pattern. The X-ray diffraction analysis reveals that all the prepared pure SnO_2 samples and annealed at temperatures from 300^oC

to 700^{o}C are in pure crystalline phase with rutile tetragonal symmetry in $P4_2/mnm$ space group. The crystallite size obtained from the Debye Scherrer formula is varying from 4 to 17nm for the annealing temperature from 300^{o}C to 700^{o}C. But the lattice strain is decreased with increasing crystallite size. The peak appeared at 621 cm^{-1} that relates to the O–Sn–O bridge functional groups of SnO_2 proves the presence of SnO_2 as crystalline phase. The shape and size of the particle are analysed by SEM and TEM micrographs.

ii. A series of polycrystalline $Sn_{1-x}Ni_xO_2$ ($0.01 \leq x \leq 0.04$) nanoparticles are synthesized by microwave assisted solvothermal method. The X-ray diffraction analysis reveals that the entire samples prepared are in pure crystalline phase with crystallite size varying from 13 to 15 nm. The changes in the positions and shapes of IR peaks indicate that Ni is incorporated in the SnO_2 host. SEM micrographs show the agglomeration of $Sn_{1-x}Ni_xO_2$ nanoparticles. The rutile structure of SnO_2 is not affected by Ni doping in SnO_2. TEM images of powder nanoparticles demonstrate that the particle size of the samples is in an average diameter of 11-19 nm for the Ni doped SnO_2.

iii. X-ray diffraction measurements reveal the single phase formation of $Sn_{1-x}Mn_xO_2$ nanoparticles. Crystallite size and crystallanity of nanoparticles are found to get decreased with the increase in dopant ratio. But the lattice strain is increased with the decrease in crystallite size. FTIR spectrum displays the vibrational band at 626 cm^{-1} due to O-Sn-O bending vibration in

SnO_2. The existence of large spherical aggregates of nanoparticles is confirmed by SEM image. The incorporation of Mn in SnO_2 is proved by the result of EDAX. TEM micrograph illustrates that the particle size is 14-45 nm for the pure SnO_2 and 13-24 nm for Mn doped SnO_2. This confirms the reduction in the particle size caused by Mn doping in SnO_2. SAED pattern also proves the good crystalline nature of the sample.

iv. Nanoparticles of the basic composition $Sn_{1-x}Co_xO_2$ with x = 0.01, 0.02, 0.03 and 0.04 are successfully synthesized. The XRD spectra exhibit the rutile type tetragonal structure of all the samples with no impurity phase. The structural change obtained from the diffraction peaks demonstrates the inclusion of Co^{2+} ions into the SnO_2 lattice which indicates that the crystal lattice has no noticeable change due to Co doping. The peak appeared at 653 cm^{-1} proves the O–Sn–O functional groups of SnO_2. All the peaks observed in the EDAX spectra belong to the expected elements Sn, O and Co suggest that the Co^{2+} ions are incorporated in the SnO_2 lattice. The tiny particles are joined together and form an agglomerated spherical morphology. It is understood by the SEM picture. TEM image provides the information about the particle size of Co doped SnO_2 nanoparticles in the range of 18-48 nm.

v. $Sn_{1-x}Cu_xO_2$ powders with nanosized particles are successfully synthesized. The X-ray diffraction reveals that all the samples formed are in single phase without any detectable secondary or impurity phases. The XRD patterns have a good agreement with JCPDS card number 77-0451. The crystallite size gets decreased, whereas, the effective lattice strain is found to get increased with

the increasing Cu concentration upto 3%. SEM images explain the clustered morphology of the nanoparticles and EDAX result proves the existence of Cu in SnO_2 matrix. From the FTIR spectrum, we can observe that there is a sharp peak at 640 cm^{-1} which is due to O-Sn-O vibrations. TEM image of $Sn_{0.98}Cu_{0.02}O_2$ nanoparticles reveals the spherical particles with the individual particle size ranging from 6.06 nm to 18.64nm. The doping of Cu in SnO_2 has decreased the particle size compared to the pristine SnO_2.

3) Optical Studies :

i. The optical band gap of SnO_2 nanoparticles is found to be 4 eV which is greater than the band gap reported for bulk SnO_2 (3.65 eV) due to the size induced quantum confinement effect. Photoluminescence studies show the emission peaks at 374 nm and 568 nm due to the oxygen vacancies.

ii. The band gap values of Ni doped SnO_2 nanoparticles are increasing with an increase in the dopant ratio. The values are in the range of 3.64 eV-3.99 eV. PL measurements illustrate the emission nature of our prepared samples in visible region which is indicated by the sharp emission peak at 560 nm due to oxygen vacancy defect. The intensity of the visible emission increases as the dopant concentration increases.

iii. It is very interesting to see that the band gap energy for $Sn_{1-x}Mn_xO_2$ nanoparticles annealed at 500°C gets increased when the particle size gets decreased with Mn doping in SnO_2 nanoparticles. The visible emission due to the generation of oxygen vacancy defects in the doped samples is

enhanced by the Mn doping in SnO_2. This is revealed in photoluminescence spectrum.

iv. The band gap is found to be 4.00, 3.38, 3.25, 3.21 and 2.9 eV for 0.00, 0.01, 0.02, 0.03 and 0.04 Co/Sn molar ratios, respectively. Co - doped SnO_2 shows a red-shift of the E_g edge from 4.00 to 2.9 eV. The doped samples show UV emission 355-370 nm, weak blue emission 450-480 nm and strong red emission 645 nm due to the oxygen vacancy defect and tin interstitial defect.

v. In Cu doped SnO_2 nanoparticles, the band gap is found to get increased from 3.20eV to 3.91 eV with a decreasing particle size indicating that there is a blue shift in the absorption edge. This blue shift reveals that the strong quantum confinement effect exists in the doped samples. The photoluminescence spectra of Cu doped SnO_2 show weak blue and strong red emission peaks in the visible region due to the crystal defects.

4) Magnetic Studies :

i. Bulk SnO_2 system has diamagnetic nature. But our magnetic measurements show that the pristine SnO_2 nanoparticles exhibit weak ferromagnetism with paramagnetic nature of having the magnetization value 3.0543×10^{-3} emu/g. The observed ferromagnetism is due to the presence of large number of oxygen vacancies which are confirmed by EDAX and PL studies.

ii. M-H curve shows that Ni doped SnO_2 nanoparticles exhibit ferromagnetism at room temperature. 3% Ni doped SnO_2 is found to have maximum

saturation magnetization of $3.5168x10^{-3}$ emu/g. The ferromagnetic nature in Ni doped SnO_2 samples is arised due to the larger amount of induced defects and oxygen vacancies. When the tin oxide is doped with the transition metal ion Ni, it becomes good ferromagnetic semiconductors.

iii. Room temperature ferromagnetism is observed in $Sn_{1-x}Mn_xO_2$ with x = 0.01, 0.02, 0.03 and 0.04. RTFM is originated from the oxygen vacancy in the system. In this series, the particle size decreases for increasing dopant concentration. So it is observed in 1% mol concentration of Mn in SnO_2 that the ferromagnetism saturates at low magnetic fields and diamagnetism dominates at high magnetic fields. But in other percentage mol concentration of Mn doped SnO_2, the oxygen vacancy population may be high because of the less particle size.

iv. The room temperature ferromagnetism in Co doped in SnO_2 nanoparticles due to the presence of the defects and the oxygen vacancies is observed. The strong optical absorption with magnetic properties at room temperature may serve the nanomaterials as a probable product for many spintronics, optoelectronics and DMS based applications. The decrease in ferromagnetism arises owing to the reduction in distance between the Co^{2+} ions.

v. The hysteresis loop of $Sn_{1-x}Cu_xO_2$ presents that 3% and 4% Cu doped SnO_2 samples illustrate the RTFM behaviour. But 1% and 2% Cu doped samples exhibit the weak ferromagnetism with diamagnetic contribution. Therefore

SnO_2 nanosystem becomes diluted magnetic semiconductor by doping transition metal ion Cu in different concentrations

5) Antibacterial activities :

The antibacterial studies using the samples Mn doped SnO_2 and Co doped SnO_2 have been inspected against some gram positive and gram negative bacterial strains. The result shows the enhanced antimicrobial activity in 4 % cobalt or manganese doped samples than that of pure SnO_2 nanoparticles.

Future Scope :

The present thesis gives an original experimental approach to prepare pure SnO_2 and transition metal doped SnO_2 nanoparticles and explores the structural, photoluminescence and magnetic properties of the prepared samples. Microwave assisted solvothermal method is proved to be a valuable technique for the preparation of fine nanoparticles with the low-cost, high-efficiency and simplicity. Our future plan is given below

- SnO_2 NPs can be potentially used as an antibacterial reagent. The three major factors for the estimation of the metal oxide NPs are nanoparticle composition, solubility and interaction modes with the biological systems. Our aim is to investigate the antibacterial and antifungal activities of SnO_2 NPs with different dopants in different concentrations.
- SnO_2 nanoparticle thin films doped with different metal ions reveal high selectivity for specific gases. The further step in our work will be the development of gas sensor device working at a favourable room temperature.