INTRODUCTION

At present nanotechnology attracts lot of attention of researchers, scientists, engineers and technologists owing to its vital applications. Nanotechnology has recently become one of the most active research fields in the areas of technology, modern science and engineering. The concept of Nanotechnology and Nanomaterials was firstly introduced by the Nobel Prize Winner Richard Feynman’s at Caltech in December 29, 1959. He described a process by which the ability to manipulate individual atoms and molecules might be developed, using one set of precise tools to build and operate another proportionally smaller set, upto the expected scale. The history of Nanomaterials is quite long; nevertheless, major developments within nanoscience have taken place during the last decades. Research in nanomaterials is the multidisciplinary efforts that involves interaction between researchers in the subject of physics, chemistry, mechanics, materials science and even biology and medicine.

Nanotechnology is a collective definition referring to every technology and science which operates on a nanoscale and to the scientific principles and new properties that can be found and mastered when operating in this range. Nanotechnology is defined as nanotechnology is the design, characterization, production and application of structures, devices and systems by controlling shape and size at nanometer scale. In the nanoscale, which is normally seen as going from 100 nm and down to just a few nanometers, the materials have properties that can be very different from those at a larger scale. The prefix ‘nano’ is derived from the Greek word for dwarf. A nanometer (nm) is one thousand millionth of a meter, i.e. $10^{-9}$ m. The illustration of nanomaterials such as, the size of a human hair is 80 000 nm wide and a virus is around 100 nm in diameter. The simplest example of nanotechnology is one nanometer about ten atoms in a line make up.

There are two principal ways for manufacturing nanoscale materials 1) the top-down approach: it starts with a large structure and proceeds to make it smaller through successive cuttings 2) the bottom-up approach: it starts with individual atoms and builds them up to a nanostructure. When we bring constituents of materials down to the nanoscale, the properties change. Some materials used for electrical insulations can become conductive and other
materials can become transparent or soluble. For example gold nanoparticles have a different colour, melting point and chemical properties, due to the nature of the interactions among the atoms that make up the gold, as compared to a nugget of gold. Nano gold does not look like bulk gold, the nanoscale particles can be orange, purple, red or greenish depending on the size of the particle [3]. All these new properties that open up when bringing the material down in scale is of great interest for the industry and society as it enables new applications and products.

The nanotechnology has attracted much attention because when the size of material entities are in the order of nanometers (10^{-9} m), the materials properties qualitatively change due to quantum-size effect, surface-to-volume ratio and boundary effect of fundamental structure. Nanotechnology develops rapidly and owing to an overwhelming application. Nanotechnology includes (a) nano-physics; (b) nano-chemistry; (c) nanomaterials science; (d) nanobiology; (e) nano-electronics; (f) nano-machining; and (g) nano-mechanics.

Nanomaterials are defined with at least one dimension between 1 and 100 nm. Generally, nanomaterials can be classified into three groups according to the number of dimensions: (a) zero dimension materials- materials with nanoscale size in all three dimensions, for example, nanoparticles and nanoclusters; (b) one dimensional materials- materials with nanoscale size in one dimension, for example, nanotubes, nanowires, nanocables, and nanobelts; (c) two dimensional materials- materials with nanoscale size in only two dimension, for example, super thin films, multiple layer films and supper lattices.

Properties of nanomaterials are different and often superior to their conventional counterparts available in polycrystalline form as they depend on the microstructure which determined by the chemical composition, grain size, atomic structure, crystallographic orientation, coordination number, and dimensionality. Because of the fine grain dimensions, significant volume fraction of atoms in nanomaterials is located at the grain boundaries that confer special attributes to them. Nanoparticles, due to their smaller size and large surface to volume ratio, exhibit interesting novel properties which include nonlinear optical behavior, increased mechanical strength, enhanced diffusivity, high specific heat, magnetic behavior, and electric resistivity, etc. Researchers have proposed a huge range of potential scientific application of metal nanoparticles such as in the fields of biotechnology, sensors, medical diagnostics, catalysis, high performance engineering materials, magnetic recording media, optics and conducting adhesives.
PROBLEM UNDER STUDY

Zinc Oxide (ZnO) is a semiconductor with a wide band gap of about 3.37 eV. The stable structure of ZnO is wurtzite (hexagonal, with a = 3.25 Å and c = 5.12 Å), in which each atom surrounded by four atoms of oxygen in tetrahedral coordination. It is very interesting from viewpoint of forming a ferromagnetic material due to the wide band gap. Combined with the high conductivity that can be achieved by doping this leads to application in surface acoustic wave devices and transparent conducting electrodes. Finally, ZnO is also a strong piezoelectric material, in which the piezoelectric properties can change the characteristics of potential energy barriers at interfaces, and can be exploited in metal oxide varistors. As grown ZnO is an n-type semiconductor and its n-type conductivity can be controlled by growing it in an oxygen deficient atmosphere or by doping it with group III elements like Al, Ga or In. Thus Mn doped ZnO has the potential to be a highly multifunctional material with coexisting magnetic, semiconducting, and optical properties.

Zinc Sulfide (ZnS), is an II-VI semiconductor with a direct band gap of 3.6 eV at room temperature and 40 meV binding energy. It has two types of crystal structures i.e. Cubic (Zinc blend) and wurtzite (Hexagonal). It is very important from the viewpoint of forming transport magnetic and semiconducting properties due to wide band gap. ZnS is very good luminescence material by doping it leads due to the application in photocatalysis. It is also one of the promising optoelectronic semiconductor and used frequently in light emitting diodes, piezoelectric devices and photodetectors. Nanodimensional ZnS has found to exhibit excellent optical and optoelectronic properties which differ greatly from the bulk ZnS. However when magnetic Mn introduced into nanoparticles of nonmagnetic ZnS semiconductor, then interesting luminescence, magnetic, semiconducting, magneto-optical properties are expected.

In addition to applications in ZnO and ZnS materials, incorporating Mn metal ions substitutionally in II-VI ZnO and ZnS should be less difficult than incorporating them in other semiconductor hosts, since when 3d ions have valence state of +2, equal to that of Zn, ionic radius differences between Zn and 3d ions are minimized and defects formation for holding charge neutrality is suppressed. This favors substitution of the Mn metal ion at cation site and helps in achieving higher dopant concentrations. It also means that, in perfectly stoichiometric sample, substitutional Mn introduces a magnetic moment without contributing carries.
Thus it is necessary to efficiently dope 3d ions in the valence state of $2^+$ into ZnO and ZnS. It is very important for spintronics, photocatalysis, electronic and optical devices applications. Therefore Mn doped ZnO and ZnS systems have been systematically investigated.

SYSTEM USED IN PRESENT STUDY

With these motivations, we have prepared two nanomaterial systems using sol-gel, chemical and co-precipitation techniques namely

1) $\text{Zn}_{1-x}\text{Mn}_x\text{O}$
2) $\text{Zn}_{1-x}\text{Mn}_x\text{S}$

The substitution of transition metal ion like Manganese (Mn) atom is selected because of suitability of doping 3d ions in ZnO and ZnS samples. It is interesting to synthesis functional diluted magnetic semiconductors (DMSs) whose structural, magnetic and optical properties are controllable by changing the carrier concentration, which will enable us to study the role of introducing magnetic ions into nanoparticles of ZnO and ZnS systems.

The $\text{Zn}_{1-x}\text{TM}_x\text{O}$ and $\text{Zn}_{1-x}\text{TM}_x\text{S}$ (where TM = Mn$^{2+}$) systems are characterized by X-ray diffraction (XRD) by means an atomized diffractometer with CuK$_\alpha$ radiation to identify crystal structure, lattice parameter and grain size. The particle size and morphology of samples are characterized by transmission electron microcopy (TEM). The presence of various functional groups in the systems has been confirmed using FTIR analysis. The optical properties of the synthesized systems have been studied using UV-Visible (UV-VIS) spectroscopy. The vibrating sample magnetometer (VSM) is employed to analyze the magnetic properties of the system.

ORGANIZATION OF THE THESIS

The first chapter includes history of nanotechnology and nanomaterials, overview of semiconducting nanomaterials, theoretical aspects, properties of nanomaterials and motivation for studying nanomaterials are discussed in detail.

The second chapter contains the common methods used for synthesis of nanomaterials like chemical route, sol-gel, coprecipitation, solid state reaction route, hydrothermal technique etc. This chapter includes the different characterization techniques used to calculate the present study such as X-ray diffraction technique (XRD), Transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), Ultra Violet Visible Spectroscopy (UV-VIS) and Vibrating sample magnetometer (VSM).
The third chapter describes the synthesis of Zn$_{1-x}$Mn$_x$O system by sol-gel method. The structural properties such as lattice parameter, volume cell, X-ray density, c/a ratio, u parameter, porosity etc. The X-ray diffraction patterns show that all samples have wurtzite (hexagonal) structure. The lattice parameters and volume cell go on increasing with increasing the Mn content. The u parameter is also increasing with increasing the Mn concentration. The grain size was calculated using the Scherrer equation. It is found that the grain size decreases with increasing Mn concentration. The morphology and particles size were calculated using transmission electron microscopy. The selected-area electron diffraction (SAED) pattern shows that the nanoparticles are in crystalline nature. Prominent IR peaks are analyzed and assigned by FTIR measurement. Absorption bands show the presence of resonance interaction between vibrational modes of oxide ions in the crystal. The UV-visible spectrophotometer measurements show the changing in the band-gap when Mn doping increases. The magnetization measurement indicates that the magnetization of these nanoparticles changes with increasing Mn concentration.

The fourth chapter illustrates the synthesis of Zn$_{1-x}$Mn$_x$O system by Co-precipitation method. The crystallographic parameters such as lattice parameter, volume cell, X-ray density, c/a ratio, u parameter, porosity etc. were studied. The X-ray diffraction exhibit that all samples have wurtzite (hexagonal, phase, space group p6$_3$mc) structure with high crystallites. From this study no trace of manganese metal, oxides or any binary zinc manganese phase is clearly observed. The lattice parameters of Zn$_{1-x}$Mn$_x$O system gradually increasing with increasing the Mn concentration. The increment in the unit cell volume with increasing Mn concentrations indicates the incorporation of Mn at Zn sites. The u parameter is increasing with increase in the Mn concentration and c/a ratio slightly decreases. The grain size was calculated using the Scherrer equation; it is found that the grain size decreases with increasing Mn concentration. The obtained TEM micrograph of Zn$_{1-x}$Mn$_x$O nanoparticles indicates that most of the individual particles are of size in the range 20-50 nm, which are consistent with the results obtained from the XRD data. The selected-area electron diffraction (SAED) pattern shows that the nanoparticles are in crystalline nature. Prominent IR peaks are analyzed and assigned by FTIR measurement. Absorption bands show the presence of resonance interaction between vibrational modes of oxide ions in the crystal. The magnetization measurements show that magnetization of these nanoparticles changes with increasing the Mn
concentration. The optical properties are carried out using UV spectra which shows that the variation of the band-gap with as increasing Mn concentration.

The fifth chapter elucidates the synthesis of Zn\(_{1-x}\)Mn\(_x\)S system by Co-precipitation method. The structural properties such as lattice parameter, volume cell, X-ray density, porosity etc. The X-ray diffraction exhibit that all samples are in cubic zinc blende structure. The lattice parameter were calculated from XRD data and found that they are slightly increasing with increasing the Mn content. The average grain size was determined from X-ray diffraction data using the Scherrer equation. It is found that the grain size is gradually changing with increasing Mn concentration. The particle size and morphology of the Zn\(_{1-x}\)Mn\(_x\)S nanoparticles have determined by transmission electron microscopy. The selected-area electron diffraction (SAED) patterns show that the nanoparticles are in crystalline nature. The magnetization measurements show that magnetization of these nanoparticles change with increasing the Mn concentration. The optical properties are carried out using UV spectra which shows that the variation of the band-gap with as Mn concentration increases. Prominent IR peaks are analyzed and assigned by FTIR measurement.

The sixth chapter contains the synthesis of Zn\(_{1-x}\)Mn\(_x\)S system by chemical route. The structural properties such as lattice parameter, volume cell, X-ray density, porosity etc. The X-ray diffraction exhibit that all samples are in cubic zinc blende structure. The lattice parameter slightly increasing with increasing the Mn content. The average grain size was determined from X-ray diffraction data using the Scherrer equation it is found that the grain size is gradually changing with increasing Mn concentration. The particle size and morphology of the Zn\(_{1-x}\)Mn\(_x\)S nanoparticles have determined by transmission electron microscopy. The selected-area electron diffraction (SAED) patterns show that the nanoparticles are in crystalline nature. The magnetization measurements show that magnetization of these nanoparticles changes with increasing Mn concentration. Prominent IR peaks are analyzed and assigned by FTIR measurement. The optical band gaps are evaluated using UV spectra. It shows that the change in the band-gap with increasing Mn concentration.

The seventh chapter interprets the results with conclusion and future scope for both systems i.e. Zn\(_{1-x}\)Mn\(_x\)O and Zn\(_{1-x}\)Mn\(_x\)S.