1. INTRODUCTION

1.1 Nanoscience and Nanotechnology [1-11]

Nano, the Greek word for 'dwarf' indicates one billionth of something \(1 \times 10^{-9}\). While the word nanotechnology is relatively new, the existence of functional devices and structures of nanometer dimensions is not, new, and in fact such structures have existed on Earth as long as life itself. The abalone, a mollusk, constructs very strong shells having iridescent inner surfaces by organizing calcium carbonate into strong nanostructured bricks held together by a glue made of a carbohydrate – protein mix. The shells represent a natural demonstration that a structure fabricated from nanoparticles can be much stronger. Purple of cassius, a popular dye in olden days is subsequently found to be made of tin oxide and Au nanocrystals. Small colloidal particles of silver are a part of the process of image formation in photography.

It is not clear when humans first began to take advantage of nanosized materials. It is known that in the fourth – century A.D. Roman glassmakers were fabricating glasses containing nanosized metals. An artifact from this period called the Lycurgus cup resides in the British Museum in London. The cup, which depicts the death of King Lycurgus, is made from soda lime glass containing sliver and gold nanoparticles. The colour of the cup changes from green to a deep red when a light source is placed inside it. The great varieties of beautiful colors of the windows of medieval cathedrals are due to the presence of metal nanoparticles in the glass.
Nanoscience is the study of phenomena and manipulations of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at a large scale. Materials in the nanoscale consist only of a few atoms or molecules clustered together. At this scale, quantum confinement effects begin to dictate a material's properties what makes these nanoparticles interesting and endows them with their unique properties is that their sizes are smaller than their critical lengths that characterize many physical phenomena. Generally, physical properties of materials can be characterized by some critical length, a thermal diffusion length or scattering length.

Nanotechnologies are the design, characterization, production and application of structures, devices and systems by controlling shape and size on the nanoscale. Nanotechnology is the application of nanoscience to useful devices. Nanotechnology is a widely spreading technology in the field of agriculture, medicines, textiles, defence etc. The ability to work with atoms at the nanoscale or with nano materials on the molecular level, with atomically precise design, promises to open up a lot of areas of technological development.

1.2 What are Nanomaterials?

Nanophase materials are three dimensionally modulated, synthetic materials with average grain, phase, or other structural domain sizes below 100nm. Ultrafine microstructures having an average phase or grain size of the order of a nanometer are classified as nanostructured materials. Nanostructured materials include atomic clusters, layered films, filamentary structures have different morphologies such as nanorods, nanosheets, nanotubes, nanoplatelets, nanowhiskers, nanorings, nanobelts
etc [4]. Nanomaterials have large surface area. So they have enhanced chemical, mechanical, optical and magnetic properties, and this can be exploited for a variety of structural and non-structural applications. Some nanomaterials are exceptionally strong, hard and ductile at high temperatures. However, they are chemically very active because the number of surface molecules or atom is very large compared with the molecules or atoms of the bulk material.

A working definition for nanomaterials and nanotechnology is "the design, characterization, production and applications of the structures, devices and system by controlled manipulation of size, and shape at the nanometer scale (atomic, molecular and macromolecular scale) that produces structures, devices and systems with atleast one novel/ superior characteristic or property"[5].

The basic nano structured materials are [3, 11-13]:

- Nanoparticles: ultrafine solid particles on a nanoscale including nanopowders and nanocrystals;
- Nanotubes: hollow nanoscale particles including nanotubes, nanohorns and nanocapsules;
- Nanostructured materials and coatings: materials made of structural elements (clusters, crystals and molecules) with dimensions in the nano-range and which may form films or be free standing; and
- Nanocomposites: mixtures of components at least one of which has nanoscale dimensions.

When particles become small enough to be nanoparticles, their mechanical properties change, and the way light and other electromagnetic radiation is affected by them changes (visible light wavelengths are on the order of a few hundred nanometers). Using nanoparticles in composite materials can enhance their strength,
reduce weight, increase chemical and heat resistance and change their interaction with radiation.

1.3 Synthesis of Nanomaterials [5-6, 10,13-19]

A current paradigm of synthesizing and processing of advanced materials emphasizes the tailored assembly of atoms and particles from the atomic or molecular scale to the macroscopic scale.

Nanostructured materials can be made by attrition of parent coarse-grained materials using the top-down approach from the macroscale to the nanoscale, or conversely, by assembly of atoms or particles using the bottom-up approach. The control of arrangement of atoms from the nanoscale to the macroscale is indeed the strength of materials chemistry.

There are two types of techniques in the preparation of nanomaterials. They are:

1. Physical approach, and
2. Chemical approach.

1.3.1 Physical approach

It is a top-down approach including milling or attrition, repeated quenching, and lithography.

By attrition or milling, nanoparticles ranging from a couple of tens to several hundreds of nanometers in diameter can be achieved. Nanoparticles obtained by attrition have relatively broad size distribution and varied morphology, and contains
impurities from the milling medium. Such prepared nanostructures are commonly used for the fabrication of nanocomposites and nanograin bulk materials.

Repeated quenching or thermal cycling may also break a bulk material into small pieces, if the materials have very small thermal conductivity but a large volume as a function of temperature.

Lithography is a top down approach which plays an important role in the synthesis and fabrication of nanostructures.

Physical techniques include

i) Arc discharge method
ii) Laser ablation
iii) Aerosol synthesis
iv) Inert gas condensation
v) High-energy ball milling (mechanical alloying method)
vi) Chemical vapour deposition
vii) Plasma synthesis
viii) Electro-deposition

(i) **Arc discharge method**

A common technique for the production of single walled carbon nanotubes (SWNTs) is the electric arc discharge method in which carbon is vaporized between two carbon electrodes. Small diameter, single-wall nanotubes can be synthesized using a dc arc welder to maintain the optimal settings between two horizontal electrodes in helium or argon atmosphere. Nanotubes of dichalcogenides such as MOS\(_2\), MoSe\(_2\), and WS\(_2\) are also obtained by this technique. Nanoparticles of metal
oxides, carbides and nitrides can also be prepared by carrying out the discharge in suitable gas medium or by loading the electrodes with suitable precursor.

(ii) **Laser ablation**

In laser ablation, high – power laser pulses are used to evaporate matter from a target surface such that the stoichiometry of the material is preserved in the interaction. This method is applicable to high melting point elements and transition metals. This method is particularly suitable to carry out in situ studies on highly toxic and radioactive materials often in trace. Iron, gold, palladium and compounds of sulphides have been reported by this method. This method is capable of high rate of production of 2.3g/min.

(iii) **Aerosol synthesis**

In this method, a liquid precursor is first prepared. The precursor can be a simple mixture solution of desired constituent elements or a colloidal dispersion. The resulting particles are spherical and their size is determined by the size of initial droplets and concentration of solid. Aerosol can be relatively easily produced by sonication or spinning. This technique has also been used in the preparation of polymer colloids. The starting materials are droplets of organic monomers that can be either polymerized in contact with an initiator in gaseous state or copolymerized with another organic reactant. Usually particles formed by this technique are larger particles, with diameters ranging from ~ 1-20 micro meters.
(iv) Inert gas condensation

Gas condensation was the first technique used to synthesize nanocrystalline materials and alloys. This method is extremely slow. Gas condensation allows us to produce nanoparticles with well-controlled size distribution. In this process the metal is evaporated by several methods including evaporation, sputtering, laser ablation, etc where it subsequently nucleates and grows into nanoparticles as a result of interaction with an inert gas.

(v) High-energy ball milling (mechanical alloying method)

This is the only top-down approach for nanoparticle synthesis of magnetic, catalytic and structural nanoparticles. Ball milling and subsequent annealing is a simple method for the production of CNTs. Using this method more multiwalled nanotubes and few single walled nanotubes can be produced.

Common drawbacks include low surface, highly poly disperse size distribution and partially amorphous state of the powder. These powders are highly reactive with oxygen, hydrogen and nitrogen. It would not be possible to produce an alloy of Al – Ta, because of the difference in melting points of Al (933K) and Ta (3293K) by any conventional process. It can be fabricated by mechanical alloying using ball milling process.

(vi) Chemical vapour deposition

Chemical vapour deposition (CVD) is the process of chemically reacting a volatile compound of a material to be deposited, with other gases, to produce a non-volatile solid that deposited atomistically on a suitably placed substrate.
In thermal CVD the reaction is activated by a high temperature above 900°C.

In plasma CVD the reaction is activated by plasma at temperatures between 300 and 700°C.

In laser CVD pyrolysis occurs when laser thermal energy heats an absorbing substrate.

In photo-laser CVD the chemical reaction is induced by ultra violet radiation which has sufficient photon energy to break the chemical bond in the reactant molecules. In this process, the reaction is photon activated and deposition occurs at room temperature.

(vii) **Plasma synthesis method**

Plasma synthesis method has been successfully used in the synthesis and preparation of advanced materials such as new ceramics, nanometric metallic powders, biomaterials and superconductors. The typical size of the nanoparticles produced by this method ranges from 20 to 100nm depending on the quenching conditions employed.

(viii) **Electro – deposition**

Template – assisted electrodeposition is an important technique for synthesizing metallic nanomaterials with controlled shape and size by this method, employing either an active or restrictive template as a cathode in an electrochemical cell (using the surface of the cathode as a template various desired nanostructures or morphologies can be synthesized for specific applications).
1.3.2 Chemical approach

This is a bottom-up approach which refers to the building up of materials from the bottom atom by atom, molecule by molecule or cluster by cluster. The bottom up approach plays an important role in the fabrication and processing of nanostructures and nanomaterials. Nanoparticles of various oxides can also be synthesized by confining chemical reaction, nucleation and growth process in small spaces such as micelle approaches. Various synthesis methods or techniques can be grouped into two categories:

a) thermodynamic approach, and
b) kinetic approach.

In the thermodynamic approach, synthesis process consists of:

i) Generation of supersaturation,
ii) Nucleation, and
iii) Growth.

In the kinetic approach, formation of nanoparticles is achieved by either limiting the amount of precursors available for the growth such as used in molecular beam epitaxy or confining the process in a limited space such as aerosol synthesis or micelle synthesis.

(i) Solvothermal synthesis

In solvothermal method, nanophase materials are produced by chemical reactions in an aqueous or organic medium under simultaneous application of heat and pressure of an alkali or acid. By this method oxides can be synthesized with and without the aid of surfactants. Zeolites, inorganic structures, and solid materials are
also synthesized by this method. Ceramics of various materials are also reported to be
prepared by this chemical method. A number of fundamental properties of the solvent
are greatly affected by pressure and temperature, for example, the viscosity and
dielectric constants are considerably reduced. The solvents used in this methods are
ethanol, methanol, toluene and t-butanol.

Synthesis under solvothermal condition offers some significant advantages
over other chemical methods.

1) First, it is easy to control particle size and morphology by varying the
   synthesis conditions (temperature, pressure, time, concentration, pH,
shearing forces and nature of additives).

2) Secondly, many nanomaterials can be directly synthesized (one-step
   synthesis) in the desired crystalline phase at relatively low temperature.

Solvothermal process opens a fruitful route for improving the synthesis of
well-known nanomaterials, furthermore, allowing the preparation of nanophase
materials which are difficult to obtain by other methods. This is one of the simple
techniques for the preparation of nanomaterials with high yield and number of
materials have been grown which are well documented.

(ii) Reverse micellar/ micro-emulsion method

In reverse micellar synthesis reactions proceed among the reactants that are
available only inside the micelle and the particle stops growing when the reactants are
consumed. Micelles are often globular and roughly spherical in shape. But ellipsoids,
cylinders and bilayers are also possible. This method is a simple and powerful
technique which does not require specialized or expensive equipments. Using this
method colloidal metals, colloidal Fe$_3$O$_4$, colloidal AgCl, nanocrystalline Fe$_2$O$_3$, TiO$_2$, Al$_2$O$_3$ and high – T$_c$ oxide YBa$_2$Cu$_3$O$_7$ and various nanodispersed polymer particle can be synthesized. Thus reverse micellar method is versatile because a variety of nanomaterials (binary, ternery and quaternary oxides) of wide ranging compositions have been prepared as pure homogeneous phases.

(iii) Sol-gel synthesis

Sol-gel method is a versatile process used in making various colloidal dispersions of inorganic and organic - inorganic hybrid materials, particularly oxides and oxide based hybrids. From such colloidal dispersions powders and thin films can be readily prepared. In a typical sol-gel process, a colloidal suspension or a sol is formed from hydrolysis and polymerization reactions of precursors which are usually inorganic metal salts or metal organic compounds such as metal alkoxides and aloxysilanes. Sol-gel formation occurs in three stages. This method involves the formation of a concentrated suspension of a metallic oxide or hydroxide (Sol), which is subsequently dehydrated by evaporation or solvent extraction, resulting in a semi-rigid mass (gel). A wide range of pure and mixed oxides can be produced on controlled heating of this gellated material.

(iv) Microwave method

In this method, the principal microwave heating frequencies are between 900 and 2450 MHz. At lower microwave frequencies, conductive currents flowing within the materials due to movement of ionic constituents can transfer energy from microwave field to the material. At higher frequencies, the energy absorption is
primarily due to molecules with a permanent dipole which tend to reorient under the influence of microwave electric field.

The major disadvantage of using microwave for industrial processing are rapid heat transfer and volumetric and selective heating. Microwave radiation is applied to prepare various oxide nanomaterial including TiO$_2$.

(v) **Sonochemical process**

Sonochemistry is the research area in which molecules undergo a chemical reaction due to the application of powerful ultrasound radiation having frequency in the range of 20kHz – 10MHz. This method is useful in the synthesis of a wide range of nanostructured inorganic materials for industrial applications.

(vi) **Co-precipitation**

This method is a useful method for the preparation of ceramic oxide powders. In the case of a multi-component system, this technique is usually limited to the cations of chemically similar properties. The main disadvantage of this method is that it produces materials with broad size distribution. The method does not work well in the following cases.

a) The two reactants have very different solubilities in water.

b) The reactants do not precipitate at the same time.

1.4 **Types of Nanostructured Materials [1-8]**

Based on the dimensionality, nanostructured materials are classified as zero, one, two or three dimensional structures and are shown in Figure 1.
i) Zero dimensional atom clusters and cluster assemblies or quantum dots. Sol-gel process has been commonly used to generate clusters.

ii) One-dimensional or nanowires which has got immense applications. These are having layered or lamellar structure. Vapour deposition, sputtering techniques and electrodeposition techniques have been used to synthesize the one-dimensional layered nanostructured materials. The magnitude of length and width are much greater than the thickness of the layered nanocrystals.

iii) Two dimensional nanostructured materials with planar structure of thickness of the order of few nanometers with definite length and breadth. These will be filamentary in nature and length is substantially larger than the width or diameter.

iv) The crystal size of which is of the order of a few (1 to 100nm) nanometers equiaxed in nature and is termed as nanostructured crystallites or 3D (Three dimensional) nanostructure.

Figure 1: The evolution of density of states with dimensionality. The plots show the density of states versus energy (E) for a bulk solid, quantum well, quantum wire and quantum dot.
1.5 Properties of Nanomaterials

The particle size of the materials has significant influence on its physical and chemical properties. Especially, when the particle size is reduced to nanometer scale, it behaves completely different from their bulk counterpart. Unusual physic-chemical properties of nanoparticles are due to three main reasons. (i) The size of nanoparticles is comparable to the Bohr radius of the excitons. This significantly alters the optical, luminescent and redox properties of nanoparticles when compared to the bulk material. (ii) The surface atoms constitute a considerable fraction of the total number of the atoms of the nanoparticle. The surface contributes largely to the thermodynamic characteristics of solids and also determine the melting temperature and structural transitions of nanoparticles in the bulk material, atoms are evenly surrounded and the cohesive forces between the atoms tend to balance. However, there are atoms on only one side of a free nanoparticle surface, and there is an internal cohesive force. As the particle size decreases, the net internal cohesive force increases, and as a consequence the surface energy that depends on the internal cohesive force should increase with decreasing particle size. (iii) The natural size of the nanoparticles is comparable with the size of molecules. This determines the peculiarities of the kinetics of chemical processes on the surface of nanoparticles.

In general, it is easily noticeable that, the reduction in the particle size results in

a) Increase in surface to bulk atom ratio, and
b) Increase in the surface area.
The size dependent nanoparticles include

i) Chemical properties - reactivity, catalysis
ii) Thermal property - melting temperature
iii) Mechanical property - adhesion, capillary forces
iv) Optical properties - absorption and scattering of light
v) Electrical properties - tunneling of current
vi) Magnetic properties - Super paramagnetic effect

Because of the increase in surface to volume ratio, nanostructured materials processes:

i) Increased strength/hardness,
ii) Enhanced diffusivity,
iii) Enhanced ductility/toughness,
iv) Reduced density,
v) Reduced elastic modulus,
vi) High electrical resistivity,
vii) Increased specific heat,
viii) Higher thermal expansion coefficient,
ix) Lower thermal conductivity, and
x) Super soft magnetic properties.

1.6 Applications of Nanocrystalline Materials

Nanotechnology is an exciting area of scientific development which promises 'more for less'. It offers ways to create smaller, cheaper, lighter and faster devices that can do more and cleverer things, use less raw materials and consume less energy. There are many examples of the application of nanotechnology from the simple to the complex.
Nanotechnology is not just about miniaturizing things. At nanoscale, different laws come into play. Properties of traditional materials change and the behaviour of surfaces starts to dominate the behaviour of bulk materials, opening up new realms.

As atoms come together to form molecules, and molecules come together to form crystals of clusters, the inherent macroscale properties are determined. By controlling molecular structure in material synthesis, mankind has gained unprecedented control over the basic material properties, such as conductivity, strength, capacity, ductility, and reactivity, yielding innovative applications ranging from batteries to automotive materials. This is a passive nano technique that primarily focuses on tuning the properties of resulting bulk materials. The active nano technique facilitates creation of functional electronic and ultimately mechanical devices at the nanoscale.

Some existing applications include:

- clay nanoparticles in packaging materials, where reduced porosity leads to less gas entering (e.g. less gas such as oxygen that spoils foods);
- rolled graphite nanotubes used in coatings on car bumpers that better hold their shape in a crash;
- carbon nanotubes which are sources of field-emitted electrons and create enhanced phosphorescence e.g. in "jumbotron" lamps used at many athletic stadiums.
- nanoparticles of zinc oxide in sunscreens, more efficient at absorbing UV than more traditional white titanium dioxide lotions and leaving the lotion smooth and transparent;
- textiles which are dirt and crease resistant due to nanocoatings;
- nanoparticles used as antiseptics, for abrasives and in paints;
- nanocoatings for spectacle glasses (making them scratchproof and crack resistant)
- nanocoatings for tiles to reduce slipping;
- electrocoatings or self-cleaning nanofilm coatings on windows, which in sunshine breaks down dirt and helps the water falling on it to carry the dirt away;
- nanofilms with non-stick properties used as anti-graffiti coatings for walls;
- ceramic coatings for solar cells to improve scratch and erosion resistance;
- glues containing nanoparticles with variable optical properties are used in optoelectronics (e.g. for coupling fibres to other optical components); and
- conductive nanofilms used in casings for electronic devices, such as computers, to provide shielding against electromagnetic interference.

Applications under development, some of which are close to market, include:

- "smart" fabrics that can change their physical properties according to surrounding conditions, or even monitor vital signs;
- drug delivery mechanisms including antibacterial and antiviral nanoparticles;
- nanoceramics for more durable and better medical prosthetics;
- improved catalysis for fuel production; and
- nanoengineered members for energy efficient water purification.

1.7 Dilute Magnetic Semiconductors

One of the more interesting classes of materials to exhibit a wide range of unique electrical, magnetic, and optical properties are diluted magnetic semiconductors (DMSs). As their name suggests, DMSs result from the alloying of magnetic transition metals and semiconducting compounds. The most widely studied II-VI-based DMSs have been those containing Mn\(^{2+}\) as the substitution magnetic cation [20]. In recent years, Fe- and Co-based DMS’s have also been successfully grown and extensively investigated [21]. It is widely accepted that some of the more important types of investigations made on II-VI-based DMSs have concentrated on
systematic studies of their electronic band structure, and how it is affected by the type of anion and both by the type and relative concentration of host group-II cation and substitutional magnetic ion.

Photoemission spectroscopy studies of Mn\(^{2+}\) 3d states in Cd\(_{1-x}\)Mn\(_x\)Y \((Y=S, Se, Te)\) [22], showed that the Mn\(^{2+}\) 3d partial density of states extends over all the valence bands as a result of strong \(p-d\) hybridization, which was inferred to vary in two important ways: (1) The amount of \(p-d\) hybridization increases directly with Mn concentration \(x\); and (2) It increases in going from Te \(\rightarrow\) Se \(\rightarrow\) S in the series. This is attributed to the difference between the Mn 3d\((t_2)\) and anion \(p\)-state energy levels, varying systematically both with Mn concentration and anion type. It should be noted that controversy still exists concerning the different degree of hybridization between Mn 3d and anion \(p\) orbitals in the Zn\(_{1-x}\)Mn\(_x\)Y \((Y=S, Se, Te)\) series [23]. Theoretical calculations showed that the hybridization energy between the Mn\(^{2+}\) 3d and local anion \(p\)-level valence electrons increases slightly in going from Te \(\rightarrow\) Se \(\rightarrow\) S for both Cd\(_{1-x}\)Mn\(_x\)Y and Zn\(_{1-x}\)Mn\(_x\)Y \((Y=S, Se, Te)\) systems [24]. This was also supported by the electronic band-structure calculations [25]. Obviously, the electronic band structure of a solid is directly affected by its physical structure, and vice versa. Accordingly, DMS lattice constants were found to decrease in going from Te \(\rightarrow\) Se \(\rightarrow\) S in Cd\(_{1-x}\)Mn\(_x\)Y, in agreement with a model for which the amount of \(p-d\) orbital overlap is directly determined by the size of the anion [22, 26].

1.8 Transition Metal Oxides and Sulphides

Manganese oxides with a rather complex oxide system, forming several phases such as MnO, MnO\(_2\), Mn\(_2\)O\(_3\), Mn\(_3\)O\(_4\) are of consider importance in many
technological applications. Polymorphs of Mn$_2$O$_3$ is known to be an active catalyst for removing carbon monoxide and nitrogen oxide from waste gas [27,28]. MnO nano-clusters show ferromagnetic behaviour while bulk MnO is antiferromagnetic with a transition temperature of 118 K and are rock-salt oxides with NaCl type structure at room temperature [29-31]. Transition metal compounds show a variety of physical and chemical properties. The electrical properties range from insulators to superconductors. Such a variety of properties is clearly related to the partially filled d-shell in transition-metal ions [32].

The transition metal oxides have three oxidation states namely Mn$^{2+}$, Mn$^{3+}$ and Mn$^{4+}$. It has been proposed that the structure of Mn$_3$O$_4$ is Mn$^{2+}$ (Mn$^{2+}$ Mn$^{4+}$)O$_4$. Mn$^{2+}$ in tetrahedral sites is partially covalent. Octahedral Mn$^{2+}$ and Mn$^{4+}$ would be ionically bound. In this model Mn$^{2+}$ octahedral - tetrahedral interactions would be antiferromagnetic according to both superexchanges and semicovalent exchanges predicts antiferromagnetic exchanges. Thus this structures would be ferromagnetic just like Fe$^{2+}$ (Fe$^{2+}$ Fe$^{3+}$)O$_4$. But down to 72 K, Mn$_3$O$_4$ is found to be paramagnetic and ferromagnetic below 43K and at 33K a rearrangement of moments occurs such that the chemical and magnetic unit cells become identical [33-35]. The above distorted spinel structure was due to Jahn-Teller distortion at the Mn$^{3+}$ sites. The ionic formula of Mn$_3$O$_4$ is usually written as Mn$^{2+}$ [Mn$^2_2$]O$_4$ corresponding to a "normal" spinel. This spinel hausmannite Mn$_3$O$_4$ has a sp$^3$ hybridisation [36-38].
Neutron diffraction studies of the three polymorphic forms of MnS have shown that the antiferromagnetic structures developed in these materials may be correlated with crystal structure [39]. More specially, in \( \alpha \)-MnS, second nearest neighbour managanese atoms are joined by sulphur atoms located on octahedral site.
whereas in the two β forms, tetrahedrally coordinated sulphur atoms join nearest neighbour manganese atoms. Furthermore, the separation and spatial arrangement of manganese atoms are the same in both α- MnS and the zinc blende form of MnS. The observed magnetic structures indicate that strong antiferromagnetic correlations exist between second nearest neighbours in the case of α- MnS and between nearest neighbours in the two β - forms. Indirect exchange coupling thus appears to involve octahedral sulphur bonds in the first instance and tetrahedral bonds in the second.

In an effort to further elucidate the role of the anion in antiferromagnetism, these studies have been extended to the homologous series consisting of MnS₂, MnSe₂ and MnTe₂. These compounds crystallize with the pyrite structure (Figure 3), which is a NaCl - like arrangement of M and X₂ groups with the axes of the X₂ groups parallel to the various body diagonals.

Figure 3: The pyrite structure
The transition magnetic semiconductor MnS\textsubscript{2} crystallites with pyrite structure is cubic above the Neel point, with space group Pa\textsubscript{3} and consists of an NaCl like arrangement of Mn\textsuperscript{2+} and (S\textsubscript{2})\textsuperscript{2+} ions, with the axes of the (S\textsubscript{2})\textsuperscript{2-} groups directed along the various body diagonal of the cell [40].

1.9 Present Work

Now a day's awareness about nanotechnology is developing steeply step by step in this world [1-11] Nanostructures have attracted much interest because of their unique electronic, optical, magnetic and mechanical properties as a result of their low dimensionality and the quantum confinement effect [41,42].

Nanostructured materials are very interesting for the wide range of new physical properties that they exhibit as well as for their applications in different fields (e.g., magnetorecording, permanent magnets, sensors, biomedicine, etc) [43-45]. Due to finite size effects, some basic magnetic properties of materials, e.g., the spontaneous magnetization, the Curie temperature, and the anisotropy energy, are strongly influenced by the particle size. As the particle size decreases, an increasing surface and interface effects become more and more important. Because of the presence of defects, missing bonds, fluctuations in number of atomic neighbours and inter-atomic distances, the surface is characterized by topological and magnetic disorder. Such disorder propagates from the surface to the particle core, actually making no longer valid the picture of the particle as a perfectly ordered single domain, whose spins rotate in a synchronous way as a large single spin[46-51]. The resulting magnetic behaviour of very small particles is complex and the effect of the interplay of some surface related phenomena is not well understood yet: surface
anisotropy, which can give a dominant contribution to the total particle anisotropy, core-surface exchange interaction (exchange anisotropy, in the case of different magnetic phases) and possible competition between surface and core effects.

Nanorods and nanowires represent a class of one-dimensional nanostructures in which the carrier motion is restricted in two directions. Due to quantum confinement or surface effects, they usually show interesting properties that cannot be observed for their bulk counterpart of the same chemical composition [53,54].

The most stable oxide of manganese Mn$_3$O$_4$ which is eco friendly is a transition metal magnetic semiconductor which have vast application, such as high density magnetic storage media, catalyst, ion exchange, molecular adsorption, electrochemical material, varistors and solar energy transformation [55-61]. One of the managanese oxides, Mn$_3$O$_4$, has been widely used as the main source of ferrite materials [62], which have extensive applications in electronic and information technologies. This material has also attracted interest as an active catalyst for the reduction of nitrobenzene of oxidation of methane [62-64]. Moreover, Mn$_3$O$_4$ has been found to be an effective and inexpensive catalyst to limit the emission of NO$_x$ and CO [65,66], which provides a powerful method to control air pollution. Recently, so far, most of the investigations on magnetic nanoscale materials have been performed due to their unique physical properties arising from the quantum size effect which makes them different from that of their bulk counterpart [60,67-70].

The properties of semiconductor nanostructured materials depend not only on their chemical composition but also on their shape and size. Mn$_3$O$_4$ was often synthesized by the high temperature calcinations of either higher manganese oxides
(MnO₂, Mn₅O₈, and Mn₂O₃), or MnII and MnIII oxysalts, hydroxides [71-73]. In the last decade, various different shape and size Mn₃O₄ nanocrystals have been synthesized by various techniques, for instance, single-crystal Mn₃O₄ nanorods were obtained by simple chemical or by physical methods. Temperature, time of reaction, and starting materials have high influence in their structure and morphology.

MnS₂ is a semiconducting transition - metal dichalcogenides of cubic pyrite-type structure with a band gap in the near infrared region. The sulphur atoms in the pyrite structure are four - fold co-ordinated. MnS₂ is paramagnetic at room temperature but becomes antiferromagnetic at about 49K [74].

MnS₂ can be got naturally and the ionicity of the M-X bond in MnS₂ is considerably larger than in FeS₂, and MnS₂ comes closest to a molecular structure of the alkali cyanide type where the covalent bonds are combined with the ionic interactions [39,75].

These transition metal sulphides have been widely used for sulphur removal (hydrodesulphurization), nitrogen removal (hydrodenitrogenation) and product quality improvement in hydro processing of petroleum - based feed stocks. Also MnS₂ finds applications in hydrostatic pressure, as rectifiers in early radios. Technically they are used to catalyze the break down of polychlorinated molecules [76-78].

Pyrite-type structures of transition-metal dichalcogenide have undergone intensive investigations in recent years due to their varied electrical and magnetic properties. Magnetic structure [79,80] and ordering, [81,82] antiferromagnetic phase transition [83-85] and spin correlations of the manganese disulphide have drawn particular attention in stating precisely its magnetic properties.
By combining this transition metal oxides and transition metal sulphides, semiconductor quantum dots of multiphased nanocomposites can be synthesized. A composite material is a combination of two or more separate materials that has characteristics not shown by either of the materials separately on a macroscopic scale to form a useful material. These multiphased nanocomposites offer unique properties that arise from their small size, large surface area and the interactions of phases at their interfaces, and are attractive for their potential to improve performance of drugs, biomaterials, catalysts and other high-value-added materials [5].

\( \text{Mn}_3\text{O}_4 \) nanocomposites find application as humidity sensors, catalysts, thermistor applications, high charge storage capacity devices, electrochemical superconductors, super capacitors, etc [86-91].

Remediation of waste water containing organic constituents is of great importance, because organic substance like benzene, phenol and alcohols, etc may lead to serious intimidation to human and animal life. Organic effluents from pharmaceutical, chemical and petrochemical industry usually contaminate water system by dissolving into ground water. Up to date, several processes have been developed for treating waste water that contains toxic organic compounds such as wet oxidation with or without solid catalysts [92-95], biological oxidation, supercritical oxidation and adsorption [96-97].

Doping means impurity which is in a feeble quantity. The dopant occupies the interstitial space. When one compound is mixed with other compound, the atoms are replaced.
Doping of material can alter the properties of the material. The alloying of two or more metals has always been systematically used in order to modify and improve the properties of the metallurgical materials. The mixing of ionic solids has been equally investigated in the purpose of obtaining new materials with specific properties. A very important situation that is special to ionic crystals arises when these crystals are doped (or added) with impurities. The behaviour depends on the valence state of impurity ions. When an ion like Ca$^{2+}$ replaces a Na$^{2+}$ ion in NaCl crystal it results in the creation of a positive ion vacancy or a negative ion interstitial. Anion impurities also produce corresponding charge compensating point defects. Whether an impurity ion goes to substitutional position or interstitial position, is determined by the ionic radius of the doped (or added) ion and also on the electronic configuration of the ion. If the impurity ion behaves in the same way as the lattice ion, a wide range of solubility may be possible. To describe this, the term mixed crystal is used.

A mixed crystal is obtained by crystallizing together two isomorphous crystals like NaCl and KCl. Isomorphism is not only the condition for the formation of mixed crystal, the lattice constants of the component crystals should be comparable. That is, when two substances A and B have closely similar structures (isomorphic structures) with not much different cell dimensions, it is found that the atoms of one can replace those of the other indiscriminately in the lattice, resulting in a mixed crystal AB [98]. The sizes of the atoms or ions and their electronic configurations are the important considerations. Any proportion of these two substances A and B may be contained in the crystal AB with cell dimensions intermediate between those two compounds.
MnO and MnS crystals are isomorphous to each other (may be at high and ambient temperature) and their lattice constants are comparable, the difference is very negligible. So, based on this condition, it may be possible for us to get mixed crystals (solid solutions) of the form MnS\(_x\)O\(_{1-x}\).

In the present study, we proposed to use the simple solvothermal method using a domestic microwave oven [99-101]. Also, we aimed at preparing new nanocomposites. As several phases are possible for manganese oxides and manganese sulphides, depending on the precursors, rate of reaction, solvent, temperature, etc we will be getting as the product one or more phases in each case (manganese oxides or managenese sulphides).

In our laboratory, previous experience has shown that it is possible for us to get Cd (OH)\(_2\) nanoparticles in the ambient conditions while performing a reaction between cadmium acetate and urea with ethylene glycol as the solvent using this simple solvothermal method [102]. However, ZnO nanoparticles is formed directly in the ambient conditions by a reaction between zinc acetate and urea eventhough Zn (OH)\(_2\) is expected to form at the first instant. It is understood that special annealing in this case is not necessary [101]. Similarly, it is possible for us to get by this method the ZnS, CdS and PbS nanoparticles from their metal acetates and thiourea directly in the ambient conditions without any special annealing [101, 103-112].

The stoichiometric composition of copper sulphide exists in five significant forms such as chlacocite(Cu\(_2\)S), djurleite (Cu\(_{1.6}\)S), digenite (Cu\(_{1.8}\)S or Cu\(_9\)S\(_5\)), anilite (Cu\(_{1.75}\)S or Cu\(_7\)S\(_4\)) and covellite (CuS) [113-116]. It has been observed that by performing a reaction between copper acetate and thiorurea with ethylene glycol as
the solvent in the ambient conditions using a domestic microwave oven the digenite (Cu$_9$S$_5$) is formed [117].

In a preliminary experiment made by us we were able to prepare Mn$_3$O$_4$ [118] and MnS$_2$ [119] nanocrystals instead of the other phases of manganese oxide and manganese sulphide (including MnO and MnS) in the ambient conditions using manganese acetate and urea, manganese acetate and thiourea respectively for Mn$_3$O$_4$ and MnS$_2$ with ethylene glycol as the solvent. This, in addition to the importance of these manganese oxide and manganese sulphide nanocrystals (See sections 2.1 and 2.2) prompted us to consider these nanocrystals for our present study.

Transparent conducting oxides (TCOs) are the metal oxides having good optical transparency and high electrical conductivity. ZnO, SnO$_2$, CdO and In$_2$O$_3$ are not isomorphous to each other. However phase-segregated binary systems have been successfully formed and found to be good TCOs with increased conductivity without degrading the transparency. The phase-segregated binary systems include ZnO- SnO$_2$, CdO - SnO$_2$ and ZnO - In$_2$O$_3$ [120-121].

As Mn$_3$O$_4$ and MnS$_2$ are not isomorphous systems, it may not be possible for us to get lattice mixing sufficiently for the formation of solid solutions using these systems. However, for the formation of mixed nanocrystals in the present study, reactants (manganese acetate, urea, and thiourea and zinc acetate for doping) in suitable proportions were used, and the end members as they were. So, new nanocomposites are expected to be formed with the compositions as MnS$_x$O$_{1-x}$ or (MnS$_2$)$_x$(Mn$_3$O$_4$)$_{1-x}$, the later is the most probable.
Although several reports are available on pure and doped individual nanoparticles of Mn$_3$O$_4$ and MnS$_2$, there is no report available on the two component Mn$_3$O$_4$ - MnS$_2$ nanocomposites. This has promoted the candidate interested on this two-component nanocomposite material without and with doping.

For more information regarding manganese compounds based nanomaterials, the readers are requested to see Chapter 2 in this thesis.

In the present research work, pure Mn$_3$O$_4$ – MnS$_2$ and Zn$^{2+}$ doped nanocomposites of different combinational ratios were prepared by the simple microwave assisted solvothermal method. A total of 15 samples (5 pure and 10 Zn$^{2+}$ doped) were prepared. For pure the combination is $(\text{MnS}_2)_x (\text{Mn}_3\text{O}_4)_{1-x}$ (where $x = 0, 0.25, 0.5, 0.75$ and 1). Impurity (Zn$^{2+}$) was added in two different concentrations in the solutions used in the reaction, viz. 2.5 and 5 wt.%. The reaction time, colour and yield percentage, in each case were observed.

X-ray diffraction patterns were recorded for all the samples using an automated X-ray diffractometer. The crystalline structure was identified by the peaks observed in the X-ray diffraction patterns and the grain size was calculated using the Debye-Scherrer formula.

FT-IR spectral measurements were carried out using 8400S model spectrometer to identify the functional groups and chemical bonds present in all the samples. Thermo gravimetric analysis (TG) and differential thermal analysis (DTA) were done for all the pure samples (5 samples) to find the decomposition of the sample.
SEM photographs were taken using JEOL/EO JSM – 6390, to find the surface morphology of the samples. Energy dispersive spectroscopic (EDAX) measurements were carried out for all the samples to determine the chemical compositions in each sample. ICP-OES studies were also made to find the chemical composition using PERKIN ELMER OPTIMA 5300DV ICP-OES.

UV-Vis spectra of all the samples were recorded using an UV-Vis spectrometer and analysed (Shimadzu UV-2400 PC).

EPR (Electron paramagnetic resonance) studies were conducted by Bruker EMX plus Resonometer and VSM (Vibrating sample magnetometer) studies were made by Lakeshore 7400 for all the 15 samples to understand the magnetic behaviour of the samples.

The electrical parameters like dielectric constant, dielectric loss factor, AC electrical conductivity and DC electrical conductivity were determined by using the parallel plate capacitor method. A brief introduction has been seen in the present Chapter.