CHAPTER 1

GENERAL INTRODUCTION

1.1 Introduction

Atoms and molecules constitute a realm of matter whose dimensions are generally less than 1nm, while solids consist of an infinite array of bound atoms or molecules and the size of it is greater than 100nm. A gap exists between these two regimes. This gap is filled with the nanosize regime which deals with particles of size 1-100nm or approximately $10^{-6}$ atoms or molecules per particle called nanoparticles belonging to a new class of materials called nanomaterials. The interest in producing these new materials arose from the fact that by controlling the sizes of atomic groups (particle, grain, phase, cluster) in the size range 1-100nm, one could start to alter and assign the properties to the assembled new materials.

Today there is a flourishing worldwide nanoscience research effort, drawing ideas and methods from Chemistry, Physics, Materials science and Engineering. The researchers attempt to make and organise objects on 1-100nm length scale and also to understand the evolution of the bulk properties from molecular properties. In metals, semiconductors and insulators where strong chemical bonding is present, delocalisation of valence electrons can take place and the extent of delocalisation can vary with the size of the particles. This effect coupled with structural changes with size variation can lead to different chemical and physical properties, depending on the size of the particles. For example, nanostructured metals can have low melting point and improved mechanical properties. Nanostructured ceramic materials can be sintered at a much lower temperature than conventional powders, thus enabling their full densification at lower temperature. They are found to be very effective in catalytic applications.
The development of semiconductor nanoparticles is an area of intense research efforts. They are often referred to as quantum dots.\textsuperscript{17} They possess quantum size effects\textsuperscript{2,4,5} caused by the confinement of delocalised electrons in confined grain sizes which leads to high technological applications.\textsuperscript{6} Bandgap engineering by size and dimension quantisation is important in nanosized semiconductor particles because it leads to electrical, optical, magnetic and optoelectronic properties substantially different from those observed for bulk materials.\textsuperscript{6,9,18} Today active research is going on and scientists have developed various experimental methods for the production of nanoparticle materials and arriving at their characteristics.

1.2 The Terminology

The terminology associated with nanoparticle material research is ever expanding. Groups of atoms is the centre of attraction for many researchers from various fields of science and technology.\textsuperscript{19} Recently nanoparticle research is going through the problem of various terms being used to denote nanoparticles. Clusters of atoms consisting of hundred to thousands on the nanometer scale are commonly known as nanoclusters.\textsuperscript{20} These small groups of atoms go by different names such as nanoparticles,\textsuperscript{20} grains,\textsuperscript{4,6} nanophases,\textsuperscript{6} aggregates,\textsuperscript{21} atomic clusters,\textsuperscript{1} nanocrystals,\textsuperscript{20} ultrafine grained solids, quantum boxes,\textsuperscript{20} quantum dots,\textsuperscript{20} small particles, fine particles, ultrafine particles,\textsuperscript{6} colloidal particles,\textsuperscript{6} crystallites\textsuperscript{2} etc.

But, more recently nanocrystals are characterised as single crystals with size range from a few nanometer up to 100nm.\textsuperscript{21} They may be aggregated into larger units called nanoparticles or nanoclusters with a size range 1-100nm. Materials assembled of nanometer sized building blocks (microstructures) are called nanostructured materials, nanophase materials, nanomaterials, nanocrystalline materials or supramolecular solids.\textsuperscript{1,2} But according to Zhong Lin Wang\textsuperscript{22} nanomaterials can be classified into nanostructured materials and nanophase/nanoparticle materials. The former is concerned with condensed bulk
materials that are made of grains with grain sizes in the nanometer size range, while the latter are usually the dispersive nanoparticles. Another term commonly used is nanoporous materials, which are substances with pores or voids of nanoscale dimensions. These materials can be single crystals such as Zeolites or molecular sieves with cage like nanopores. Due to active research in this field, we can expect that more terminologies may enter into this field.

1.3 Historical Development

Nanophase materials are artificially synthesised or man made materials, which are of recent origin. But it has been found that some nanostructured materials have been with us from the beginning of the universe. Evidence from the earliest meteorites that have been found and studied suggests the existence of nanophase primordial materials condensed from solar nebula. In nature a large number of mineral species occur as small crystallites. For example, we have iron and manganese oxyhydroxide minerals and other species whose formation processes and growth conditions limit their ultimate size. But the planned synthesis of nanomaterials has begun only after billions of years after the origin of the universe.

The colloid science started its development in 1861. The scientist Ostwald classified dispersed systems of particles with sizes 1-100nm as colloids. After that the scientists Einstein and John Tyndall characterised colloids around 1900. The recent studies on nanoparticles began with the work of Kubo in 1962. He had predicted that the physical property of a small metal particle will be quite different from those of bulk materials. He noted that Al made up of particles of sizes less than 10nm are electrically neutral, since it is difficult to add or remove an electron from this particle.

The concept of atomic precision was first suggested by the Physics Nobel Laureate Richard Feynman in 1959 in a celebrated lecture to the American Physical Society. He said, “The principles of physics, as far as I
can see, do not speak against the possibility of maneuvering things atom by atom. Ultimately we can do chemical synthesis. Put the atoms down where the chemist says, and so you can make the substance". His words have come true with the development of nanoscience research. In 1970, research on small particles included atomic and electronic structure determination using experimental studies and theoretical methods. In 1980, atom clusters with selected size ranges had been produced and chemical and physical property studies began. There has been a huge increase in research on atom clusters and increased understanding of their potential, as a constituent of nanomaterials. The synthesis of materials by consolidation of small particles started with the work of H. Gleiter. The cluster assembled nanophase materials have been getting great attention during the last several years. Recently carbon clusters called fullerenes and nanotubes have been arousing the interest of scientists.

Advancements in microscopy technology have made it possible to visualise images of nanostructures and have largely dictated the development of nanotechnology. Nanotechnology is the science and engineering of making materials, functional structures and devices on the nanometer scale. Nanotechnology has become a vital and active area of research which is rapidly developing in industrial sectors and spreading over to almost every field of science and engineering. In the coming years Nanotechnology is expected to grow into a multibillion dollar industry and will become the most dominant technology of the 21st century. Nanotechnology now starts to fulfil its business potentials- from better tennis balls to stain- resistant khaki cloth and cancer drugs.

1.4 Methods of Nanoparticle Synthesis

Various methods have been reported by many scientists for the production of nanoparticles of materials of interest and of varying size range. Control of the size and shape of the particles and its reproducibility
are the prime important factors in the methods for the synthesis of nanophase materials. Beyond that, chemical control of the phases and cleanliness of the interfaces must be controlled as well. Small particles can be formed either by ‘nucleation’ from the atomic level or by the mechanical ‘breaking down’ of bulk materials. In nucleation a phase change is involved, either from liquid or vapour to solid.4

Generally four methods have been used to produce nanophase material depending on the nature of the final product. The first method involves the production of isolated, ultrafine crystallites having uncontaminated free surfaces followed by a consolidation process at room temperature or at high temperature. The specific processes involved to produce these isolated nanoparticles are inert gas condensation method,4,23,31 decomposition of the starting chemicals or precursors28 and precipitation from solutions.6 Second method is chemical vapour deposition (CVD), physical vapour deposition (PVD)32 and some electro-chemical methods33 that have been used to deposit atoms or molecules of materials on suitable substrates (thin film techniques). Nanocomposites can be produced in this way. Third method is the introduction of defects in perfect crystal such as dislocations and grain boundaries, a new class of nanoparticles can be synthesised. Such deformations are usually brought about by high energy ball milling or high energy irradiation.34 Fourth method is to make nanoparticles by crystallisation or precipitation from unstable states of condensed matter such as crystallisation from glasses or precipitation from supersaturated solid or liquid solutions.35 Apart from these general methods, several modifications in these processes have been developed to generate compounds and alloys of specific compositions and properties.

All these nanophase materials can be synthesised basically by two types of synthetic techniques6 namely (1) physical method6,36 and (2) chemical method.6,37
The most widely used technique in physical method is inert gas evaporation,\textsuperscript{4} which is used to metals\textsuperscript{26} and nanophase ceramics\textsuperscript{14} which are consolidated under vacuum conditions. Other techniques are Joule heated ovens, sputtering, mechanical attrition etc.\textsuperscript{4} In sputtering, the material of interest is subjected to an accelerated and highly focussed beam of inert gases such as argon or helium ejecting atoms or molecules. In high-energy ballmilling\textsuperscript{38} or high-energy shear process\textsuperscript{39} nanoparticles are formed by deformation of the coarser material into fine powder and structural deformation takes place by the application of high mechanical energy. Although this method is useful in generating large quantity of the material, it suffers from the problem of contamination resulting from the sources of grinding media. Other techniques are laser ablation,\textsuperscript{40} plasma method\textsuperscript{41,42} electron beam heating\textsuperscript{43,44} etc.

Chemical synthesis method is more advantageous due to its chemical homogeneity and mixing of the constituents at a molecular level. Chemical precipitation method is the most commonly used one for the preparation of nanophase materials.\textsuperscript{45-47} Here there is the possibility of agglomeration which can alter the properties of materials. The concentration of the reactants, reaction temperature and pH value of the solution are all-important factors, which affect the size and formation of particles. By co-precipitation method a multivalent material is often made at a suitable pH value.\textsuperscript{48} For example nano ZnFe$_2$O$_4$ can be made by this method.

Sol-gel technique can be used to produce ceramic materials through the processes, gelation, precipitation and hydrothermal treatment.\textsuperscript{49-51} The advantage of this technique is high thermal stability, high mechanical strength, and low temperature of the method in comparison to high temperature methods like calcination and evaporation. Using chemical capping method one can attain larger control over the synthesis parameters.\textsuperscript{52} Microemulsion method has been used to produce metallic, semiconductor, silica, magnetic and superconductor nanoparticles.\textsuperscript{53} Semiconductor clusters are also prepared by the use of colloids,
miscelles, polymers, glasses etc. These methods have the drawback of varying size distribution of particles. Attempts are being carried out to produce monodisperse nanoparticles. Nanoparticle synthesis can be summarised as shown below.

1.5 Characterisation of Nanoparticles

Characterisation of nanoparticles is indispensable to understand the behaviour and properties of nanomaterial aiming at implementing nanotechnology, controlling their behaviour and designing new material systems with super performance. Characterisation contains two main categories, structure analysis and property measurements. Structure analysis is carried out by a variety of microscopy and spectroscopy techniques.

Direct imaging of nanoparticles is possible using transmission electron microscopy (TEM) and scanning probe microscopies\textsuperscript{22,24} [scanning tunnelling microscopy (STM) and atomic force microscopy (AFM)]. TEM imaging in
conjunction with selected area electron diffraction (SAED) is valuable for the analysis of crystalline samples. Using TEM, one can measure the size of the particle, its shape and structure (morphology) having size greater than 2nm. Using high-resolution transmission electron microscope (HRTEM) we can study the isolated particles within the whole ensemble. In reciprocal space method, diffraction and interference effects of photons or electrons provide sample-averaged information about structure. X-ray diffraction (XRD), extended X-ray absorption fine structure (EXAFS) and small-angle X-ray scattering (SAXS) techniques come under this category. For ordered system of nanoparticles, XRD can be used to determine the structure, whereas for disordered materials, EXAFS technique is found to be more useful. Both complement each other. EXAFS probes the local environment of a particular element and it is a spectroscopic method. SAXS can provide direct information about the external form of particles and average particle size in the range 1-200nm can be determined. Structural information can also be obtained from neutron diffraction studies which is similar to XRD.

Scanning tunnelling microscopy (STM) presents a new class of near field microscopy with nanometer till atomic resolution in real space. This was originally used for surface analysis of particles. Further development of STM resulted in scanning probe microscopes (SPM). Examples are scanning force microscope (SFM) or atomic force microscope (AFM) and scanning near field optical microscope (SNOM). Scanning tunnelling electron microscopy (STEM) can be used in various forms to give information about nanoparticles. Electron energy loss spectroscopy (EELS) and X-ray energy dispersive spectroscopy (XEDS) are techniques available in STM instruments for the elemental analysis of small particles.

Positron annihilation spectroscopy (PAS) and precise densitometry are techniques used to determine the porosity of nanophase materials. PAS is sensitive to small pores whereas for larger ones the Brunauer-Emmet-Teller
(BET) nitrogen adsorption method can be used. Positron lifetime spectroscopy is a suitable method for the study of nanocrystalline materials because it gives information about lattice defects and structural disorders in terms of free volume associated with them. Time of flight mass spectrometry is a technique, which can be used for the gas phase, generated atomic clusters. Small particles can also be characterised using their chemical activity as a probe.11

It is interesting to study the optical properties of nanoparticles.9,57-59 The quantum size effect on the optical absorption spectrum of nanoparticles is well known. As the particle size decreases, there is a reduction in the repetition period of a system of small particles, leading to breakdown of the law of conservation of momentum, which is valid only for large crystals. It is found that Fourier transform infrared (FTIR)6,60-62 and Raman spectroscopy 63,64 can be used to characterise these systems, especially for its surface study.

Electrical and electrochemical analysis of nanophase materials are useful for the fabrication of nanostructured electrodes.65 The measurement of electrical conductivity and dielectric constant gives valuable information about electronic processes, ionic processes, different polarisation mechanisms and different relaxation processes in nanostructured materials.60,66-70 Impedance spectroscopy has emerged as a powerful experimental tool for the study of electrical properties of grains, grain boundaries and electrode effects in nanophase materials.71-74

Solid state nuclear magnetic resonance methods with magic angle spinning (MAS NMR)75-77 is very sensitive to local chemical environment of a particular nucleus under study and is complementary to the longer-range structure afforded by imaging and diffraction techniques. From chemical shift values of NMR components, structural information related to tetrahedral condensation, network distortions or cations sharing oxygen with tetrahedra can be obtained.
Magnetic properties of nanophase materials are considerably different from those of corresponding bulk materials. For example, superparamagnetism is exhibited by very small particles and magnetic susceptibility measurements with temperature can be used as a technique to characterise nanophase materials. Magnetic studies can be carried out using vibrating sample magnetometer (VSM) and superconducting quantum interference devices (SQUID) magnetometer. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) can be used to study the thermodynamical behaviour of nanoparticles. Large amount of energy is stored in the grain boundaries and in other types of defects, nanophase materials are in metastable state of thermal inequilibrium. Hence one can get information regarding the long-term thermal stability of such systems by studying the transition from nanophase-state to thermal equilibrium state. Computer simulations can also be used as a tool for the study of nanoparticles.

### 1.6 Unique Properties of Nanoparticles

The unique properties and the improved performance of nanomaterials are determined by the sizes of particles, surface to volume ratio of atoms, surface structures of particles and interparticle interaction. The structure and properties of collection of condensed atoms in a single particle vary with particle size from atomic or molecular state to bulk solid state. The way in which this property variation takes place is the fundamental basis for the development of theoretical models for condensed matter.

As the particle size decreases, the ratio of atoms on the surface of the particle to its volume increases till nearly all of the atoms occupy the surface positions. The surface atoms are in disordered state having large number of dangling bonds and the microstructure of a grain varies with particle size. The finite size of the particles confines the spatial distribution of the electrons leading to quantisation of energy levels and hence quantum size effect, which originate from two interrelated causes. Firstly, the effective wavelength
of excitation is comparable with the cluster size, resulting in boundary scattering effects. Secondly the characteristic size of the nanoparticles is reduced to the point where critical length scales of phenomena such as mean free paths of electrons or phonons, a coherency length, a screening length, etc. become comparable with the characteristic size of the particle. For example, if the thickness of the layers of a superlattice is comparable with the wavelength of electrons at the Fermi edge, discrete energy levels for electrons and holes are formed in the quantum wells. Such size effects modify mechanical, optical, magnetic and thermodynamic properties.

The well-established bonding such as ionic, covalent, metallic and secondary are the basis of solid structure. The bonding nature of very small particle will be different from that of bulk materials and that may be observed through spectroscopy. As the particle size increases from molecular level to bulk lattice, the bonding nature and structure of the particle changes and at a particular size level the bonding becomes just that of the bulk solid. The blue shift observed in absorption or luminescence spectra of nanocrystal ZnO is a quantum size effect. If the crystallite size becomes comparable or smaller than the de Broglie wavelength of the charge carriers generated by the absorbed light, the confinement increases the energy required for absorption. This energy increase shifts the spectra towards shorter wavelength side (blue shift). Nanoparticles have discrete excited electronic states and an increased band gap in comparison with the bulk lattice. In CdSe nanocrystals a red shift is observed in the spectrum as the particle size increases. The melting point of gold nanoparticle of size 2.5 nm is found to be 700 K where as that of bulk is 1300 K.

1.7 Nanophase Materials / Nanostructured Materials

1.7.1 Structure

Nanostructured materials or bulk nanoparticle materials are formed by the assembling of a large number of nanoparticles and can be categorised in
terms of modulation dimensionality.\textsuperscript{2,4,5} Depending on the atomic arrangement in the material it can be divided into crystals and amorphous solids (glasses).\textsuperscript{26} In glasses, atomic structure or chemical composition varies in space continuously throughout the solid on an atomic scale. But materials assembled with a nanometer sized microstructure (nanocrystal or nanoparticle) are microstructurally heterogeneous consisting of the building blocks called grains and the regions between adjacent building blocks (grain boundaries).\textsuperscript{2,9} It is this inherently heterogeneous structure on a nanometer scale that is crucial for many of their properties and distinguishes them from glasses and conventional polycrystalline materials. In ordinary polycrystalline materials, grain boundaries occupy a small percentage (less than 1\%) of the volume of the grain, whereas nanostructured materials can occupy as much as 50\%. Thus nanostructured materials consist of grains (bulk region) and large number of grain boundaries or interfaces. Other structural features such as pores, grain-boundary junction and other crystal lattice defects play significant roles in their properties along with the microstructure and size of the grain or particle.\textsuperscript{2} In a nanostructured material, as the crystal size is of the order a few nanometres, the average density and co-ordination between nearest neighbours is changed. Hence the properties of these materials will be different from those of a single crystal.\textsuperscript{23,89}

1.7.2 Grains, Pores and Grain Boundaries

Grain structure of nanophase materials has resulted from direct observation using TEM. The studies revealed that the grains of nanostructured materials are essentially equiaxed, similar to the atom clusters from which they are formed.\textsuperscript{4} A change in shape of the particles may have occurred due to consolidation. Otherwise the density would be less than 78\%, the theoretical limit for close packing of identical spheres. The observed density was greater than 78\% indicating a deformation of the clusters during consolidation process. Extrusion like deformation of the clusters may be filling the pores among the
grains. Electron and X-ray scattering experiments show that the grains in the nanophase compact are randomly oriented with respect to one another. Studies on nanophase materials also show that porosity in metals and ceramics of comparable sizes to the grains may be interconnected and intersect with the material surface. Consolidation at higher temperature can remove the porosity without grain growth. The atomic structures of nanophase materials are randomly oriented in grain boundaries whereas it is orderly oriented in the boundaries of coarser grained polycrystalline materials. The random orientation may be associated with the structure of individual boundaries or the structural co-ordination among boundaries. Further HRTEM images revealed that nanophase grain-boundaries may be possessing low energy, exhibiting flat facets interspersed with steps. If sufficient local atomic motion occurred during consolidation process, then only such structures would have appeared allowing the system to reach a local energy minimum. Two conclusions can be derived from this observations:

1. There is considerable diffusion of atoms constituting the grain boundary volumes in nanophase materials during consolidation of clusters to accommodate themselves into relatively low energy configurations.

2. Though there is large amount of energy stored in the grain boundary region, the local driving force for grain growth is small.

1.7.3 Properties

Small sized nanoparticles coupled with their surface cleanliness can react with one another rather aggressively, even at low temperatures. For example, nanophase TiO$_2$ exhibits significant improvement in sinterability (400-600°C) which results in improved mechanical properties relative to coarser grained materials. The melting point of nanophase materials is considerably lowered compared to its bulk substances. For example, the melting point of bulk CdS is 1680K whereas that of 1.2nm radius CdS
crystallite is 600K.\textsuperscript{1} The factors which determine the melting point are latent heat of fusion, surface tension and density of the particles. The reduced coordination number of the surface atoms greatly increases the surface energy so that atom diffusion occurs at relatively low temperature.

The surface of a nanocrystal experiences a relaxation and the bulk of the nanocrystal may expand in lattice dimensions.\textsuperscript{21,94} Lattice contraction is observed in nanosized Si, Sn, Pt and Bi particles whereas lattice expansion is observed in BaTiO\textsubscript{3} and CeO\textsubscript{2} nanomaterial by photoelectron spectroscopy and simulation methods.\textsuperscript{21} The mechanical properties such as creep and super plasticity and the physical properties depend on the atomic diffusion and is found to be very rapid in nanophase materials.\textsuperscript{4} It is found that atomic transport is faster in consolidated metals like Cu and Pd and ceramics like TiO\textsubscript{2} exhibiting surface diffusion like behaviour compared to coarser grained materials. The surface diffusion has the possibility of doping nanophase materials at relatively low temperatures along their grain boundary networks and interconnected porosity via the rapid diffusion available. This property can be used to synthesise materials with tailored chemical, mechanical or physical properties.

In nanophase materials, due to large number of surface atoms with dangling bonds on the nanoparticle surface, it can be seen that they are far more reactive than any other samples of coarser grained materials and act as a very good catalyst. It is found that nanophase Cu and Pd, assembled from clusters are having hardness and yield-strength values upto 500\% greater than that of conventionally produced metals indicating improved mechanical properties.\textsuperscript{4} The increased strength is due to the difficulty of moving dislocation in the spatially confined grains of nanophase materials. But in the case of ceramics, due to significant porosity and ultrafine grain sizes, the mechanical property behaviour is different from metallic property.\textsuperscript{95,96} Coarser grained ceramics are brittle while nanophase ceramics are found to be ductile due to the grain
boundary sliding and diffusion process in nanomaterials. Similar behaviour can be observed in the microhardness of nanoparticles of metals and ceramics.

In semiconductor nanocrystals or quantum dots, the spatial distribution of excited electron hole pairs are confined within a small volume resulting in the enhanced non-linear optical properties. The quantum confinement of carriers converts the density of states to a set of discrete quantum levels, which is the fundamental for semiconductor lasers. When the size of a semiconductor nanocrystal is very small, its electronic properties are significantly affected by the transport of a single electron, giving the possibility of producing single electron devices. Nanostructured porous Si has been found to give visible photoluminescence which can be correlated with its electronic properties, possibly leading to a new approach for opto-electronic device. The discovery of fullerenes ($C_{60}$) and carbon nanotubes comprised of cylindrical concentric graphite sheets are very useful for nanochemical reactions and unique electronic properties. The unique tube like structure is likely to produce extraordinary mechanical strength and high elastic limit and is ideal for probe tips in STM and AFM.

The magnetic properties of nanophase materials differ from the bulk mainly in two points. The large surface to volume ratio results in a different local environment for the surface atoms in their magnetic coupling with neighbouring atoms, leading to the mixed volume and surface magnetic characteristics. Ferromagnetic materials are 'multiple magnetic domains' materials whereas small particles of this material consist of only single magnetic domain and superparamagnetism exists. Magnetic nanocrystals have applications in information storage, colour imaging, magnetic refrigeration and ferrofluids. Metallic heterostructured multilayers comprised of alternating ferromagnetic and non-magnetic layers such as Fe-Cr and Co-Cr have been found to exhibit giant magneto resistance (GMR), a significant change in the
electrical resistance experienced by current flowing parallel to the layers when an external field is applied.

1.8 Applications

1.8.1 Technological

In recent years, there has been increased interest in nanostructured or nanophase materials due to its technological as well as industrial applications. Most of these materials are studied using spectroscopic, photochemical, photocatalytic and optical properties. Many properties of the material were studied based on the intrinsic surface reactivities coupled with high surface-to-volume ratio of atoms. The unfilled bonding or dangling bonds of a nanoparticle paves the way for adsorption for the incoming species of molecules. The possible application of adsorption is in air purification cartridges for buildings, military vehicles, air planes and other enclosed areas. Nanoparticles of Zn, Fe and Sn have high reactivities for chlorocarbons in an aqueous environment. Using this property it can be used for water purification.

Based on the unique surface structure, electronic states and largely exposed surface area, nanomaterials are largely used for catalytic applications. Also the high reactivity of surface atoms makes the material an effective tool for creating entirely new materials with improved electronic, magnetic and optical properties. Carbon fullerenes and nanotubes can serve as cells/sites for nanochemical reaction due to large surface area.

Semiconductor nanoparticles hold the potential for making more efficient solar cells. Another dream of scientists in this field concerns the use of quantum confined semiconductor systems for optical transitions, spatial light modulations, and other devices depending on non-linear optical properties. The semiconductor materials composed of layers of different phases/compositions are
particularly interesting if the layer thickness is less than the mean free path of the electrons, providing an ideal system for quantum well structure. This material is best for fabricating electronic and photonic nanodevices. Nanotube has been hailed as a strong, semiconducting ingredient that will make materials stronger and help miniaturise electronic system. Their ability to act as filters may one day be exploited to build artificial livers. It has been made possible to make nanotubes generate electricity by running water past a conducting nanotube. In the molecules of a polar liquid like water, some atoms are slightly positively charged while others carry a balancing negative charge. When the positive part of the liquid’s molecules are close to the surface of a single walled nanotube, they attract electrons, which are carried along with the liquid as it flows past. Because electrons can only flow lengthwise along the tubes, the flow of polar molecules will produce a small, but potentially useful current.

Nanotech organic films will be the data storage medium of the near future using micro electro-mechanical systems to read and write on that medium. Information will be stored in clusters of molecules within the inexpensive films. By current conventional technology, a CD can hold 500 megabits of data per square inch whereas by this method 32.6 Gigabits of data can be stored. Nanocomposite research is an important area in nanoscience. The combination of inorganic and organic in a composite can lead to the improvement in the material property and also to the creation of new properties that do not exist for either material individually. In the field of X-ray photoconductive materials, the nanocomposite approach combines the properties of both organic and inorganic. Nanocomposite ceramics may find use in several engineering applications such as high efficiency gas turbines, aerospace and automotive components.

It has been proved that nanoparticles of ceramic materials can be compressed at relatively low temperatures into solids that possess better flexibility and malleability. After further development the use of ceramics as
a replacement for metals may be possible. It has been noted that aerogel-prepared materials generally have very low densities, can be translucent or transparent and have low thermal conductivity and unusual acoustic properties. They have found various applications including detectors for radiation, superinsulators, solar concentrators, coatings, glass precursors, catalysts, insecticides and destructive adsorbents. Recently it has been reported that the world’s strongest, lightest material called aerogel is developed, which is a high-tech amalgam of highly porous glass (silica) and plastic (polyurethane) as light as air. These new materials show promise as shielding for armoured vehicles, lightweight body armour for soldiers and strongest building material, safer aircraft and space vehicle.

The large surface area of porous material is ideal for catalysis. The synthesis of mesoporous material is useful for environmental cleaning and energy storage. Ordered self assembly of hollow structures of silica, carbon, and titania has drawn much attention recently because of their applications in low-loss dielectrics, catalysis, filtering and photonics. Magnetic nanoparticles are very useful in information storage, colour imaging, bioprocessing, magnetic refrigeration and ferrofluids.

1.8.2 Commercial

Although much of the work being done in nanoscience is development of the material, there are indeed nanostructured products currently available in the market. They key factor for industrial use of nanostructured material is the large-scale production of the material with less cost. Certain materials like nanostructured silica and iron oxide have been produced commercially for more than half a century. In early 1940s silica nanoparticles were manufactured and sold in US and Germany. From that time onwards, nanosized amorphous silica particles have been in great use in many everyday consumer items. During that time magnetic fluids containing suspended iron oxide nanoparticles were in use, which were produced by the technology developed at NASA. More than this,
Nanosized particles were incorporated in commercially available polishing slurries, fire retardant materials, sunscreens, magnetic recording tapes, etc. Nanocrystalline alumina, titania, antimony oxide, non-oxide ceramics and other materials have entered the market recently. Besides powders of these ceramic nanoparticles, metallic nanoparticles are extensively manufactured in Japan by Vacuum Metallurgical Co. Ltd. for use in magnetic recording tapes.

In order to commercialise nanomaterials, large quantity production of the material with less cost must be developed with suitable preparation techniques. The main barrier to commercialisation of nanoparticles is that nanoparticle research is being done in laboratories at a small scale.

The magazine “Time” reported the recent industrial applications of nanotechnology and the advanced developments in this field. Most nanotech companies are investing more in research and development with the prediction that 21st century is for nanotechnology. The National Science Foundation in the US foresees a $1 trillion market by 2015 for nanoproducts, and businessmen and governments around the world are rushing to get a partnership. Similarly government in Asia and Europe are investing $2 million in nanotechnology research and development. According to Mark Modzelewski, executive director of Nanobusiness Alliance, NY City, “Nanotech is a three legged race right now”. The technology will evolve- “radically” he says as its benefits seep into virtually every crevice of human industry, from toys to tanks. The book “The investor’s Guide to Nanotechnology and micromachines” authored by Glenn Fishbine is an indication of the flourishing trend of nanotechnology in industrial sector. Companies like Intel, Samsung, Dupont etc. are funding nanotech development for years.

Nowadays nanotechnology finds widespread use in consumer goods, computers, pharmaceuticals, and energy efficient car industries. The company in New Jersey, ‘In Mat’ is making environmentally safe liquid containing, 1nm-thick sheets of clay. When the material coats the inside of a tennis ball, it traps
air far more effectively than standard rubber alone and doubles the life of the ball. This ball is available in US tennis shops and last year this was the official ball of Davis Cup competition. The same company is producing a tyre-sealant made of nanoparticles, by which the tyres can run cooler and safer, are lighter and increase a car's fuel efficiency. A Nano-Tex company owned by Burlington industries in North Carolina, US is producing wrinkle free and stain resistant cotton fabrics by adding 'nano whiskers' to ordinary cotton by a chemical process. The companies Eddie Bauer and Lee produces khaki jeans made of this material, which are wrinkle free and stain resistant. This company is also developing fabrics that disperse and dry sweat.

Another company Nantero expects to produce a commercial prototype for a chip with non-volatile random access memory (NRAM) with which an “instant-on” computer, which does not need boot up time, can be built. By this we can save 5 minutes, which is the booting time for ordinary computers. The NRAM technology uses arrays of 2nm strands of carbon atoms, called carbon nanotubes, which convey electrons faster than copper and 100 times strong as steel. Pairs of tubes store data by locking together when a current runs through them and stay together even when the computer power is switched off and back on. They can also store data 10 times as much in a silicon chip of the same size. Nanotubes could be the first commodity in the nanotech economy. Dozens of companies like IBM, Hewlett Packard, Samsung, NEC, etc. are buying large amount of nanotubes called 'soot' for research. The company Nano-Lab, in Massachusetts USA sold nanotubes worth $2 lakh in 2001. HP researchers unveiled a way of manufacturing molecular scale circuitry that will be cheaper and use less power than current silicon chips and have the potential to store entire libraries of information.

Another application of nanoparticles is in pharmaceuticals. A biotech company “C-Sixty” is building fullerenes into molecules that will attach to and deactivate HIV molecules, blow up cancer cells and repair neurological damage
in a nerve illness called Lou Gehrig’s disease. C₆₀ (fullerene) is a universal molecule with its peculiar structure and shape can be weaponised to attack any enzyme or receptor that plays a role in a disease’s development. Another scientist Dr. James Baker, head of the University of Michigan’s Centre for Biologic Nanotechnology, is developing nanoscale molecules called dendrimers to fight against cancer cells. The company called Nano Bio developed a liquid namely ‘Nano Defend’ designed to decontaminate clothing and surfaces that have come into contact with anthrax or small pox. With the help of nanoparticles common drugs can work more efficiently. For example, Naproxen Sodium is a painkiller that takes 2 hours to exert its pain relieving effect. But the same material made up of nanocrystals is found to be 8 times faster than commercial product, taking only 15 minutes to release its effect.

Another application of nanoparticles is in car industry. The car manufacturing companies like Toyota and General Motors are using strong, lightweight material made up of nanocomposites. Improvement in strength and reduction in weight will lead to fuel saving. It is found that nanoparticles like platinum make fuel cells more efficient.

Recently nanoparticle TiO₂ coating on glasses have exhibited interesting antifogging and self-cleaning properties. CdS nanocrystals can be used as precursors for the processing of buffer/window layers for thin film solar cells. Nanoparticles are found to be more efficient in cosmetic industry. All modern audio and videotapes depend on the magnetic properties of fine particles. The phenomenon of giant magneto resistance (GMR) is now shown to be present even in equiaxetl nanocrystalline materials. The change in resistance is about 10 to 50 times larger, than the change in conventional magnetoresistive materials, when the magnetic field is applied. The materials exhibiting large GMR can be an important candidate for the reading heads of the next generation information storage systems.
Nanoparticles of spherical shape are important for applications in chemical catalysis. For smaller metal particles the number of surface atoms is more in number and more reactive compared to bulk atoms and therefore they can easily form alloys. For example, nanocrystalline alloys of nickel- molybdenum act as advanced electrode materials for high efficiency alkaline fuel cells.

21st century is expected to be the century of nanotechnology and we can expect that more efficient and long lasting materials made of nanoparticles will come into our daily use.

1.9 Present Work

The present work consists of the synthesis of nanoparticles of Ag₃PO₄, FePO₄ and ZnFe₂O₄ for three reactant concentrations each. Silver phosphate is a material used in pharmaceuticals, photographic emulsions, electrodes in voltammetry, and as a catalyst. FePO₄ is a ceramic material as well as a biomaterial. It is ferroelectric and an antiferromagnetic material. ZnFe₂O₄ is a spinel ferrite as well as a ceramic magnetic material, which is of great interest because of its large technological applications. It also provides the opportunity to study the effect of grain size on structural, morphological and magnetic properties of nanoparticles and to understand theoretically the interactions at nanoscale. The effect of reactant concentration on particle size and hence the vibrational, electrical and magnetic properties of these materials were studied. The size and structure of the particles were studied using TEM and XRD. Morphology was studied using SEM. Vibrational properties were studied using FTIR. Thermal analysis (TG/DTA) was carried out to study the thermal stability of these materials. Impedance spectroscopy was used to analyse the grain and grain boundary contribution to the impedance of the nanoparticles. The dielectric properties of these materials were analysed in detail. Magnetic moment and molar susceptibility were calculated using VSM at room temperature. Temperature variation of magnetic susceptibility was measured using SQUID magnetometer. ESR measurements too were carried out to know the magnetic property of FePO₄.
1.10 References


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