Chapter 1

General Introduction
1.1 Introduction

Man has always been in search of materials for specific applications to fulfil his need and greed. The use of materials such as stone, wood, cloth, metals, alloys, loadstone, ceramics, glass, coal, petroleum fuels, plastics, semiconductors, radioactive materials, etc., have been turning-points in the history of mankind. Though the search for new materials with better properties had well begun in the stone ages itself, the systematic study of synthesis, processing and characterization of materials – materials science – emerged as a distinct branch of science with technological and commercial importance only during the twentieth century.¹

Over the last two decades, a variety of new and somewhat exotic technical terms having the prefix “nano” – nanostructured, nanoscale, nanophase, nanocrystalline, nano-lithography, nanoelectronics, etc., – had entered the vocabulary of the materials scientists and the advanced materials industry. Correspondingly, the last two decades have witnessed a tremendous increase in the interest of the academics and the industry in materials that are aptly described by this new terminology – nanostructured materials.²⁻²¹ Nanostructured materials are also referred to as nanocry stalline materials, nanophase materials and nanomaterials. This new class of materials shows properties vastly superior to those exhibited by single crystalline, conventional polycrystalline and amorphous materials and is of great theoretical and technological importance. The synthesis, characterization and
processing of nanostructured materials have become an emerging and rapidly growing field of materials research.

1.2 Nanostructured Materials

Nanostructured materials are single-phase or multi-phase polycrystals, the crystal size of which is of the order of a few nanometers (typically 1 to 100 nm) in at least one dimension. These materials may contain crystalline, quasicrystalline or amorphous phases and can be metals, ceramics, semiconductors or composites. Nanostructured materials are broadly classified into four categories – zero dimensional, one dimensional, two dimensional and three dimensional – according to the number of dimensions in which the crystallite sizes are confined to or spatially modulated in the nanometer range. A schematic representation of the four categories is shown in Figure 1.1.

![Figure 1.1](image)

Figure 1.1. Schematic representation of the four categories of nanostructured materials, classified according to integral modulation dimensionality (a) zero dimensional, (b) one dimensional, (c) two dimensional and (d) three dimensional.
Zero dimensional nanostructures are nanometer-sized particles (isolated, substrate-supported or embedded) with sizes limited to a few nanometers in all the three dimensions. Multilayers with thickness and breadth limited to a few nanometers and thin wires having diameters in the nanometer range constitute one dimensional nanostructures. Two dimensional nanostructured materials are either thin films with thickness of the order of a few nanometers or ultra-fine grained overlayers, coatings or buried layers. Bulk solids with a nanometer scale microstructure extending in all the three dimensions constitute the fourth category - three dimensional nanostructured materials. All these materials have a significant percentage of their atoms associated with interfaces such as grain boundaries, interphase boundaries or surfaces. The properties of these materials are affected significantly by their structural or compositional modulation, spatial confinement, interfaces or a combination of these parameters.

Nanostructured samples of several metals, alloys, semiconductors, ceramics and composites have been synthesized and their physical and chemical properties have been investigated in detail. Theoretical investigations and experimental results show that almost all the properties of materials are drastically changed when the average grain size is of the order of a few nanometers. More importantly, in the nanosize regime, the physical and chemical properties of materials strongly depend on the average grain size. The properties of nanostructured materials are so much different from those of their bulk counterparts that some scientists are even inclined to classify them as a new (fifth) aggregate state of matter: solid phase, nanophase, liquid phase, gas phase and plasma phase. It is the wide range of exquisite physical and chemical properties, which can be controlled effectively by varying the size, structure, or composition that make nanostructured materials a topic of great interest for the scientists, technologists and the advanced materials industry. For the more academically inclined solid state and theoretical physicists, the nanosize regime provides an arena for probing important theoretical problems such as the evolution of the electronic band structure and hence electrical, optical, thermal, etc., properties when bulk solids are formed by the aggregation of atoms, ions or molecules. Questions such as, “above what critical size a metal becomes metallic or a semiconductor becomes semiconducting” is of
common interest to both theoreticians and technologists. Thus the world of nanostructures offers interesting challenges to the academic community besides providing an opportunity for the technologists to synthesize new materials possessing unusual properties which may be exploited for important commercial applications.

1.3 History of Nanostructured Materials - From Big Bang to Bucky Balls

Nanostructured materials apparently had its genesis with the Big Bang, even though the controlled and deliberate nanostructuring of materials by man began only in the twentieth century.¹⁴ The structural evaluation of the earliest meteorites suggests that atoms first consolidated into nanoscale clusters, which then aggregated into larger masses under the action of gravity. Numerous examples of natural nanostructures can also be found in biological systems, from seashells to human body.

Michael Faraday²⁵, in the 1856 Bakerian Lecture observed that “gold wire deflated by explosions of a Leyden battery produces a divided condition, very different to that presented by gold leaves. The ruby colour of the deposit observed on the transmission could be transformed to the green colour of gold leaves by applying a compressive force”. Though Faraday never measured the average size of the finely divided particles of gold, this was perhaps the first observation that the properties of very small particles can differ from those of the bulk material and that the control of their separation and coalescence leads to profound changes in their properties.²⁶

Scientists have been dealing with nanometer-sized particles albeit in dispersed systems, ever since the founding of colloidal chemistry in the 1860s. British chemist Thomas Graham, in 1861, coined the term “colloid” as colloid chemistry was beginning to develop. Wolfgang Ostwald classified dispersed systems of particles with sizes of about 1 – 100 nm as colloids. John Tyndall, Hermann Helmholtz, Lord Rayleigh, James Clerk Maxwell and Albert Einstein were among the renowned physicists who studied the characteristics of colloids around 1900. During these early years of study of dispersed systems, the main experimental tools of observation were viscometers, potentiometers, permeable membranes and optical microscopes. In 1930s
Ame Tiselius began the study of protein and other biological colloids by developing a precise electrical migration device. In several respects, colloid chemistry may rightly be viewed as the foundation for the new field of nanostructured materials. During the 1930s, A. H. Pfund in the United States and H. C. Burger and P. H. Van Cittert in Germany pioneered the now commonly used gas condensation technique for nanoparticle synthesis. By the early 1940s, precipitated and fumed SiO$_2$ nanoparticles were being commercially manufactured and used for diverse applications such as rubber reinforcement and as nondairy coffee creamer in many developed countries.

By the second half of the twentieth century, the scientific community began to realize and appreciate the immense potential of materials in the form of very fine particles. As long ago as 1959, Richard Feynman at Caltech spoke in a prescient lecture to the American Physical Society about the creation of materials with new properties by the manipulation of matter on a small scale:

*I can hardly doubt that when we have some control of the arrangement of things on a small scale we will get an enormously greater range of possible properties that substances can have.*

These prophetic words of Feynman, appreciated and quoted by one and all working in the field of nanostructured materials, caught the imagination of an entire generation of scientists and played the role of a catalyst for the rapid growth and diversification of this new field.

A very important event in the history of theoretical formulations in the field of small particles was the introduction of the novel concept of *quantum confinement* by Ryogo Kubo at the University of Tokyo in the early 1960s. Kubo showed that the electrons in metallic ultra-fine particle are in a unique situation and do not obey Fermi statistics because the number of such electrons is small. Hence, for particles smaller than 10 nm, it is difficult either to add or remove a single electron, and such particles have a strong tendency to remain electrically neutral. The ways in which this
phenomenon affects the specific heat, magnetization and superconductivity is now called the *Kubo effect*. Also, in the 1960s, Ryozi Uyeda and his coworkers at Nagoya University in Japan used electron microscopy and electron diffraction techniques to determine the morphologies and crystal structures of nanometer-sized particles of metals and metallic compounds. They also made advances in producing relatively clean ultra-fine particles through evaporation and condensation in an inert gas atmosphere.

In 1971, the Research and Development Corporation of Japan instituted a five-year development effort focused on metallic nanopowder production for magnetic recording tapes. During the seventies, ultra-fine powders of many metals such as Cu, Ag, Al, Ni, Co and Fe were being manufactured by the Vacuum Metallurgical Co. Ltd Japan. During the same period, magnetic fluids containing suspended ultra-fine particles of iron oxide, synthesized using the technology developed at the National Aeronautics and Space Administration (NASA) entered the market in United States.

The synthesis of bulk materials by consolidation of small particles was first suggested in the early 1980s by Herbert Gleiter at the University of Saarlandes in Germany and was applied initially to metals and then to nanophase ceramics. In 1981 a second five-year project on ultra-fine particles was launched in Japan, headed by Chikara Hayashi, within a programme named Exploratory Research for Advanced Technology Programme (ERATO). The main objectives of the project was to study in detail the physical, chemical and biological properties of a wide variety of nanostructured materials and to evaluate the possibility of using these new materials in industry, medicine and scientific research. Further developments during 1980s include the advent of new methods such as high-energy mechanical milling, electrochemical deposition, amorphous crystallization, etc., for the synthesis of nanostructured materials and tremendous improvements in the field of electron microscopy. Also, intensive study of synthesis and characterization of semiconductor nanocrystals, *quantum dots*, which has great technological importance in fields such as electronics, photonics, quantum cascade lasers, etc., was initiated at many centres during the 1980s. By the end of the eighties, efforts to transfer the new technologies based on nanomaterials
from the laboratories to the industry began with the formation of companies, such as Nanophase Technologies Corp. USA, Nanodyne, Inc. USA, etc.\textsuperscript{18,20}

The 1990s and the first two years of the twenty first century have witnessed a giant leap forward in the field of nanostructured materials with the development of more precise, accurate and powerful characterization tools such as Scanning Tunneling Microscope (STM), Atomic Force Microscope (AFM), etc. The use of powerful computer simulation and modeling techniques to formulate the structure and properties of nanophase materials have contributed to the rapid advances in the understanding of the properties of materials in the nanosize regime. An important application of STM emerged with the realization that the STM tip may be used to modify the surface of a sample in a number of ways. The ability of the STM tip to draw nanometer-sized lines and dots provided a new tool for nano-lithography and virtually revolutionized miniaturization of electronic and optical devices.\textsuperscript{34-36} Also, tremendous progresses were made in the field of nanocomposites also, which promises to be an area of extreme technological and industrial importance.\textsuperscript{37} Another type of nanomaterials which are considered to be of immense technological importance is carbon nanostructures – \textit{fullerenes, carbon nanotubes and carbon onions}.\textsuperscript{38-40} In 1996, the Nobel Prize in chemistry was awarded to Harold Kroto, Robert Curl and Richard Smalley for their pioneering work on the discovery of the fullerene, C\textsubscript{60}, which is a cluster formed by sixty carbon atoms forming a closed cage structure. Fullerenes, also called \textit{Bucky Balls} together with carbon nanotubes is expected to be a key material in the fields of molecular electronics, organic superconductors and novel optical display devices, according to the preliminary studies.\textsuperscript{39,40}

During the 1990s, the scientific community addressed for the first time the importance of having a common platform for researchers working in this emerging field to interact with one another, and the first International Conference exclusively to discuss the developments in the field of nanostructured materials was held in Mexico in 1992. The Conference continues to be held once in every two years. A number of new scientific journals devoted for research in the field of nanomaterials and nanotechnology - \textit{Journal of Nanoparticle Research, Nanotechnology, Nanoletters},
Journal of Nanoscience and Nanotechnology, etc., to name a few – came into existence and reports on the theoretical and experimental fronts of nanomaterials research routinely appear in reputed journals such as Physical Review, Physical Review Letters, Journal of Applied Physics, Applied Physics Letters, etc. Now, one can hardly find a volume of any standard journal dealing with materials science or solid state physics without a few articles on this new class of materials.

1.4 Characteristic Features of Nanostructured Materials

Some of the characteristic features that distinguish nanostructured materials from their bulk counterparts and form the basis for their modified physical and chemical properties are:

- **Large surface area-to-volume ratio:** One distinct feature of materials in the nanosize regime is that a significant percentage of the atoms are associated with interfaces such as surfaces, grain boundaries or inter-phase boundaries. This is true irrespective of the actual shape of the building blocks of the microstructure since for any geometrical shape the surface area to volume ratio increases with decrease in size.

Calculations assuming different probable geometrical shapes for the nanograins show that the fraction of atoms associated with the interfacial region can be as much as 70-80% for 2-3 nm grains, ~ 50% for 5 nm grains, ~ 30% for 10 nm grains and ~ 3% for 100 nm grains. In contrast, for conventional coarse-grained polycrystalline samples with average grain sizes of the order of a few micrometers, the fraction of the atoms associated with the surface will be much less than 0.01%. Thus, even for nanostructured samples having relatively larger average particle size (~ 100 nm), the fraction of the atoms associated with the interfacial region is much larger than that for conventional coarse-grained polycrystalline samples. Hence, it is reasonable to expect that with decrease in the average particle size, the characteristics of the surface atoms become increasingly sharper and the distinct contribution of the surface atoms should be taken into account while analyzing the experimental results and attempting to explain the unusual properties of nanostructured samples.
**Size effects:** Size effects result if the size of the building blocks of the microstructure (e.g. the grain size or the layer thickness) is reduced to a value comparable to the critical length scales associated with one or more physical phenomena (e.g. the mean free paths of electrons or phonons, a coherency length, a screening length, etc.).\[^{14,21}\] Such size effects modify the optical, electrical, magnetic, mechanical, etc., properties of nanostructured materials and are of great technological importance. An example of size effect is the “blue shift” in the optical absorption and luminescence spectra of nanostructured semiconductors such as ZnS, CdS, ZnO, etc., when the grain size falls below the Bohr radii of the excitonic states which lies in the range 5 – 50 nm.\[^{14,24,41-44}\] The “blue shift” is often referred to as a “**quantum size effect**”.\[^{21}\]

Another interesting example of size effect is the strengthening of normally soft metals when their grain sizes are reduced below ~ 50 nm.\[^{14}\] The strengthening of metals on nanostructuring occurs because when the grain sizes are reduced to a few nanometers, the sources of dislocations which are responsible for easy deformation becomes difficult to activate under conventional applied stresses.

**Change of dimensionality:** In the case of nanostructured samples in the form of thin needle-shaped or flat two dimensional crystallites, only two or one dimension of the building blocks become comparable with the length scale of one or more physical phenomena. In these cases, the nanostructured materials become a two dimensional or one dimensional system with respect to these phenomena.\[^{21}\]

**Unique microstructure:** Nanostructured materials have a unique microstructure, which may be distinguished from those of single crystals, coarse-grained polycrystals, glasses and gels having the same average chemical composition.\[^{6,7,15,18,21}\] As far as the atomic arrangement is concerned, all existing solids may be classified into crystals and glasses, which differ by the presence or absence of long-range order, whereas short-range order is similar. Two dimensional hard sphere models of a perfect crystal (hexagonal array of atoms) and a glassy structure are shown in Figures 1.2 (a) and (b) respectively. In most materials with
glassy structure, the density and the nearest neighbour configuration varies typically by a few percent relative to the perfect crystal and the atomic arrangement and/or chemical composition varies in space continuously throughout the solid on an atomic scale. In contrast, the microstructure of nanostructured materials is characterized by the absence of even "short-range" order and is often referred to as "gas-like".

Figure 1.2. Schematic cross-section through hard sphere model of (a) perfect crystal and (b) glassy structure

Figure 1.3. Schematic cross-section through hard sphere model of a nanostructured material.
A schematic cross-section through a hard sphere model of a nanostructured material is shown in Figure 1.3. All atoms are assumed to be chemically identical in this representation. In Figure 1.3, as far as the atomic structure is concerned, two kinds of atoms may be distinguished: “crystal atoms” the nearest neighbour configurations of which correspond to the lattice configuration; and “boundary atoms” characterized by the nearest neighbour configurations that are different from the lattice configurations. Hence in terms of the nearest neighbour configurations, a nanostructured material consists of a crystalline component formed by all the “crystal atoms” and a boundary component formed by all the “boundary atoms”. The atomic arrangements at the interiors of all the nanograins (dark circles in Figure 1.3) constituting the nanostructured material are identical. However, the atomic arrangements at various interfaces differ from one another since the crystal misorientations and the boundary inclinations are different for different boundaries. The boundary regions (open circles in Figure 1.3) are characterized by a reduced atomic density and interatomic spacings deviating from the ones in a perfect lattice. As nanostructured materials contain very large number of interfaces, typically \( \sim 10^{19} \) boundaries / cm\(^3\), the interfacial component is the sum over all these \( \sim 10^{19} \) atomic arrangements, all of which may be different. If the interatomic spacings in all of these interfaces are uncorrelated in the sense that certain interatomic spacings do not occur preferentially, the interfacial component is expected to exhibit no short-range order. This does not imply that the grain boundaries are completely disordered. In fact every boundary is assumed to have a two dimensionally ordered structure, the periodicity and interatomic spacings of which are different from boundary to boundary. Thus in the interfacial regions of nanostructured materials, the atoms can only relax into structures compatible with the adjacent crystal lattices unlike in glasses where no constraints of this type exist. In this respect, nanostructured materials are often referred to have a “gas-like” microstructure, lacking even “short-range” order.

Compared to the bulk crystalline density, the atomic density in the core regions of the grain boundaries of nanostructured materials is reduced typically by about 15 to 30%, which is almost an order of magnitude more than the density difference between the glassy and crystalline states in most materials. The atomic density in the
boundaries of a typical nanocrystalline material is probably lower than that in coarse-grained polycrystals due to the limited rigid body translations in nanocrystalline materials. The boundaries of different atomic arrangements formed on opposite sides of a nanometer-sized crystallite in a nanostructured material require different rigid body translations to maximize the atomic density in both interfaces. When the crystallite size is a few nanometers, the different rigid body translations would require unrealistic elastic distortions of the small crystal, which is unlike in conventional coarse-grained polycrystals. The unique atomic arrangement in the interfacial region of nanostructured materials plays a prominent role in determining their unusual physical properties.

1.5 Synthesis of Nanostructured Materials

Over the last two decades, several methods have been developed for the synthesis of nanostructured materials. The field is so rapidly evolving that novel methods and improvements of existing ones are reported time and again. The most commonly employed techniques for synthesizing nanostructured materials include inert gas condensation, sputtering, laser ablation, physical and chemical vapour deposition techniques (PVD & CVD), high energy milling, spray conversion processing, plasma processing, sol-gel process, controlled chemical precipitation, micro emulsion technique, electrodeposition, etc. The grain size, morphology and texture can be varied by suitably modifying the process variables in each of these methods and each technique has its own advantages, specificities and limitations. A brief description of some of the important techniques for the synthesis of nanostructured materials is presented in this section.

The inert gas condensation technique and its various modified forms have been employed with great success and reproducibility for synthesizing nanostructured samples of a large number of metals such as Al, Ag, Au, Ti, Mo, W, and Cu, and metal oxides such as TiO₂, NiO, ZrO₂, MgO, Al₂O₃, and Er₂O₃. Inert gas condensation technique involves the evaporation of the metal or mixture of metals inside an ultra-high vacuum (UHV) chamber filled with an inert gas such as Ar or He.
Evaporation may be brought about by heating, sputtering, laser ablation, etc. As a result of the inter atomic collisions with the inert gas atoms in the chamber, the evaporated metal atoms lose their kinetic energy and condense to form small crystallites of nanometer dimensions which accumulate in the form of a loose powder on a cold finger. The powder is scrapped off the cold finger and compacted to obtain three dimensional nanostructured samples under ultra-high vacuum so that the cleanliness of the particle surfaces and subsequent interfaces are maintained and the possibility of any gas adsorption at the interfaces is minimized.

Sputtering of solid surfaces using suitable ions (e.g. Ar ions or Kr ions) under vacuum conditions are employed for the synthesis of nanometer-sized clusters. One obvious drawback of sputtering process is that it usually produces small amounts of clusters with a broader size distribution. Laser ablation technique is more or less similar to sputtering except that a high power pulsed laser, usually in the ultraviolet region, is used to vaporize the cluster ions from solid surfaces. Sputtering and laser ablation techniques are not suitable for large-scale production of nanostructured samples and are most often used for cluster ion production inside or in the proximity of a mass spectrometer.

Another technique commonly used for the synthesis of nanostructured oxides and nanocomposites is the spray conversion process. In this technique, aqueous solutions of metal salts such as chlorides or nitrides are aerosolized and rapidly spray dried to produce extremely fine particles. Starting with mixtures of aqueous solutions of salts of different metals, one can obtain nanocomposites such as WC-Co. The particle size, morphology and stoichiometry can be controlled by adjusting the processing parameters such as the concentration of the salt solution, drying temperature or by the use of suitable additives. Plasma processing technique, which involves the vaporization of micrometer sized particles in an Ar plasma for a very short time interval, ~ 0.01 to 0.001 seconds, has been used for producing nanostructured samples of metals such as Al, Mo, W, Zr, and Ag as well as oxides such as Al₂O₃.
High-energy ball milling has been reported to be a relatively simple and cost effective method for the synthesis of nanostructured materials.\textsuperscript{57-61} It has been reported that by this method, the grain size of pure bcc metals (Cr, Nb, W, etc.), metals with hcp structure (Zr, Hf, Co, Ru, etc.), inter-metallic compounds (CuEr, NiTi, AlRu, SiRu, etc.) and alloys (Fe-Ta-W, Ti-NiC, Al-Fe, Ag-Fe, Fe-Al, etc.) can be reduced to nanometer sizes. However, ball milling techniques are found to be unsuitable for metals with fcc structure which are too soft for effective energy storage and sinter to larger particles during milling.\textsuperscript{6} Another serious limitation of the method is the possible contamination of the sample during milling.

Sol-gel process is one of the most effective and widely employed methods for the generation of nanostructured ceramics.\textsuperscript{62-68} In sol-gel process, the starting material is either a metal alkoxide or colloidal dispersions of hydrous oxides. The starting material is processed to produce a dispersed oxide, which forms a sol in water or dilute acid. Removal of the liquid from the sol yields the gel, which on calcination produces the oxide. By controlling the sol-gel transition, the particle size of the sample can be reduced to nanometer ranges. A significant advantage of the sol-gel technique is the low processing temperature. Also, this method provides excellent control over the grain size, shape and stoichiometry and has been employed for the synthesis of nanostructured samples of TiO\textsubscript{2}, NiO, Fe\textsubscript{2}O\textsubscript{3}, SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, BaPbTiO\textsubscript{3}, etc.

Controlled chemical precipitation is one of the simple, convenient and commonly employed techniques for nanostructuring. Nanostructured samples of a wide range of oxides, carbonates, sulfides, selenides, halides, etc., have been synthesized through the controlled precipitation route.\textsuperscript{69-79} In this method, nanostructuring is effected by increasing the nucleation rate and inhibiting the grain growth during precipitation by adjusting the processing parameters such as concentration of the reactants, temperature, etc., and/or by using suitable stabilizers (capping agents). Excellent control over the particle size, high degree of reproducibility and cost effectiveness are some of the noteworthy features of the precipitation technique. Microemulsion technique may be regarded as a variant of the controlled precipitation technique in which better size control is achieved through the
use of microscopically structured liquid mixtures—microemulsions—such as water-soap-heptane, in which the aqueous cores can be used as nanometer-sized reactors for the precipitation of nanoparticles.  

Though all the aforementioned techniques and their various modified forms have been used with different levels of success to produce nanostructured samples of a variety of materials, the inert gas condensation, high energy milling, chemical precipitation and spray conversion processing techniques are the ones most commonly used to synthesize three dimensional equiaxed nanocrystallites, while vapour deposition, sputtering and electrodeposition techniques are used widely to synthesize layered nanostructures. The sol-gel process can be used to generate clusters as well as nanostructured thin films.

1.6 Characterization of Nanostructured Materials

Nanostructured samples should be characterized on both atomic and nanometer scales for a complete understanding of the structure-property correlations. Structural features of importance include, the grain size, size distribution, morphology, state of agglomeration, the nature and morphology of grain boundaries and inter-phases in interfaces, perfection of intra-grain atomic arrangements, nature and density of defects, composition profile across grains and interfaces, trapped species during processing, porosity in the case of three dimensional nanostructures, etc. Understanding of the electronic structure and thermal, mechanical, electrical, magnetic, optical, etc., properties of nanostructured materials is necessary for the successful exploitation of this new class of materials for technological applications as well as to evaluate, confirm, reject, complement and modify the existing theories or to formulate new ones. Almost all the known experimental techniques for materials characterization are found useful for the characterization of nanostructured materials. A brief description of some of the most commonly employed techniques for the characterization of nanostructured materials is presented in this section.
Direct observation using microscopic techniques such as Transmission Electron Microscopy (TEM), High Resolution Transmission Electron Microscopy (HRTEM), Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), Field Ion Microscopy (FIM) and Scanning Tunneling Microscopy (STM) have been widely used for determining the grain size/layer thickness, size distribution and morphology of nanostructured samples. Less direct techniques such as X-ray diffraction (XRD) and Small Angle X-ray scattering (SAX) are also widely employed for this purpose. The atomic arrangements in different kinds of nano materials can be studied using High Resolution Transmission Electron Microscopy (HRTEM), Scanning Tunneling Microscopy (STM), X-ray diffraction (XRD), Extended X-ray Absorption Fine Structure (EXAFS) studies, Mössbauer spectroscopy, Positron Annihilation Spectroscopy (PAS), Small Angle Neutron Scattering (SANS), and hydrogen absorption studies. Microchemical analysis of nanosized samples requires much advanced state-of-the-art instrumental capabilities such as the atom-probe FIM or STM to obtain the desired lateral scale resolution. Porosity in three dimensional nanostructured samples may be estimated using Positron Annihilation Spectroscopy (PAS), precise densitometry, porosimetry measurements like BET (Brunauer-Emmett-Teller) Nitrogen absorption technique and Small Angle Neutron Scattering (SANS).

Electron spectroscopic techniques such as Ultraviolet Photoemission Spectroscopy (UPS) and X-ray Photoelectron Spectroscopy (XPS), and optical techniques such as uv-visible absorption and luminescence measurements can be used for gathering information on the electronic energy states of nanostructured samples. Vibrational spectra of nanostructured materials are known to be markedly varied from those of their bulk counterparts due to the breakdown of the vibrational selection rule ‘$k \neq 0$ forbidden’ in the nanosize regime, and also due to the significant contribution of the surface region resulting from the large surface area to volume ratio. Hence both Raman and infrared (IR) spectroscopy studies are routinely employed for the characterization of nanophase samples.
Due to the large surface area to volume ratio and the unique microstructure, nanostructured samples may often be in a metastable state.\textsuperscript{18} Thermal analysis techniques such as Differential Scanning Calorimetry (DSC) and Differential Thermal Analysis (DTA) can be effectively used for studying the thermal stability, phase transitions, grain growth and densification of nanostructured samples.\textsuperscript{18,105-107} The specific heat and entropy measurements at liquid He temperature is important in understanding the collective behaviour of electrons in nanometer-sized systems.\textsuperscript{5,108}

Study of mechanical properties of nanocrystalline metals, alloys and ceramics are of great technological and commercial importance. Microhardness and hardness measurements, and ultrasonic techniques are some of the commonly employed methods for investigating the mechanical properties.\textsuperscript{6} Both ac and dc electrical properties of consolidated nanostructured samples, thin films and layered structures are of great technological and academic interest. Study of electrical properties of nanophase samples using electrometers and impedance bridges could furnish information as diverse as the effect of finite size on the charge carriers, structural uniformity of the sample, nature of interfaces, nature and concentration of defects, etc.\textsuperscript{78,79,109,110}

Magnetic properties of nanometr-sized samples are exciting from both theoretical and application points of view since the domain size of magnetically ordered materials falls in the nanometer range.\textsuperscript{111-113} Magnetic characterization of nanostructured samples is often done using static magnetization studies using either Vibrating Sample Magnetometer (VSM) or Superconducting Quantum Interference Device (SQUID) magnetometer.\textsuperscript{114-117} AC susceptibility measurements\textsuperscript{118}, Mössbauer spectroscopy\textsuperscript{115} and neutron diffraction studies\textsuperscript{119} are also employed for the characterization of nanostructured samples of magnetic materials.

Computer simulation and modeling techniques are routinely employed for the interpretation of the experimental observations on nanostructured materials and to achieve a better understanding of the structure-property correlations in this new class of materials.\textsuperscript{120,121} Rapid advances and diversification of the field of nanomaterials
demand the advent of more precise and sophisticated novel techniques for investigations in the nanosize regime.

1.7 Properties and Potential Applications of Nanostructured Materials

During the past several years exciting progress has been made by scientific community in synthesizing, processing and characterizing nanostructured samples of a host of materials. Though theoretical formulations for interpreting many of the experimental observations on nanometer-sized samples are still only evolving, many important technological applications based on this new class of materials are on the verge of realization or have already been realized. Since the physical properties of materials are drastically varied on nanostructuring, the potential fields of application of this new class of materials are as diverse as novel structural materials, magnetic recording and imaging technology, sensors, lasers and molecular electronics. A brief description of some of the exquisite properties of nanophase materials that find applications in different fields of modern technology is presented in this section.

Nanostructuring has been reported to improve drastically the mechanical properties of metals, intermetallic compounds and ceramics.\textsuperscript{6,14,18} For instance, nanophase samples of metals such as Cu, Pd, Ni, Fe, Ti, Ag, etc., and intermetallic compounds such as Nb\textsubscript{3}Sn, Ni\textsubscript{3}Al, TiAl, Ti\textsubscript{3}Al, Al\textsubscript{3}Nb, Ni-P, Fe-B-Si, Fe-Mo-Si-B, etc., have hardness and yield strength values 4 to 5 times larger than those of the conventional coarse-grained samples with the same average chemical composition.\textsuperscript{18,122-127} The increased strength arises from the increased difficulty of creating and moving dislocations in spatially confined grains of nanophase samples. Also, it has been observed that generally brittle ceramics become ductile, permitting large plastic deformations at low temperatures, if the ceramic materials are generated in the nanocrystalline form.\textsuperscript{6,14,128} The ductility exhibited by nanostructured ceramic samples arises from the grain boundary sliding, grain rotation and grain shape accommodation. Enhanced self-diffusivity of nanostructured ceramic samples results in comparatively lower sintering temperatures for nanometer-sized samples in comparison with those of coarse-grained samples. The increased diffusivity and the
consequent reactivity lead to increased solid solubility limits in metallic nanostructures which could result in alloying of extremely insoluble systems such as Ag-Fe, W-Ga, Ir-Cu, Si-Fe, V-C, Si-La, etc.\textsuperscript{12,18,129} All these pairs of elements exhibit no measurable solute solubility if prepared in the form of coarse-grained polycrystals. Improved mechanical properties of nanophase materials find applications in fields such as novel structural materials, cutting tools with improved strength and precision, impact resistant materials, automobile industry, machine parts, defense applications, etc. The possibility of synthesizing new alloys of conventionally immiscible elements is of interest to a wider spectrum of technologists from diverse fields of materials industry.

The optical properties of non-interacting assemblages of nanometer-sized semiconductor clusters are exciting from both scientific and technological points of view. In such non-interacting semiconductor clusters, assembled in liquid or solid media, the loosely bound valence electrons are confined in space more than they would be in a bulk sample with same average chemical composition. Spatial confinement of valence electrons in semiconductor clusters is generally referred to as quantum confinement. The frequency of light absorbed/emitted by non-interacting semiconductor clusters is shifted to lower wavelength region due to the quantum confinement of valence electrons resulting in a “blue shift”. The extent of “blue shift” depends on the degrees of quantum confinement and hence on the cluster size.\textsuperscript{14,24,41-44} Such “quantum size effects” exhibited by semiconductor nanostructures find important applications in fabrication of quantum cascade lasers and light emitting diodes and in optical computing technology.\textsuperscript{14,36,41-44} Increased efficiency of luminescence of nanostructured semiconductor samples in comparison with that of their coarse-grained polycrystalline counterparts, owing to their large surface area to volume ratio, is advantageously exploited in many applications such as novel display devices.\textsuperscript{19} It is reported that nanoparticle samples of semiconductors such as CdSe and InSe can be used as solar cell materials with many advantages over the conventional solar cell materials now in use.\textsuperscript{130,131} Three dimensional structures consolidated from nanometer-sized grains of ceramic materials like Y$_2$O$_3$, Si$_3$N$_4$, etc., can be made transparent, translucent or opaque by adjusting the grain size, state of aggregation and porosity, and is of potential use in optical filtration technology.\textsuperscript{132,133} Also,
nanostructured thin films and coatings are employed in many optical devices such as high-energy laser mirrors and laser gyroscopes where surface roughness has to be limited to nanometer dimensions.\textsuperscript{36}

Nanostructured samples of magnetic materials have been synthesized and studied by many investigators primarily for understanding the domain structure responsible for different kinds of magnetic ordering.\textsuperscript{111,112} Nanometer-sized samples of magnetic materials exhibit many novel properties such as superparamagnetism, superantiferromagnetism, varied values of saturation magnetization, coercivity and magnetic transition temperatures and are of importance in diverse fields such as the high density magnetic recording media, ferrofluid technology, magnetic imaging technology, etc.\textsuperscript{18,113-118} The phenomenon of giant magnetoresistance (GMR) exhibited by nanostructured samples of many alloys and composites are expected to be crucial in the technology for the reading heads of next generation information storage systems.\textsuperscript{18,134} The excellent soft magnetic properties of many nanostructured materials can be useful in producing tape-wound cores for common mode chokes, saturable reactors, high frequency transformers and magnetic heads.\textsuperscript{18} Also, nanocomposites such as $\gamma$-Fe$_2$O$_3$ stabilized in an ion-exchange resin and Gd$_3$Ga$_{3.25}$Fe$_{1.75}$O$_{12}$ exhibit magnetocaloric effect at much higher temperatures in comparison to the conventionally used magnetic refrigerator materials and have the potential to be exploited for the development of novel magnetic refrigeration systems which could replace conventional chlorofluorocarbon (CFC) based refrigerators.\textsuperscript{18,135}

Nanostructured samples of metals such as Ni and ceramics such as TiO$_2$ are reported to show improved catalytic properties due to large surface area to volume ratio.\textsuperscript{18,136} Enhanced catalytic action of nanostructures could play crucial roles in fields such as chemical industry, water purification, catalytic conversion of automobile exhaust gas, etc. Gas and humidity sensors based on nanostructured samples of transition metal oxides have many advantages like lower activation temperature, better sensitivity, etc., over the conventional sensors.\textsuperscript{36} Fine particles of latex, which is an organic polymer, are commonly used as a vehicle for biological and chemical manipulation in pharmaceutical industry.\textsuperscript{4} Aerosols, which are fine dispersion of a
solid phase in a gas, are routinely used in fields like agriculture, forestry, defense and medicine. Systematic study of the properties of nanostructured materials over the last two decades have made this new class of materials the most probable answer for the quest for materials with tailor-made properties. Nanostructured materials are all set to play a major role in the advancement of almost every realm of modern technology.

1.8 Present Work

Nickel oxide (NiO) is an important material due to its complex band structure and interesting electrical, optical and magnetic properties which find applications in diverse fields such as smart windows, active optical fibers, electrochromic displays and temperature sensors. Over and above the potential technological applications, nickel oxide is interesting from the academic point of view since it is perhaps one of the most widely studied yet not well-understood transition metal oxides.

At ordinary temperature, nickel oxide has a crystal structure slightly distorted from the ideal cubic NaCl structure. Electrically, nickel oxide is classified as a Mott-Hubbard insulator, the very low conductivity of which is in contradiction with the band theory of solids. Further, at room temperature nickel oxide is an antiferromagnet with a two sublattice magnetic ordering resulting from the superexchange interactions involving Ni$^{2+}$ ions and nonmagnetic O$^{2-}$ ions. In the nanosize regime, the physical properties of nickel oxide including electrical and magnetic properties are expected to show marked changes. The research work included in this thesis is a detailed account of the synthesis of nanostructured nickel oxide samples having different average grain sizes ranging from 2–3 nm to 18 nm and the study of their properties using different experimental techniques.

In the present work, nanostructured nickel oxide samples having different average grain sizes ranging from 2–3 nm to 18 nm were synthesized through a two-step process. The average grain sizes of the samples were determined from the X-ray
diffraction analysis. Transmission Electron Microscopy (TEM) and Electron Diffraction techniques were also used for the characterization. The dc and ac electrical properties of the nanostructured samples were studied in detail and were compared with those of their single crystalline and coarse-grained polycrystalline counterparts. Ni 2p X-ray Photoelectron Spectroscopy (XPS) studies of samples were carried for understanding the effects of nanostructuring on the electronic structure of the material. Fourier Transform Infrared (FTIR) spectroscopy study of nanostructured nickel oxide samples in the far IR region was carried out for investigating the surface modes and other size effects in the vibrational spectra. Static magnetic properties of the nanostructured samples at room temperature were studied using a Vibrating Sample Magnetometer (VSM). Also, using FTIR measurements in the far IR region the antiferromagnetic resonance (AFMR) in nanostructured nickel oxide was investigated.

1.9 References

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