CHAPTER 1

GENERAL INTRODUCTION

The concepts that seeded nanotechnology were first reinvested by Richard Feynman in his famous talk ‘There's Plenty of Room at the Bottom’ in 1959 in which he quoted “The principles of physics, as far as I can see, do not speak against the possibility of manoeuvring things atom by atom. Put the atoms down where the chemist says, and so you make the substance” [Richard Feynman 1960]. Nanoscience is indeed a manifestation of this idea and the result is that today; it turns out to be vital for the society not only from a scientific point of view but also from a layman’s perception.

Over a decade later, in his explorations of ultra precision machining, Professor Norio Taniguchi coined the term nanotechnology. His definition referred to “production technology to get extra high accuracy and ultra fine dimensions, i.e., the preciseness and fineness on the order of 1 nm (nanometer), \(10^{-9}\, \text{m}\) in length” [Taniguchi 1974]. The emergence of nanotechnology as a new branch of science, in the 1980s was caused by the convergence of experimental advances such as the invention of the scanning tunneling microscope in 1981 and the discovery of fullerenes in 1985 by Harry Kroto, Richard Smalley, and Robert Curl [Wolf 2006]. Also, in 1986 the conceptual framework for the goals of nanotechnology was published in the book ‘Engines of Creation: The Coming Era of Nanotechnology’ by Eric Drexler paved the path of nanoscience.

To define, nanoscience is the combination of our ability to see and manipulate matter on the nanoscale and understanding of atomic scale interactions. Advances in the materials processing along with the abrupt rise in the sophistication of characterisation techniques made nanoscience simply one that primarily deals with synthesis, characterization, exploration and exploitation of nanostructured materials. The assurance of the nanoscale science and technology is on the established truth that the materials at the nanoscale have properties quite different from the bulk materials and in fact these properties could be refrained according to our needs.

Although the nanoscience and nanotechnology are quite new, the history of nanoscale materials were traced back to centuries. Chinese are known to use gold nanoparticles as an inorganic dye to introduce red colour into their ceramic porcelains more than thousand years ago [Lorenzo Camusso and Sandro Bortone 1992]. Different sized gold and silver particles...
created colours in the stained glass windows of medieval churches hundreds of years ago. The world famous cultural symbol of Kerala, the ‘Aranmulakannadi’ has a secret compound in its making which is also made into nanopowder. Thus this technology is not new but is the combination of existing technologies and our new found ability to observe and manipulate at the atomic scale, this makes nanotechnology so compelling in various viewpoints. Today scientists and engineers are finding a wide variety of ways to deliberately make materials at the nanoscale to take advantage of their enhanced properties.

In the future, nanotechnology will let us to snap together the fundamental building blocks of nature easily, inexpensively and in most of the ways permitted by the laws of nature. This new pollution free manufacturing technology will also let us economically fabricate a profusion of new products that are remarkably light, strong, smart, and durable.

1.1 NANOMATERIALS

Nanomaterials are a new step in the evolution of understanding and utilization of materials. They are considered to be the cornerstones of nanoscience and nanotechnology. Nanostructures refer to the matter whose length scale, in any dimension, is approximately 1 to 100 nanometres. Nanomaterials can come in a wide range of morphologies and cover diverse range of materials: ceramics, polymers, metals or composite materials.

Nanomaterials are not a simple extension of miniaturization from microscale down to nanoscale. Micro scale materials mostly exhibit the same physical properties as bulk materials. However, properties of nanomaterials are significantly different from those of bulk materials, such as the lower melting point, the enhanced mechanical strength and the shift of absorption spectrum are of interest because at this scale unique optical, magnetic, electrical and other properties emerge. These emergent properties have the potential for great impacts in the fields of optics, electronics, catalysts, biomedicines and others. The research of nanomaterials focuses on the creation and exploitation of materials which have morphological characteristics from atoms to bulk materials and with at least one dimension in the nanoscale range.

Nanomaterials encompass an entirely different arena; the nano world lays midway between the scale of bulk materials and atomic quantum phenomena. Nanomaterials have structural features in between those of atoms and bulk materials. Properties of nanomaterials are significantly diverse from their corresponding macro-micro counterparts. This is mainly due to the nanometre size of the materials which render them (i) large fraction of surface atoms (ii) high surface energy (iii) spatial confinement and (iv) reduced imperfections [Cao 2004]. Due to their smaller dimensions nanomaterials have extremely large surface area to
volume ratio, which makes a large fraction of atoms of the materials to be in the surface or interfacial atoms resulting in more ‘surface ‘dependent material properties.

Many of the properties of nanostructures are size dependent. In other words, properties of nanostructured materials can be tuned considerably by simply adjusting its size, shape or extent of agglomeration [Brus 1991, Nozik and Memming 1996]. The peculiar physical properties of nanomaterials arise from many different fundamentals. The huge surface energy is responsible for the reduction of thermal stability and the super-paramagnetism. Increased surface scattering is responsible for the reduced electrical conductivities. The quantum confinement of nanomaterials has profound effects on the properties of nanomaterials. The energy band structure and charge carrier density in the materials can be modified quite differently and in turn will modify the electronic and optical properties of the materials. Nanosturctures and nanomaterials favours a self-purification process in that the impurities and intrinsic material defects will move to near the surface upon thermal annealing. This increased perfection thus enhances chemical stability and mechanical properties of individual nanosized materials.

1.2 DIFFERENT TYPES OF NANO MATERIALS

Nanostructures are those with at least one dimension falling in nanometre scale. They can be created in many variants and dimensions and include nanoparticles, nanorods and nanowires, thin films and bulk materials made of nanoscale building blocks or consisting of nanoscale structures. Furthermore, nanomaterials can come in a wide range of morphologies from spheres, through flakes and platelets, to dendritic structures, tubes, and rods.

As defined by Richard W. Siegel [Siegel 1994]: Nanomaterials can be nanoscale in zero dimension, one dimension (1D), two dimensions (2D) and three dimensions (3D). Materials wherein all the dimensions are measured within the nanoscale are of zero-dimension. The most common representation of zero-dimensional nanomaterials are nanoparticles, atomic clusters etc. In one dimension variant one of the measurements is outside the nanoscale. This leads to needle like-shaped nanomaterials. 1D materials include nanotubes, nanorods and nanowires. 2D nanomaterials exhibit plate-like shapes where two of the dimensions are not confined to the nanoscale. They include nanofilms, nanolayers and nanocoatings. Bulk or 3D nanomaterials are materials that are not confined to the nanoscale in any dimension. These materials are thus characterized by having three arbitrarily dimensions above 100 nm. In terms of nanocrystalline structure, bulk nanomaterials can be composed of a multiple arrangement of nanosize crystals, most typically in different orientations. With respect to the presence of features at the nanoscale, 3D nanomaterials can contain dispersions of
nanoparticles, bundles of nanowires, and nanotubes as well as multi-nanolayers. Figure 1.1 shows different classification of nano structures.

Nanomaterials consisting of nanometre sized crystallites or grains and interfaces may be classified according to their chemical composition and shape or dimensionality. According to the shape of the crystallites or grains we can broadly classify nanomaterials into four categories:

- Clusters or powders (D=0)
- Multilayers (D=1)
- Ultrathin nanolayers or nanofilms or buried layers (where the layer thickness or the rod-diameters are <50 nm) (D=2)
- Nanomaterials composed of equiaxed nanometre-sized grains (D=3)

There are many types of intentionally produced nanomaterials and a variety of others are expected to appear in the future. Generally they fall into two category: fullerenes and inorganic nanoparticles, which is further sorted into four as carbon based materials, metal based materials, dendrimers and composites.

![Figure 1.1 Classifications of nanomaterials](image)

Carbon based materials are composed mostly of carbon, most commonly taking the form of a hollow spheres, ellipsoids, or tubes. Spherical and ellipsoidal carbon nanomaterials are referred to as fullerenes, while cylindrical ones are called nanotubes. Metal based
materials include quantum dots, nanogold, nanosilver and metal oxides, such as titanium dioxide. A quantum dot is a closely packed semiconductor crystal comprised of hundreds or thousands of atoms, and whose size is of the order of a few nanometers to a few hundred nanometers. Dendrimers are nanosized polymers built from branched units. The surface of a dendrimer has numerous chain ends, which can be tailored to perform specific chemical functions. Composites combine nanoparticles with other nanoparticles or with larger, bulk-type materials.

The unique properties of these various types of intentionally produced nanomaterials give them novel electrical, catalytic, magnetic, mechanical, thermal, or imaging features that are highly desirable for applications in commercial, medical, military and environmental sectors. These materials may also find their way into more complex nanostructures and systems. As new uses for materials with these special properties are identified, the number of products containing such nanomaterials and their possible applications continues to grow.

1.3 UNIQUE PROPERTIES OF NANOMATERIALS

Exceptional properties of nanomaterials have revolutionized various fields of science. The peculiarity of these properties is that we can tune it to desired level by simply controlling the size, morphology and composition. Some of the novel properties of these materials are detailed below:

1.3.1 OPTICAL PROPERTIES

Optical properties are the most fascinating properties of nanomaterials and have been extensively studied because of its wide range of applications using a variety of optical spectroscopic techniques. The reduction of materials dimension has pronounced effects on the optical properties. The size dependence on optical properties can be generally classified into two. One is due to the increased energy level spacing as the system becomes more confined and the other is related to surface plasmon resonance.

Nanoparticles often have unexpected optical properties because they are small enough to confine their electrons and produce quantum effects. When the size of a nanocrystal (i.e. a single crystal nanoparticle) is smaller than the de Broglie wavelength, electrons and holes are spatially confined and electric dipoles are formed and discrete electronic energy levels would be formed in all materials. Similar to a particle in a box, the energy separation between adjacent levels increases with decreasing dimensions. The electronic configurations of nanomaterials are significantly different from that of their bulk counterpart. These changes arise through systematic transformations in the density of electronic energy levels as a function of the size and these changes result in strong variations in the optical properties with
size [Rossetti 1983, Guzelian et al 1996]. Since the absorption edge is due to the band gap, the band gap increases as the particle size decreases. Also the intensity of the absorption increases as the particle size decreases [Lue 2001]. The quantum size effect is most pronounced for semiconductor nanoparticles, where the band gap increases with a decreasing size, resulting in the inter band transition shifting to higher frequencies [Brus 1991, Nozik and Memming 1996, Alivisatos 1996].

Surface Plasmon Resonance phenomenon also plays an important role in determining the optical properties of nanoparticles. Surface plasmon resonance is the coherent excitation of all the free electrons within the conduction band, leading to an in-phase oscillation [Kerker 1969, Bohren and D.R. Huffman 1983]. When the size of a metal nanocrystal is smaller than the wavelength of incident radiation, a surface plasmon resonance is generated [Kreibig and Vollmer 1995]. The plasmon band red shifts with increasing particle size. At the same time, the plasmon bandwidth increases with increasing particle size. The increase of both absorption wavelength and peak width with increasing particle size has been clearly demonstrated experimentally [Link and El-Sayed 1999]. The luminescence energy and efficiency are subjected to the size effect. Such direct size dependence on the particle size is regarded as extrinsic size effects.

1.3.2 ELECTRICAL PROPERTIES

The increased volume fraction of atoms lying at the grain boundaries is expected to increase the electrical resistivity of nanocrystalline material than that in the corresponding coarse-grained polycrystalline materials. The electrical resistivity of nanocrystalline material is high in both coarse-grained metals and amorphous alloys. At a constant temperature, resistivity increases with decreasing grain size and it is found to be proportional to the temperature for different grain size in wide temperature range. The temperature coefficient of electrical resistivity has been found to decrease with a decreasing grain size.

The effects of size on electrical conductivity of nanostructures and nanomaterials are complex since they are based on distinct mechanisms. These mechanisms can be generally grouped into four categories: i) surface scattering including grain boundary scattering, ii) change of electronic structure, iii) quantized transport and iv) effect of microstructures. In nanowires and thin films surface scattering of electrons results in reduction of electrical conductivity when the critical dimension of thin film and nanowires is smaller than the electron mean-free path, the motion of electron will be interrupted to collision with the surface [Skove and Stillwell, 1965]. A reduction in characteristic dimension below a critical size, i.e. the electron de Broglie wavelength, would result in a change of electronic structure,
leading to widening and discrete band gap. Such a change generally would also result in a reduced electrical conductivity. Quantum transport phenomenon such as on ballistic conduction, coulomb charging and tunnelling conduction in small devices and materials has been studied extensively [Datta 1995, Ferry et al. 1994]. Ballistic conduction occurs when the length of the conductor is smaller than the electron mean-free path. An important aspect of ballistic transport is that no energy is dissipated in the conduction and there exist no elastic scattering. Ballistic conduction of carbon nanotubes was first demonstrated by Frank and his co-workers [Van Wees et al 1988, Frank et al 1998]. Ballistic conduction occurs when the length of the conductor is smaller than the electron mean-free path, where no energy is dissipated. Electrical conductivity may change due to the formation of ordered microstructure, when the size is reduced to a nanometre scale as in polymer fibre. The enhancement was explained by the ordered arrangement, e.g. polymer chains. Smaller the diameter, the better alignment of polymer is expected.

In addition, increased perfection, such as reduced impurity, structural defects and dislocations of nanoparticles would affect its electrical conductivity. Nanoparticles are employed because of their remarkably lower melting temperature compared to bulk materials. A lower synthesis temperature also favours a better alignment and thus a higher electrical conductivity [Scott et al 1989, Cai et al 1991]. This low melting temperature of nanoparticles is due to the large ratio of surface atoms to inner atoms.

A specific parameter introduced by nanomaterials is the surface/interface-to-volume ratio. A high percentage of surface atoms introduce many size-dependent phenomena. The finite size of the particles confines the spatial distribution of the electrons, leading to the quantized energy levels due to size effect i.e. increased electronic energy levels when the dimensions of materials are below a certain size [Choi et al 2000, Zhang et al 2000]. It is known that the electron energy band structure and band gap are sensitive to lattice constant. The lattice relaxation introduced by nanocrystal size could affect its electronic properties.

All of the above conclusions are consistent with the theoretical analysis of scattering of electrons by grain boundaries. If the crystal size is smaller than the electron mean free path, grain boundary scattering is dominated and hence the electrical resistivity as well as temperature coefficient is expected to increase.

1.3.3 DIELECTRIC PROPERTIES

With the recent advancements of electronics, the demand of capacitors with high volumetric efficiency, extended temperature ratings, smaller size and lower cost as required by multilayered capacitors, is constantly on the rise. Hence, it has become extremely
important to synthesize dielectric materials with higher density and higher surface area, more uniform size distribution and less brittleness at elevated temperatures. This necessitates investigation of nanosized particles of well known dielectric materials.

The dielectric properties of a solid give a good insight into the electric field distribution within it [Anderson 1963, Tareev 1979]. In general case, all the electrical parameters such as dielectric constant ($\varepsilon_r$), dielectric loss factor ($\tan\delta$), electrical ac conductivity ($\sigma_{ac}$) and electrical dc conductivity ($\sigma_{dc}$) increase with increase in temperature exhibiting a normal dielectric behaviour. Thus $\varepsilon_r$ and $\tan\delta$ values decrease with increase in frequency up to a particular value. The dielectric constant is attributed to four types of polarization which are space charge, dipolar, ionic and electronic [Hench and Ulrich 1986]. At lower frequencies, all four types of polarizations contribute, the rapid increase in dielectric constant is mainly due to space charge and are strongly temperature dependent [Hench and Ulrich 1986]. The dipolar orientation effect can be seen in some materials at high frequencies and ionic and electronic polarization below 1 kHz. The dielectric parameters were estimated by Meena and co-workers on many nanocrystalline materials which show increase in dielectric constant with increase in temperature [Meena and Mahadevan 2008]. The dielectric constant decreases with decreasing size of the nanostructure due to the increasing contribution of the surfaces [Delerue and Lannoo 2004]. This is due to the fragmentation of crystals when approaching to the molecular state which results in a decrease in bond polarity and hence in the reduction of the difference in dielectric constant and refractive index ($\varepsilon_r - n^2$) [Batsanov et al. 2009].

1.3.4 MELTING POINT AND SINTERABILITY OF NANOPARTICLES

Nanoparticles of metals, inert gases, semiconductors and molecular crystals are all found to have lower melting temperatures as compared with their bulk forms, when the particle size decreases below 100nm. The lowering of the melting points is in general explained by the fact that the surface energy increases with a decreasing size. Three different criteria have been explored for the size dependence of melting temperature of nanoparticles - the disappearance of the state of order in the solid, the sharp variation of some physical properties, such as evaporation rate and the sudden change in the particle shape. Melting temperatures of various nanowires have also been found to be lower than that of bulk forms [Link et al. 2000, Wu and Yang 2000].

Since nanocrystalline materials contain a very large fraction of atoms at the grain boundaries, the numerous interfaces provide a high density of short circuit diffusion paths. Consequently they are expected to exhibit enhanced diffusivity in comparison to polycrystalline bulk materials with the same chemical composition, which can affect the
mechanical properties significantly. An important consequence of the increased diffusivity and reduced melting point is that sintering of nanocrystalline powders can occur at temperatures lower than those required for coarse grained polycrystalline powders [Kenji et al. 1988, David et al. 1990]. In the case of ceramics, whose sinterability is a major issue, high surface to volume ratio of nanocrystals lead to enhanced sinterability and result in microstructure, retaining the initial nanocrystals. This microstructure is the source of unique mechanical, electrical, dielectric, magnetic and optical properties of nanocrystals [Gleiter 1992, Gleiter 2000]. The decrease in the phase transition temperature can be attributed to the changes in the ratio of surface energy to volume energy as a function of particle size. The ferroelectric–paraelectric transition temperature or the Curie temperature of ceramics decreases sharply below a certain size [Newnham et al 1992].

Figure 1.2 Different stages of sintering process

1.3.5 OTHER PROPERTIES

Nanomaterials have received much interest by virtue of their excellent properties suited for applications in various fields such as electronic, pharmaceutical, biomedical, cosmetic, energy and catalysis. Physical, chemical, and biological properties of materials in nano-scale differ in fundamental from those of individual atoms and molecules or bulk
materials. When the particle size is reduced, both the number of atoms located at the surface and the ratio of the surface area to volume are increased. This would enhance the surface active sites and lead to some extraordinary chemical and physical properties and promise significantly enhanced functions in practical applications.

Magnetic nanoparticles show a variety of unusual magnetic behaviour when compared to the bulk materials, mostly due to surface or interface effects, including symmetry breaking, electronic environment or charge transfer and magnetic interactions. The large surface area to volume ratio results in a substantial proportion of atoms having different magnetic coupling with neighbouring atoms leading to differing magnetic properties. For example, nanometre sized ferromagnetic materials turn to paramagnetic and behaves differently from the conventional paramagnetics which is referred to as superparamagnetics [Bean and Livingston 1959, Lue 2001]. Nano scale particles of magnetite show superparamagnetism at a transition temperature, which is smaller than the transition temperature of bulk material [Goya et al 2003]. High energy products and relatively high coercivities can be developed in nano composite magnets which have high value of remanence and low cost. Magneto restrictive materials i.e., magnetic materials which are deformed due to presence of magnetic field are of great scientific importance. Magneto restrictive nano scale films can allow such functions, which cannot be done using existing integrated circuits. For example these constitute driving elements of micro robots, pumps, motors, resonators with magnetically adjustable frequency and stress controlled inductance etc.

Chemical properties of nanomaterials also change at nanoscale. Higher the percentage of surface atoms the reactivity of nanomaterials increases. The predominance of surface is a major reason for the change in behaviour of materials at the nanoscale. As up to half of all the atoms in nanoparticles are surface atoms, properties such as electrical transport are no longer determined by solid-state bulk phenomenon. For example, catalytic materials have a greater chemical activity per atom of exposed surface as the catalyst is reduced in size at the nanoscale.

Novel nanotechnologies have allowed great improvements in the synthesis of catalyst with well controlled size, shape and surface properties. Nanomaterial-based catalysts are usually heterogeneous catalysts. The extremely small size of the particles maximizes surface area exposed to the reactant, allowing more reactions to occur. Nano-catalyst has great enhanced reactivity and selectivity as compared to their bulk counterparts [Thomas and Thomas 1997]. Among this core-shell nanostructures which are nanoparticles encapsulated and protected by an outer shell that isolates the nanoparticles and prevents their migration and coalescence during the catalytic reactions. Photo catalytic activity of nanomaterials has
become a comprehensively studied area of research during the past three decades due to its practical interest in applications including water–air de-pollution, cancer therapy, sterilization, artificial photosynthesis photochromism, solar chemicals production and many others [Colmenares and Luqueb 2014].

The mechanical properties of materials increase with a decreasing size. Nanostructured materials may have different elasto-plasticity from that of large-grained bulk materials [Champion et al. 2003]. Other mechanical properties of nanostructured materials, such as Young's modulus, stiffness, flexibility and super plasticity, have also been studied; however, no solid understanding on the size dependence has been established.

A reduction in grain size can significantly change the thermal properties of ceramics. The difference between materials with different grain sizes vanishes at elevated temperatures. Even though some researchers have confirmed that the coefficient of thermal expansion increased with a decrease in grain size [Eastman 1994], others reported that it was approximately the same for both the nanocrystalline and coarse grained materials [Suryanarayana and Koch 2000]. The small grain size and the large amount of grain boundaries also result in unusual thermo-mechanical properties, e.g. extreme hardness and super plasticity [Hahn and Averback 1991].

A major bottleneck in the ongoing research in this area is the effective and efficient storage of hydrogen. Nanomaterials offer great promise for this problem. Storage and retrieval of hydrogen involves an important phenomenon called ‘sorption’. Adsorption and desorption are the two processes involved and the associated thermodynamics is vital in the design and optimization of the materials for hydrogen storage. Nanomaterials are a natural choice for increasing the kinetics of uptake and release; the sorption characteristics can be fine-tuned by controlling the particle sizes [Zaluska et.al 2001]. Nanoparticles help promote fast hydrogen exchange by shortening diffusion distances for hydrogen. This is facilitated by the increased porosity and smaller size leading to increased diffusion-limited rates. Surface energies and materials properties at the nanoscale help tune the energetics of adsorption and desorption to reduce the release temperature and hasten the release process.

One promising solution, providing clean and sustainable power, is fuel cells. Instead of burning fuel to create heat, fuel cells convert chemical energy directly into electricity [Basu 2007]. This energy conversion technology currently receives intensive research and development focus because of its high energy conversion efficiency (typically, 40–60% or up to 85% efficiency if waste heat is captured for use), virtually no pollution and potential large-scale applications. The large-scale practical application of fuel cells will be difficult to realize
if the expensive platinum-based electro catalysts are replaced by other efficient, low cost, and stable electrodes. Along with the intensive research efforts in reducing or replacing Pt-based electrode in fuel cells, a new class of carbon nanomaterials has been discovered, which act as alternative ORR (oxygen reduction reaction) catalysts, could dramatically reduce the cost and increase the efficiency of fuel cells [Zhang and Dai 2012].

1.4 NANOCERAMICS

A ceramic is an inorganic, nonmetallic solid prepared by the action of heat and subsequent cooling. Ceramic materials may have a crystalline or partly crystalline structure, or may be amorphous (e.g., a glass). Crystalline ceramic materials are not amenable to a great range of processing. Methods for dealing with them tend to fall into one of two categories – either makes the ceramic in the desired shape, by reaction in situ, or by "forming" powders into the desired shape, and then sintering to form a solid body. Nanoceramics are new class of ceramic materials or nanoceramics may be more advanced versions of previously used ceramics, or they may be new types of ceramics made possible by the use of nanotechnology in the manufacturing process. Indeed, the development of new ceramics is perhaps the main area of research in the field of nanoceramics. The major drive for wider interest in nanoceramics and its composites has been the fact that one can potentially achieve better and some unusual material properties by manipulating length scale in the nano range. Therefore, better performance and newer application of the materials have now been made possible.

Nano ceramics/nano composites are defined as novel bulk materials or coatings with micro structural architecture characterized by at least one of the ceramic phases having the length scale between 1 to 100nm. Nanoceramics have been defined in two ways. In the past, it was defined as ceramics produced with some form of nanotechnology involved in the production process. Presently, however, a more specific definition is used: nanoceramics are ceramic materials comprised of particles of a certain size, usually 100 nanometres diameter or less.

These nanoceramics have a number of properties that distinguish them from ceramics of a more standard particle size. The first is that due to the smaller size of their constituent particles, nanoceramics present more surface area to anything they come into contact with. This can have benefits in applications where a high reaction rate is needed: since the nanoceramic has a greater surface area, more of it is able to react quickly with the targeted reactant. Due to their particle size, nanoceramics can also display improved insulating or conducting properties, depending on the nanoceramic being manufactured.
Nanoceramics have applications in many present and emerging technologies. Due to their insulating and/or conducting properties, nanoceramics have uses in the construction of the next generation of high-speed computer chips and in other aspects of electronics. For the same reasons, they also have applications in power generation. In medicine, nanoceramics are starring to be used to develop new bone implants and artificial organs, since working at the nanoscale allows device manufacturers to fine-tune how the implant will interact with the human body, thus improving the chance of the body accepting it. Aside from these, nanocermaics have applications in space exploration, weapons manufacturing, construction, consumer goods and transport.

1.5 **MOLYBDENUM AND TUNGSTEN BASED CERAMIC MATERIALS**

Molybdenum and tungsten are rare earth metals with exceptional inherent properties which makes them ideal for many potential applications in diverse fields. The molybdenum and tungsten belong to the same group in the periodic table means that they have similar atomic structure and chemical properties. Carl Wilhelm Scheele was the pioneer to succeed in producing white molybdenum oxide and tungstic acid from their respective ores.

Tungsten and molybdenum materials are used for many years in the field of lighting materials. They have many unique and advantageous properties at an elevated temperature such as a very high melting point, a low coefficient of thermal expansion and a high level of thermal conductivity. Molybdenum and Tungsten belong to the group of refractory metals as they have a high melting point coupled with a low vapour pressure, high modulus of elasticity and high thermal stability. Refractory metals are also typically characterized by a low coefficient of thermal expansion and relatively high density.


Figure 1.3 Crystal structure of orthorhombic MoO$_3$

Molybdenum trioxide forms crystals with different structures. The most common and thermodynamically stable phase is $\alpha$-MoO$_3$, which consists of orthorhombic lattices with a layered structural arrangement of edge and corner-linked MoO$_6$ octahedra. On the other hand, monoclinic molybdenum trioxide, $\beta$-MoO$_3$, is a metastable phase that is transformed into the $\alpha$-phase by heating above 673 K. It has a ReO$_3$-type structure in which MoO$_6$ octahedra share only the corners with each other [Machiels et al 1986, Takanori et al 2011]. WO$_3$ shows different crystal structures at different temperatures. The most common monoclinic crystal structure of WO$_3$. The tungsten oxides consist of WO$_6$ octahedra arranged in various sharing (corners, edges, planes) configurations. The main differences between the phases are shifts in the position of the W atoms within the octahedra and variations in W-O bond lengths. The stable monoclinic WO$_3$ have a ReO$_3$-type structure (corner sharing arrangement of octahedra). An infinite array of corner- sharing WO$_6$–octahedral is formed. These octahedrons are in planes perpendicular to the [001] hexagonal axis and they form four member rings in the $xy$ or
(001) plane. These layers are stacked in arrangement and are held together by weak van de Waal’s forces [Genin et al 1992, Wilson et al 2003, Imre et al 2012].

![Crystal structure of monoclinic WO₃](image)

**Figure 1.4 Crystal structure of monoclinic WO₃**

The most famous class of molybdenum and tungsten based ceramics are scheelite group of compounds having general formula AMO₄ (A = Ba, Sr, Ca, Pb… and M=W or Mo) in which A atom has eight fold oxygen co-ordination and molybdenum/tungsten atom form [MO₄]²⁻ tetrahedron. They remain in tetragonal structure within a wide range of temperatures and pressures [Christofilos 1995, Basiev et al 2000].

et al 2005, Voronina et al 2003]. Recently, PbWO$_4$ has attracted special interest because of plans to use it as a scintillator in detectors at the Large Hadron Collider in CERN [Itoh and Fujita 2000].


Figure 1.5 Scheelite crystal structure

1.6 MOTIVATION AND SCOPE OF THE PRESENT WORK

Ceramics of rare earth metals are of immense intense to the research community due to their novel properties and widespread applications. As the demand and competition in the market increases, the need for new efficient functional materials also ascends. In the recent years, attempts are done to synthesis materials with excellent characteristic properties in nano scale so that we can tune its properties according to our need by manipulating its particle size, morphology and processing parameters. Molybdenum and tungsten based ceramic materials have created a great impact because of their remarkable optical properties and applications.

Since the properties of materials can be tuned by its microstructure, different synthesis methods were employed. Samples prepared through most of the methods are relatively large in particle size with irregular morphology and of inhomogeneous composition. Also in most of these methods a prolonged processing temperature is needed to obtain the required phase. But in order to control the grain growth and to retain the nanocrystallinity of the compounds, we adopted an easy and time saving single step modified combustion technique in which the as-prepared powder obtained is phase pure.

The optical properties of molybdenum and tungsten based ceramics are still a matter of curiosity. So the study of these materials could not be completed without optical characterisation. A detailed analysis on the luminescence, optical band gap studies were carried out and explained in terms of lattice structure. Even though the luminescent behaviour of these compounds remains much investigated, its dielectric properties, sintering behaviour, mixed oxides compositions are not much explored. At the point of application view, we had made an attempt to study low temperature sintering and dielectric behaviour of molybdenum and tungsten based nanoceramics in addition to the detailed investigation on its structure and optical characteristic properties.

There have been reports that nanomaterials could be sintered at a temperature much less than their corresponding conventional samples to a high density. Reduction of the sintering temperature without affecting the dielectric properties is a challenging problem in Low-temperature co-fired ceramic (LTCC) materials research. The LTCC technology plays an important role in the miniaturization and integration for wireless communication. It requires the microwave dielectric ceramics with low sintering temperature than the melting point of inner electrode materials, such as Ag, Cu. Usually, glass/polymer–ceramic composite materials are used for LTCC applications. But their high values of dielectric loss, thermal mismatch and high sintering temperature impose restrictions on their effective use as LTCC.
So, a glass-free LTCC material with appropriate dielectric properties is strongly desired for the multilayer structure applications. A pure ceramic material with good dielectric properties and that could be sintered at a temperature below 950°C without any sintering aid could be considered as an ideal LTCC material. In view of this fact we had tried to sinter all the samples of present study at low temperature by preparing its nanoceramics, without compromising its dielectric behaviour. In search for new materials, scheelite structures appear especially attractive because of their excellent dielectric properties and relatively low sintering temperature materials.

A mixed oxide composition of scheelite molybdate and tungstates by varying the composition of different elements were also done so that we could tailor the properties of these compounds according to our needs. The structural, optical and dielectric characterization of these newly synthesized nano compounds were also presented.

The experimental details, the characterization techniques, synthesis route and the results obtained along with detailed discussions are given in the consequent chapters of this thesis.