CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

Nanotechnology is the creation of functional materials, devices, and systems through control of matter on the nanometer (1 to 100 nm) length scale and the exploitation of novel properties and phenomena developed at this scale (Wilson et al 2002). A scientific and technical revolution has begun that is based upon the ability to systematically organize and manipulate matter on the nanometer length scale. The literal meaning of nano is dwarf or an abnormally short person (Booker & Boysen 2005). However in scientific language it is a billionth ($10^{-9}$) part of some unit scale. Nanometer is so small that if you imagine only ten atoms of hydrogen placed in a line touching each another it will measure one nanometer. One nanometer is one-millionth of a millimeter and a single human hair is around 80,000 nanometers in width (Poole & Owens 2003, Moriarty 2001).

The scientific story of nanomaterials however began much later. One of the first scientific reports is the colloidal gold particles synthesized by Michael Faraday as early as 1857. His gold samples are still in British Museum in U.K showing beautiful magenta-red colour (not golden!) solution. Decorative glass windows with beautiful designs in old churches and palaces indeed use nanoparticles of iron, cobalt, nickel, gold, silver etc. Nanostructured catalysts have also been investigated for over 70 years. By the early 1940's, precipitated and fumed silica nanoparticles were being
manufactured and sold in USA and Germany as substitutes for ultra-fine carbon black for rubber reinforcements (Yury Gogosti 2006).

Nanosized amorphous silica particles have found large-scale applications in many everyday consumer products, ranging from non-dairy coffee creamer to automobile tyres, optical fibers and catalyst supports. In the 1960s and 1970s metallic nanopowders for magnetic recording tapes were developed. In 1976, for the first time, nanocrystals produced by the now popular inert-gas evaporation technique were published by Granqvist & Buhrman (1976). Recently it has been found that the Maya blue paint is a nanostructured hybrid material. The origin of its color and its resistance to acids and biocorrosion are still not understood but studies of authentic samples from Jaina Island show that the material is made of needle-shaped palygorskite (clay) crystals that form a super lattice with a period of 1.4 nm, with intercalates of amorphous silicate substrate containing inclusions of metal (Mg) nanoparticles. The beautiful tone of the blue color is obtained only when both these nanoparticles and the super lattice are present, as has been shown by the fabrication of synthetic samples Granqvist & Buhrman (1976).

Probably most celebrated historical comment on the advancement of nanomaterials was the public speculation by physicist Richard Feynman in 1959 at a meeting of the American Physical Society about the effects of manipulating minuscule bits of condensed matter in his famous talk “There’s plenty of room at the bottom” (Bhushan 2004). Today nanophase engineering expands in a rapidly growing number of structural and functional materials, inorganic and organic, allowing to manipulate the mechanical, catalytic, electric, magnetic, optic and electronic functions. The production of nanophase or cluster-assembled materials is usually based upon the creation of separated small clusters which then are fused in a bulk-like material or on their embedding into compact liquid or solid matrix materials. e.g. nanophase
silicon, which differs from normal silicon in physical and electronic properties, could be applied to macroscopic semiconductor processes to create new devices. For instance, when ordinary glass is doped with quantized semiconductor “colloids,” it becomes a high-performance optical medium with potential applications in optical computing (Dutta & Hoffman 2003).

1.2 NANOMATERIALS

At the beginning of last century, increasing attention was focused on the physical chemistry of colloidal suspension. By referring to them as the "world of neglected dimensions", Oswald was the first to realize that nanoscale particles should display novel and interesting properties largely depending on their shapes. However it is only in the last two decades that significant interest has been devoted to inorganic particles consisting of few hundred or a few dozen of atoms, called clusters. This interest has been extended to a large variety of metals and semiconductors and is due to the special properties exhibited by these nanometer sized particles, which differ greatly from those of the corresponding macro crystalline material (Yury Gogosti 2006).

Matters that is constituted of atoms and molecules as such, has been widely classified and satisfactorily explained. However, an ensemble of atoms or molecules forming the so-called ‘Clusters’ is far from being properly understood. Elemental clusters are held together by various forces depending on the nature of the constituting atoms.

- Inert gas clusters are weakly held together by vander-waals interactions, eg: (He)$_n$.
- Semiconductor clusters are held with strong directional covalent bonds, eg: (Si)$_n$.
Metallic clusters are strongly held together by delocalized non-directional bonding, eg: $(\text{Na})_n$.

Either elemental clusters or a mixture of different elements constitute the vast expanding field of materials sciences called 'nanomaterials'. Depending on the number of atoms forming the clusters determines the percentage of atoms that are exposed on the surface of the clusters. As an example of such an ensemble of metal atoms show the decreasing numbers of surface atoms with increasing size of the clusters. When an ensemble of atoms adds up to form a few nanometer sized clusters, they form what we call nanoparticles since only a few atoms forming clusters, are called molecular clusters.

Nanocrystalline materials are single- or multi-phased polycrystalline solids with a grain size of a few nanometers ($1 \text{ nm} = 10^{-9} \text{ m} = 10 \text{ Å}$), typically less than 100 nm. Since the grain sizes are so small, a significant volume of the microstructure in nanocrystalline materials is composed of interfaces, mainly grain boundaries, i.e., a large volume fraction of the atoms resides in grain boundaries. Consequently, nanocrystalline materials exhibit properties that are significantly different from and often improved over their conventional coarse-grained polycrystalline counterparts (Suryanarayana and Froes 1992). Materials with microstructural features of nanometric dimensions are referred to in the literature as nanocrystalline materials (a very generic term), nanocrystals/nanostructured materials/ nanophased materials. Nanocrystalline structures are not really very new. Nanocrystalline phases were detected in samples of lunar soils. Many conventional catalytic materials are based on very fine microstructures. Nanostructures formed chemically under ambient conditions can also be found in natural biological systems from seashells to bone and teeth in the human body. These materials are notable in that they are simultaneously hard,
strong, and tough. Therefore, a number of investigations have been conducted to mimic nature (biomimetics) and also artificially synthesize nanostructured materials and study their properties and behavior. These investigations have clearly shown that one could engineer (tailor) the properties of nanocrystalline materials through control of microstructural features, more specifically the grain size (Burda et al 2005). Classifications and important aspects of nanomaterials are presented in the following sections.

1.2.1  Grain Size Determination

Most of the novel properties of nanostructures are due to their extremely small grain sizes. Hence, the grain sizes determination of nanomaterials is of primary importance. Unfortunately, size determination of nanoparticles is a great task before the scientists. Utility of conventional techniques like X-ray diffraction for particle size determination is often questioned when applied to nanoparticles (Dieckmann et al 2009; Pyrz & Buttrey 2008; Rehani et al 2006). This is understandable because long range order which is a prerequisite in X-ray diffraction is not satisfied here.

Although techniques like TEM, STM, SEM should be of use, there are difficulties of proper sample preparation suitable for size determination. As the properties are size-dependent one should often like to know the size distribution in a synthesized material and obtained as narrow size distribution. It can be noticed that particles have different shapes even for almost same size.
1.2.2 Structure of Nanomaterials

Figure 1.1 shows a schematic representation of hard-sphere model of an equiaxed nanocrystalline metal (Chimi et al. 2001). Two types of atoms can be distinguished: crystal atoms with nearest neighbor configuration corresponding to the lattice and the boundary atoms with a variety of interatomic spacings, differing from boundary to boundary (Baier et al. 2011, Nowak & Carter 2009). A nanocrystalline metal contains typically a high number of interfaces (~6x10^{25} m^{-3} for a 10 nm-grainsize) with random orientation relationship, and consequently, a substantial fraction of the atoms lies in the interfaces. Assuming, for simplicity, that grains have the shape of spheres or cubes, the volume fraction of nanocrystalline materials associated with the boundaries, C, can be calculated as:

\[ C = \frac{3}{d}, \]  

where \( \Delta \) is average thickness of grain boundaries and \( d \) is the average grain diameter. Thus, the volume fraction of atoms in the grain boundaries can be as much as 50% for 5 nm grains and decreases to about 30% for 10 nm grains and 3% for 100 nm grains. In contrast, for coarse-grained materials with a grain size of >1 \( \mu \)m, the volume fraction of atoms in the grain boundaries is negligibly small. From the foregoing, it is clear that nanocrystalline metals can be considered to consist of two structural components – the numerous small crystallites with long-range order and different crystallographic orientations which consists the “crystalline component” and a network of inter-crystalline regions, the structure of which differs from region to region; this will be referred to as the “interfacial component”. The interatomic spacings in the interfacial component have a wide distribution and further the average atomic density is considerably less than the crystal density depending
on the type of chemical bonding between the atoms. Both these characteristics of the interfacial component (reduced density and wide distribution of interatomic spacings) have been confirmed by experiments like X-ray diffraction, small-angle X-ray scattering, EXAFS (Extended X-ray Absorption fine Structure), and other techniques (Baker et al 2009; Frenkel et al 2011).

Figure 1.1 Schematic representation of an equixed nanocrystalline metal distinguishing between the atoms associated with the individual grains (filled circles) and those constituting the grain boundary network (open circles) (Baker et al 2009)

1.2.3 Morphology of Nanophase Materials

In nanocrystalline single-phase alloys and pure metals, the most important structural parameter is the grain size. The properties of materials are mostly dependent on the grain size and therefore, an accurate determination of the grain size is important. Both direct (imaging) and indirect (scattering) techniques have been employed to determine the grain
sizes (Hao et al 2010; Jun et al 2006; Kinge et al 2008; Na et al 2009). Transmission electron microscopy (TEM) techniques (especially, the high-resolution TEM studies) are ideal to directly determine the grain sizes of nanocrystalline materials using the dark-field technique. The width of the Bragg reflection in an X-ray (large-angle) diffraction pattern can provide grain (or crystal, i.e., the size of the coherently diffracting domain) size information after the appropriate corrections (for instrumental and strain effects) are incorporated. The TEM techniques can clearly indicate whether there is a distribution of grain sizes and it is also possible to obtain a grain size histogram by measuring the grain sizes and counting the number of grains. On the other hand, the X-ray diffraction technique gives only the average crystal size and this value depends strongly on which function is used when averaging over the size distribution. A number of recent studies discuss the techniques for an accurate measurement of grain sizes and application of X-ray peak shape analysis techniques to nanocrystalline materials (Rehani et al 2006).

1.2.4 Atomic Structure of the Grains and the Grain Boundaries

The structure of the grains (crystallites) in nanocrystalline materials has been normally accepted to be the same as in a coarse-grained material. Consequently, there have not been many investigations into this aspect. High-resolution TEM experiments have indicated that nanocrystalline materials consist of small crystallites of different crystallographic orientations separated by grain boundaries. Even though not frequently reported, the grains contained a variety of crystalline defects such as dislocations, twin boundaries, multiple twins, and stacking faults.

The structure of the grain boundaries has received a lot of attention and has been discussed extensively in the literature, especially to decide
whether it is different in the nanocrystalline and coarse-grained materials of the same composition. The grain boundary structure determines the diffusivity, and consequently the rate of deformation by grain boundary diffusion (Coble creep) and the rates of sintering and grain growth. The conclusions differ and some believe that the structure is fundamentally different in both the types of materials while others believe that it is the same. The present status of the structure of grain boundaries in nanocrystalline materials can be found in some recent review articles (Baier et al. 2011).

Gleiter (1989 & 1995) and others (Suryanarayana and Froes 1992) studied the structure of nanocrystalline materials using a number of techniques and showed that the grain boundaries in nanocrystalline materials may be random, rather than possessing either the short-range or long-range order normally found in conventional coarse-grained materials. This randomness has been associated with either the local structure of individual boundaries or the structure co-ordination among boundaries (Suryanarayana and Froes 1992). It was also noted that the boundaries in the as prepared nanocrystalline Pd are in a state with lower atomic short-range order than conventional grain boundaries in polycrystalline materials. The grain boundary free energy of as prepared nanocrystalline Pd was also computed to be twice that of the relaxed state. EXAFS studies also indicated a much larger reduction in the atomic co-ordination numbers than that detected by X-ray studies, supporting the concept of widely disordered grain boundaries in nanocrystalline materials (Frenkel et al. 2011, Baker et al. 2009).

1.3 CLASSIFICATION OF NANOMATERIALS

All conventional materials like metals, semiconductors, glass, ceramic or polymers can be obtained in principle with a nanoscale dimension. The spectrum of nanomaterials ranges from inorganic or organic, crystalline
or amorphous particles, which can be found as single particles, aggregates, powders or dispersed in a matrix, over colloids, suspensions and emulsions, nanolayers and –films, up to the class of fullerenes and their derivates. Also supramolecular structures such as dendrimers, micelles or liposomes belong to the field of nanomaterials (Koch 2002).

Nanocystalline materials can be classified into different categories depending on the number of dimensions in which the material has nanometer modulations. Thus, they can be classified into (a) layered or lamellar structure, (b) filamentary structure, and (c) equiaxed nanostructured materials. A layered or lamellar structure is one dimensional (1D) nanostructure in which the magnitudes of length and width are much greater than the thickness that is only a few nanometers in size. One can also visualize a two-dimensional (2D) rod-shaped nanostructure that can be termed filamentary and in this the length is substantially larger than width or diameter, which are of nanometer dimensions. The most common of the nanostructures, however, is basically equiaxed (all the three dimensions are of nanometer size) and are termed nanostructured crystallites (three-dimensional [3D] nanostructures) (Cao 2004).

The nanostructured materials may contain crystalline, quasicrystalline, or amorphous phases and can be metals, ceramics, polymers, or composites. If the grains are made up of crystals, the material is called nanocrystalline. On the other hand, if they are made up of quasicrystalline or amorphous (glassy) phases, they are termed nanoquasicrystals and nanoglasses, respectively (Suryanarayana 1995). Gleiter (1995) has further classified the nanostructured materials according to the composition, morphology, and distribution of the nanocrystalline component.
Amongst the above, maximum research work is conducted on the synthesis, consolidation, and characterization of the 3D-nanostructured crystallites followed by the 1D-layered nanostructures. While the former are expected to find applications based on their high strength, improved formability, and a good combination of soft magnetic properties, the latter are targeted for electronic applications. Relatively very few investigations have been carried out on the 2D-filamentary nanostructures.

1.4 PROPERTIES OF NANOMATERIALS

Because of the very fine grain sizes and consequently high density of interfaces, nanocrystalline materials exhibit a variety of properties that are different and often considerably improved in comparison with those of conventional coarse-grained materials. These include increased strength/hardness, enhanced diffusivity, improved ductility/toughness, reduced density, reduced elastic modulus, higher electrical resistivity, increased specific heat, higher coefficient of thermal expansion, lower thermal conductivity, and superior soft magnetic properties. But, it is becoming increasingly clear that the early results on the properties of nanocrystalline materials are not very reliable, mainly due to the significant amount of porosity present in those samples. Thus, for example, the room temperature ductility in ceramic samples has not been reproduced. The properties of nanocrystalline materials are summarized and compared them with those of coarse-grained materials in the following sub headings.

It has been well established that all materials –may be metals, semiconductor, insulators –have size dependent physio-chemical properties below a certain critical size. The critical size depends upon the details of the materials viz. its composition and structure. The physical and chemical properties of nanostructured materials (such as optical absorption and
fluorescence, melting point, catalytic activity, magnetism, electric and thermal conductivity etc.) typically differ significantly from the corresponding coarser bulk material.

1.4.1 Size Effects

The effects of particle size on optical properties are more pronounced in semiconductor nanoparticles. In metals, the Fermi level is in the center of the conduction band where the energy levels are closely spaced, whereas in semiconductors, the band edges control the optoelectronic behavior. If a semiconductor nanoparticle is so small that the particle diameter is of the same magnitude as the wavelength of the electron wave functions, it is known as a Quantum Dot (QD). The electrons in a QD will be spatially “confined” instead of merging together to form a band structure (Park et al 2007).

1.4.2 Structural Properties

There are reasons to believe that the small cluster or nanoparticles are not just the fragments of bulk materials. There can be entirely different structures as well as bonds and bond strengths in nanomaterial. Temperature and pressure also have profound effect on crystal structure. Even though some nanomaterials with slightly large number of atoms (>50-60 atoms) may acquire bulk crystalline structure, it is found that the lattice parameters may not be the same as in the bulk materials. For example it has been shown by rigorous analysis of X-ray Diffraction patterns of ZnS that as small as 1.4 nm particles had liquid like disorder. However, larger nano crystals of ZnS show same sphalerite (cubic) structure as in the bulk. It has been observed that there is a lattice of ~1% for 1.4 nm ZnS nanoparticles. Other small particles also show up to ~2-3% lattice constant deviations compared to
bulk crystalline materials. With increase in temperature the disordered structure of small particle of ZnS were found to transform to wurtzite (Hexagonal structure). Further the chemical capping, often used in the synthesis of nanoparticles, gets removed and particles tend to agglomerate or coalesce forming larger particles. Effect of pressure on structural properties (using X-ray Diffraction) has also been well investigated for some nanoparticles. It has been found that indeed the structural transformations do take place in case of nanoparticles with applied pressure. However the pressures required for this are larger for nanoparticles than for corresponding bulk material and depend upon the particle size, e.g. CdSe nanoparticles. Thus CdSe nanoparticles of 2 to 4 nm size required 4.9 GPa to 3 GPa pressure to transform them from wurtzite to rock salt structure. Bulk CdSe needs just 2.0 GPa for the same transformation. (Sulbha K. Kulkami et al 2005).

1.4.2.1 Grain growth

The experimental observations suggest that grain growth in nanocrystalline materials is very small up to a reasonably high temperature. The kinetics of normal grain growth under isothermal annealing conditions can be represented by the equation (Suryanarayana & Korth 1999),

\[ d^2 - d_0^2 = k t \]  

(1.2)

where,

- \( d \) is the grain size at time \( t \),
- \( d_0 \) is the mean initial grain size (at \( t = 0 \))
- \( K \) is a constant.

The above equation is obeyed only at temperatures close to the melting point.
If \( d \gg d_0 \), the empirical equation becomes

\[
d = K' t^{1/n}
\]  

(1.3)

where,

- \( K' \) is another constant
- \( n \) is the grain growth exponent (values ranging between 2 and 3)

The activation energy for grain growth, \( Q \) can be calculated from the equation,

\[
K' = K'_0 \exp \left( -\frac{Q}{RT} \right)
\]  

(1.4)

where,

- \( K'_0 \) is a pre-exponent constant
- \( R \) is the gas constant.

Grain growth studies were conducted by observing the grain size in the prepared materials and observing its change as a function of temperature, using direct microscopic observations.

1.4.3 Diffusion and Sinterability

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 an enhanced diffusivity in comparison to single crystals or conventional coarse-grained polycrystalline materials with the same chemical composition (Horvath 1989). This enhanced diffusivity can have a significant effect on mechanical properties such as creep and superplasticity, ability to efficiently
dope nanocrystalline materials with impurities at relatively low temperatures, and synthesis of alloy phases in immiscible metals and at temperature much lower than those usually required for coarse-grained materials.

The measured diffusivities in nanocrystalline copper are about 14-20 orders of magnitude higher than lattice diffusion and about 2-4 orders of magnitude larger than grain boundary diffusion. For example, the measured diffusivity at room temperature is $2.4 \times 10^{-20}$ m$^2$/s for 8 nm-grain sized copper samples compared to $4.8 \times 10^{-24}$ m$^2$/s for grain boundary diffusion and $4 \times 10^{-40}$ m$^2$/s for lattice diffusion (Schumacher et al 1989). Similarly enhanced diffusivities were also observed for solute diffusion in other metals. It may be mentioned in this context, that some investigators (Bokstein et al 1995) ascribe this increased diffusivity to the presence of porosity in the consolidated samples. For example, if the presence of porosity is properly taken into account, the diffusivity of nanocrystalline materials has been found to be comparable to that of grain boundary diffusivity. The increased diffusivity (and consequently the reactivity) leads to increased solid solubility limits (the solid solubility of Hg in nanocrystalline Cu has been reported to be 17 at.% against an equilibrium value of <1 at.% ) (Ivanov 1992), formation of intermetallic phases (formation of Pd$_3$Bi at 120°C, a temperature much lower than normally required for coarse-grained materials ) (Siegel & Hahn 1987) and sometimes new phases, and increased sinterability of nanocrystalline powders.

1.4.4 Melting Properties

A variety of nanoparticles like Au, Ag, CdS etc, have been investigated for their thermal stability and melting. Melting begins at the surface. As the particle size decreases, surface to bulk atoms ratio increases dramatically. In small particles or clusters the central atom may be considered
as surrounded by first, second, third ... compact shells of atoms. Number of atoms in shells is given as $10n^2 + 2$. Thus, first shell would have 12 atoms; second shell would have 42 atoms and so on. It can be easily seen that number of surface atoms is quite large in nanoparticles and surface to bulk atoms ratio goes on increasing with decreasing particle size (or shells). Large surface is related to large surface energy. This energy can be lowered by melting (there can be some exceptions also). Melting temperature of gold nanoparticles of 3-4 nm size is reduced by ~500 °C compared to bulk melting point. Melting of nanoparticles is usually determined either by X-ray diffraction or electron diffraction. Heating increases the lattice parameter and at melting long range order is lost (Sulbha K. Kulkami 2006).

1.4.5 Chemical Properties

The change in structure as a function of particle size is intrinsically linked to the changes in electronic properties. The ionization potential (the energy required to remove an electron) is generally higher for small atomic clusters than for the corresponding bulk material. Furthermore, the ionization potential exhibits marked fluctuations as a function of cluster size. Such effects appear to be linked to chemical reactivity, such as the reaction of $(\text{Fe})_n$ clusters with hydrogen gas.

Nanoscale structures such as nanoparticles and nanolayers have very high surface area to volume ratios and potentially different crystallographic structures which may lead to a radical alteration in chemical reactivity. Catalysis using finely divided nanoscale systems can increase the rate, selectivity and efficiency of chemical reactions such as combustion or synthesis whilst simultaneously significantly reducing waste and pollution. Gold nanoparticles below 5 nm in diameter are known to adopt octahedral structures rather than the normal face centered cubic arrangement. This
structural change is accompanied by an extraordinary increase in catalytic activity. Furthermore, nanoscale catalytic supports with controlled pore sizes can select the products and reactants of chemical reactions based on their physical size and thus case of transport to and from internal reaction sites within the nonporous structure. Additionally, nanoparticles often exhibit new chemistries as distinct from their larger particulate counterparts; for example, many new medicines are insoluble in water when in the form of micron-sized particles but will dissolve easily when in a nanostructured form (Robert Kel Sall et al 2005).

Due to their enhanced chemical activity, nanostructural materials can be used as catalysts to react with such noxious and toxic gases as carbon monoxide and nitrogen oxide in automobile catalytic converters and power generation equipment to prevent environmental pollution arising from burning gasoline and coal. Fuel cell technology is another important application of the noble metal nanoparticles relating the catalysis of the reactions. In the present, the fuel cell catalysts are based on platinum group metals (PGM). Pt and Pt-Ru alloys are some of the most frequently used catalysts from this group. In fact, the use of these metals is one major factor for cell costs, which has been one of the major drawbacks preventing it from growing into a more important technology. One possibility to produce economical catalysts is the use of bimetallic nanoparticles (Migual Jose-Yacaman, 2009)

1.4.6 Optical Properties

Nanocrystalline systems have attracted much interest for their novel optical properties, which differ remarkably from bulk crystals. Key contributory factors include quantum confinement of electrical carriers within nanoparticles, efficient energy and charge transfer over nanoscale distances and in many systems a highly enhanced role of interfaces. With the growing
technology of these materials, it is increasingly necessary to understand the detailed basis for nanophotonic properties. The linear and nonlinear optical properties of such materials can be finely tailored by controlling the crystal dimensions, and the chemistry of their surfaces; fabrication technology becomes a key factor for the applications. Surface Plasmons (SP) are the origin of the color of nanomaterials. An SP is a natural oscillation of the electron gas inside a given nanosphere. If the sphere is small compared to a wavelength of light, and the light has a frequency close to that of the SP, then the SP will absorb energy.

The frequency of the SP depends on the dielectric function of the nanomaterial, and the shape of the nanoparticle. For a gold spherical particle, the frequency is about 0.58 of the bulk plasma frequency. Thus, although the bulk plasma frequency is in the UV, the SP frequency is in the visible (close to 520 nm). In small nanoclusters the effect of reduced dimensionality on electronic structure has the most profound effect on the energies of the highest occupied molecular orbital (HOMO), essentially the valence band, and the lowest unoccupied molecular orbital (LUMO), essentially the conduction band. Optical emission and absorption depend on transitions between these states; semiconductors and metals, in particular, show large changes in optical properties, such as colour, as a function of particle size.

Colloidal solutions of gold nanoparticles have a deep red colour which becomes progressively more yellow as the particle size increases; indeed gold colloids have been used as a pigment for stained glass since the seventeenth century. Semiconductor nanocrystals in the form of quantum dots show similar size-dependent behaviour in the frequency and intensity of light emission as well as modified non-linear optical properties and enhanced gain for certain emission energies or wavelengths. Other properties which may be affected by reduced dimensionality include photo catalysis,
photoconductivity, photoemissions and electroluminescence. Suppose we have a suspension of nanoparticles in a host. If a wave of light is applied, the local electric field may be hugely enhanced near an SP resonance. If so, one expects various nonlinear susceptibilities, which depend on higher powers of the electric field, to be enhanced even more (Migual Jose Jacuman, 2009).

Glues containing nanoparticles have optical properties that give rise to uses in optoelectronics. Casings, containing nanoparticles used in electronic devices, such as computers, offer improved shielding against electromagnetic interference. Electro chromic devices are similar to liquid-crystal displays (LCD), are been developed with nanomaterials. The incorporation of nanomaterials in surface coatings can provide long-term abrasion resistance without significantly effecting optical clarity, gloss, color or physical properties (Migual Jose Jacuman, 2009).

1.4.6.1 Optical absorption: band gap

The optical properties of nanocrystalline materials have been found to be exciting from both the scientific and technology point of view. The simplest experiment to determine the size dependence in semiconductor nanoparticles is to study absorption spectrum of the material as a function of wavelength of incident photons. When photons are incident on semiconductor material they will be absorbed only when the minimum energy of photons is enough to excite an electron from the valence band to conduction band, i.e. when the photon energy equals the energy gap of the semiconductor. If lower energy photons are incident there cannot be any absorption. Therefore there is a sudden rise in absorption when photon energy is same as energy gap. This is the onset of absorption. If the energy gap increases there should be a shift in the onset of absorption towards shorter wavelength. As shown in Figure 1.2 one expects a ‘blue shift’ with absorption in smaller and smaller clusters,
which is indicative of increasing energy gap. For very small clusters one uses the terminology borrowed from chemistry viz. Highest occupied Molecular orbital (HOMO) and lowest unoccupied Molecular orbital (LUMO) instead of top of valence band and bottom of conduction band in case of extended solid.

This change in absorption would have an interesting effect on the originally coloured materials. It is known now from literature that Cd$_3$P$_2$ is a dark brown semiconductor with energy gap of approximately 0.5 eV. When its clusters are made, it progressively passes through a series of colours like brown, red, yellow and white with particle size changing from ~30 Å to ~15 Å. For ~15 Å particles the band gap increases to 4eV.

Figure 1.2 Optical absorption spectra for nanoparticles of different sizes
The same is true for ZnS. The bulk semiconductor with energy gap of 3.5eV is white in colour. As the clusters become smaller and energy gap increases it becomes yellowish. It is quite easy to show by chemical analysis techniques that this white material is ZnS and nothing else. Observation of different colours due to ZnSe in glass matrix led scientists to think that ZnSe nanoparticles of different sizes may have been formed.

The band gap of semiconductors and the optical transparency behavior of materials could be changed by controlling the grain and/or pore size in the nanocrystalline state for small particle sizes. For example, the band gap of CdSe semiconductor could be changed from 3.0 eV for clusters of 1.2-1.5 nm to 2.3 eV for cluster sizes of 3.0-3.5 nm due to quantum confinement effects; the bulk material has a band gap of 1.8 eV (Steigerwald & Brus 1989). By controlling the pore size in nanocrystalline Y$_2$O$_3$ to be equivalent to the wavelength of light, scattering could be affected and so the material becomes opaque. On the other hand, when the pore size is much smaller than the wavelength of light, scattering did not take place and so the material was fairly transparent (Skandan et al 1991). The optical absorption characteristics can also be modified by allowing interaction to occur between the nanosized CdS clusters (Stucky & MacDougall 1990). The band gap becomes a function of the grain zone showing a ‘Blue shift’ with decrease in particle size.

1.4.7 Luminescence Properties

Luminescence may be defined as emission of light from certain substance, when excited with radiations like X-ray/UV/electrons and mechanical stress/chemical reaction/electric discharge/thermal heating etc. The emitted radiation from a luminescent material is free from heating effect and hence is also called as ‘cold emission’. Different types of luminescence
with mechanisms involved are given in Table 1.1. Manganese is a particularly effective activator in a wide variety of host lattices, when incorporated in amounts ranging from a small trace up to an order of several percent. The emission spectrum of manganese activated phosphors lies in green, yellow or orange spectral regions. Most of the host materials are silicates, phosphates, sulphides, alkali halides and oxides of Ca, Mn, Zn, Ba etc.

Photoluminescence occurs when a system is excited to a higher energy level by absorbing a photon, and then spontaneously decays to a lower energy level, emitting a photon in the process. To conserve energy, the emitted photon cannot have more energy than the exciting photon, unless two or more excitation photons act in tandem. Intermediate nonradiative downward transitions are also possible. The electron can also be stored in an intermediate state for a long time, resulting in delayed luminescence.

Photoluminescence is divided into two types, depending upon the nature of the ground and the excited states. In a singlet excited state, the electron in the higher-energy orbital has the opposite spin orientation as the second electron in the lower orbital. These two electrons are said to be paired. In a triplet state these electrons are unpaired, that is, their spins have the same orientation. Return to the ground state from an excited singlet state does not require an electron to change its spin orientation. A change of spin orientation is needed for a triplet state to return to the singlet ground state (Figure 1.3). 

Fluorescence is the emission which results from the return to the lower orbital of the paired electron. Such transitions are quantum mechanically, “allowed” and the emissive rates are typically near $10^8 \text{s}^{-1}$. These high emissive rates result in fluorescence lifetimes near $10^{-8} \text{s}$ or 10 ns. The lifetime is the average period of time a fluorophore remains in the excited state. Phosphorescence is the emission which results from transition between states of different multiplicity, generally a triplet excited state returning to a
singlet ground state. Such transitions are not allowed and the emissive rates are slow. Typical phosphorescent lifetimes range from milliseconds to seconds, depending primarily upon the importance of deactivation processes other than emission.

![Diagram of singlet and triplet states](image)

**Figure 1.3 Fluorescence and phosphorescence mechanism**

**Table 1.1 Various types of Luminescence Mechanisms**

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<thead>
<tr>
<th></th>
<th>Description</th>
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<tbody>
<tr>
<td>a)</td>
<td>Bio-luminescence: Emission of light by living animals and plants</td>
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<tr>
<td>b)</td>
<td>Cathdo-luminescence: Emission of light after bombardment of electrons</td>
</tr>
<tr>
<td>c)</td>
<td>Cando-luminescence: Emission of light by mixed oxides in a gas or hydrogen flame</td>
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<tr>
<td>d)</td>
<td>Chemi-luminescence: Luminescence occurring during the course of a chemical reaction and consecutive to the absorption of energy by the molecules</td>
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</table>
1.4.8 Electronic Properties

The changes which occur in electronic properties as the system length scale is reduced are related mainly to the increasing influence of the wave-like property of the electrons (quantum mechanical effects) and the scarcity of scattering centres. As the size of the system becomes comparable with the de Broglie wavelength of the electrons, the discrete nature of the energy states becomes apparent once again, although a fully discrete energy spectrum is only observed in systems that are confined in all three dimensions. In certain cases, conducting materials become insulators below a critical length scale, as the energy bands cease to overlap. Owing to their intrinsic wave-like nature, electrons can tunnel quantum mechanically between two closely adjacent nanostructures, and if a voltage is applied between two nanostructures which aligns the discrete energy levels in the DOS, resonant tunneling occurs, which abruptly increases the tunneling current.

In macroscopic systems, electronic transport is determined primarily by scattering with phonons, impurities or other carriers or by scattering at rough interfaces. The path of each electron resembles a random walk, and transport is said to be diffusive. When the system dimensions are smaller than the electron mean free path for inelastic scattering, electrons can travel through the system without randomization of the phase of their wave functions. This gives rise to additional localization phenomena which are specifically related to phase interference. If the system is sufficiently small so that all scattering centres can be eliminated completely, and if the sample boundaries are smooth so that boundary reflections are purely specular, then electron transport becomes purely ballistic, with the sample acting as a waveguide for the electron wave function.
Conduction in highly confined structures, such as quantum dots, is very sensitive to the presence of other charge carriers and hence the charge state of the dot. These Coulomb blockade effects result in conduction processes involving single electrons and as a result they require only a small amount of energy to operate a switch, transistor or memory element. All these phenomena can be utilized to produce radically different types of components for electronic, optoelectronic and information processing applications, such as resonant tunneling transistors and single-electron transistors (Cao 2004).

1.4.9 Mechanical Properties

The strength and hardness of the nanocrystalline materials are 4-5 times greater, when compared to the coarse grained material and the elastic constant of these materials have been found to be reduced by 30% or less. The various results on the variation of hardness with grain size reveal a fact that at very small grain sizes, the hardness also decreases with a decrease in grain size. The critical grain size at which this reversal takes place is dependent on the material.

Many mechanical properties, such as toughness, are highly dependent on the ease of formation or the presence of defects within a material. As the system size decreases, the ability to support such defects becomes increasingly more difficult and mechanical properties will be altered accordingly. Novel nanostructures, which are very different from bulk structures in terms of the atomic structural arrangement, will obviously show very different mechanical properties. For example, single- and multi-walled carbon nanotubes show high mechanical strengths and high elastic limits that lead to considerable mechanical flexibility and reversible deformation.
As the structural scale reduces to the nanometer range, for example, in nanolayered composites different scale dependence from the usual Hall-Petch relationship for yield strength often becomes apparent with large increases in strength reported. In addition, the high interface to volume ratio of consolidated nanostructured materials appears to enhance interface-driven processes such as plasticity, ductility and strain to failure. Many nanostructured metals and ceramics are observed to be super plastic, in that they are able to undergo extensive deformation without necking or fracture. This is presumed to arise from grain boundary diffusion and sliding, which becomes increasingly significant in a fine-grained material. Overall these effects extend the current strength-ductility limit of conventional materials, where usually a gain in strength is offset by a corresponding loss in ductility (Miguel Jose Jacuman, 2009).

1.4.10 Magnetic Properties

The extrinsic magnetic properties of particles depend strongly upon their shape and size. Among the magnetic properties, $H_c$ shows a remarkable size effect and saturation magnetization is independent of the particle size (Bhargava & Gallagher 1994). When the particle size is reduced in ferromagnetic and ferroelectric materials to sizes of the order of microns, the particles become single domains. As the particle size reduced further, the materials become superparamagnetic or super ferroelectric respectively, at temperature below Curie point. At these conditions they do not exhibit any hysteresis effects and they retain very high permeability and lose their magnetism or polarization when the external field is removed. The superparamagnetic nanoparticles can be used for separation processes in biochemistry. The potential applications of nanoscale magnetic particles are in colour imaging, ferro fluids and magnetic refrigeration. Co, Fe, Ni metals
are used for this purpose since they are easy to synthesis and cost effective (Chen & Zhang 1998).

Magnetic nanoparticles are used in a range of applications, including Ferro fluids, colour imaging, bioprocessing, refrigeration as well as high storage density magnetic memory media. The large surface area to volume ratio results in a substantial proportion of atoms (those at the surface which have a different local environment) having a different magnetic coupling with neighbouring atoms, leading to differing magnetic properties. While bulk ferromagnetic materials usually form multiple magnetic domains, small magnetic nanoparticles often consists of only one domain and exhibit a phenomenon known as superparamagnetism. In this case the overall magnetic coercivity is then lowered: the magnetizations of the various particles are randomly distributed due to thermal fluctuations and only become aligned in the presence of an applied magnetic field.

Giant magneto resistance (GMR) is a phenomenon observed in nanoscale multi-layers consisting of a strong Ferro magnet (for e.g., Fe, Co) and a weaker magnetic or non-magnetic buffer (for e.g., Cr, Cu), it is usually employed in data storage and sensing. In the absence of a magnetic field, the spins un-alternating layers are oppositely aligned through anti-ferromagnetic coupling, which gives maximum scattering from the interlayer interface and hence a high resistance parallel to the layers. In an oriented external magnetic field the spins align with each other and this decreases scattering at the interface and hence resistance of the device (Migual Jose Jacuman, 2009).

1.4.11 Thermal Properties

Since nanocrystalline materials contain a large amount of interfacial volume, the coefficient of thermal expansion (CTE) is expected to
be higher than in a coarse-grained material. Accordingly, measured values of CTE of nanocrystalline Cu, Pd, Fe-B-Si and Ni-P alloys were almost twice the value for single crystals (Suryanarayana 1995). For example, CTE for nanocrystalline (8 nm) Cu obtained by the inert gas condensation technique has been reported to be $31 \times 10^{-6}$ K$^{-1}$ in comparison with $16 \times 10^{-6}$ K$^{-1}$ for copper single crystals.

A comparison of the specific heats of different nanocrystalline, coarse-grained polycrystalline, and amorphous materials suggest that, at room temperature, the specific heat in the nanocrystalline state is much higher than that in the coarse-grained material and even that of the amorphous material (Nawrocki et al 1981). While most of the investigators reported a nonlinear (parabolic) variation of specific heat with temperature, some people (Hellstern et al 1989) have reported a linear variation. It has also been noted that the specific heat increase at a constant temperature was linear with the reciprocal crystal size.

The recent advances of nanotechnologies in the past decades have resulted in the burst of promising synthesis, processing and characterization technologies, which enables the routine production of a variety of nanomaterials with highly controlled structures and related properties. By controlling the structures of nanomaterials at nano scale dimensions, the properties of the nanostructures can be controlled and tailored in a very predictable manner to meet the needs for a variety of applications. Examples of the engineered nanostructures include metallic and non-metallic nanoparticles, nanotubes, quantum dots and super lattices, thin films, nano composites and nano electronic and optoelectronic devices which utilize the superior properties of the nanomaterials to fulfill the applications.
Many properties of the nanoscale materials have been well studied, including the optical electrical, magnetic and mechanical properties. However, the thermal properties of nanomaterials have only seen slower progresses. This is partially due to the difficulties of experimentally measuring and controlling the thermal transport in nano scale dimensions. Atomic force microscope (AFM) has been introduced to measure the thermal transport of nanostructures with nanometer-scale high spatial resolution, providing a promising way to probe the thermal properties with nanostructures. Moreover, the theoretical simulations and analysis of thermal transport in nanostructures are still in infancy. Available approaches including numerical solutions of Fourier’s law, computational calculation based on Boltzmann transport equation and Molecular-dynamics (MD) simulation, all have their limitations. More importantly, as the dimensions go down into nanoscale, the availability of the definition of temperature is in question.

In non-metallic material system, the thermal energy is mainly carried by phonons, which have a wide variation in frequency and the Mean Free Paths (MFP). The heat carrying photons often have large wave vectors and MFP in the order of nanometer range at room temperature, so that the dimensions of the nanostructures are comparable to the MFP and wavelengths of photons. However the general definition of temperature is based on the average energy of a material system in equilibrium.

For macroscopic systems, the dimension is large enough to define a local temperature in each region within the materials and this local temperature will vary from region to region, so that one can study the thermal transport properties of the materials based on certain temperature distributions of the materials. But for nanomaterial systems, the dimensions may be too small to define a local temperature. Moreover, it is also problematic to use the
concept of temperature which is defined in equilibrium conditions, for the non-equilibrium processes of thermal transport in nanomaterials, posing difficulties for theoretical analysis of thermal transport in nanoscales.

In spite of all the difficulties in both experimental and theoretical characterization the thermal properties of nanomaterials. Recent advances in experiments have showed that certain nanomaterials have extraordinarily thermal properties compared to their macroscopic counterparts, as will be explained in detail in this section. In nanomaterials systems, several factors such as the small size, the special shape, the large interfaces modified the thermal properties of the nanomaterials, rendering them the quite different behaviour as compared to the macroscopic materials. As mentioned above, as the dimension goes down to nanoscales, the size of the nanomaterials is comparable to the wavelength and the mean free path of the photons, so that the photon transport within the materials will be changed significantly due the photon confinement and quantization of photon transport, resulting in modified thermal properties.

For example, nanowires from silicon have a much smaller thermal conductivities compared to bulk silicon. The special structure of nanomaterials also affects the thermal properties. For example, because of it tubular structures of carbon nanotubes, they have extreme high thermal conductivity in axial directions, leaving high anisotropy in the heat transport in the materials. The in interfaces are also very important factor for determine the thermal properties of nanomaterials.

Generally, the internal interfaces impede the flow of heat due to photon scattering. At interface or grain boundary between similar materials, the interface disorder scatters phonons, while as the differences in elastic properties and densities of vibrational states affect the transfer of vibrational
energy across interfaces between dissimilar materials. As a result, the nanomaterials structures with high interfaces densities would reduce the thermal conductivity of the materials. These interconnected factors joined together to determine the special thermal properties of the nanomaterials (Hellstern et al. 1989).

1.5 APPLICATIONS

With nanotechnology, a large set of materials and improved products rely on a change in the physical properties when the feature sizes are shrunk. Nanoparticles for example take advantage of their dramatically increased surface area to volume ratio. Their optical properties, e.g. fluorescence, become a function of the particle diameter. When brought into a bulk material, nanoparticles can strongly influence the mechanical properties of the material, like stiffness or elasticity. For example, traditional polymers can be reinforced by nanoparticles resulting in novel materials which can be used as lightweight replacements for metals. Therefore, an increasing societal benefit of such nanoparticles can be expected. Such nanotechnologically enhanced materials will enable a weight reduction accompanied by an increase in stability and an improved functionality (Knauth & Schoonman 2004). There are many applications of nanotechnology; few of them are shown here.

1.5.1 Medicine

The biological and medical research communities have exploited the unique properties of nanomaterials for various applications (e.g., contrast agents for cell imaging and therapeutics for treating cancer). Terms such as biomedical nanotechnology, bionanotechnology, and nanomedicine are used to describe this hybrid field. Functionalities can be added to nanomaterials by
interfacing them with biological molecules or structures. The size of nanomaterials is similar to that of most biological molecules and structures; therefore, nanomaterials can be useful for both in vivo and in vitro biomedical research and applications. Thus far, the integration of nanomaterials with biology has led to the development of diagnostic devices, contrast agents, analytical tools, physical therapy applications, and drug delivery vehicles.

1.5.2 Memory Storage

Electronic memory designs in the past have largely relied on the formation of transistors. However, researches into crossbar switch based electronics have offered an alternative using reconfigurable interconnections between vertical and horizontal wiring arrays to create ultra-high density memories.

1.5.3 Displays

The production of displays with low energy consumption could be accomplished using carbon nanotubes (CNT). Carbon nanotubes are electrically conductive and due to their small diameter of several nanometers, they can be used as field emitters with extremely high efficiency for field emission displays (FED). The principle of operation resembles that of the cathode ray tube, but on a much smaller length scale.

1.5.4 Quantum Computers

Entirely new approaches for computing exploit the laws of quantum mechanics for novel quantum computers, which enable the use of fast quantum algorithms. The Quantum computer has quantum bit memory space
termed "Qubit" for several computations at the same time. This facility may improve the performance of the older systems.

1.5.5 Aerospace

Lighter and stronger materials will be of immense use to aircraft manufacturers, leading to increased performance. Spacecraft will also benefit, where weight is a major factor. Nanotechnology would help to reduce the size of equipment and thereby decrease fuel-consumption required to get it airborne. Hang may be able to halve their weight while increasing their strength and toughness through the use of nanotech materials. Nanotech is lowering the mass of supercapacitors that will increasingly be used to give power to assistive electrical motors for launching hang gliders off flatland to thermal-chasing altitudes.

1.5.6 Optics

The first sunglasses using protective and anti-reflective ultra-thin polymer coatings are on the market. For optics, nanotechnology also offers scratch resistant surface coatings based on nanocomposites. Nano-optics could allow for an increase in precision of pupil repair and other types of laser eye surgery.

1.6 SYNTHESIS OF NANOMATERIALS

Producing nanomaterials of consistent quality and composition is an important criterion for industrial applications. The primary requirement is the synthesis of powders and the other requirements are fabrication of green bodies and sintering of the same to achieve proper densification. It is also well known that chemically homogeneous single-phase powder with well-defined
particle size distribution as the starting material is necessary to achieve the desired properties in the densified bodies. Many methods are available for the preparation of nanoscale materials and it can be divided into two basic types such as mechanical and chemical methods (Knauth & Schoonman 2004).

1.6.1 Mechanical Methods

Mechanical methods involve the use of mechanical forces such as compressive forces, shear or impact to effect particle size reduction in bulk materials. In this method, fine particles are produced from larger ones by mechanical comminution. Comminution is achieved by crushing, grinding and milling. Powders of conventional ceramics are mainly prepared from naturally occurring raw materials by these methods.

Mechanical size reduction is a cheap method and can be used for a wide variety of materials and is suitable for bulk production (Angelo and Subramanian 2008). The most common method for reducing particle size is ball milling. A ball mill is a barrel (usually made of ceramic) that rotates on its axis and is partially filled with a grinding medium in the form of spheres, cylinders, or rods. There are many mechanical methods that can be used to achieve comminution. The possible particle size range for each is compared in Table 1.2 (Barry Corter & Grant Norton 2007).
Table 1.2 Possible particle sizes for different milling techniques

<table>
<thead>
<tr>
<th>Milling Technique</th>
<th>Particle Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jaw Crushers</td>
<td>upto 5 mm</td>
</tr>
<tr>
<td>Cone Crushers</td>
<td>upto 5 mm</td>
</tr>
<tr>
<td>Crushing Rolls</td>
<td>upto ~1 mm</td>
</tr>
<tr>
<td>Hammer mill</td>
<td>upto ~0.1 mm</td>
</tr>
<tr>
<td>Jet mill</td>
<td>1 to ~50 μm</td>
</tr>
<tr>
<td>Vibratory Mill</td>
<td>1 to ~50 μm</td>
</tr>
<tr>
<td>Ball Mill</td>
<td>0.5–10 μm</td>
</tr>
<tr>
<td>Attrition Mill</td>
<td>0.1–5 μm</td>
</tr>
<tr>
<td>Roller Mill</td>
<td>0.1–5 μm</td>
</tr>
</tbody>
</table>

1.6.2 High-Energy Ball Milling Processes

Ball milling has been utilized in various industries to perform size reduction for a long time. Recently, materials with novel microstructures and properties have been synthesized successfully via high-energy ball milling processes (Suryanarayana 2001). Although different terms have been used to describe the high-energy ball milling processes, three terms are generally used to distinguish powder particle behavior during milling: mechanical alloying (MA), mechanical milling (MM), and mechanochemical synthesis (MS). Mechanical alloying is referred to when mixtures of powders are milled together. In this case, materials transfer is involved to obtain a homogeneous alloy. Mechanical milling describes a milling process when no material transfer is involved; that is, only powder with uniform composition is milled. Mechanochemical synthesis, on the other hand, is a special MA process where chemical reactions between the powders take place during milling. The
unique feature of MS process is that grain refinement and chemical reactions take place at low temperatures under far-from-equilibrium conditions.

1.6.3 Chemical Methods

Chemical methods make use of chemical reactions to produce ceramic powders directly from their compounds (e.g. oxides) at the temperatures well below the melting point of the materials concerned. Chemical reactions offer attractive means of producing ceramic powders having a wide range of characteristics like purity, size and shape. The thermodynamics and kinetic aspects of the process are very important in chemical methods. Powders can be produced from solid, liquid or gaseous state from a variety of starting materials. These reactions are based on reduction of oxide, precipitation from the solution or from a salt and thermal decomposition of compounds. Chemical methods used for the production of ceramics fall under the categories such as solid state reaction, precipitation from solution and vapour phase reactions (Knauth & Schoonman 2004).

Chemical methods are most widely used in the production of advanced ceramic materials. The techniques such as solid state reaction, sol-gel process and co-precipitation are fall under the category of chemical methods of preparation of ceramic compounds. Some of the important techniques involved in the preparation of ceramic compounds with desired composition are given below.

1.6.4 Solid State Reaction

Chemical decomposition, also known as calcination, is a simple process in which a solid chemical (reactant) is heated to produce a product, also in solid form and gaseous bye-products. The starting materials employed
are usually compounds such as carbonates, hydroxides, nitrates, oxalates, alkoxides and other metallic salts. A typical example is the calcination of magnesium carbonate to produce fine magnesia and carbon dioxide gas. The final product requires crushing. Solid state reaction is also used for the production of complex oxides such as cuprates, ferrites, manganites and titanates by the reaction between two or more precursors in the solid state condition (Cao 2004). Factors such as type of reactant (carbonate or alkoxides), the initial size of the reactant particles as well as processing temperatures and time affect the final powder characteristics. This method has the advantages of low cost, simple as well as inexpensive and the ability to process complex oxides. The limitations are the formation of agglomerates requiring crushing, causing contamination and chemical inhomogeneity.

1.6.5 Aqueous Solution Synthesis

Aqueous solution synthesis is widely used for the preparation of oxide nanostructures and ceramic materials at low temperature. This method consists of heating an aqueous solution of metal salts or complexes at moderated temperatures below 100°C (Wahab et al 2007). Therefore, such technique does not require high-pressure containers and is also entirely recyclable, safe and environment friendly because only water is used as a solvent. Such a process avoids the safety hazards or organic solvents and their eventual evaporation and potential toxicity.

The morphology of the resulting nanostructures can be tuned by changing parameters such as temperature, precursor concentrations and pH. More importantly, doping during the aqueous chemical growth is very simple and typically involves mixing the precursors in an appropriate ratio. In addition because no organic solvents or surfactants are present, the purity of the materials is substantially improved. The residual salts are easily washed
out by water due to their high solubility. In most cases no additional heat or chemical treatment is necessary, which represents a significant improvement compared with surfactant-, template-, or membrane based synthesis methods. Until recently, there has been a great interest to synthesize and develop rare earth doped nanostructures from the chemical methods, given that direct chemical approaches are generally compatible with large-scale production, and the resulting colloidal suspensions are ready for application in self-assembly strategies that have become a mainstay of nanotechnology.

Compared to vapor phase synthesis, solution phase growth requires much lower temperature, resulting a lower synthesis cost. Due to the vast availability of solvents and solutes, solution phase synthesis can be carefully designed to carry out the synthesis of materials from elements such as gold and platinum, to binary compound such as TiO$_2$ (Tian et al 2003), ZnO (Cheng et al 2006), and CdTe to complicated compounds such as barium titanate (BaTiO$_3$) and magnesium hydroxide sulfate hydrate. On the other hand, vapor phase synthesis is quite limited to simple materials such as metal elements or metal binary compounds. A series of morphologies have been successfully synthesized with this approach. A number of solution phase syntheses have been developed to synthesize nanomaterials, including co-precipitation, micro-emulsion, hydrothermal, and template-assisted synthesis. Due to the complexity and non-ideality of the reaction conditions, the mechanism of nanostructure growth is less understood.

1.6.6 Co-precipitation

In solution-drying method the segregation of metal ions occurs during the drying and decomposition process which leads to inhomogeneity and this is a major problem. This problem could be solved by simultaneous precipitation of the metal compounds at the same rate, followed by
calcinations of the metal compounds at elevated temperatures. This method is known as the co-precipitation process and it has extensively used for the precipitation of a large number of ceramic powders (Kishio et al 1989; Iademoto et al 2009). The co-precipitation process involves precipitation of the cations from solution, either in the form of simple compound or in the form of complex compound, in such a fashion that all the cations are precipitated at the same time and at the appropriate rates (Walton 1979, Nielsen 1964).

In this process, larger quantity of a soluble component (for example, a metal salt) can be dissolved in a solution at high temperature than at a lower temperature. At supersaturation large number of nuclei forms suddenly. Their formation lowers the solution concentration below the concentration at which nucleation occurs, but enough excess solute remains for the existing nuclei to grow. If the solution is kept uniform, growth of all the particles proceeds at the same rate, producing powders with extremely uniform size distribution. The variation of solute concentration with time during the nucleation and growth of particles from solution is shown in Figure 1.4. This diagram is often referred as LaMer diagram after the work of LaMer and Barnes (Destrée and Nagy 2006).

![LaMer Diagram](image-url)
The above figure relates the variation of concentration with time during a precipitation reaction and is based on the principle that the nucleation is the limiting step in the precipitation reaction. In the first step, the concentration increases continuously with increasing time. As the concentration reaches the critical supersaturation value, nucleation occurs. This leads to a decrease of the concentration. Between the concentrations $C_{\text{max}}^*$ and $C_{\text{min}}^*$ the nucleation occurs. Later, the decrease of the concentration is due to the growth of the particles by diffusion. This growth occurs until the concentration reaches the solubility value (Walton 1979, Nielsen 1964).

A true co-precipitation process is distinct from successive precipitation, permits almost molecular level mixing of the constituent cations. With proper monitoring of the pH and temperature of the precipitating medium, the solubility of the precipitate can be controlled to yield good quality powder. This process can be scaled up for the production of large quantities of ceramic powder.

Co-precipitation is a process involving a series of steps that include nucleation, growth, and coarsening. Due to the complexity of these steps, a fundamental understanding of coprecipitation is not yet available. However, the process is described in the following brief overview: 1) Desired products are generally sparingly soluble in a certain solvent. 2) Supersaturation is a deterministic factor in the growth of the products. 3) High supersaturation leads to nucleation to form a large number of clusters or nuclei. 4) The clusters grow into crystals as ions or molecules are supplied to the crystals. 5) Secondary growth processes such as Ostwald ripening or aggregation can dramatically affect the size and morphology of the final product.
Various nanoparticles such as elemental metal and metal oxide have been synthesized with the coprecipitation method. For example, different-sized silver nanoparticles can be synthesized by reducing the silver nitrate with different agents. Particles 3-5 nm and those 15-26 nm in diameter can be obtained if sodium borohydride and ascorbic acid, respectively, are the reducing agents. Co-precipitation can be achieved in a nonaqueous medium. It has been reported that gold nanoparticles were synthesized from reducing chloroauric acid (HAuCl$_4$) using formamide as a reducing agent and the poly(vinylpyrrolidone) (PVP) as a stabilizer. The reaction can take place at room temperature. It is believed that the nonaqueous solvent can reduce the aggregation and control the size of the final product.

1.6.7 Sol–Gel Process

The sol-gel process, as the name implies, involves the evolution of inorganic networks through the formation of a colloidal suspension (sol) and gelation of the sol to form a network in a continuous liquid phase (gel). The precursors for synthesizing these colloids consist of a metal/metalloid surrounded by various reactive ligands. Metal alkoxides are most popular because they react readily with water. At the functional group level, three reactions are generally used to describe the sol-gel process: hydrolysis, alcohol condensation, and water condensation. However, the characteristics and properties of a particular sol-gel inorganic network are related to a number of factors that affect the rate of hydrolysis and condensation reactions, such as pH, temperature and time of reaction, reagent concentrations, catalyst nature and concentration, aging temperature and time, and drying.

Sol-gel method is a versatile method useful for preparing metal oxides. Stoichiometrical homogeneous control of the doping is easily
achieved, since liquid precursors are used, it is possible to cast the glass and ceramics in a range of shapes, such as thin film, fibers, and monoliths, etc, without the need for machining or melting. The precursors such as metal alkoxides, with very high purity make it easy to fabricate materials with high quality and cost effective and the temperature required in the process is low and no delicate vacuum system is needed. Despite its advantages, sol-gel method still has some limitation. Sol-gel technique is not widely used in industries due to weak bonding, low wear-resistance, high permeability and difficulty in controlling the porosity. Figure 1.5 shows the flow chart of the materials derived from sol-gel method.

In sol–gel processing, a reactive metal precursor such as metal alkoxide is hydrolyzed with water and the hydrolyzed species are allowed to condense with each other to form nanoparticles (Livage 1988). The hydrolysis of metal alkoxides involves nucleophilic reaction with water, which is as follows (Pierre 1991, Brinker & Sherrer 1999)

\[
M(OR)_y + xH_2O \rightarrow M(OR)_{y-x}(OH) + xROH
\]  

(1.4)

where, \( M(OR)_y \rightarrow \) Metal alkoxides

\( M \rightarrow \) Metals like Si, Ti, Cu etc.,

\( R \rightarrow \) Alkyl group (R=CH\(_3\), C\(_2\)H\(_5\) etc.,)
Figure 1.5  Flow chart of materials derived from sol-gel process

Condensation occurs when either hydrolyzed species react with each other and release a water molecule, or a hydrolyzed species reacts with an un–hydrolyzed species and releases an alcohol molecule. The rates at which hydrolysis and condensation reactions take place are important parameters that affect the properties of the final product (Hutlova et al 2003). Typically, slower and more controlled hydrolysis process leads to smaller nanoparticles. The following are some of the advantages of sol–gel process:

- Sol–gel method is the easiest and feasible way of producing novel nanocrystalline materials in an efficient and cost effective manner.
- Constrained growth of materials and homogeneity is possible
- Any combination of materials can be prepared at low processing temperatures.
The introduction of metal alkoxide precursors for sol–gel synthesis made possible for the preparation of high purity nanocrystals.

Sol–gel process has some of the disadvantages and it is listed below:

- The starting materials are very expensive.
- The removal of solvent and organic by–products from gel is relatively difficult.
- The volume shrinkage upon sol–gel transition is large. To overcome these advantages many attempts have been carried out by changing the materials and/or procedure.

1.6.8 Microemulsion

Micelles are aggregates of dispersed surfactants when the surfactant concentration is greater than the critical micelle concentration (CMC), which is the concentration when adding more surfactant cannot further reduce the surface tension of the system. In polar media such as water, the hydrophobic parts of the surfactants tend to locate away from the polar phase while the hydrophilic parts of the surfactant will point toward the solvent interface. Micelles can also be formed in nonpolar media such as benzene in which the hydrophobic parts point out toward the solvent and the hydrophilic parts point inward, forming an assembly known as a “reversed micelle”. A micelle or reversed micelle may take several forms, such as spheres, disks, or rods, depending on the composition of the surfactant molecules and the conditions of the aqueous system (Liu et al 2001).
Having unique properties, micelle can dissolve in both hydrophobic and hydrophilic compounds. Due to the duality of solvent, they have been used as micro reactors. They also have been used as templates which will be summarized in a later part of this thesis. When a reverse micelle containing dissolved metal salts is mixed with another micelle containing a suitable reducing agent, the metal ions can be reduced to produce element metal. Barium hexaaluminate 3-10 in size were synthesized with reverse micelle and used for the catalytic combustion of methane. Due to the weak interaction between the solvent and the reactant, reverse micelles can be used to control the size of the final product (Liu et al 2001). With this method, magnetic iron oxide nanoparticles ranging from 2 to 9nm were also reported (Gabbala et al 2004).

1.6.9 Hydrothermal Synthesis

As defined, hydrothermal synthesis is a subset of solvothermal synthesis which involves water at elevated conditions. The basic principle is that small crystals will homogeneously nucleate and grow from solution when subjected to high temperatures and pressures (Li 1989). During the nucleation and growth process, water is both a catalyst and occasionally a solid-state phase component. Under the extreme conditions of the synthesis vessel (autoclave or bomb), water often becomes supercritical, thereby increasing the dissolving power, diffusivity, and mass transport of the liquid by reducing its viscosity. In addition, the ability to tune the pressure of the vessel provides an avenue to tailor the density of the final product. When compared to other methodologies, hydrothermal synthesis is environmentally benign, inexpensive, and allows for the reduction of free energies for various equilibria (Roy 1956).
Materials that are made hydrothermally are generally high-quality, single crystals with a diversity of shapes and sizes. Although hydrothermal synthesis is an established synthesis route within the ceramics industry, it has recently been rekindled within the scientific community by synthesizing one-dimensional nanostructures, such as carbon nanotubes and oxide nanowires. As of recent, hydrothermal synthesis has been used to synthesize well-aligned ZnO nanorods on GaN substrates for optical applications.

The solvothermal method is a method that takes advantage of the properties of supercritical fluids which is a fluid that is heated at elevated temperature and pressure above its boiling point and that exhibits both liquid and gas properties. The interfacial tension is greatly reduced and mass transfer between different phases is enhanced. When the solvent is water, it is commonly referred to as “hydrothermal”. Although some synthesis did take place under supercritical conditions, most of the nanomaterial syntheses were simply carried out at much lower temperatures and pressure.

Many important nanomaterials such as TiO$_2$, ZnO (Liu et al 2003, Zhang et al 2005) and CdTe have been synthesized using this method. Nanostructured titania, one of the most important photocatalysts, has been synthesized extensively with hydrothermal method. Walsh systematically investigated the effects of hydrothermal conditions on TiO$_2$ nanotube growth. It was found that the diameters of the nanotubes depended on the reaction temperature and ratio of reactants, and higher temperatures resulted in large nanotubes and wide size distribution. Some researchers took advantage of high temperature and converted amorphous TiO$_2$ into anatase or rutile crystallite TiO$_2$ using different acids as catalysts under hydrothermal conditions. With citric and nitrate acid, nanorods the in rutile phase could be obtained and HF could convert amorphous TiO$_2$ to the anatase phase.
1.6.10 Template Directed Growth

Nanostructures growth can be realized by using template-directed methods, in which a periodic structured template (for example an anodic alumina membrane or a polymeric membrane) is exploited to lead the growth of the material. These pores of the template can be filled by using other techniques such as thermal evaporation, PLD or electro deposition. After the deposition of materials, the templates can be effectively etched out leaving the nanostructures. For example nanodots have been deposited by PLD using an anodic alumina membrane. Nanorods have been obtained by evaporation on a gold membrane.

This Template directed approach can be employed to synthesis nanostructures of complex materials which are otherwise difficult to synthesis by other common methods. Other solution-based methods used to synthesize ZnO nanostructures are, like electrochemical methods, sonochemical synthesis and microwave-assisted synthesis. In addition to these, several less popular techniques and combination of these techniques have been employed for the growth of nanostructures and the details on these can be found in one of the several reviews on nanostructures (Antonelli & Ying 1988, Antonelli et al 1996).

1.6.11 Sonochemical Synthesis

Sonochemistry is chemistry assisted/enhanced by ultrasound. The chemical effects of ultrasound arise from acoustic cavitation: the formation, growth and implosive collapse of bubbles in liquid (Suslick 1990). This means that chemical reactions that take place under more conventional conditions are accelerated, or even yield totally different products (Wills et al 1999; Shafi et al 1998). The reason for this can be due to either physical or
chemical effects of cavitation. The physical effects can enhance the reactivity of a catalyst by enlarging the surface area, or accelerate a reaction by proper mixing of reagents. Chemical effects of ultrasound enhance reaction rates because of the formation of highly reactive radical species formed during cavitation. Cavitation in a liquid occurs due to the stresses induced in the liquid by passing of a sound wave through the liquid.

Sound waves comprises of longitudinal waves that consists of compression and decompression/rarefaction cycles as they passes through the medium (Trentler et al 1995). If the pressure during the decompression cycle is low enough, the liquid can be turn apart to leave small bubbles. These cavitation bubbles are at the heart of sonochemistry systems. These bubbles are now subjected to the stresses induced by the sound waves. This causes the bubbles to grow during a decompression phase, and contract or even impose during a compression phase.

These bubbles are filled with vapour and gas and can produce radicals during such an implosion. The implosive collapse of the bubble generates localized hot spots through adiabatic compression or shock wave formation within the gas phase of the collapsing bubble. Cavitation bubble collapse is a remarkable phenomenon induced throughout the liquid by the power of sound. In aqueous systems at an ultrasonic frequency of 20 kHz each cavitation bubble collapse acts as a localized hotspot generating transient temperatures of about 5000 K and in excess of 1800 atmospheric pressures (Trentler et al 1995). These extreme conditions attained during bubble collapse have been exploited to prepare nanoparticles of metals, metal carbides, metal oxides, and metal sulphides (Sriharsha Theerdhala 2007).
1.7 OBJECTIVE AND SCOPE

In an electro-optical industry, metal molybdates and tungstates are two families of important materials that have promising applications in photoluminescence, optical fibers, and scintillators (Qiang Gong et al 2006). To enhance their physical properties, the materials usually need to have high crystallinity and to have various regular shapes. Especially, bivalent metal tungstates with common composition A$^{2+}$WO$_4$ crystallize in a wolframite-type structure with space group P2/c at an ionic radius rA$^{2+}$ < 77 pm are chemically stable and are spread in nature as minerals (Victor V. Atuchin et al 2011). These kind of wolframite-type tungstates are widely used in nanotechnologies such as catalysis, electronics, optical devices and scintillator. The first row d-block elements such as transition metal tungstates with the chemical formula of AWO$_4$, (A = Mn, Fe, Co, Ni, Cu, Zn) crystallizes in the wolframite structure, which makes these materials an ideal tunable platform whose properties can be exploited through forming solid solutions (Joseph E. Yourey et al 2012).

As a member of this metal tungstate family, cobalt tungstate (CoWO$_4$), has attracted a great deal of attention because of its wide range of physical and chemical properties. This compound is isostructural with CdWO$_4$ and NiWO$_4$, crystallizing in a wolframite-type monoclinic structure belonging to the P2/c space group and having two formula units per primitive cell, and it can be described as consisting of hexagonal close-packed oxygen atoms with certain octahedral sites filled by Co$^{2+}$ and W$^{6+}$ cations in an ordered fashion (Hyun-Woo Shim et al 2011). It has also been applied in the fields of luminescent materials, photocatalysts, optical fibers, gas sensors, solid-state laser hosts, and so on. In particular, CoWO$_4$ is an attractive anode material for secondary Li-ion batteries (Sagrario M. Montemayor & Antonio
F. Fuentes 2004). Thus, the synthesis of well-crystallized CoWO₄ crystallites, especially CoWO₄ nanoparticles, has recently drawn increasing attention.

Doping is the process widely used to control the structure, particle size, morphology, surface features and chemical composition of host materials. The compound has been shown to be doped with transition-metal and rare-earth ions, and these doped congeners have found application in upconversion luminescence (Uma Subramanian et al 2013). On the basis of optoelectronic and chemical properties originating from the 4f shell of rare earth ions, it is received extensive attention as the dopant (Lin Xiu et al 2009). Recently, nanocrystalline CoWO₄ has been synthesized in various methods, like chemical precipitation (Hongfei Jia et al 2012), melt salt method (Zuwei Song et al 2009), hydrothermal (Rajagopal et al 2010, Liang Zhen et al 2008), spray pyrolysis (Somchai Thongtem et al 2009), chemical route (Angana Sen & Panchanan Pramink 2000) etc. while being doped with rare-earth (RE) ions are limited and obtain the enhanced luminescence properties.

In earlier, the reactivity in the solid state between CoWO₄ and some rare tungstates RE₂WO₆ (RE = Sm, Eu, Gd) were investigated by Tomaszewicz (2006). Recently, Naik et al (2010) have reported the optical absorption and photoluminescent studies of cerium-doped cobalt tungstate nanomaterials. In their report, undoped and Ce³⁺-doped CoWO₄ nanoparticle (22–65 nm) phosphors were showed the PL emission at 468 nm and its intensity was found to vary with sintering temperature and the concentration of Ce³⁺ doping. However, the PL pattern and peak positions did not show any change. For bulk samples PL intensity was 40 times less than that of the nanosamples and insensitive to Ce³⁺ doping concentrations and the maximum PL emission was observed for nano-CoWO₄ samples doped with 1.5–2% Ce³⁺ ions and sintered at 600ºC.
This thesis reports explorative research concerning the luminescence properties of rare-earth-doped CoWO$_4$ material for optical applications. The focuses is on searching for improved or unconventional properties in existing materials and in addition design, synthesis of novel materials through special crystal chemical substitutions. The structure of rare-earth doped CoWO$_4$ and photoluminescence studies has not been found in the literature. Finally, the invention of rare-earth doped CoWO$_4$ materials and understanding of the relationship between luminescence properties and structure/composition are also challenging parts of the work described in this thesis from an application and scientific point of view, respectively. Here, it is noted that no attempt has been made to give a detailed spectroscopic study, which is an interesting subject of subsequent studies.

The key objectives of the research work are

(a) Synthesis of rare-earth metal ions doped $\text{Co}_{1-x}\text{RE}_x\text{WO}_4$ (RE = Yb, Nd, Gd & Dy) nanocrystals by easy and effective chemical precipitation technique.

(b) As-synthesized nanocrystals were characterized by various analytical techniques to evaluate their physical and optical properties.

(c) By varying the dopant ions, the morphology, energy band gap and luminescent characteristics of the host material were investigated.

(d) Tunable optical features of the lanthanide series rare-earth metal ion doped CoWO$_4$ towards optical applications was reported.
In this research work, it is expected to give the better understanding of optical behavior of wolframite type CoWO$_4$ with respect to the lanthanide series rare-earth metal ions for opto-electronics applications. With the size and concentration of the dopant have directly influences on the optical features of the host matrix. This kind of investigation is essential for newly emerging electronic devices.