Chapter 1
Introduction and Aim of the Present Work

This chapter presents a brief review of the nanomaterials and their applications. Various properties of nanomaterials and their preparation methods have been discussed briefly. Literature review of wide band gap semiconductors ZnO, Bi$_4$V$_2$O$_{11}$ and SnO$_2$ are presented here. The main objectives of the investigations carried out in this thesis are presented
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1.1 Introduction

Nanomaterials are foundations of nanoscience and nanotechnology. Nanostructure science and technology is a wide and interdisciplinary area of research and progress activity that has been growing explosively global in the past few years. It has the potential for revolutionizing the ways in which materials and products are created and the range and nature of functionalities that can be accessed. It is already having a significant commercial impact, which will assuredly increase in the future.

1.2 What are nanomaterials?

Nanoscale materials are defined as a set of substances where at least one dimension is less than approximately 100 nanometers. A nanometer is one millionth of a millimetre approximately 100,000 times smaller than the diameter of a human hair. Nanomaterials are of interest because at this scale unique optical, magnetic, electrical, photocatalytic and other properties emerge significantly. These emergent properties have the potential for great impacts in optoelectronics, spintronics, medicine, waste water treatment and other fields.

1.3 The history of nanotechnology

Nanotechnology was first suggested, by the Nobel Prize winning physicist Richard Feynman, he proposed that someday it would be possible to put the entire 24 volume Encyclopaedia Britannica on the head of a pin. He established that theoretically, atleast such a feat is possible [Wallis (1992)]. His leading talk on nanoscience in 1959 entitled "There Is Plenty Room At the Bottom" has become a classic milestone. Feynman proposed that tiny robots might be able to build chemical materials. He noted that they could be used to build nanomachines. He had also pointed out that a new class of miniaturized devices would be needed to manipulate and measure the properties of the nanostructures. In the 1980's these instruments were developed. They could begin to do what Feynman talked about. The scanning tunnelling microscope (STM), atomic force microscope (AFM) and the near-field
microscopes provided the eyes and fingers required for nanostructure measurement and manipulation [Pacific Northwest National Laboratory (2002)].

Nanotechnology is an interdisciplinary research field in which many physicists, chemists, biologists, materials scientist and other experts are involved. The term of nanomaterials covers numerous types of nanostructured materials which possess at least one dimension in the nanometer range. Various nanostructures which include zero dimension nanostructures such as metallic, semiconducting and ceramic nanoparticles; one dimension nanostructures such nanowires, nanotubes and nanorods; two dimension nanostructures such as quantum well structures. Besides this individual nanostructures, ensembles of these nanostructures form high dimension arrays, assemblies, and superlattices.

Due to their small dimensions, nanomaterials have enormously large surface area to volume ratio, which makes a large fraction of atoms of the materials to be on the surface or interfacial atoms, resulting in more surface dependent material properties. Mainly when the sizes of nanomaterials are comparable to Debye length, the entire material will be affected by the surface properties of nanomaterials [Ogawa et al. (1982), Luth (1995)]. This in turn may improve or modify the properties of the bulk materials. For example, metallic nanoparticles can be used as very active catalysts. Chemical sensors from nanoparticles and nanowires enhanced the sensitivity and sensor selectivity. The quantum confinement of nanomaterials has reflective effects on the properties of nanomaterials. The energy band structure and charge carrier density in the materials can be altered quite differently from their bulk counterpart and this in turn will modify various properties of the materials. Synthesis and processing of nanomaterials and nanostructures are the critical aspect of nanotechnology. Studies on new physical properties and applications of nanomaterials and nanostructures are probable only when nanostructured materials are made available with desired size, morphology, crystal and chemical composition. Work on the manufacture and processing of nanomaterials and nanostructures started long time ago, far earlier than nanotechnology emerged as a new scientific field. Such research has been extremely intensified in the last decade, resulting in awesome literatures in
many journals across different disciplines. The research on nanotechnology is evolving and growing very quickly. There are two principal methods of engineering nanoscale materials; the top-down nanofabrication starts with a large structure and proceeds to make it smaller through sequential cuttings while the bottom-up nanofabrication starts with individual atoms and builds them up to a nanostructure. When we bring constituents of materials down to the nanoscale, the properties change. Lasers and light emitting diodes (LEDs) from both quantum dots and quantum wires are very favourable in the future developments of optoelectronics. High density information storage using quantum dot devices is also a fast developing area. Reduced imperfections are also an important factor in determination of the properties of the nanomaterials.

1.4 Where are nanomaterials found?

Some nanomaterials occur naturally, but of particular interest are engineered nanomaterials, which are designed for, and already being used in many commercial products and processes. They can be found in such things as sunscreens, cosmetics, sporting goods, stain-resistant clothing, tires, electronics, as well as many other everyday items, and are used in medicine for purposes of diagnosis, imaging and drug delivery. Engineered nanomaterials are resources designed at the nanometer level to take advantage of their small size and novel properties which are generally not seen in their conventional, bulk counterparts. The two main reasons why materials at the nano scale can have different properties are increased surface area to volume ratio and quantum confinement effect. Nanomaterials have a much greater surface area to volume ratio than their conventional forms, which can lead to greater chemical reactivity and affect their strength. Also at the nano scale, quantum effects can become much more important in determining the materials properties and characteristics, leading to novel optical, electrical and magnetic behaviours. Nanomaterials are already in commercial use, with some having been available for several years or decades. The range of commercial products available today is very broad, including stain-resistant and wrinkle-free textiles, sunscreens, electronics,
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paints and varnishes. Nanocoatings and nanocomposites are finding uses in diverse consumer products, such as windows, sports equipment, bicycles and automobiles. There are novel UV-blocking coatings on glass bottles which protect beverages from damage by sunlight, and longer-lasting tennis balls using butylrubber/nano-clay composites. Nanoscale titanium dioxide, for instance, is finding applications in cosmetics, sun-block creams and self-cleaning windows, and nanoscale silica is being used as filler in a range of products, including cosmetics and dental fillings.

1.5 Advances in nanomaterials

One of the first scientific reports is the colloidal gold particles synthesised by Michael Faraday as early as 1857. 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 ultrafine carbon black for rubber reinforcements. Nanosized amorphous silica particles have found large-scale applications in many every-day consumer products, ranging from non-diary coffee creamer to automobile tires, optical fibres and catalyst supports. In the 1960s and 1970’s metallic nanopowders for magnetic recording tapes were developed. In 1976, for the first time, nanocrystals produced by the now popular inert-gas evaporation technique was published by Granqvist and Buhrman. Today nanophase engineering expands in a rapidly growing number of structural and functional materials, both inorganic and organic, allowing manipulating mechanical, catalytic, electric, magnetic, optical 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 into 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.
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1.6 Classification of Nanomaterials

Nanomaterials have extremely small size which having at least one dimension 100 nm or less. Nanomaterials can be nanoscale in one dimension (e.g. nanowires), two dimensions (e.g. thin films), or three dimensions (e.g. nanostrars). They can exist in single, fused, aggregated or agglomerated forms with spherical, tubular, and irregular shapes. Common types of nanomaterials include nanotubes, quantum dots and fullerenes. Nanomaterials have applications in the field of nano technology, and displays different physical chemical characteristics from normal chemicals (i.e., silver nano, carbon nanotube, fullerene, photocatalyst, carbon nano, silica).

1.7 Why are nanomaterials important?

These materials have created a high interest in recent years by virtue of their unusual mechanical, electrical, optical, photocatalytic and magnetic properties. Some examples are given below: (i) Nanophase ceramics are of particular interest because they are more ductile at elevated temperatures as compared to the coarse-grained ceramics. (ii) Nanostructured semiconductors are known to show various non-linear optical properties. (iii) Nanosized metallic powders have been used for the production of gas tight materials, dense parts and porous coatings. (iv) Single nanosized magnetic particles are mono-domains and one expects that also in magnetic nanophase materials the grains correspond with domains, while boundaries on the contrary to disordered walls. Very small particles have special atomic structures with discrete electronic states, which give rise to special properties in addition to the superparamagnetism behaviour. Magnetic nanocomposites have been used for mechanical force transfer (ferrofluids), for high density information storage and magnetic refrigeration. (v) Nanostructured metal clusters and colloids of mono- or plurimetallic composition have a special impact in catalytic applications. They may serve as precursors for new type of heterogeneous catalysts and have been shown to offer substantial advantages concerning activity, selectivity and lifetime in chemical transformations and electrocatalysis. (vi) Nanostructured metal-oxide thin films are receiving a growing attention for the realization of gas sensors (NO\textsubscript{x}, CO, CO\textsubscript{2}, CH\textsubscript{4})
and aromatic hydrocarbons) with enhanced sensitivity and selectivity. Nanostructured metal-oxide (MnO₂) finds application for rechargeable batteries for cars or consumer goods. Nanocrystalline silicon films for highly transparent contacts in thin film solar cell and nano-structured titanium oxide porous films for its high transmission and significant surface area enhancement leading to strong absorption in dye sensitized solar cells. (vii) Polymer based composites with a high content of inorganic particles leading to a high dielectric constant are interesting materials for photonic band gap structure.

**1.8 Quantum confinement**

For bulk semiconductor, the dimension of the exciton can be theoretically calculated by exciton Bohr radius [Efros and Rosen (2000), Efros and Elfros (1982)].

\[
a_B = \frac{\hbar e}{2\mu \varepsilon}
\]  

where \( h \) is defined as Planck’s constant, \( \varepsilon \) is the dielectric constant, \( \mu \) is the exciton reduced mass [Efros and Elfros (1982)]. However, if the radius of a semiconductor nanocrystal is reduced to less than its exciton Bohr radius, we can visualize that the exciton will be strongly confined in this limited volume and the electronic structure of the three-dimensionally confined electrons and holes will be drastically altered. The term quantum confinement describes this confinement of the exciton within the physical boundaries of the semiconductor. The exciton Bohr radius \( a_B \) is often used to judge the extent of confinement in a semiconductor nanocrystal with radius, \( a \). In the analysis of experimental data, one needs to consider three different regimes: \( a > a_B \), \( a \sim a_B \) and \( a < a_B \), which are named as weak confinement, intermediate confinement and strong confinement regimes, respectively [Efros and Rosen (2000)].

To form the theoretical models of electronic structure for quantum dots one uses quantum mechanics to describe the behaviour of electrons in a semiconductor. In quantum mechanics electrons exhibit a wave-particle duality and can be termed by a wave function. According to Heisenberg’s uncertainty principle, position \( x \) and momentum \( p \) of an electron cannot be accurately determined instantaneously. For a
plain wave, the position is unknown and can possibly be situated at any position, but the momentum has an accurately defined value $\hbar k/2\pi$, where $k$ is the wave vector. However, for an electron confined in a restricted space such as in a semiconductor crystal, the uncertainty in position decreases, but the momentum is no longer well defined and $k$ has an uncertain value. Because the energy $E$ is related to the momentum $p$ or $k$ vector, it will also have uncertain energy levels. In a bulk semiconductor, carrier motion is limitless along all three spatial directions. However, a nanostructure has one or more of its dimensions concentrated to a nanometre length scale and this creates a quantisation of the carrier energy corresponding to motion along these directions.

### 1.8.1 Confinement in one dimension

Quantum wells are structures in which a thin film (confinement film) of a smaller band gap semiconductor is inserted between two films (barrier film) of a wider band gap semiconductor. The heterojunction between the smaller and the wider band gap semiconductors forms a potential well restricting the electrons and the holes in the smaller band gap material. This is the case of a type I quantum well. In a type II quantum well, the electrons and the holes are restricted in different films. Thus the motions of the electrons and the holes are restricted in one dimension. This system represents a two-dimensional electron gas (2DEG), when electrons are present in the conduction band. Total energy of the electron is the sum of permissible energies related with the motion of these carriers along one direction (say $z$ direction) and the kinetic energy due to free motion of carriers in other two directions (say $x$, $y$ directions)

$$E_{\text{Total}} = \frac{\hbar^2}{8\pi^2m} \left( \frac{n_z\pi}{a} \right)^2 + \frac{\hbar^2}{8\pi^2m} \left( k_x^2 + k_y^2 \right)$$

(1.2)

where 'a' is the thickness of the confinement film, which corresponds to the width of the potential well, $n_z = 1, 2, 3,....$ and $k_x$ and $k_y$ are the wave vectors along $x$ and $y$ directions. Lasers fabricated using single or multiple quantum wells constructed on wide band gap semiconductors as the active region have been widely studied over the
last two decades. Quantum well lasers offer upgraded performance with lower threshold current and lower spectral width as associated to that of regular double heterostructure lasers. Quantum wells allow the possibility of independently varying barriers and confinement layer compositions and widths, and thus distinct determination of optical confinement and electron injection. One of the main differences between the single quantum well and the multiple quantum well lasers is that the confinement factor of the optical mode is ominously smaller for the former. This results in advanced threshold carrier and current densities for single quantum well lasers; however the confinement factor of single quantum well lasers can be ominously increased using a graded-index layer structure [Hersee et al. (1984)]. The emissions from the quantum well-structured determine the quality of confinement and barrier layer and the interface between these layers.

### 1.8.2 Confinement in two dimensions

The term nanowire is extensively used to represent one-dimensional nanostructures that have a definite axial direction while their side surfaces are less well-defined [Westwater et al. (1997), Zhang et al. (2000)]. The wire- or rod-like shape of one-dimensional nanostructures has caused them to be the source of somewhat growing research of the past several years. In specific, their novel electrical and mechanical properties are the subject of strong research. Quantum wires represent two-dimensional confinement of electrons and holes. Such confinement permits free-electron behaviour in only one direction, along the length of the wire (say the y direction). For this reason, the system of quantum wires describes a one-dimensional electron gas (IDEG) when electrons are present in the conduction band. The classification of one-dimensional nanostructures involves a wide variety of morphologies. These contain whiskers, nanowires, nanorods, fibers, nanotubules, nanocables, and nanotubes, among others. Nanowires and nanorods are one-dimensional nanostructures whose width does not exceed 100 nanometers. Nanowires have been successfully synthesized out of a extensive variety of materials, including titanium oxide [Lei et al. (2001)], indium oxide [Liang et al. (2001)], indium-tin oxide
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[Nguyen et al. (2003)], aluminum [Ono et al. (2003)], tungsten oxide [Qi et al. (2003)] and zinc oxide [Ajimsha et al. (2008)] etc. Here, total energy of the electron is the sum of allowed energies related with the motion of these carriers along two direction (say y, z direction) and the kinetic energy due to free motion of carriers in the other direction (say x direction)

\[
E_{Total} = \frac{\hbar^2}{8\pi^2m} \left( \frac{n_y \pi}{a} \right)^2 + \frac{\hbar^2}{8\pi^2m} \left( \frac{n_z \pi}{b} \right)^2 + \frac{\hbar^2}{8\pi^2m} \left( k_x^2 \right)
\]  

(1.3)

where ny, nz are integers and a, b are confined sizes of the materials along z and y directions.

The term nanotubes represent two separate types of nanostructure. The first is any structure that appears to be like a nanowire with a hollow centre. The side surfaces of the nanotube in this sense may be well-faceted. Many materials have been used to make these structures. The difference of nanowires and nanorods from nanotubes is the geometry of their cross-section. Nanotubes are hollow and have a cross-section approaching the perimeter of a circle or the outside of a rectangle. Nanowires and nanorods have solid cores. Their cross-section resembles a filled-in circle or hexagon. Research on one-dimensional nanostructures took-off freshly with the publication in 1991 of Iijima’s seminal paper outlining the discovery of carbon nanotubes, “helical microtubules of graphitic carbon” [Iijima (1991)]. Carbon nanotubes are made up of a hexagonal network of carbon atoms creating a crystalline graphite sheet. This sheet is roled up to form a tubular structure. If the tube entails of only a single carbon sheet that meets end on end, then the carbon nanotube is referred to as a single walled carbon nanotube (SWCNT). However, if the nanotubes consist of multiple sheets rolled up coaxially or if the nanotube rolls up somewhat spirally, then the carbon nanotube is mentioned to as a multi walled carbon nanotube (MWCNT).

1.8.3 Confinement in three dimensions

Quantum dots symbolize the case of three-dimensional confinement, hence the case of an electron confined in a three-dimensional quantum box, typically of dimensions ranging from nanometres to tens of nanometres. These dimensions are
smaller than the de Broglie wavelength of thermal electrons. A quantum dot is often termed as an artificial atom because the electron is dimensionally confined just like in an atom (where an electron is confined near the nucleus) and similarly has only distinct energy levels. The electrons in a quantum dot represent a zero-dimensional electron gas (0DEG). Here, total energy of the electron is the sum of allowed energies related with the motion of these carriers along all three directions (say x, y, z direction)

\[ E_{\text{Total}} = \frac{\hbar^2}{8\pi^2 m} \left( \frac{n_x \pi}{a} \right)^2 + \frac{\hbar^2}{8\pi^2 m} \left( \frac{n_y \pi}{b} \right)^2 + \frac{\hbar^2}{8\pi^2 m} \left( \frac{n_z \pi}{c} \right)^2 \]  

(1.4)

where \( n_x, n_y, n_z \) are integers and \( a, b, c \) are confined sizes of the materials along z, y and x directions. Quantum dots are zero-dimensional nanostructures of semiconductors. Quantum dots were first theorized in the 1970s and initially synthesized in the early 1980s. If semiconductor particles are made small enough, quantum effects begin to assert themselves. These effects limit the energies at which electrons and holes can exist in the particles. Because energy is related to wavelength of the resulting photon, this means that the optical properties of the particle can be finely tuned liable on its size. Quantum mechanics regulates that only certain distinct energy levels are allowed in a single atom. If two indistinguishable atoms are held at large distances from each other, electrons in each level will have exactly the same energy. As those two atoms are brought nearer to one another, they interact, and no two electrons with the same spin can have the same energy. This governing principle is called the Pauli Exclusion Principle. When a large number of atoms are brought together to form a solid, the distinct allowed energy levels of the separate atoms becomes a continuous energy band. In bulk structures, these properties can only be changed by adding constituents to generate defects, interstitials, or substitutions in the material. The notable phenomenon in QDs is that the optical and electronic properties can be specifically tuned by changing the size of the dots in addition to adding dopants. The electronic and optical properties that were thought to be inherent to a material can be transformed when the material was in a small enough (nanoscale) size. As the dimensions of a material decrease in size, quantum confinement effects
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begin to occur. Quantum confinement occurs when material dimension is smaller than exciton Bohr radius [Bawendi et al. (1992)]. This restricts carriers’ movement, resulting in the above stated discrete energy levels and differences in material properties. Quantum confinement effects in QDs have a significant impact on the optical properties of the material. Quantum dots are often described in terms of the degree of confinement. The strong confinement regime is defined to represent the case when the size of the quantum dot (e.g., the radius R of a spherical dot) is smaller than the exciton Bohr radius \(a_B\). In this case, the energy separation between the sub-bands (various quantized levels of electrons and holes) is much larger than the exciton binding energy. Hence, the electrons and holes are largely symbolized by the energy states of their respective sub-bands. As the quantum dot size increases, the energy separation between the various sub-bands becomes comparable to and eventually less than the exciton binding energy. The latter represents the case of a weak confinement regime where the size of the quantum dot is much larger than the exciton Bohr radius. The electron-hole binding energy in this case is nearly the same as in the bulk semiconductor. Because of its unique properties, quantum dots have some promising potential applications. The more creative research involves using quantum dots for biological imaging [Chan and Nie (1998), Bruchez et al. (1998)] and computing [Li et al. (2003)] applications. Zinc sulphide has also plays an important role in quantum dot based nanosensors. Quantum computing creates use of the electronic properties of quantum dot.

1.9 Nanostructure fabrication methods

Nanomaterials deal with very fine structures: a nanometer is a billionth of a meter. This indeed allows us to think in both the ‘bottom up’ or the ‘top down’ approaches to synthesize nanomaterials, i.e. either to assemble atoms together or to dis-assemble (break, or dissociate) bulk solids into finer pieces until they are constituted of only a few atoms. This domain is a pure example of interdisciplinary work encompassing physics, chemistry, and engineering upto medicine. There are many different ways of creating nanostructures: of course, macromolecules or
nanoparticles or buckyballs or nanotubes and so on can be synthesized artificially for certain specific materials. They can also be arranged by methods based on equilibrium or near-equilibrium thermodynamics such as methods of self-organization and self-assembly (sometimes also called bio-mimetic processes). Using these methods, synthesized materials can be arranged into useful shapes so that finally the material can be applied to a certain application, some of the methods are briefly described below.

1.9.1 Mechanical grinding

Mechanical attrition is a typical example of ‘top down’ method of synthesis of nanomaterials, where the material is prepared not by cluster assembly but by the structural decomposition of coarser-grained structures as the result of severe plastic deformation. This has become a popular method to make nanocrystalline materials because of its simplicity, the relatively inexpensive equipment needed, and the applicability to essentially the synthesis of all classes of materials. The major advantage often quoted is the possibility for easily scaling up to tonnage quantities of material for various applications. Similarly, the serious problems that are usually cited are; 1. contamination from milling media and/or atmosphere, and 2. to consolidate the powder product without coarsening the nanocrystalline microstructure. In fact, the contamination problem is often given as a reason to dismiss the method, at least for some materials. Here we will review the mechanisms presently believed responsible for formation of nanocrystalline structures by mechanical attrition of single phase powders, mechanical alloying of dissimilar powders, and mechanical crystallisation of amorphous materials. The two important problems of contamination and powder consolidation will be briefly considered.

Mechanical milling is typically achieved using high energy shaker, planetary ball, or tumbler mills. The energy transferred to the powder from refractory or steel balls depends on the rotational (vibrational) speed, size and number of the balls, ratio of the ball to powder mass, the time of milling and the milling atmosphere. Nanoparticles are produced by the shear action during grinding. Milling in cryogenic
liquids can greatly increase the brittleness of the powders influencing the fracture process. As with any process that produces fine particles, an adequate step to prevent oxidation is necessary. Hence this process is very restrictive for the production of non-oxide materials since then it requires that the milling take place in an inert atmosphere and that the powder particles be handled in an appropriate vacuum system or glove box. This method of synthesis is suitable for producing amorphous or nanocrystalline alloy particles, elemental or compound powders. If the mechanical milling imparts sufficient energy to the constituent powders a homogeneous alloy can be formed. Based on the energy of the milling process and thermodynamic properties of the constituents the alloy can be rendered amorphous by this processing.

1.9.2 Wet chemical synthesis of nanomaterials

In principle we can classify the wet chemical synthesis of nanomaterials into two broad groups: 1. The top down method: where single crystals are etched in an aqueous solution for producing nanomaterials, For example, the synthesis of porous silicon by electrochemical etching. 2. The bottom up method: consisting of sol-gel method, precipitation etc. where materials containing the desired precursors are mixed in a controlled fashion to form a colloidal solution.

1.9.2.1 Sol-gel process

The sol-gel process, 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 usually of a metal or metalloid element surrounded by various reactive ligands. The starting material is processed to form a dispersible oxide and forms a sol in contact with water or dilute acid. Removal of the liquid from the sol yields the gel, and the sol/gel transition controls the particle size and shape. Calcination of the gel produces the oxide. Sol-gel processing refers to the hydrolysis and condensation of alkoxide-based precursors such as Si(OEt) 4 (tetraethyl orthosilicate, or TEOS). The reactions
involved in the sol-gel chemistry based on the hydrolysis and condensation of metal alkoxides $\text{M(OR)}_n$ can be described as follows:

$$\text{MOR} + \text{H}_2\text{O} \rightarrow \text{MOH} + \text{ROH} \quad \text{(hydrolysis)}$$

$$\text{MOH} + \text{ROM} \rightarrow \text{M-O-M} + \text{ROH} \quad \text{(condensation)}$$

Sol-gel method of synthesizing nanomaterials is very popular amongst chemists and is widely employed to prepare oxide materials. The sol-gel process can be characterized by a series of distinct steps.

1. Formation of different stable solutions of the alkoxide or solvated metal precursor.

2. Gelation resulting from the formation of an oxide- or alcohol-bridged network (the gel) by a polycondensation reaction that results in a dramatic increase in the viscosity of the solution.

3. Aging of the gel (Syneresis), during which the polycondensation reactions continue until the gel transforms into a solid mass, accompanied by contraction of the gel network and expulsion of solvent from gel pores. Ostwald ripening (also referred to as coarsening, is the phenomenon by which smaller particles are consumed by larger particles during the growth process) and phase transformations may occur concurrently with syneresis. The aging process of gels can exceed 7 days and is critical to the prevention of cracks in gels that have been cast.

4. Drying of the gel, when water and other volatile liquids are removed from the gel network. This process is complicated due to fundamental changes in the structure of the gel. The drying process has itself been broken into four distinct steps: (i) the constant rate period, (ii) the critical point, (iii) the falling rate period, (iv) the second falling rate period. If isolated by thermal evaporation, the resulting monolith is termed a \textit{xerogel}. If the solvent (such as water) is extracted under supercritical or near super critical conditions, the product is an \textit{aerogel}.

5. Dehydration, during which surface-bound M-OH groups are removed, thereby stabilizing the gel against rehydration. This is normally achieved by calcining the monolith at temperatures up to 800 °C.
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6. Densification and decomposition of the gels at high temperatures (T>800 °C). The pores of the gel network are collapsed, and remaining organic species are volatilized.

1.9.2.2 Co-precipitation

Diffusion distances for the reacting cations are large in the ceramic method. Thus diffusion distances are reduced markedly (to few angstroms) by incorporating the cations in the same solid precursor. Co-precipitation involves the separation of a solid containing various species chemically bound to one another from a liquid or a solution phase [Ferreira et al. (2007)]. A homogenous co-precipitation process can result in the formation of crystalline or amorphous solids. Co-precipitation of well-defined stoichiometry with respect to the metal ions is obtained only when the following conditions are satisfied.

1. The precipitating agent is a multivalent organic compound which can coordinate with more than one metal ion, and the precipitation rate is fast.

2. The solid precipitating out of the solution should be really insoluble in the mother liquor.

The anions generally preferred for co-precipitation of oxidic materials are carbonates, oxalates, citrates etc. The precipitates (carbonates, oxalate etc.) are heated at appropriate temperatures in a suitable atmosphere to obtain the desired product. But the method does not work well in cases where the two reactants have very different solubilities in solution, and the reactants do not precipitate at the same rate. The method is not often suitable for the preparation of high purity, accurately stoichiometric phases. It is difficult to control the stoichiometry if all the relevant metal ions do not form really insoluble precipitates. Thus solid state precursors have several advantages:

1. The reacting cations are uniformly blended together thereby avoiding the diffusion problem and compositional inhomogeneity in the final product.

2. The product is formed at a much lower temperature than in a conventional ceramic synthesis thus permitting an examination of sub-solidus regions of the phase
diagram which would otherwise be inaccessible. The products formed at lower temperatures possess larger surface areas which is an important requirement in catalyst preparations.

1.9.2.3 Hydrothermal

This method finds application in materials science and solid state chemistry, as it is an important method for crystal growth and for the synthesis of new materials with useful properties. It provides additional parameters for obtaining information on the structures, behaviour and properties of solids. It is performed on an apparatus consisting of a steel pressure vessel closed at one end. The other end has screw cap with a gasket of soft copper to provide a seal. It uses water under pressure and at temperatures above its normal boiling point as a means of speeding up the reactions between solids. The water acts as liquid or vapor or serves as the pressure transmitting medium. As some or all of the reactants are partially soluble in water under pressure, this enables reactions to take place with the aid of liquid or vapor phases. This method is suited for the synthesis of phases that are unstable at higher temperatures. Since, hydrothermal reactions must be carried out in closed vessels, the pressure-temperature relation of water at constant volume is important. The critical temperature of water is 374 °C. Below this temperature, two fluid phases, liquid and vapor can coexist. Above 374 °C, only one fluid phase, supercritical water exists.

Possible advantages of the hydrothermal method over other types of crystal growth include the ability to create crystalline phases which are not stable at the melting point. Disadvantages of the method are the use of expensive autoclaves, and the inability to monitor the reaction.

1.9.3 Gas phase synthesis of nanomaterials

The gas-phase synthesis methods are of increasing interest because they allow elegant way to control process parameters in order to be able to produce size, shape and chemical composition controlled nanostructures. Before we discuss a few selected pathways for gas-phase formation of nanomaterials, some general aspects of gas-
phase synthesis needs to be discussed. In conventional chemical vapour deposition (CVD) synthesis, gaseous products either are allowed to react homogeneously or heterogeneously depending on a particular application.

1. In homogeneous CVD, particles form in the gas phase and diffuse towards a cold surface due to thermophoretic forces, and can either be scrapped off from the cold surface to give nano-powders, or deposited onto a substrate to yield what is called ‘particulate films’.

2. In heterogeneous CVD, the solid is formed on the substrate surface, which catalyses the reaction and a dense film is formed. In order to form nanomaterials several modified CVD methods have been developed. Gas phase processes have inherent advantages, some of which are noted here:

- An excellent control of size, shape, crystallinity and chemical composition
- Highly pure materials can be obtained
- Multicomponent systems are relatively easy to form
- Easy control of the reaction mechanisms

Most of the synthesis routes are based on the production of small clusters that can aggregate to form nano particles (condensation). Condensation occurs only when the vapour is supersaturated and in these processes homogeneous nucleation in the gas phase is utilised to form particles. This can be achieved both by physical and chemical methods.

1.9.4 Furnace

The simplest fashion to produce nanoparticles is by heating the desired material in a heat-resistant crucible containing the desired material. This method is appropriate only for materials that have a high vapour pressure at the heated temperatures that can be as high as 2000°C. Energy is normally introduced into the precursor by arc heating, electron beam heating or Joule heating. The atoms are evaporated into an atmosphere, which is either inert (e.g. He) or reactive (so as to form a compound). To carry out reactive synthesis, materials with very low vapour
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Pressure have to be fed into the furnace in the form of a suitable precursor such as organometallics, which decompose in the furnace to produce a condensable material. The hot atoms of the evaporated matter lose energy by collision with the atoms of the cold gas and undergo condensation into small clusters via homogeneous nucleation. In case a compound is being synthesized, these precursors react in the gas phase and form a compound with the material that is separately injected in the reaction chamber. The clusters would continue to grow if they remain in the supersaturated region. To control their size, they need to be rapidly removed from the supersaturated environment by a carrier gas. The cluster size and its distribution are controlled by only three parameters:

1. The rate of evaporation (energy input),
2. The rate of condensation (energy removal), and
3. The rate of gas flow (cluster removal).

Because of its inherent simplicity, it is possible to scale up this process from laboratory (mg/day) to industrial scales (tons/day).

1.9.5 Flame assisted ultrasonic spray pyrolysis

In this process, precursors are nebulized and then unwanted components are burnt in a flame to get the required material, eg. ZrO$_2$ has been obtained by this method from a precursor of Zr(CH$_3$CH$_2$CH$_2$O)$_4$. Flame hydrolysis that is a variant of this process is used for the manufacture of fused silica. In the process, silicon tetrachloride is heated in an oxy-hydrogen flame to give highly dispersed silica. The resulting white amorphous powder consists of spherical particles with sizes in the range 7-40 nm. The combustion flame synthesis, in which the burning of a gas mixture, e.g. acetylene and oxygen or hydrogen and oxygen, supplies the energy to initiate the pyrolysis of precursor compounds, is widely used for the industrial production of powders in large quantities, such as carbon black, fumed silica and titanium dioxide. However, since the gas pressure during the reaction is high, highly agglomerated powders are produced which is disadvantageous for subsequent processing. The basic idea of low pressure combustion flame synthesis is to extend
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the pressure range to the pressures used in gas phase synthesis and thus to reduce or avoid the agglomeration. Low pressure flames have been extensively used by aerosol scientists to study particle formation in the flame.

A key for the formation of nanoparticles with narrow size distributions is the exact control of the flame in order to obtain a flat flame front. Under these conditions the thermal history, i.e. time and temperature, of each particle formed is identical and narrow distributions result. However, due to the oxidative atmosphere in the flame, this synthesis process is limited to the formation of oxides in the reactor zone.

1.9.6 Chemical Vapour Condensation

The evaporative source used in GPC is replaced by a hot wall reactor in the Chemical Vapour Condensation (CVC) process. Depending on the processing parameters nucleation of nanoparticles is observed during CVC of thin films and poses a major problem in obtaining good film qualities. The original idea of the novel CVC process which is schematically shown below where, it was intended to adjust the parameter field during the synthesis in order to suppress film formation and enhance homogeneous nucleation of particles in the gas flow. It is readily found that the residence time of the precursor in the reactor determines if films or particles are formed. In a certain range of residence time both particle and film formation can be obtained. Adjusting the residence time of the precursor molecules by changing the gas flowrate, the pressure difference between the precursor delivery system and the main chamber occurs. Then the temperature of the hot wall reactor results in the fertile production of nanosized particles of metals and ceramics instead of thin films as in CVD processing. In the simplest form a metal organic precursor is introduced into the hot zone of the reactor using mass flow controller. Besides the increased quantities in this continuous process compared to GPC has been demonstrated that a wider range of ceramics including nitrides and carbides can be synthesised. Additionally, more complex oxides such as BaTiO$_3$ or composite structures can be formed as well. Appropriate precursor compounds can be readily found in the CVD literature. The extension to production of nanoparticles requires the determination of a modified
parameter field in order to promote particle formation instead of film formation. In addition to the formation of single phase nanoparticles by CVC of a single precursor the reactor allows the synthesis of

1. Mixtures of nanoparticles of two phases or doped nanoparticles by supplying two precursors at the front end of the reactor, and

2. Coated nanoparticles, i.e., n-ZrO$_2$ coated with n-Al$_2$O$_3$ or vice versa, by supplying a second precursor at a second stage of the reactor. In this case nanoparticles which have been formed by homogeneous nucleation are coated by heterogeneous nucleation in a second stage of the reactor.

Because CVC processing is continuous, the production capabilities are much larger than in GPC processing. Quantities in excess of 20 g/hr have been readily produced with a small scale laboratory reactor. A further expansion can be envisaged by simply enlarging the diameter of the hot wall reactor and the mass flow through the reactor.

**1.9.7 Sputtered Plasma Processing**

In this method is yet again a variation of the gas-condensation method excepting the fact that the source material is a sputtering target and this target is sputtered using rare gases and the constituents are allowed to agglomerate to produce nanomaterial. Both dc (direct current) and rf (radio-frequency) sputtering has been used to synthesize nanoparticles. Again reactive sputtering or multitarget sputtering has been used to make alloys and/or oxides, carbides, nitrides of materials. This method is specifically suitable for the preparation of ultrapure and non-agglomerated nanoparticles of metal.

**1.9.8 Microwave Plasma Processing**

This technique is similar to the previously discussed CVC method but employs plasma instead of high temperature for decomposition of the metal organic precursors. The method uses microwave plasma in a 50 mm diameter reaction vessel made of quartz placed in a cavity connected to a microwave generator. A precursor
such as a chloride compound is introduced into the front end of the reactor. Generally, the microwave cavity is designed as a single mode cavity using the TE10 mode in a WR975 waveguide with a frequency of 0.915 GHz. The major advantage of the plasma assisted pyrolysis in contrast to the thermal activation is the low temperature reaction which reduces the tendency for agglomeration of the primary particles. This is also true in the case of plasma-CVD processes. Additionally, it has been shown that by introducing another precursor into a second reaction zone of the tubular reactor, e.g. by splitting the microwave guide tubes, the primary particles can be coated with a second phase. For example, it has been demonstrated that ZrO$_2$ nanoparticles can be coated by Al$_2$O$_3$. In this case the inner ZrO$_2$ core is crystalline, while the Al$_2$O$_3$ coating is amorphous. The reaction sequence can be reversed with the result that an amorphous Al$_2$O$_3$ core is coated with crystalline ZrO$_2$. While the formation of the primary particles occurs by homogeneous nucleation, it can be easily estimated using gas reaction kinetics that the coating on the primary particles grows heterogeneously and that homogeneous nucleation of nanoparticles originating from the second compound has a very low probability.

1.9.9 Particle precipitation aided CVD

In another variation of this process, colloidal clusters of materials are used to prepare nanoparticles. The CVD reaction conditions are so set that particles form by condensation in the gas phase and collect onto a substrate, which is kept under a different condition that allows heterogeneous nucleation. By this method both nanoparticles and particulate films can be prepared. An example of this method has been used to form nanomaterials eg. SnO$_2$, by a method called pyrosol deposition process, where clusters of tin hydroxide are transformed into small aerosol droplets, following which they are reacted onto a heated glass substrate.

1.9.10 Combustion Synthesis

Combustion synthesis is the self-propagating high-temperature synthesis (SHS) of compounds by combustion reaction that propagates over starting reactive
mixture owing to layer-by-layer heat transfer. The initial reagent powder mixtures (loose or pelleted), when ignited, spontaneously transform into products (usually in the form of powders, foams or particle conglomerates), because of highly exothermic reactions. Oxides are usually prepared by using nitrate mixtures (oxidizer) of the desired metals along with a fuel (e.g. hydrazine, glycine or urea) in solution, evaporating the solution to dryness and heating the resulting solid to obtain spontaneous combustion, yielding an oxide product. Reaction is normally initiated from the sample surface with a heat flux (heated wire, electric spark or laser beam).

After initiation, reaction self-propagates through the mixture. The duration of heating is markedly shorter than the time of reaction (combustion). SHS occurs when two requirements are met (a) the initial mixture of reactants should be well dispersed and contain high chemical energy to allow high combustion temperature; (b) combustion products should be refractory at the high combustion temperatures. In order to carry out combustion synthesis, the powdered mixture of reactants (0.1-100 \( \mu \)m particle size) is generally placed in an appropriate gas medium that favours an exothermic reaction on ignition. Air is generally sufficient in case of oxides. The combustion temperature can vary between 1500 and 3500 K depending on the reaction. Reaction times are short since the desired product results soon after the combustion. Short synthesis time, high rates of synthesis, non-necessity of high temperature furnace and relatively low power requirements are the salient features of the method. Although these advantages make SHS technique attractive for laboratory use, process scale-up and control are not straightforward because of the extreme processing conditions. Expulsion of gases during combustion in a large reactor can be explosive.

1.10 Properties of nanomaterials

1.10.1 Structural properties

The rise in surface area and surface energy with reducing particle size leads to changes in interatomic spacings. For Cu metallic clusters the interatomic spacing is detected to be decreasing with decreasing cluster size. This is due to the compressive
strain induced by the internal pressure arising from the small radius of curvature in the nanoparticle. Conversely, for semiconductors and metal oxides there is evidence that interatomic spacings increase with decreasing particle size. A further effect is the apparent steadiness of metastable structures in small nanoparticles and clusters, such that all traces of the usual bulk atomic arrangement is lost.

1.10.2 Chemical properties

The alteration in structure as a function of particle size is intrinsically associated to the changes in electronic properties. The ionization potential (the energy required to remove an electron) is usually higher for small atomic clusters than for the corresponding bulk material. Furthermore, the ionization potential exhibits marked variations as a function of cluster size. Such effects appear to be linked to chemical reactivity of the materials. 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. Nanoparticles often exhibit new chemistry as discrete from their bigger 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.

1.10.3 Magnetic properties

Magnetic nanoparticles are used in a variety of applications, including ferrofluids, 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 divergent magnetic properties. Ferromagnetic particles become unstable when the particle size decreases below a certain size, since the surface energy offers a sufficient
energy for fields to spontaneously switch polarization directions. As a result, ferromagnetics become paramagnetics. An operational definition of superparamagnetism would contain at least two requirements. Firstly, the magnetization curve should not show hysteresis, since that is not a thermal equilibrium property. Secondly, the magnetization curve for an isotropic sample must be temperature dependent to the extent that curves taken at different temperatures must approximately superimpose when plotted against H/T after correction for the temperature dependence of the spontaneous magnetization. Whereas bulk ferromagnetic materials usually form multiple magnetic domains, small magnetic nanoparticles often contain 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 variations and only become aligned in the existence of an applied magnetic field.

Giant magnetoresistance (GMR) is a phenomenon detected in nanoscale multilayers [Baibich et al. (1988)] consisting of a strong ferromagnet (e.g., Fe, Co) and a weaker magnetic or non-magnetic buffer (e.g., Cr, Cu); it is usually employed in data storage and sensing. In the absence of a magnetic field the spins in alternating layers are oppositely aligned through antiferromagnetic 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 reduction in scattering at the interface and hence resistance of the device.

1.10.4 Optical properties

The lessening of materials’ dimension has prominent effects on the optical properties. The size dependence can be generally classified into two groups. One is due to the increased energy level spacing as the system becomes more confined, and the other is related to surface Plasmon resonance. The quantum size effect is most prominent for semiconductor nanoparticles, where the band gap increases with a decreasing size, resulting in the interband transition shifting to higher frequencies [Nozik and Menning (1996), Wang and Heron (1991)]. In a semiconductor, the
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energy separation, i.e. the energy difference between the completely filled valence band and the empty conduction band is of the order of a few electron volts and increases rapidly with a decreasing size [Wang and Herron (1991)]. Quantum confinement produces a blue shift in the band gap as well as presence of discrete sub-bands corresponding to quantization along the direction of confinement. The optical properties of nanostructured semiconductors are highly size dependent and thus can be altered by varying the size alone, keeping the chemical composition intact. The luminescent emission from the semiconductor nanostructures can be tuned by varying the size of the nanoparticles. In the case of nanostructured semiconductor lasers, the carrier confinement and nature of electronic density of states of the nanostructures make it more efficient for devices operating at lower threshold currents than lasers with bulk materials. The size dependent emission spectra of quantum wells, quantum wires and quantum dots make them attractive lasing media. The performance of quantum dot lasers is less temperature dependent than conventional semiconductor lasers [Huang (2001)]. The same quantum size effect is also known for metal nanoparticles. However, in order to detect the localization of the energy levels, the size must be very small, as the level spacing has to exceed the thermal energy (~26 meV). Surface Plasmon resonance is the coherent collective excitation of all the free electrons within the conduction band, leading to an in-phase oscillation [Kerker (1969), Bohren and Huffman (1983)]. When the size of a metal nanocrystal is smaller than the wavelength of incident radiation, a surface Plasmon resonance is generated [Kreibeg and Vollmer (1995)]. The width of the resonance varies with the characteristic time before electron scattering. For larger nanoparticle, the resonance sharpens as the scattering length increases. Noble metals have the resonance frequency in the visible range of electromagnetic spectrum.

1.10.5 Electronic properties

The changes which occur in electronic properties as the system length scale is reduced are related mainly to the increasing effect of the wave-like property of the electrons (quantum mechanical effects) and the scarcity of scattering centres. As the
size of the system becomes analogous 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 restricted 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 tunnelling occurs, which shortly increases the tunnelling 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 wavefunctions. This gives rise to additional localization phenomena which are specifically associated to phase interference. If the system is sufficiently small so that all scattering centres can be removed 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 wavefunction. All these phenomena can be utilised to produce radically different types of components for electronic, optoelectronic and information processing applications, such as resonant tunnelling transistors and single-electron transistors.

1.10.6 Biological properties

Biological systems contain many examples of nanosized materials and nanoscale systems. Biomineralization of nanocrystallites in a protein matrix is highly important for the formation of bone and teeth, and is also used for chemical storage and transport mechanisms within organs. Biomineralization involves the operation of gentle biological control mechanisms to produce materials with well-defined characteristics such as particle size, crystallographic structure, morphology and
architecture. Generally complex biological molecules such as DNA have the capability to undergo highly precise and hierarchical self-assembly, which makes them ideal for the assembling of nanosized building blocks. Biological cells have dimensions within the range 110 mm and contain many examples of extremely complex nano assemblies, including molecular motors, which are complexes embedded within membranes that are driven by natural biochemical processes.

1.10.7 Photocatalytic properties

Semiconductor photocatalysis is initiated by electron-hole pairs after band gap excitation. When a photocatalyst, such as titanium dioxide (TiO₂) absorbs Ultraviolet (UV)* light radiation from sunlight or illuminated light source (fluorescent lamps), it produces pairs of electrons and holes. The electron of the valence band of titanium dioxide becomes excited when illuminated by light. The excess energy of this excited electron promotes the electron to the conduction band of titanium dioxide, therefore, creating the negative-electron (e⁻) and positive-hole (h⁺) pair. This stage is referred as the semiconductor's 'photo-excitation' state. The energy difference between the valence band and the conduction band is known as the 'Band Gap'.

Photocatalyst (e.g., TiO₂) + hv → e_CB⁻ + h_VB⁺

These holes further can undergo any of the following processes: (i) recombine with the excited state conduction band electrons and dissipate the input energy as heat, with no chemical effect, (ii) get trapped in metastable surface states, or (iii) react with electron donors or acceptors adsorbed on the semiconductor surface [Folli et al. (2009)]. In the absence of suitable electron and hole scavengers, the stored energy is dissipated in a few nanoseconds by recombination [Folli et al. (2009)]. If a suitable scavenger or surface defects state is available to trap the electron or hole, recombination is prevented and subsequent redox reactions may occur with adsorbed species, such as water, oxygen, and other organic and inorganic compounds. A simplified mechanism for a photocatalytic process for the degradation of organic compounds on a semiconductor is presented in Fig. 1.1.
The prime requisite of a photocatalyst is that the valence band (VB) and the conduction band (CB) of the semiconductor photocatalyst should be positioned in such a way that, the oxidation potential of the hydroxyl radicals ($E_0 (\text{H}_2\text{O}/\text{OH}^\cdot) = 2.8$ V vs NHE) and the reduction potential of superoxide radicals ($E_0 (\text{O}_2/\text{O}_2^-) = -0.28$ V vs NHE), lie well within the band gap. In other words, the redox potential of the VB hole must be sufficiently positive to generate hydroxyl radicals and that of the CB electron must be sufficiently negative to generate superoxide radicals.

1.11 Phosphors and luminescence mechanisms

Phosphors are luminescent materials that emit light when excited, and are usually microcrystalline powders or thin-films designed to provide visible colour emission. A phosphor usually comprises of a host crystal material and one or more intentionally introduced impurities, called activators. The concentration of activators can be as low as tens of ppm, such as for donor acceptors, or can be as high as 20% for rare earth dopants. The band gap of a phosphor host is generally larger than 3 eV to be transparent to visible light, and so either a wide-band-gap semiconductor or an insulator is used as the host. Luminescence is the emission of electromagnetic radiation (photon) usually in the visible region which is not thermal in origin, involving a radiative transition. According to the types of excitation, the phenomena of luminescence can be classified as: photo-, cathodo-, electro-, and
thermoluminescence etc., which is excited by photons, electrons, current, and heat, respectively [Shionoya and Yen (1998)]. In addition to classification by excitation, two other terms are also often used and are related to the decay time ($\tau$): fluorescence ($\tau < 10\text{ms}$) and phosphorescence ($\tau > 0.1\text{s}$) [Shionoya and Yen (1998), Feldman et al. (2003)]. The luminescence of phosphors can be traced to two mechanisms: luminescence in semiconductors and luminescence of localized centers. Luminescence of semiconductors normally occurs, after band-to-band excitation, between impurity states within the band gap, such as donor-acceptor pair luminescence. In the case of luminescent centers, the transitions occur between energy levels of single ions. In the Fig. 1.2, left and middle diagram shows the excitation and emission can be both localized onto one centre (called an activator) or separated from each other: excitation on the sensitizer ($S$) is followed by emission on the activator ($A$) [Feldmann et al. (2003)]. The excitation and emission of semiconductors are shown in the right diagram of the Fig. 1.2. In semiconductors, most important impurities are donors and acceptors that dominate semiconductive properties, and they act as luminescence activators. In this unlocalized type of luminescence, the electrons and holes of the host lattice, i.e., free electrons in the conduction band and free holes in the valance band, participate in the luminescence process. In Fig. 1.2, $A$ and $A^*$ represents the ground and excited state of activator, $S$ and $S^*$ represents the ground and excited state of sensitizer and $D$ and $A$ represents the donor and acceptor levels of semiconductor.

**Fig. 1.2:** Schematic of luminescence mechanisms of phosphors: in localized centers (left, middle) and in semiconductors (right).
After decades of research and development, thousands of phosphors have been prepared and some of them are widely used in many areas [Shionoya and Yen (1998)]. In practical applications, phosphors are often excited by cathode rays, x-rays, or UV emission of a gas discharge, which corresponds to applications in displays, medical imaging and lighting, respectively, such as cathode ray-tube (CRT) colour television, x-ray fluorescent screens and fluorescent lamps.

Materials with nano dimensions such as quantum dots, nanowires, nanorods and nanotubes, have attracted a great deal of attention recently due to their interesting properties that cannot be obtained from the conventional macroscopic materials. Various technological applications require materials that are ordered on all length scales, from the molecular to nano. These novel nanoscale materials are expected to have potential applications in areas such as optoelectronic devices, photo catalyst fabrication and drug delivery systems. Nanophosphor materials are of potential interest in non-linear optics and in fast optical switching. Quantum dots of II-VI semiconductors have attracted particular attention, because they are easy to synthesize within the size range required for quantum confinement. A reduction in the particle size strongly influences the crystallinity, melting point and structural stability. The unique characteristics of the nanomaterials are believed to have originated from the quantum confinement effects due to the change in the band structure into discrete quantum levels as a result of the smaller size of the nanoparticles. Luminescent quantum dot is a new paradigm of phosphor known as quantum phosphor. Different from regular microcrystalline phosphors, these nanocrystals exhibit extremely small sizes of 1~10 nm in diameter and size dependent tunable emission from the same pure semiconductor material. The research on quantum dot technology was pioneered by Brus and others since the early 1980’s, [Brus (1983), Brus (1991)] who demonstrated a wide range of size quantization effects that could be obtained as the size of a semiconductor was reduced to the nanoscale regime. This quantum dot technology enables great flexibility in tuning the optical properties of a material by controlling its physical size [Brus (1983), Brus (1991), Burda et al. (2005)]. For example, the band gap of CdS was found to increase from 2.5 eV, the bulk value, to >3.5 eV as the
particle diameter was decreased from 10 nm to 1 nm [Burda et al. (2005)]. Concurrently, the spectral properties of the luminescence changed and the decay time became extremely fast, ~1-10 ps. As the dot diameter becomes progressively smaller, the energy band shifts to larger values. This indicates that quantum dots can be engineered to emit in selected spectral regions and in combinations, can cover the entire visible spectrum. Quantum dots have been widely used as fluorescence tags and have many potential applications in optoelectronic devices such as photovoltaic cells, LEDs and nano-lasers [Burda et al. (2005)]. By far the most common application is in fluorescence tagging to replace molecular dyes. For example, injecting a tagging substance into a biological cell makes it possible to identify that cell from its fluorescence amid other cells.

1.12 Wide band gap semiconductors

The nanostructures can be realized through different types of structures as well as through different materials. The focus of the present thesis is the growth and characterization of different nanostructures of wide band gap semiconductors.

1.12.1 Zinc oxide

Zinc Oxide (ZnO) is an oxide of the group II metal oxide, and belongs to the P63mc space group. Under most growth conditions, ZnO is an n-type semiconductor, though p-type conductivity of ZnO has also been reported for growth under certain conditions [Kim et al. (2003), Ryu et al. (2003), Joseph et al. (2001), Senthil et al. (2010)]. ZnO exhibits a wurtzite structure (hexagonal symmetry) or rock salt structure (cubic symmetry). However, ZnO crystals most commonly stabilize with the wurtzite structure (hexagonal symmetry), whereas the crystals exhibit the rock salt phase (cubic symmetry) at high pressure. The wurtzite crystal structure of ZnO is shown in Fig. 1.3. Even though it is tetrahedrally bonded, the bonds have a partial ionic character. The lattice parameters of ZnO are \( a = 0.32495 \text{ nm} \) and \( c = 0.52069 \text{ nm} \) at 300, with a \( c/a \) ratio of 1.602, which is close to the 1.633 ratio of an ideal hexagonal close-packed structure. In the direction parallel to the c-axis, the Zn-O distance is
0.1992 nm, and it is 0.1973 nm in all other three directions of the tetrahedral arrangement of nearest neighbours. In a unit cell, zinc occupies the (0, 0, 0.3825) and (0.6667, 0.3333, 0.8825) positions and oxygen occupies the (0, 0, 0) and (0.6667, 0.3333, 0.5) positions [Pearson (1967)]. The wurtzite structure of ZnO has a direct energy bandgap of 3.37 eV at room temperature. Doping in ZnO is much easier compared with other covalent-bond wide bandgap semiconductors, such as GaN. By appropriate doping, the electrical conductivity of ZnO can be tailored from semiconducting to semimetal, keeping high optical transparency to the visible and UV spectral regime. ZnO nanotips are attractive for field emission due to their low emission barrier, high saturation velocity, and high aspect ratio. ZnO is more resistant to radiation damage than Si, GaAs, and GaN [Look (2001)], which is preferred for the long-term stability of field emission emitters in high electric fields. These properties make ZnO an ideal candidate among transparent conducting oxides (TCOs) for field emission displays. ZnO is a wide band gap (3.37 eV) compound semiconductor that is suitable for short wavelength optoelectronic applications. The high exciton binding energy (60 meV) in ZnO crystal can ensure efficient excitonic emission at room temperature. Room temperature ultraviolet (UV) luminescence has been reported in nanoparticles and thin films of ZnO. ZnO is transparent to visible light and can be made highly conductive by doping.

Fig. 1.3: The wurtzite structure of ZnO (Zn white, O blue; highlighted atoms are inside unit cell).
ZnO is a versatile functional material that has diverse growth morphologies such as, nanoparticles [Ajimsha et al. (2008)], core/shell nanoparticles [Zeng et al. (2007)] nanowires and nanorods [Baruah et al. (2008)], nanocombs [Huang et al. (2006)], nanorings [Hughes et al. (2005)], nanoloops and nanohelices [Kong et al. (2003)], nanobows [Hughes et al. (2004)], nanobelts [Sun et al. (2008)] nanocages [Snure et al. (2007)], nanocomposites [Bajaj et al. (2010)] and quantum wells [Misra et al. (2006)]. These structures have been successfully synthesized under specific growth conditions [Wang et al. (2004)]. Nanostructures have attracted attention because of their unique physical, optical, and electrical properties resulting from their low dimensionality. ZnO has an effective electron mass of ~0.24 m_e and bulk ZnO has a small exciton Bohr radius (~1.8 nm) [Gil et al. (2002), Wong et al. (1999)]. The quantum confinement effect in ZnO nanowires should be observable at the scale of an exciton Bohr radius. An example is the well-width-dependent blue shift in the PL spectra observed in both of ZnO/MgZnO MQWs and nanorods [Park et al. (2003)], with the ZnO well widths ranging from 1 to 5 nm. Blue shift of emission from free excitons was reported for ZnO nanorods with diameters smaller than 10 nm, which was ascribed to the quantum size effect [Maejima et al. (2003)]. The temperature dependent blue emission from Zn/ZnO core/shell nanostructures synthesized by laser ablation in liquid medium [Zeng et al. (2007)]. Au is commonly used as a catalyst for growing ZnO nanowires by vapor liquid solid process [Hashimoto et al. (1996)]. The origin of the green luminescence has been attributed to the oxygen vacancies or zinc interstitials [12-13]. Djurisic et al. [14] suggested that the green emission originates from surface defects whereas Norberg et al. [15] have shown a direct relation between the presence of OH group and green emission. The luminescence properties of ZnO nanoparticles are very sensitive to the surface defects and size. ZnO nanoparticles prepared using the wet chemical method generally has traces of intermediate complexes or unreacted precursor which act as defects centers [16]. Nanobelts of ZnO are usually grown [Pan et al. (2007)] by sublimation of ZnO powder without introducing a catalyst and the hydrothermal growth of ZnO nanoscrewdrivers and their gas sensing properties [Wang et al. (2007)]. The dependence of confinement
layer thickness on the PL emission of ZnMgO/ZnO/ZnMgO multiple quantum well structures were reported recently [Misra et al. (2006)]. They also presented room temperature luminescence from this symmetric multiple quantum well structures. Rare earth and transition metals were doped in ZnO nanostructures for luminescent and magnetic applications [Ishizumia et al. (2005), Cui et al. (2006)]. Nanostructured ZnO materials have received broad attention due to their distinguished performance in electronics, optics and photonics. With reduction in size, novel electrical, mechanical, chemical and optical properties are introduced, which are largely believed to be the result of increased surface area and quantum confinement effects. ZnO nanostructures have a wide range of technological applications like surface acoustic wave filters [Emanetoglu et al. (1999)], photonic crystals [Chen et al. (2000)], photodetectors [Liang et al. (2001)], light emitting diodes [Saito et al. (2002)], photodiodes [Lee et al. (2002)], gas sensors [Mitra et al. (1998)], optical modulator waveguides [Koch et al. (1995)], solar cells [Gratzel et al. (2005)] and varistors [Lin et al. (1999)]. ZnO is also receiving a lot of attention because of its antibacterial property and its bactericidal efficacy has been reported to increase as the particle size decreases [Padmavathy and Vijayaraghavan (2008)].

1.12.2 Bismuth Vanadate

Bismuth Vanadate (Bi₄V₂O₁₁), a member of the Aurivillius layered oxides is usually represented as Bi₄V₂O₁₁ due to the presence of the intrinsic oxygen vacancies. The two structural transitions between the three polymorphs (α, β and γ) of Bi₄V₂O₁₁ and further extended the studies involving the partial substitution of the vanadium by other metal ions, thus resulting in a new family of bismuth containing oxides [Abraham et al. (1988)]. They are being popularly identified as the BIMEVOX (BI= bismuth, ME = metal dopant, V = vanadium, OX = oxide) oxides [Abraham et al. (1990)]. A view of the crystal structure of Bi₄V₂O₁₁ is shown in Fig. 1.4. The structure consists of [Bi₂O₃]²⁺ layers alternating with (VO₃₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋_- sheets
have basal edge-shared BiO$_4$ groups with the bismuth occupying the apex of a square pyramid and the oxygen forming the basal plane. The average V-O polyhedron appears as oxygen deficient octahedral units that are connected by the sharing of their corners.

\[
\begin{align*}
\alpha\text{-Bi}_4\text{V}_2\text{O}_{11} & \quad \xrightarrow{450 \, ^\circ C} \quad \beta\text{-Bi}_4\text{V}_2\text{O}_{11} & \quad \xrightarrow{570 \, ^\circ C} \quad \gamma\text{-Bi}_4\text{V}_2\text{O}_{11}
\end{align*}
\]

\[\text{Fig. 1.4: Structural representation of } \alpha\text{-Bi}_4\text{V}_2\text{O}_{11}.\]

\(\alpha\text{-Bi}_4\text{V}_2\text{O}_{11}\) was indexed using a monoclinic cell with the parameters \(a = 5.533, b = 5.611,\) and \(c = 15.288\) Å [Abraham et al. (1988)]. \(\beta\text{-Bi}_4\text{V}_2\text{O}_{11}\) was indexed on a orthorhombic cell with the parameters \(a = b = 11.285\) and \(c = 15.400\) Å, while \(\gamma\text{-Bi}_4\text{V}_2\text{O}_{11}\) was indexed on a tetragonal cell, with the cell parameters \(a = b = 4.004\) and \(c = 15.488\) Å [Abraham et al. (1988)]. Numerous studies have been carried out to relate the structure and the nature of defects with the ionic conductivity of these Bi$_4$V$_2$O$_{11}$ oxides [Mairesse et al. (2003), Mairesse et al. (1988) 861, Abrahams et al. (2002)]. Various experimental conditions, such as quenching and/or annealing, and purity of V$_2$O$_5$ play a significant role towards the oxygen stoichiometry found in Bi$_4$V$_2$O$_{11}$. The experimental band gaps obtained from the UV-visible diffuse reflectance measurements
Introduction

of these samples were known in the range 1.99 to 2.04 eV [Abrahams et al. (1998)]. A wide range of substitution of various cations in different oxidation states for bismuth (Na\(^+\), K\(^+\), Ca\(^{2+}\), Sr\(^{2+}\), Ba\(^{2+}\)) and/or vanadium (Cu\(^{2+}\), Ni\(^{2+}\), Al\(^{3+}\), Ga\(^{3+}\), Ti\(^{4+}\), Nb\(^{5+}\), W\(^{6+}\)) have been investigated in detail over the years [Sharma et al. (1992), Aboukais et al. (1993), Watson et al. (1997), Kendall etal. (1996), Nadir and Steinfink (1999), Kant et al. (2008)]. Depending upon the extent of the cation substitution, the resulting compositions were stabilized either in the \(\alpha\)- or in the \(\gamma\)-Bi\(_4\)V\(_2\)O\(_{11}\) structures [Sharma et al. (1992), Aboukais et al. (1993), Watson et al. (1997), Kendall et al. (1996), Nadir and Steinfink (1999), Kant et al. (2008)].

There has been an exponential growth of scientific studies involving semiconductor materials as photocatalysts, especially to identify semiconducting oxides with appropriate band gaps as an alternate for TiO\(_2\). Bi\(^{3+}\)-containing mixed metal oxides have long been considered as potential visible light photocatalysts for both water splitting and for environmental remediation, the reason being the formation of valence band with hybridised O 2\(p\) and Bi 6\(s\) orbitals [Kudo et al. (1999), Park and Woodward (2000)]. In spite of this favoured electronic structure, only a very few Bi\(^{3+}\) oxides have been identified as visible light photocatalysts. Monoclinic BiVO\(_4\) with a scheelite structure as a highly efficient photocatalyst for water splitting, for the evolution of H\(_2\) and O\(_2\) and for the photodegradation of organic pollutants such as Methylene Blue (MB), Rhodamine B (Rh B) solutions under visible light irradiation [Kudo et al. (1999), Tokunga et al. (2001)]. Subsequently, hydrothermal synthetic methods have been reported for the synthesis of BiVO\(_4\), to enhance its visible light photocatalytic activities [Yu et al. (2006), Wang et al. (2009), Yu et al. (2009)]. Bi\(_2\)PbNb\(_2\)O\(_9\), a member of Aurivillius series of oxides has been identified as a novel photocatalyst showing high photocatalytic activities capable of degrading several organic pollutants and for the production of H\(_2\) or O\(_2\) by water splitting under visible light irradiation (\(\lambda \geq 420\) nm) [Kim et al. (2004)]. Although, CaBi\(_2\)O\(_4\) has been identified [Tang et al. (2004)] as a very efficient visible light photocatalyst for the decomposition of acetaldehyde and MB solutions, its successful applicability is limited by the difficulty associated in
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synthesizing the oxide itself [Luo et al. (2008)]. $\text{Bi}_2\text{WO}_6$ [Zhang et al. (2005), Fu et al. (2007)], $\text{Bi}_2\text{MoO}_6$ [Zhao et al. (2009)] and $\text{Bi}_2\text{GaTaO}_7$ [Luan et al. (2004)] exhibit visible light photocatalytic activity for the decomposition of dye solutions such as Rh B and MB solutions. Other mixed metal oxides such as $\text{Bi}_2\text{Ti}_2\text{O}_7$ [Yao et al. (2004)], $\text{LiBi}_3\text{M}_3\text{O}_{14}$ (M = Nb, Ta) [Muktha et al. (2005)], $\text{Bi}_2\text{M}_2\text{O}_7$ (M = Al, Ga, In) [Zou et al. (2001)], $\text{Bi}_2\text{MTaO}_7$ (M = In, Fe, Ga) [Wang et al. (2005)] and $\text{BiMO}_4$ (M = Nb, Ta) [Muktha et al. (2006)] have been known for the decomposition of organic contaminants under UV light irradiation. The photocatalytic activities for water splitting were investigated for the oxides $\text{ABi}_2\text{Nb}_2\text{O}_9$ (A = Ca, Sr, Ba) under UV light irradiation [Li et al. (2010)]. The efficiency of $\text{BiVO}_4$ as a visible light photocatalyst, encouraged us to investigate the yet another member of the well-known oxide ion conductor, $\text{Bi}_4\text{V}_2\text{O}_{11}$ belonging to the Bi-V-O system [Boivin et al. (1998)].

Reports of novel $\text{Bi}^{3+}$ based visible light photocatalytic oxides, such as $\text{Bi}_2\text{YVO}_8$, $\text{Bi}_2\text{AlVO}_7$ and $\text{Bi}_2\text{GaVO}_7$ [Luan et al. (2008), Luan et al. (2009), Luan et al. (2007)] have been added recently to the literature. $\text{Bi}_2\text{YVO}_8$ was reported to be a new compound containing $\text{Bi}^{3+}$ and $\text{Bi}^{5+}$ ($\text{Bi}_{1.06}^{3+}\text{Bi}_{0.94}^{5+}\text{Y}_{0.98}^{3+}\text{V}_{1.03}^{5+}\text{O}_{7.95}^{2-}$) ions, crystallizing in the $I4/mmm$ space group with the lattice parameters of $a = 3.9188(2)$ and $c = 15.3105(9)$ Å [Luan et al. (2008)]. $\text{Bi}_2\text{YVO}_8$ with a band gap of 2.09 eV was shown to split water under UV light and to degrade MB solution under visible light irradiation [Luan et al. (2008)]. $\text{Bi}_2\text{AlVO}_7$ ($a = 3.99294$ and $c = 15.3469$ Å) [Luan et al. (2009)] and $\text{Bi}_2\text{GaVO}_7$ ($a = 3.0994$ and $c = 15.2291$ (Å) [Luan et al. (2007)] crystallizing in tetragonal crystal system with space group $I4/mmm$, were known to decompose MB solutions under visible light. Their band gaps were 2.06 and 2.13 eV for $\text{Bi}_2\text{AlVO}_7$ and $\text{Bi}_2\text{GaVO}_7$, respectively [Luan et al. (2009), Luan et al. (2007)]. Close examination of the XRD patterns of these phases and the lattice parameters reported for these oxides resembled closely to that of $\gamma$-$\text{Bi}_4\text{V}_2\text{O}_{11}$. 

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1.12.3 Tin Oxide

Tin Oxide (SnO₂) is a wide band-gap (3.6 eV) semiconductor with good chemical and mechanical stability and is optically transparent in the visible range of electromagnetic spectrum [Batzill et al. (2005)]. The unit cell of SnO₂ is shown in Fig. 1.5, where the big spheres represent oxygen atoms and smaller sphere represents Sn atoms. The Sn atoms in the crystal have an octahedral coordination whereas O atoms have trigonal planar coordination. SnO₂ being a wide band-gap material is expected to be electrically insulating in stoichiometric composition. However, low formation energy of oxygen vacancies and tin interstitials results in readily formation of these native point defects in SnO₂, and thereby responsible for often observed high conductivity of undoped, but non-stoichiometric, SnO₂ [Kilic and Zunger (2002)]. The n-type conductivity of SnO₂ is reported due to large amount of defects related to oxygen vacancies which creates the donor levels about 114 meV below the bottom of the conduction band [Kilic and Zunger (2002)]. It has been identified that the adsorbed oxygen from atmosphere on the surface of SnO₂ interacts with a combination of bridging oxygen and in-plane oxygen vacancies, and this interaction forms the basis of gas detection mechanism [Batzill et al. (2005)].

It is reported that (110) and (101) planes of SnO₂ crystal are F (plane) faces while the (111) plane is K (kinked) i.e. (110) and (101) are smoother than (111) plane.
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[Batzill et al. (2005)]. According to Periodic Bond Chain (PBC) theory (110) plane is the most stable face of SnO₂ because of the fact that F faces are strongly bound to each other in direction parallel to the face. In an ionic form, Sn²⁺ has a 5s² electron configuration. The surface energies of the low index surfaces of SnO₂ with bulk composition termination are calculated theoretically by Density Functional Theory (DFT) [Batzill et al. (2005)]. For these surfaces with surface-tin atoms in their Sn⁴⁺ oxidation state, the (110) surface exhibits the lowest energy surface followed by the (100), (101), and (001) surfaces. It is reported that the Sn ions on the perfect surface of SnO₂ are all in the nominal Sn⁴⁺ state, as in the bulk [Batzill et al. (2005)]. The conduction and valence bands do not appear to be bent at this surface, i.e., surface is in a flat-band state. For this reason, the surface and the bulk exhibit same resistivity values. The surface (110) is thermodynamically the most stable one [Batzill et al. (2005)]. The interesting defect properties of this surface arise because of the bridging of oxygen ions, lying above the main surface plane. These oxygen ions can be removed easily either by heating or by particle bombardment. When oxygen ions are removed, the two electrons left behind occupy orbitals, a mixture of 5s and 5p, on surface Sn⁴⁺ ions, converting them to Sn²⁺. The dual valency of Sn facilitates reversible transformation composition of the surface from stoichiometric surface (Sn⁴⁺ surface cations) into a reduced surface with Sn²⁺ surface cations depending on the oxygen chemical potential of the system [Batzill et al. (2005)]. Reduction of the surface influences the surface electronic structure by formation of Sn 5s derived surface states that lie deep within the band gap and also may cause a lowering of the work function.

On the other hand stoichiometric (101) surface is known to exhibit higher surface energy as compared to the (110) surface [Batzill et al. (2005)]. The reduced surface (101) shows a surface termination with a perfect Sn²⁺O²⁻ stoichiometry which satisfies the valency of Sn. Whereas, for a reduced (110) surface, no analogous arrangement of atoms exists that can readily satisfy the Sn²⁺ oxidation state [Batzill et al. (2005)]. This explains the stability of the (101) surface, while the (110) surface forms complex reconstructions despite the fact that the surface energy of the stoichiometric (110) is lower than that of (101). Thus, (110) surface adsorbs more
oxygen from the atmosphere as compared to (101) surface due to which when reducing
gas comes into contact of (110) surface, it interacts with adsorbed oxygen species and
releases electrons to the SnO$_2$ surface, thereby reducing the resistance of SnO$_2$ surface
[Haridas et al. (2011), Verma et al. (2012)]. However, (101) surface adsorbs
comparatively lesser oxygen from atmosphere, thus more Sn$^{2+}$ sites are available for
oxidizing gases to interact from SnO$_2$ surface. Thus, oxidizing gases trap free electrons
from (101) surface resulting in reduction in conductivity and increases resistance of
SnO$_2$ film [Choi et al. (2008), Law et al. (2002)].

1.13 Objective of the present work

The objective of the present work is to synthesis the semiconducting
nanomaterials and characterize for their structural, morphological, optical and
magnetic and catalytic properties. The present study has been made with respect to the
following points:

- Synthesis of semiconducting nanomaterials (ZnO, Bi$_4$V$_2$O$_{11}$, SnO$_2$).
- Effect of annealing and hydrothermal reaction temperature of ZnO
  nanoparticles in order to understand the mysterious visible broad emission in
  PL.
- Induced defects (in ZnO nanoparticles) by rare earth elements doping to tailor
  the optical, magnetic and photocatalytic properties.
- Synthesis of Bi$_4$V$_2$O$_{11}$ nanoparticles for organic dye degradation (Rh B and
  MB) using photocatalytic and sonocatalytic experiments. Also, to understand
  the effect of phase change of the catalyst (Bi$_4$V$_2$O$_{11}$) on the degradation rate of
  organic dye.
- Effect of annealing on optical and photocatalytic activity (for the degradation
  of MB dye) of SnO$_2$ nanoparticles.