1.1 Introduction

Nanotechnology involves the creation and manipulation of materials at the nanometre (nm) scale either by scaling up from single groups of atoms or by refining or reducing bulk materials. A nanometre is $1 \times 10^{-9}$ m or one millionth of a millimetre. To give a sense of this scale, a human hair is of the order of 10,000 to 50,000 nm, a single red blood cell has a diameter of around 5000 nm, viruses typically have a maximum dimension of 10 to 100 nm and DNA molecule has a diameter of 2 to 12 nm. The use of the term “Nanotechnology” can be misleading since it is not a single technology or scientific discipline, but it is a multidisciplinary grouping of Physical, Chemical, Biological, Engineering and Electronic.

Nanotechnology is a rapidly developing and expanding discipline and has aroused growing media and public interest. New materials are being discovered and astonishing claims are being made concerning their properties, behaviours and applications. Development of new nanomaterials is a major theme of all of these programmes. Ordinary materials such as carbon or silicon, when reduced to the nanoscale, often exhibit novel and unpredictable characteristics such as extraordinary strength, chemical reactivity, electrical conductivity and other characteristics that the same material does not possess at the micro or macro-scale. The nanomaterials have already been produced with different morphologies such as nanotubes, nanowires, nanorods, cuboids etc, which has special properties than spherical size materials.

Nanotechnologies are gaining more importance in commercial applications. Nanoscale materials are currently being used in electronic, magnetic, optoelectronic, biomedical, pharmaceutical, cosmetic, energy, catalytic and material applications. Areas producing the greatest revenue for nanoparticles are reportedly chemical-mechanical polishing, magnetic recording tapes, sunscreens, automotive catalyst supports, bio-labelling, electro-conductive coatings and optical fibres.

Despite the current interest nanoparticles are not a new phenomenon for scientists being aware of colloids and sol particles, for more than 100 years.
The scientific investigation of colloids and their properties were reported by Faraday (1857) in his experiments with gold. He used the term “divided metals” to describe the material which was produced. Zsigmondy (1905) describes the formation of a red gold sol which is now understood to comprise particles in the 10 nm size. Throughout the last century the field of colloidal science has developed enormously and has been used to produce many materials including metals, oxides, organic and pharmaceutical products.

Many other well known industrial processes produce materials which have dimensions in the nanometre size range. One example is the synthesis of carbon black by flame pyrolysis which produces carbon with a very high surface to volume ratio. This is highly agglomerated but has a primary particle size which can be in the order of 100 nm. Worldwide production of carbon black was approximately six million tons in 1993 (IARC, 1996). Other common materials produced by flame pyrolysis or similar thermal processes include fumed SiO$_2$, ultrafine TiO$_2$ and Ni.

Nano sized particles are also found in the atmosphere where they originate from combustion sources (traffic, forest fires), volcanic activity, and atmospheric gas to particle conversion processes such as photochemically driven nucleation. In fact, nanoparticles are the end product of a wide variety of physical, chemical and biological processes, some of which are novel and radically different.

The term "nano" comes from a Greek prefix, meaning dwarf. Nanoscale objects have atleast one dimension that measures between 1-100 nm. Nanophase materials of all types are being considered for advanced applications in 21st Century. The synthesis, characterization and processing of nanostructured materials are part of an emerging and rapidly growing fields [1]. Nanomaterials have a particular distribution of crystallites or domains at a nanometer scale in a peculiar fashion. A strong macroscopic interaction occurs between the basic units of crystallites. It determines the modified physical and chemical properties of nanostructured materials. These nanostructures are intensely interesting for many reasons [2].
Fig. 1.1 Examples of nanostructures in nature and nanotechnology

Nanotechnologists use similar principles to deliberately engineer at the nanoscale to create products that make use of these unusual properties. Starting with nanostructures, scientists rearrange them to assemble functional systems that can be incorporated into products with unique properties. Fig. 1.1 shows two examples. First, the propensity for carbon to form tubes at the nanoscale can be used to generate arrays over micron sized conductors that illuminate flat panel displays for mobile phone and secondly nanoparticles can be manipulated to create effective, fully transparent UV blocking creams. These are two of many examples of stronger, stickier, smoother and lighter products being developed.

In general, as per the human nature, one believes some information only if one could see it. Science always believes on proof and repeatability of the results, therefore nanotechnology has developed only after the invention of electron microscope. The proverb ‘necessity is the mother of invention’ has some meaning. In that way if one looks at the nanotechnology the applications are countless. Properties of nanomaterials that are different from bulk are
variation of the redox properties, band gap variation, enhancement in toughness and strength, anomalous melting points and unusual crystal structures (in metals). Nanotechnology is one of the frontier areas of science due to its versatile applications in various fields.

1.2 History of Nanotechnology and Nanomaterials

The origins of nanotechnology received more attention after 1959, when Richard Feynman, Physicist and Nobel Prize winner, presented a talk to the American Physical Society in annual meeting entitled *There’s Plenty of Room at the Bottom* [3]. In his talk, Feynman presented ideas for creating nanoscale machines to manipulate, control and image matter at the atomic scale. In 1974, Norio Taniguchi introduced the term ‘nanotechnology’ to represent extra-high precision and ultra-fine dimension, and also predicted improvements in integrated circuits, optoelectronic, mechanical devices and computer memory devices [4]. This is the so called ‘top-down approach’ of carving small things from large structures. In 1986, K. Eric Drexler in his book *Engines of Creation* discussed the future of nanotechnology, particularly the creation of larger objects from their atomic and molecular components, so called ‘bottom-up approach’ [5]. He proposed ideas for ‘molecular nanotechnology’ which is the self assembly of molecules into an ordered and functional structure. The invention of the scanning tunneling microscope by Gerd Binnig and Heinrich Rohrer in 1981 (IBM Zurich Laboratories), provided the real breakthrough and the opportunity to manipulate and image structures at the nanoscale. Subsequently, the atomic force microscope was invented in 1986, allowing imaging of structures at the atomic scale. Another major breakthrough in the field of nanotechnology occurred in 1985 when Harry Kroto, Robert Curl and Richard Smalley invented a new form of carbon called fullerene (buckyballs), a single molecule of 60 carbon atoms arranged in the shape of a soccer ball. This led to a Nobel Prize in Chemistry in 1996. Since that time, nanotechnology has evolved into one of the most promising fields of science, with multi-billion dollar investment from the public and private sectors and the potential to create
multi-trillion dollar industries in the coming decade. The nanomaterials began immediately after the big bang theory when nanostructures were formed in the early meteorites. Nature evolved many other nanostructures like seashells, skeletons etc. Nanoscaled smoke particles were formed during the use of fire by early humans. 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 [6]. Nanostructured catalysts have also been investigated over 70 years. By the early 1940’s, precipitated and fumed silica nanoparticles were being manufactured and sold in USA and Germany as substitute for ultrafine carbon black for rubber reinforcement [7]. Nanosized amorphous silica particle has found large-scale applications in many every-day consumer products, ranging from non-dairy coffee creamer to automobile tires, optical fibers and catalyst support. In the 1960s and 1970s metallic nanopowders for magnetic recording tapes were developed [8].

Today nanophase engineering expands in a rapidly growing number of structural and functional materials, inorganic and organic, allowing to manipulating mechanical, catalytic, electric, magnetic, optical and electronic properties. The production of nanophase or cluster-assembled materials is usually based upon the creation of separated small clusters, which are fused into a bulk material such as 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 [9].

1.3 Importance of Nanoparticles

The nanomaterials have created a high interest in recent years by virtue of their unusual mechanical, electrical, optical and magnetic properties. The production of nanophase materials is usually based upon the creation of
separated small clusters, which are fused into a bulk-like material. Some examples are given below:

(a) Nanophase ceramics are of particular interest because they are more ductile at elevated temperatures as compared to the coarse-grained ceramics.

(b) Nanostructured semiconductors are known to show various non-linear optical properties. Semiconductor quantum dot particles also show quantum confinement effects which may lead to special properties, the luminescence in silicon powder and silicon germanium quantum dots as infrared optoelectronic devices.

(c) Nanosized metallic powders have been used for the production of gas tight materials, dense parts and porous coatings. Cold welding properties combined with the ductility make them suitable for metal-metal bonding especially in the electronic industry.

(d) Single nanosized magnetic particles are mono-domains and one expects that also in magnetic nanophase materials that 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 super-paramagnetism behaviour. Magnetic nanocomposites have been used for mechanical force transfer (ferrofluids), for high density information storage and magnetic refrigeration.

(e) 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 which have been shown to offer substantial advantages concerning to activity, selectivity and lifetime in chemical transformations and electrocatalysis (fuel cells). Enantioselective catalysis were also achieved using chiral modifiers on the surface of nanoscale metal particles.

(f) 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 (MnO\textsubscript{2}) finds application for rechargeable batteries for cars and 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.

Polymer based composites with a high content of inorganic particles leading to a high dielectric constant are interesting materials for photonic band gap structure.

It has been realized that materials in nanodimensions exhibit properties very different from their bulk counterparts. Increasing knowledge about the unique properties of nanoparticles has lead to renewed interest in them for potential applications. The applications of nanoparticles extend to wide-ranging areas such as catalysis, biosensors, diagnostics, cell labeling, solar cells, fuel cells, photonic band gap materials, single electron transistors, nonlinear-optical devices and surface enhanced Raman spectroscopy. The realization of their various potential applications is only limited by our imagination.

Our focus has been on the production processes rather than on those which utilize nanoparticles to manufacture other products. Our view of a production process includes synthesis, in which the material is formed, and recovery in which the product is collected, modified, divided and packed for dispatch. Since these are new materials, most of the research and industry effort is on the development of processes and materials and scale-up of these processes to industry scale. As understanding about the properties of a new material increase, effort will tend to shift towards applications and more exposures might be expected. Secondly, in the early stages of the life cycle of a new material, many of the potential applications will be speculative and may never come to fruition.

1.4 Morphology of Nanoparticles

As the particle size ranging from 1 to 100 nm shows unusual properties of materials. From the literature survey it is seen that ZnO nanowires are used to sense the ethanol in the range of 1 to 100 ppm, V$_2$O$_5$ nanofibres shows
Chapter-I: Introduction

extremely high sensitivity for 1-butylamine and moderate sensitivity for ammonia. The optical properties of metal nanoparticles have received attention for making use of them in optical sensors, colour glasses and photoelectrochemical cells. Metal nanowires and nanoparticles are used in the nanocircuits. In medicine, gold nanoparticles are utilized for drug delivery and identification of affected cells. It is important that the only triangular nanoparticles can be easily identified the cancer cells. Since, they posses sharp edges, they easily penetrate the cancer cells and the cancer cells can be destroyed using the same. The most of triangular particles are bound to cell, they will be killed using far IR radiation. It is also reported that in particular, nanorods, nanowires, cuboids are showing enhanced photocatalytic activity than the spherical size.

1.5 Methods for Synthesis of Metal Oxide Nanoparticles

Mainly two approaches have been used for the synthesis of nanomaterials. Top–down and Bottom–up are the two approaches. Top–down approach involves mainly physical methods where a bulk material is sliced into pieces till the desired size is achieved. Lithographic techniques, laser induced chemical etching and ball milling fall in to this category. However, these methods are effective only down to the micrometer level. Reaching nanometer scale makes these methods more expensive and technically difficult. The bottom–up approaches mainly involve chemical and biological methods to make nanoparticles. These involve controlled condensation of solute molecules that is formed during a chemical reaction. The restriction of the condensation or the growth leads to the formation of particles of desired size and shape [2]. However unlike the chemical synthesis of molecules of a desired structure, the synthesis of nanomaterials with uniform size and shape is difficult. Thus, large scale synthesis of nanomaterials remains a challenge.

The development of systematic studies for the synthesis of oxide nanoparticles is a current challenge and, essentially, the corresponding preparation methods may be grouped in two main streams based upon the
liquid-solid and gas-solid nature of the transformations [10]. Liquid-solid transformations are possibly the most broadly used in order to control morphological characteristics with certain “chemical” versatility and usually follow a “bottom-up” approach. A number of specific methods have been developed, amongst them those which are broadly in use are given below.

I) Co-Precipitation Method

This involves dissolving a salt precursor in water (or other solvent) to precipitate the hydroxide form with the help of a base. However, the use of surfactants, sonochemical methods, and high-gravity reactive precipitation appear as novel and viable alternatives to optimize the resulting solid morphological characteristics [11-12].

II) Sol-Gel Method

The sol-gel method provides a highly useful means of preparing inorganic oxides [13]. It is a wet chemical method and a multistep process involving both chemical and physical processes such as hydrolysis, polymerization, drying and densification. The name sol-gel is given to the process because of the distinctive viscosity increase that occurs at a particular point in the sequence of steps. Most of the sol-gel literature deals with synthesis from alkoxides. The important features of the sol-gel techniques are better homogeneity compared to the traditional methods, high purity, lower processing temperature and more uniform phase distribution in multicomponent systems, better size and morphological control, the possibility of preparing new crystalline and nanocrystalline materials.

The various steps in the sol-gel technique may or may not be strictly followed in practice. Thus, many complex metal oxides are prepared by a modified sol-gel route without actually preparing metal alkoxides e.g. a transition metal salt solution is converted into a gel by the addition of an appropriate organic reagent.
III) Microemulsion Technique

Microemulsions represent an approach based on the formation of ternary mixture containing water, surfactant and oil. Metal precursors on water will proceed precipitation as oxo-hydroxides within the aqueous droplets, typically leading to monodispersed materials with size limited by the surfactant-hydroxide contact [14].

IV) Solvothermal Method

In this case, metal complexes are decomposed thermally either by boiling in an inert atmosphere or using an autoclave with the help of pressure. A suitable surfactant is usually added to the reaction media to control particle size growth and limit agglomeration [15]. The solvothermal method uses a solvent under pressure and temperature above its critical point to increase the solubility of solids and to speed up reactions of solids. Most materials can be made soluble in proper solvent by heating and pressurising the system near to its critical point. Lower supersaturation state can be achieved by this method.

VI) Chemical Vapour Deposition (CVD)

There are a number of CVD processes used for the formation of nanoparticles, some of them are classical, metalorganic, plasma-assisted, and photo CVD methodologies [17]. The advantages of this methodology consist of producing uniform, pure and reproducible nanoparticles and films although requires a careful initial setting up of the experimental parameters.

VII) Pulsed Laser Deposition (PLD)

Pulsed laser deposition heats a target sample (4000 K) and leads to instantaneous evaporation, ionization, and decomposition with subsequent mixing of desired atoms. The gaseous entities formed absorb radiation energy from subsequent pulses and acquire kinetic energy perpendicularly to the target to be deposited in a substrate generally heated to allow crystalline growth [18].

Irrespective of the preparation method used to obtain ultrafine nano-oxides, the studies of nanoparticle preparation yielded compelling evidence
concerning the fact that crystallization does not follow a traditional nucleation and growth mechanism. Although subjected to further assessment, it appears that the simple idea that a small primary size would be prime nucleation as the key step of crystallization seems essentially correct and holds certain general validity, at least in solid-solid crystallization mechanisms. When additional liquid/gas phase crystallization steps are involved in the final formation of the nanoparticle, other steps like Ostwald ripening may be also of prime importance. In any case, a lot of novel insights have been recently uncover in solid-solid transformations and two main theories describe crystallization to proceed either by surface (single particle) or interface (two or multiple particle) nucleation [19].

The primacy of one of them has been postulated to be a function of the oxide chemical nature and temperature, being presumably surface effects always predominant at higher temperatures. Both theories mostly received support from kinetic approaches but very recent analyses sensitive to structural order in the amorphous precursor materials have demonstrated the key role of intraparticle local order (below 1 nm) in driving the nucleation temperature onset in a broad interval of ca. 200 K, showing that the whole crystallization mechanism of oxide nanoparticles appears only compatible with some kind of intraparticle, dimensional-restricted (surface) mechanism [20].

VIII) Microwave Assisted Sol-Gel Method

In the last decades, microwave heating has been applied in several areas as a very effective and non-polluting method of activation. Examples of this technology are materials processing, industrial and commercial applications, chemistry and biochemistry, among others. In the electromagnetic spectrum, the microwave radiation is located between infrared radiation and radio waves. The wavelengths are between 1mm and 1m with corresponding frequencies in the range of 300 GHz to 300 MHz. Besides telecommunication and microwave, radar equipments occupy many of the band frequencies in this region, most routinely used, for industrial and scientific purposes are imposed by
international convention be the 2.45GHz (wavelength of 12.2cm) [21]. The microwave energy is lying between 1.24 meV to 1.24 µeV.

Microwave is a relatively new technology alternative for materials processing that provides new approaches for enhancing the material properties as well as economic advantages through energy saving and acceleration of product development. Clearly, advantages in utilizing this technology include penetration of radiation, controlled electric field distributions, rapid heating, self-limiting reactions and selective and volumetric heating [22]. Depending on the response to microwave heating, materials can be classified into three principal groups with respect to their interaction with a microwave field: transparent or low loss materials where microwaves pass through them without any losses; conductors which reflect microwaves without any penetration; absorbing or high loss materials, which absorb microwaves and dissipate the electromagnetic energy as heat, depending on the value of the dielectric loss factor. Microwave heating of dielectric materials lies in the ability of the electric field to polarize the charge of the material where polarization cannot follow the rapid change of the electric field [23].

Microwave heating offers several potential advantages over conventional heating for inducing or enhancing chemical reactions. These include direct microwave interaction with certain classes of molecules, volumetric heating rather than heat flow through the vessel wall, less waste heat, increased control over heating rates and the possibility of selective enhancement of desired reactions. This is particularly attractive in the case of catalytic reactions, where it may be possible to selectively promote desirable reactions while suppressing undesirable ones. Also, as a fast, simple and energy efficient method, microwave synthesis has been developed and is widely used for the synthesis of zeolites and ceramic materials.

Compared with conventional methods, microwave synthesis has the advantages of very short reaction times, production of small particles with a narrow particle size distribution and high purity. These conveniences could be attributed to fast homogeneous nucleation and ready dissolution of the gel.
Unfortunately the exact nature of the interaction of the microwaves with the reactants during the synthesis of materials is somewhat uncertain and speculative. However, it is well known that the interaction between dielectric materials and the microwaves leads to dielectric heating in which electric dipoles in such materials respond to the applied electric field. In liquids, this constant reorientation leads to a friction between the molecules, which subsequently generate heat. Many microwave phenomena are poorly understood such as non-thermal effects and the superheating effect [21-23].

1.6 Properties of ZnO

1.6.1 Physical Properties

The unique and fascinating properties of II-VI compound semiconductors have triggered tremendous motivation among the scientists to explore the possibilities of using them in industrial applications, zinc oxide (ZnO) is a piezoelectric, dielectric, transparent, semiconducting oxide with a direct band gap of 3.37 eV at room temperature and a large exciton binding energy (60 MeV), which is 2.4 times the effective thermal energy (KBT = 25 MeV) at room temperature. This is one of the key parameters that ZnO exhibits near-UV emission, transparency, conductivity and resistance to high temperature electronic degradation. In addition, ZnO is the hardest of the II-VI semiconductors due to the higher melting point (1975°C) and large cohesive energy (1.89 eV). Physical properties of ZnO are given in Table 1.1.
Table 1.1: Physical Properties of ZnO

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Structure</td>
<td>Hexagonal</td>
</tr>
<tr>
<td>2</td>
<td>Lattice parameter ‘a’</td>
<td>3.2495 Å</td>
</tr>
<tr>
<td>3</td>
<td>Lattice parameter ‘c’</td>
<td>5.2069 Å</td>
</tr>
<tr>
<td>4</td>
<td>c/a</td>
<td>1.602</td>
</tr>
<tr>
<td>5</td>
<td>Density</td>
<td>5.606 g cm(^{-3})</td>
</tr>
<tr>
<td>6</td>
<td>Stable phase at 300 K</td>
<td>Wurtzite</td>
</tr>
<tr>
<td>7</td>
<td>Melting point</td>
<td>1975°C</td>
</tr>
<tr>
<td>8</td>
<td>Thermal conductivity</td>
<td>0.6, 1-1.2 µSiemen</td>
</tr>
<tr>
<td>9</td>
<td>Static dielectric constant</td>
<td>8.656</td>
</tr>
<tr>
<td>10</td>
<td>Refractive index</td>
<td>2.008, 2.029</td>
</tr>
<tr>
<td>11</td>
<td>Energy gap</td>
<td>3.37 eV, direct</td>
</tr>
<tr>
<td>12</td>
<td>Exciton binding energy</td>
<td>60 MeV</td>
</tr>
<tr>
<td>13</td>
<td>Ionicity</td>
<td>62%</td>
</tr>
</tbody>
</table>

1.6.2 Crystal Structure

Zinc oxide crystallizes in three forms: hexagonal wurtzite, cubic zinc blende and the rarely observed cubic rock salt. The wurtzite structure is most stable and thus most common at ambient conditions, shown in Fig.1.2 (a). The zinc blende form can be stabilized by growing ZnO on substrates with cubic lattice structure, shown in Fig.1.2 (b). The rock salt NaCl-type structure is only observed at relatively high pressures ~10 GPa. The hexagonal and zinc blende ZnO lattices have no inversion symmetry (reflection of a crystal relatively any given point does not transform it into itself). This and other lattice symmetry properties result in piezoelectricity of the hexagonal and zinc blende ZnO, and in pyroelectricity of hexagonal ZnO. The hexagonal structure has a point group 6 mm (Hermann-Mauguin notation) and the space group is P\(_{6}\)\(_{3}\)mc or C\(_{6v}\). The lattice constants are a = 3.25 Å and c = 5.2 Å, their ratio c/a ~ 1.60 is close to
the ideal value for hexagonal cell $c/a = 1.633$. As in most II-VI materials, the bonding in ZnO is largely ionic, which explains its strong piezoelectricity. Due to this ionicity, zinc and oxygen planes bear electric charge (positive and negative, respectively). Therefore, to maintain electrical neutrality, those planes reconstruct at atomic level in most relative materials, but not in ZnO because its surfaces are atomically flat, stable and exhibit no reconstruction.

Fig.1.2 (a) Wurtzite structure of ZnO

Fig.1.2 (b) Zinc blende structure of ZnO
1.6.3 Lattice Parameters

Lattice parameters are considered important, when one has to develop semiconductor devices. There are mainly four factors which determine the lattice parameters of the semiconductors. (i) Free-electron concentration which affects the potential of the bottom of conduction band normally occupied by electrons. (ii) Concentration of impurities, defects and the difference in ionic radii between these defects and impurities with respect to substituted matrix ions. (iii) External strains. On the other hand, the strict periodicity of the lattice is disturbed by many imperfections. These imperfections have a considerable, controlling influence on mechanical, thermal, electrical and optical properties of semiconductors. They determine the plasticity, hardness, thermal and electrical conductivities. Commonly the lattice parameters of any crystalline material are measured accurately by high resolution X-ray diffraction (HRXRD). Table 1.2 shows a comparison of measured and calculated lattice parameters of ZnO, c/a ratio reported by several groups [24-25].

Table 1.2: Measured and calculated lattice constants

<table>
<thead>
<tr>
<th>Name of the method</th>
<th>Lattice parameter a (Å)</th>
<th>Lattice parameter c (Å)</th>
<th>Ratio of c/a</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-ray diffraction method.</td>
<td>3.2496</td>
<td>5.2042</td>
<td>1.6018</td>
</tr>
<tr>
<td>Powder X-ray diffraction method.</td>
<td>3.2501</td>
<td>5.2071</td>
<td>1.6021</td>
</tr>
<tr>
<td>Linear Combination of Atomic Orbital (LCAO) method.</td>
<td>3.286</td>
<td>5.241</td>
<td>1.595</td>
</tr>
</tbody>
</table>
1.6.4 Band Structure

ZnO has wurtzite structure with direct energy band gap of 3.37 eV at room temperature. The lowest conduction band of ZnO is predominantly n-type and the valance band is p-type (six fold degenerate). The valance band splits into three subbands A, B and C by spin orbit and crystal-field interactions, as illustrated in Fig.1.3 [26]. The free excitation binding energies associated with the A, B and C valance bands are 63, 50 and 49 meV, respectively [27]. The high excitation binding energy leads to excitonic recombination even at room temperature, in contrast to conventional electron-hole-plasma (EHP) transition, which is promising for high-efficiency, low threshold photonic devices. Optical anisotropy exists near the band edge due to different selection rules for light polarization perpendicular and parallel to c-axis [28]. Transition for the A and B excitation is mainly allowed for light polarization perpendicular to C-axis, where as transition for the C excitation is mainly allowed for light polarization parallel to C-axis.

![Fig.1.3. Valance band splitting in hexagonal ZnO by crystal-field and spin-orbit coupling](image)

Fig.1.3. Valance band splitting in hexagonal ZnO by crystal-field and spin-orbit coupling
1.6.5 Technology Development

In the field of semiconductor, ZnO is not new, its lattice parameter and optical properties were studied by Bunn in 1935 and Mallow in 1954. Damen studied the vibrational properties of ZnO with Raman scattering in 1966 and its growth though the chemical vapour transport reported by Gali and Coker. ZnO has been used as LED (1968) and it’s green emission (1969), yellow emission (1970) are reported by Drapak. The main obstacle for the development of ZnO has been the lack of reproducibility and low resistivity of p-type ZnO as recently discussed by Look and Claflin in 2004. The attempt is made to prepare various morphologies in presence of various oxides mixed with ZnO and to improve its photo catalytic activity.

1.6.6 Applications of ZnO

As an important low-cost basic II-VI functional semiconductor material, ZnO has many remarkable applications in functional devices, due to its large exciton binding energy (60 meV) at room temperature. A great effort has been paid to the synthesis of ZnO nanostructures, such as nanorods, nanowires [29-30], nanobelts [31] and nano-tubes [32], which have been attracted intense attention due to their potential applications in a variety of novel nano-devices, such as field-effect transistors, single-electron transistors, photodiodes [33] and chemical sensors [34-36].

The applications of zinc oxide powder are numerous and the principle ones are summarized below. Most applications exploit the reactivity of the oxide as a precursor to other zinc compounds. For material science applications, zinc oxide has high refractive index, high thermal conductivity, antibacterial and UV-protection properties. Consequently, it is added into various materials and products, including plastics, ceramics, glass, cement, rubber, lubricants [37], paints, ointment, adhesive, sealants, pigments, foods, batteries, ferrites, fire retardants, etc. Zinc oxide is a constituent of cigarette filters for removal of selected components from tobacco smoke. A filter consisting of charcoal impregnated with zinc oxide and iron oxide removes
significant amounts of HCN and H$_2$S from tobacco smoke without affecting its flavor. Zinc oxide along with stearic acid is used in the vulcanization of rubber. Zinc oxide is widely used for concrete manufacturing. Addition of ZnO improves the processing time and the resistance of concrete against water. Many sunscreens use nanosized zinc oxide (along with nano titanium dioxide) because such small particles do not scatter light and therefore do not appear white. Zinc oxide is added to many food products, for eg. breakfast cereals as a source of zinc, a necessary nutrient. Zinc white is used as a pigment, in paints which is more opaque than lithopone, but less opaque than titanium dioxide. Chinese white is a special grade of zinc white used in artists' pigments. It is also a main ingredient of mineral makeup. Various plastics, such as polyethylene naphthalate (PEN), can be protected by applying zinc oxide coating, the coating reduces the diffusion of oxygen with PEN [38]. Zinc oxide layers can also be used on polycarbonate (PC) in outdoor applications. The coating protects PC from solar radiation and decreases the oxidation rate and photo-yellowing of PC [39]. ZnO has wide direct band gap (3.37 eV). Therefore, it’s most common potential applications are in laser diodes and light emitting diodes (LEDs) [40]. Some optoelectronic applications of ZnO overlap with that of GaN, which has a similar bandgap (~3.4 eV at room temperature). Compared to GaN, ZnO has a larger exciton binding energy (~60 meV, 2.4 times of the room-temperature thermal energy), which results in bright room-temperature emission from ZnO. It can be combined with GaN for LED-applications. For instance as TCO layer and ZnO nanostructures provide better light outcoupling [41]. Other properties of ZnO favorable for electronic applications include its stability to high-energy radiation and to wet chemical etching [42] radiation resistance [43] makes ZnO a suitable candidate for space applications. ZnO is currently the most promising candidate in the field of random lasers to produce an electronically pumped UV laser source. The pointed tips of ZnO nanorods result in a strong enhancement of an electric field. Therefore, they can be used as field emitters [44]. Aluminium-doped ZnO layers are used as transparent electrodes. The constituents Zn and Al are much
cheaper and less toxic compared to the generally used indium tin oxide (ITO). One application which has begun to be commercially available is the use of ZnO as the front contact for solar cells [45]. Transparent thin-film transistors (TTFT) can be produced with ZnO. As field-effect transistors, they even may not need a p-n junction [46] thus avoiding the p-type doping problem of ZnO. Some of the field-effect transistors even use ZnO nanorods as conducting channels [47]. The piezoelectricity in textile fibers coated in ZnO have been shown capable of fabricating "self-powered nanosystems" with everyday mechanical stress from wind or body movements [48-49]. Zinc oxide nanorods are devices detecting changes in electrical current passing through zinc oxide nanowires due to adsorption of gas molecules. Selectivity to hydrogen gas was achieved by sputtering Pd clusters on the nanorod surface. The addition of Pd appears to be effective in the catalytic dissociation of hydrogen molecules into atomic hydrogen, increasing the sensitivity of the sensor device. The sensor detects hydrogen concentrations down to 10 parts per million at room temperature [50].

1.7 Properties of Cerium Oxide

1.7.1 Physical Properties

Ceria (CeO$_2$) is an oxide with important applications in areas of catalysis, electrochemistry, photochemistry and materials science [51-55]. Also it is highly efficient ultraviolet (UV) absorber to protect light-sensitive materials, as a coating material for protection of corrosion of metals, as an oxidation catalyst and as a counter electrode for electrochemical devices [56-59]. The physical properties of CeO$_2$ are represented in Table 1.3. Cerium oxide has outstanding physical and chemical properties. Recently Zhang et al. has reported the CeO$_2$ nanocrystal microspheres as a novel adsorbent for the removal of Cr (VI) from waste water [60]. In its most stable phase, bulk CeO$_2$ adopts a fluorite-type crystal structure in which each metal cation is surrounded by eight oxygen atoms. The band gap of pure ceria is ~3.2 eV, but crystal
defects or impurities can transform the material in a good n-type semiconductor.

**Table 1.3 Physical Properties of CeO$_2$**

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1)</td>
<td>Molar mass</td>
<td>172.115 g/mol</td>
</tr>
<tr>
<td>2)</td>
<td>Appearance</td>
<td>White or pale yellow solid, slightly hygroscopic</td>
</tr>
<tr>
<td>3)</td>
<td>Density</td>
<td>$7.65$ g/cm$^3$, solid</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$7.215$ g/cm$^3$, fluorite phase</td>
</tr>
<tr>
<td>4)</td>
<td>Melting point</td>
<td>2400°C</td>
</tr>
<tr>
<td>5)</td>
<td>Solubility in water</td>
<td>Insoluble</td>
</tr>
<tr>
<td>6)</td>
<td>Band gap</td>
<td>$\sim$3.2 eV</td>
</tr>
</tbody>
</table>

In the area of catalysis, nanoparticles of ceria have been studied since the early 1970s, but they were poorly characterized. In recent years, substantial progress has been made and the use of better synthetic methods.

**1.7.2 Crystal Structure of CeO$_2$**

The fluorite structure is most stable and thus most common at ambient conditions shown in Fig.1.4. Many researchers were reported the fluorite structure of CeO$_2$. Small nanoparticles exhibited a nearly amorphous structure [58, 61-65]. Due to its fluorite structure, the oxygen atoms in a ceria crystal are all in a plane with one another, allowing for rapid diffusion as a function of the number of oxygen vacancies. As the number of vacancies increases, the ease at which oxygen can move around in the crystal increases, allowing the ceria to reduce and oxidize molecules or co-catalysts on its surface. It has been shown that the catalytic activity of ceria is directly related to the number of oxygen
vacancies in the crystal, frequently measured by using X-ray Photoelectron Spectroscopy to compare the ratios of Ce$^{3+}$ to Ce$^{4+}$ in the crystal.

**Fig. 1.4 Fluorite structure of CeO$_2$**

### 1.7.3 Applications of CeO$_2$

Nanostructured metal oxides have attracted considerable attention from many researchers due to their diversity of applications in various technological fields of science and technology. Ceria has been used in catalytic converters in automotive applications. CeO$_2$ possesses many attractive properties that make it highly promising for a wide range of applications such as solid electrolytes in solid oxide fuel cells [66], automotive three-way catalyst [67], ultraviolet absorbers [68-69] and oxygen sensors [70-71]. It is also used as a catalyst for large-scale fluid cracking in refineries and dehydrogenation of ethyl benzene to styrene [72] as a sulphur adsorbent for the removal of H$_2$S from hot fuel gas streams [73]. The reports on the synthesis and applications of coupled bicomponents ZnO-CeO$_2$ materials are important. The mixed oxide of ZnO reported that it has high photo catalytic activity due to tuning in the band gap, which is one of the key concepts for photocatalysis. Therefore we have carried out this study on microwave assisted process for preparation of ZnO, ZnO-CeO$_2$ and ZnWO$_4$ nanoparticles and properties of these nanoparticles.
1.8 Metal Oxide Nanomaterials

Metal oxides play a very important role in many areas of chemistry, physics and materials science [74]. The metal elements are able to form a large diversity of oxide compounds. These can adopt a vast number of structural geometries with an electronic structure that can exhibit metallic, semiconductor character [75]. In technological applications, oxides are used in the fabrication of microelectronic circuits, gas sensors, piezoelectric devices, fuel cells, dye sensitized solar cells, coatings for the passivation of surfaces against corrosion. In the emerging field of nanotechnology, a goal is to make nanostructures with special properties with respect to those of bulk [76-77].

Metal oxide nanoparticles can exhibit unique physical and chemical properties due to their limited size and a high density of corner surface sites. Particle size is expected to influence three important groups of basic properties in any material. The first one comprises the structural characteristics, namely the lattice symmetry and cell parameters [78]. Bulk oxides are usually robust and stable systems with well-defined crystallographic structures. However, the growing importance of surface free energy and stress with decreasing particle size must be considered. Changes in thermodynamic stability associated with size can induce modification of cell parameters [79] and in extreme cases the nanoparticle can disappear due to interactions with its surrounding environment and a high surface free energy [80].

In order to display mechanical and structural stability, a nanoparticle must have a low surface free energy. As a consequence of this requirement, phases that have a low stability in bulk materials can become very stable in nanostructures. This structural phenomenon has been detected in TiO$_2$, VO$_x$, Al$_2$O$_3$ and MoO$_x$ oxides [81]. Size-induced structural distortions associated with changes in cell parameters have been observed in nanoparticles of Al$_2$O$_3$, NiO, Fe$_2$O$_3$, WO$_3$, MoO$_3$, CeO$_2$, Y$_2$O$_3$ and ZnO [82-84]. As the particle size decreases, the increasing number of surface and interface atoms generates stress/strain and concomitant structural perturbations [85-87]. Beyond this
“intrinsic” strain, there may be also “extrinsic” strain associated with a particular synthesis method which may be partially relieved by annealing [88]. Also, non-stoichiometry is a common phenomenon. On the other hand, interactions with the substrate on which the nanoparticles are supported can complicate the situation and induce structural perturbations or phases not seen for the bulk state of the oxide [89].

1.9 Nanomaterials in Semiconductor

The important terms involved in a photoactive semiconductor are conduction band (CB), valence band (VB), band gap, traps sites and Fermi level. The bands are the allowed energy states that an electron can occupy in a material. The highest energy band occupied by an electron is called the valence band while the next available lowest empty energy level, is called the conduction band. The bands are clearly differentiated in a semiconductor than a metal. In case of semiconductor nanoparticles, as the size of the nanoparticles increases the band gap of the semiconductor decreases, which is shown in Fig.1.5
The Fermi level is a probability distribution curve that represents a 50% possibility of locating an electron at a given energy level. For an n-type semiconductor such as ZnO, TiO₂ the Fermi level is close to the conduction band. Light energy greater than the band gap of the semiconductor excite the...
electrons from the valence band to the conduction band leaving behind a hole in the valence band. For example, TiO$_2$ is a large band gap semiconductor and hence produces e-h pairs on illumination with UV light. The electrons and holes are available for carrying out redox activities at the semiconductor surface. Photogenerated e-h pairs are also delocalized in the semiconductor. These locations are called trap sites (e$_t$ and h$_t$). The e-h pairs undergo recombination which results in decreasing the efficiency of the semiconductor. The numbers of photogenerated electrons in TiO$_2$ are dictated by the ability of the surroundings to scavenge electrons and holes and the recombination between the photo generated e-h pairs.

An increase in the band gap of the semiconductor with decrease in the particle size is defined as quantization effect. Nanoparticles of semiconductors display unique size-dependent properties (quantization effect) that alter its photochemical, photophysical, photochromic, optical and electrochemical responses. Both the large (e.g. ZnO, TiO$_2$, SnO$_2$ and WO$_3$) as well as small band gap semiconductor (e.g. CdSe and CdS) display this property. Charge generation, separation, retention and transfer across a semiconductor and its surroundings is greatly affected due to the quantization effect [90-94]. The presence of surface bound species which include surrounding electrolytes, sensitizers like other semiconductors, metals and dyes play an active role in determining the mechanism of charge transfer taking place at the semiconductor and surrounding species interface. Photo-induced excitation leads to charge separation in the semiconductor followed by electron or hole transfer to the surroundings dictated by the energetics of the system. Furthermore, defects created in the semiconductor largely depend upon method and doping. These defects play a vital role in controlling the photoelectrochemical and photocatalytic behavior of the semiconductor. Two major drawbacks of any individual large band gap semiconductor have been identified as, recombination of photogenerated charges (electron and holes) and limited light harvesting ability. These factors are limiting in the economical usage of the semiconductor. The former can be minimized by using metal on a
semiconductor because metal acts as sink for the electron and decreases recombination. Sensitization with dyes is one of the most commonly used methods to overcome the limited light harvesting ability of a large band gap semiconductor [95]. A semiconductor can be sensitized using another semiconductor (e.g. TiO$_2$-CdSe) or a dye (Azo dyes) while charge recombination can be minimized using metal deposits (Ag, Pt). When a metal is used with a semiconductor, the metal facilitates in decreasing recombination of the photogenerated charges. Thus both drawbacks of the semiconductor can be effectively overcome depending upon the material used to create composite with a semiconductor.

1.10 Impact of Nanomaterials in Catalysis

Nanomaterials are believed to exhibit unique science at nanoscale regime. The interest in nanomaterials arises from the fact that their physico-chemical properties are a function of their dimensions. Some of the important features that influence the catalytic and selectivity are surface structure, mobility of the active species to restructure as well as the mobility of the adsorbates on these active species, selective pore size in case of porous catalysis and metal-support interface sites. In comparison to bulk materials in nano regime possesses several properties like short range ordering, enhanced interaction with environments due to high number of dangling bonds, great variety of the valence band electron structure and self-structuring for optimum performance in chemisorption and catalysis.

As a consequence of the size reduction, larger portion of their constituent atoms are located at the surface (surface to volume ratio) and higher the surface area, higher will be the surface atoms. In general, increase in the surface area provides more adsorption of reactant molecules on its surface, which results the higher catalytic activity. Similarly increase in the number of surface atoms creates more number of active sites, which ultimately result in higher catalytic activity. In case of fuel cell applications, the current generated at an electrode is proportional to the active surface of catalysts on the electrode.
surface, so higher power density fuel cells can be formed from nanomaterials, because nanomaterials have a higher surface to volume ratio. Researchers have also shown that the electrolytic properties of the materials are sensitive to particle size, so increased catalytic activity can be observed for nanoparticles and nanomaterials. It is important to understand that smaller the particles, the larger the portion of their constituent at the surface. A surface atom plays an important role in catalysis, as the reaction takes place at the surface of the particle. Furthermore, increasing surface area increases the relative contribution of the surface energy and therefore the thermodynamic stability is decreased with decreasing particle size [96-97].

Nanomaterials are characterized by a very high number of low coordination number species at edge and corner sites which can provide a large number of catalytically active sites. Such materials exhibit chemical and physical properties characteristic of neither that of isolated atoms nor of the bulk material. The excess surface energy makes the particles more reactive and structurally sensitive towards their environment. Modern surface science studies indicate that, during chemisorptions and catalytic reaction, these particles restructure, and the adsorbed molecules also possesses a high degree of surface mobility. The adsorbate-induced restructuring facilitates the breaking of surface chemical bonds and the rearrangement of adsorbates as the cluster assumes a thermodynamically most stable configuration. As any materials interact with their environment through solid/gas, solid/liquid, and solid/solid interfaces, the nanometer scale surface created can be modified to perform certain functions [98].

Nanosize particles play a crucial role in surface reactivity, chemisorption and catalysis. Owing to their size, the electronic structure of the particles significantly differs from that of bulk. The electronic structure of catalysts has been shown to be important in adsorption and since adsorption is a necessary step in heterogeneous catalytic reactions, it would be expected that the changes in the electronic structure would influence the rate of reaction. The small size also significantly affects the electrochemical behaviour of the
nanocrystal materials. Electrochemical model and theories on nanoparticles and charge-transfer mechanisms for some metal oxide revealed that the properties of semiconductor gradually transmit to molecular properties as the size of a crystal is successively decreased in the nanometer range [99]. While going from bulk to nano size, the semiconductor energy levels become more separated from each other and the effective band gap increases. As a result of increase in band gap, the conductivity as well as the density of states in the conduction and valence band will be reduced. Because of this unusual behaviour of metals and semiconductors while going from bulk to nano, the Fermi level and density of states at the interface will alter. Since the Fermi level is associated with the redox ability of the system, there will be a considerable change in the rate of redox processes. It would therefore be possible to control the electrocatalytic and photocatalytic activity of metals and semiconductors by changing their size [96,100].

1.11 Classification of Nanomaterials Based on its Shape

The main categories of nanoparticle according to shape and the type of application in which they may be used [101-102] are given in Table 1.4.

Table 1.4 Different shapes of nanoparticles with examples

<table>
<thead>
<tr>
<th>Morphology of the Nanostructure</th>
<th>Name of the Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanotubes</td>
<td>Carbon, (fullerenes)</td>
</tr>
<tr>
<td>Nanowires</td>
<td>Semiconductors, metals, oxides, sulfides, nitrides</td>
</tr>
<tr>
<td>Nanocrystals, quantum dots</td>
<td>Insulators, semiconductors, metals, magnetic materials</td>
</tr>
<tr>
<td>Other nanoparticles</td>
<td>Ceramic oxides</td>
</tr>
</tbody>
</table>

a) Nanotubes

Nanotubes are a particularly novel form of nanoparticle about which there is great interest and excitement. Carbon nanotubes (CNT) were first
discovered by Iijima (1991), and are a new form of carbon molecule. They are similar in structure to the spherical molecule C\textsubscript{60} (buckminsterfullerene) discovered in the 1980s, but are elongated to form tubular structures 1-2 nm in diameter [103]. In their simplest form, nanotubes comprise a single layer of carbon atoms arranged in a cylinder. These are known as single-wall carbon nanotubes. They can also be formed as multi-wall carbon nanotubes having diameters significantly greater up to 20 nm and length greater than 1 mm. CNTs have great tensile strength and are considered to be 100 times stronger than steel while being only one sixth of its weight thus making them potentially the strongest. They also exhibit high conductivity, high surface area, unique electronic properties and potentially high molecular adsorption capacity [104]. Applications which are currently being investigated include; polymer composites (conductive and structural filler), electromagnetic shielding, electron field emitters, super capacitors, batteries, hydrogen storage and structural composites [105]. Hoffman et al. identified four main synthesis methods for CNTs. These are:

- Laser ablation,
- Arc discharge,
- Chemical vapour deposition (CVD) and
- Plasma-enhanced CVD.

Many of the applications envisaged for CNTs will require bulk quantities of the material to be produced. For applications where large quantities of CNTs are required, CVD offers the most suitable approach for scaling up due to the relatively low growth temperature, high yields and high purities that can be achieved. Production of relatively large volumes of unaligned MWCNTs, have been achieved by this and other methods and these materials are beginning to be used for commercial applications [106]. A recent advance in the development of CNTs is the production of controlled architectures of aligned CNTs using an injection CVD process. The CNTs are produced by spraying a solution of ferrocene dissolved in xylene into a two-stage furnace. The carrier gas is a mixture of argon and hydrogen. The
ferrocene decomposes to provide an iron catalyst, which nucleates the nanotube growth. The xylene acts as the carbon feedstock. The vapour passes into the second furnace where the nanotubes grow on quartz substrates [107].

One major focus of current research on nanotubes is on scaling-up of production rates to kilogram quantities. Nanotubes have also been produced from other materials including silicon and germanium but the development of various forms and applications for CNTs remain the main focus of activity [108]. From an occupational hygiene perspective, the large aspect ratios of CNTs, their durability and the desire to produce bulk quantities make them of particular interest [109].

b) Nanowires

Nanowires are small conducting or semi-conducting nanoparticles with a single crystal structure and a typical diameter of a few nanometers and a large aspect ratio [110]. They are used as interconnectors for the transport of electrons in nanoelectronic devices. Various metals have been used to fabricate nanowires including cobalt, gold and copper. Silicon nanowires have also been produced.

Most approaches to the fabrication of nanowires are derived from methods currently used in the semi-conductor industry for the fabrication of microchips. Van Zant (2000) provides a comprehensive review of microchip fabrication, which makes useful background reading. Typically they involve the manufacture of a template followed by the deposition of a vapour to fill the template and grow the nanowire. Deposition processes include electrochemical deposition and CVD. The template may be formed by various processes including etching, or the use of other nanoparticles, in particular, the nanotubes [96,111].

c) Quantum Dots

Quantum dots of semiconductors, metals and metal oxides has the particle size in all dimension at the forefront of research for the last five years due to their novel electronic, optical, magnetic and catalytic properties
The number of atoms in a quantum dot, which ranges from 1000 to 100,000, makes it neither an extended solid structure nor a single molecular entity. This has led to various names being attributed to such materials including nanocrystals and artificial atoms. To date, chemistry, physics and material science have provided methods for the production of quantum dots and allow tighter control of affecting factors, for example, particle growth and size, solubility and emission properties [113].

The majority of research has centred around semiconductor quantum dots, as they exhibit distinct 'quantum size effects'. The light emitted can be tuned to the desired wavelength by altering the particle size through careful control of the growth steps. Various methods can be employed to make quantum dots however the most common is by wet chemical colloidal processes [114]. This method gives a better results and the morphology of the materials.

d) Other Nanoparticles

This catch all category includes a wide range of primarily spherical or aggregated dendritic forms of nanoparticles. Dendritic forms are where spherical or other compact forms of primary particles aggregate together to form chain like or branching structures. Welding fume is the best known example of this. This “other nanoparticle” category includes existing common nanoparticles such as ultrafine carbon black and fumed silica which are synthesized in bulk form through flame pyrolysis methods. Nanoparticles of this type may be formed from many materials including metals, oxides, ceramics, semiconductors and organic materials. The particles may be composites having, for example, a metal core with an oxide shell or alloys in which mixtures of metals are present. Many of the production processes involve the direct generation of aerosols through gas phase synthesis, similar to flame pyrolysis but other production processes including wet chemistry methods [115]. This group of particles may be classified as being less well defined in terms of size and shape, generally larger, and likely to be produced
in larger bulk quantities than other forms of nanoparticles. From an occupational hygiene perspective, the likelihood of aerosol generation and their availability in bulk quantities makes these nanoparticles of particular interest [96,116].

1.12 Properties of Metal Oxide Nanoparticles

a) Optical Properties

The optical property is one of the fundamental properties of metal oxides and can be experimentally obtained from absorption measurements. While reflectivity is clearly size-dependent as scattering can display drastic changes when the oxide characteristic size is in the range of photon wavelength, absorption features typically common and main absorption behavior of solids [117]. Due to quantum-size confinement, absorption of light becomes both discrete like and size dependent. For nano crystalline semiconductors, both linear and non-linear optical properties arise as a result of transitions between electron and hole discrete or quantized electronic levels [118]. The effective mass theory (EMA) is the most elegant and general theory to explain the size dependence of the optical properties of nano-meter semiconductors, although other theories such as the free exciton collision model (FECM) or those based on the bond length-strength correlation have been developed to account for several deficiencies of the EMA theory [119].

Other optical excitations, which showed quantum-size confinement effects, concern the excitation of optical phonons of oxides. The effects of size on the phonon spectra of oxide materials have been well established by using Raman scattering experiments on nanocrystals, in combination with the theoretical phonon confinement models [120]. Essentially, the phonon confinement model provides the theoretical background for the study of nanocrystalline materials and this is the main factor responsible for the changes observed in the Raman spectrum, which are caused by the size effect. Some examples of application of the confinement model for qualitative interpretation
of Raman results in series of nanostructured oxides like anatase ZnO, TiO$_2$, CuO, Cr$_2$O$_3$, ZrTiO$_4$, CeO$_2$ or manganese oxides are reported [11-123].

In all cases, “non-stoichiometry” size-dependent defect affects optical absorption features of nanosized oxides. Typical point defects in nanostructured oxides concern oxygen or cation vacancies or the presence of alien’s species, like Cu$^{2+}$ and Ce$^{3+}$. Vacancy defects introduce gap states in proportion to the defect number; in fact, a random distribution of vacancy defects introduce a Gaussian like density of states which may produce mid-gap states and be localized near the valence and conduction bands depending on the electronic nature (donor/acceptor) of the defect and giving characteristic “localized” features in the UV-Visible spectrum. Such point defects mainly contribute to the Raman spectra by producing a broadening of the peaks [124]. Alien cations display specific features, like the localized d-d or f-f transitions of Cu/Ce. Besides electronic modifications, point defects, the alien ions, like Cu$^{2+}$ and Ce$^{3+}$, induce strain and concomitant structural differences in atomic positions with respect to bulk positions. Strain effects are inherent to nanostructured materials and may be comprised in the general, ambiguous term of “surface” effects usually claimed to account for significant deviations in the confinement theories [125]. Surface effects and, particularly, nonstoichiometry related to the preparation method are critically important for very low particle size and to produce characteristic features in the UV-Visible spectrum for certain oxides such as SnO$_2$ or ZrO$_2$ [96,126].

b) Electrical Properties

Oxide materials can present ionic or mixed ionic/electronic conductivity and it is experimentally well established that both can be influenced by the nanostructure of the solid. The number of electronic charge carriers in a metal oxide is a function of the band gap energy according to the Boltzmann statistics. The electronic conduction is referred to as n or p hopping type depending on whether the principal charge carriers are electrons or holes. The number of “free” electron/holes of an oxide can be enhanced by introducing
non-stoichiometry and in such case are balanced by the much less mobile oxygen/cation vacancies [127]. In an analogous manner to hopping type conduction, ionic conduction takes place when ions can hop from site to site within a crystal lattice as a result of thermal activation, and is typically interpreted on the basis of a modified Fick’s second law. Four mechanism types have been observed for ionic conduction: direct interstitial, interstitialcy, vacancy and Grotthus. As charge species (defects; impurities) in polycrystalline oxides typically segregate to particle boundaries to minimize strain and electrostatic potential contributions to the total energy, there is a contribution to the conductivity parallel to the surface which becomes important at the nanoscale regime [128]. The charge carrier (defect) distribution also suffers strong modification from bulk materials, as there is presence of charge carriers through the whole material as a consequence of the shielded electrostatic potential depletion at surface layers of nanosized materials [129]. As a result of these nanoscale derived effects, it is well known that CeO$_2$ exhibits an improved n-type conductivity which may be four order of magnitude greater than the corresponding to bulk/micro-crystalline ceria and is ascribed to a significant enhancement of the electronic contribution [130]. Alteration of the transport properties is also observed in ZrO$_2$ but the physical ground is still far from being understood [131]. The strong size dependence observed for the electrical conductance in the context of gas-sensing devices has been recently reviewed for the SnO$_2$, WO$_3$, and In$_2$O$_3$ oxides. In proton conductors, like SrCe$_{0.95}$Yb$_{0.05}$O$_3$-d enhanced conduction and faster kinetics under H-atmospheres are observed in nanosized samples as these phenomena are largely determined by boundary/interfacial effects [132]. Interesting to stress here is that some of the most dramatic effects of the nanostructure on ionic transport in oxides are observed in the field of Li$^+$ ion batteries. An outstanding enhancement in conductivity due to Li$^+$ ion vacancy has been achieved using Li-infiltrated nanoporous Al$_2$O$_3$ [133].
c) Mechanical Properties

Main mechanical properties concern low yield (stress and hardness) and high (superplasticity) temperature observables. Information on oxide nanomaterials is scarce and mainly devoted to analyze sinterability, ductility and superplasticity. These mechanical properties are also found to be strain-rate dependent; an enhanced strain rate sensitivity at room temperature is observed for TiO$_2$ and ZrO$_2$ with decreasing primary particle grain size. In spite of such facts, it is clear that oxide materials (like ZnO, Al$_2$O$_3$, ZrO$_2$, CeO$_2$ and TiO$_2$) sintered under vacuum or using the spark plasma technique display enhanced field strength and hardness with respect to conventional or bulk ceramic materials and have the additional properties of being transparent (films), being potential materials for the aerospatial industry [134]. Superplasticity refers to the capacity of oxide materials. Essentially, polycrystalline tetragonal ZrO$_2$ appears as the most celebrated example of a superplasticity ceramic and together with TiO$_2$, the ZrO$_2$ are the only nano-oxides subjected to studies. At room temperature, nanocrystalline oxides may have a small amount of ductility beyond that exhibited by bulk materials but they are not superplastics. At high temperatures, they seem to exhibit significant compressive ductility and strain rate sensitivities that indicate superplasticity [135].

d) Chemical Properties

Metal oxides are used for both their redox and acid/base properties in the context of absorption and catalysis. The three key features essential for their application as absorbents or catalysts are (i) the coordination environment of surface atoms, (ii) the redox properties and (iii) the oxidation state at surface layers. Both redox and acid/base properties are interrelated and attempts can be found in the literature to establish correlations of both properties. In a simple classification, oxides having only s or p electrons in their valence orbitals tend to be more effective for acid/base catalysis, while those having d or f outer electrons find a wider range of uses [136].
The solid in a given reaction conditions that undergoes reduction and reoxidation simultaneously by giving out surface lattice oxygen anions and taking oxygen from the gas phase is called a redox catalyst. This process necessarily demands microscopy reversibility and implies dynamic operation. The commonly accepted mechanism was developed by Mars van Krevelen and essentially implies that redox systems require high electronic conduction cations to manage electrons and high oxygen-lattice mobility. Based on modern isotopic exchange experiments, the redox mechanism of chemical reactions can be more specifically divided in (i) extra facial oxygen in which adsorbed (oxygen) species react (electrophilic reaction) and (ii) interfacial oxygen where lattice oxygen vacancies are created (nucleophilic reaction) [137]. There are enormous evidences which exhibit that nucleophilic oxygen is capable of carrying out selective oxidations while it seems that electrophilic species seems to work exclusively on non-selective ones. Latter, it was shown that hydrocarbon selective oxidation starts with H-abstraction steps and that the filling of oxygen vacancies requires the cooperation of a significant number of cations. So, typically, an oxidation reaction demands to optimize three important steps: the activation of the C-H bond and molecular oxygen and the desorption of products (to limit over-oxidation). The effect of size on these key steps is unknown but can be speculated to be related to the oxidation state of surface cations and their ability to manage electrons and the influence of non-stoichiometry on the gas-phase oxygen species handling and activation [138].

Many oxides also display acid/base properties. Oxide materials can contain Bronsted and Lewis acid/base sites. Bronsted acid (A) and base (B) interactions consist of the exchange of protons as $HA + B = A^- + HB^+$. In any solid, two independent variables, the acid/base strength and amount (density per surface unit) need to be addressed to give a complete picture of its acid/base characteristics. Such characteristics are basically linked to the nature (valence/cation size) of the element present in the oxide and general views of the behavior of Bronsted/Lewis acidity as a function of solid state variables have been published. Essentially, Lewis acidity is characteristic of ionic oxides.
and practically absent in covalent oxides. The strongest Lewis acid oxides are Al₂O₃ and Ga₂O₃. As a general rule, for stronger Lewis acid, the few sites are available (amount) due to the higher level of surface hydroxylation. As mentioned, Lewis acidity is mostly associated to oxides with ionic character; Lewis basicity is mostly associated with them. This means that the stronger the Lewis acid sites, the weaker the basic sites and vice versa. On the contrary, most of the ionic metal oxides do not carry sufficiently strong Bronsted acidity to protonate pyridine or ammonia at room temperature although the more acids of them can do it at higher temperatures. In spite of this, the surface OH groups of most ionic oxides have a more basic character than acid character. Finally, strong Bronsted acidity appears in oxides of elements with formal valency five or higher (WO₃, MoO₃, N₂O₅, V₂O₅ and S-containing oxides) [139].

1.13 Advanced Oxidation Processes

Advanced oxidation processes (AOP’s), uniting together ozone and high output ultraviolet technologies, in conjunction with hydrogen peroxide and catalyst are successfully used to decompose many toxic and bio-resistant organic pollutants in aqueous solution to acceptable levels, without producing additional hazardous by-products or sludge which require further handling. Advanced oxidation processes involve the generation of hydroxyl (•OH) radicals which oxidize the pollutants. Advanced oxidation processes can be broadly classified into the following groups:

i) Homogeneous photocatalysis,

ii) Heterogeneous photocatalysis

i) Homogeneous photocatalysis

The applications of homogeneous photodegradation (single-phase system) to treat contaminated water, involves the use of an oxidant to generate radicals, which attack the organic pollutants to initiate oxidation. The major oxidants used are: Hydrogen peroxide (UV /H₂O₂), Ozone (UV /O₃), Hydrogen peroxide and Ozone (UV /O₃/ H₂O₂),
Photo-Fenton system (Fe$^{3+}$ / H$_2$O$_2$).

**ii) Heterogeneous photocatalysis**

Heterogeneous photocatalytic process consists of utilizing the near UV radiation to photo-excite a semiconductor catalyst in the presence of oxygen. Under these circumstances oxidizing species, either bound hydroxyl radicals or free holes, are generated as shown in Fig.1.6. Using photocatalysis, organic pollutants can be completely mineralized reacting with the oxidizers to form CO$_2$, water and dilute concentration of simple mineral acids. The process is heterogeneous because there are two active phases, solid and liquid. This process can also be carried out utilizing the near part of solar spectrum ($\lambda < 380$nm) which transforms into a good option to be used [140].
The semiconductor may be in the form of a powder suspended in the water or fixed on a support. The most active photocatalyst for this application is the anatase form of TiO$_2$/ZnO because of its high stability, good performance and low cost [141].

1.14 History and Current Status of Photocatalysis

Environmental pollution and energy shortage, being regarded as the top two challenges facing mankind in the next 50 years, have attracted much attention from both government agencies and scientific communities. Semiconductor based heterogeneous photocatalytic technology was developed as a promising solution to the two challenges. The utilization of semiconductors as a photocatalyst started from the first report by Fujishima and Honda in 1972 [142]. At that time, the energy crisis was spreading around the world, the water splitting into hydrogen and oxygen under ultraviolet (UV) irradiation by using TiO$_2$ photoanode inspired extensive research concerning solar energy conversion and created a new era in the field of photocatalyst. In 1977, Bard reported that CN$^-$ was photocatalytically oxidized into OCN$^-$ on TiO$_2$ [143] and the applications of photocatalysis were extended into the field of waste water treatment and environmental remediation. Since the beginning of the 1990s, environmental pollutants have aroused increased public concern. Heterogeneous photocatalytic reactions on ZnO nanoparticles (n-type semiconductors) are now recognized as an ideal technology for removal of all kinds of pollutants both in water and air [144-148]. Most of the investigations have focused on mixed-metal oxides which show relatively high reactivity and chemical stability under ultraviolet (UV) light.

Over the last 10 years the scientific and engineering interest in the application of semiconductor photocatalysis has grown exponentially. In the areas of water, air and waste water treatment the photocatalysis by metal oxides has many potential applications as an environmental control technology [149]. Many background information reviews on photocatalysis have been appeared in the literature, noteworthy recent reviews are provided by Ollis and Al-

Semiconductor photocatalysis with a primary focus on TiO$_2$ as a durable photocatalyst has been applied to a variety of problems of environmental interest in addition to water and air purification. It has been shown to be useful for the destruction of microorganisms such as bacteria [157] and viruses [158]. Semiconductors (e.g., TiO$_2$, ZnO, Fe$_2$O$_3$, CdS and ZnS) can act as sensitizers for light-reduced redox processes due to their electronic structure, which is characterized by a filled valence band and an empty conduction band [159]. The approaches also include the incorporation of transition metals doping [160-163]. Spinel zinc ferrite (ZnFe$_2$O$_4$) is a narrow band gap semiconductor that has a potential application in the conversion of sunlight, because of its sensitivity to ultra-violet light and no photochemical corrosion [164]. In contrast, on bulk semiconductor electrodes only one species, either the hole or electron, is available for reaction due to band bending [165]. However, in very small semiconductor particles and suspensions both species are present on the surface. Therefore, careful consideration of both the oxidative and the reductive paths is required.

1.15 Literature Survey

The fine powders of oxides have been prepared by many methods, including forced hydrolysis, sol-gel, hydrothermal, co-precipitation, surfactant templating and spray pyrolysis [166]. However, microwave-assisted synthesis is very beneficial to find a fast, simple and energy efficient approach to produce fine metal oxide nanoparticles [167]. Microwave assisted synthesis is relatively new technology to produce inorganic compounds since 1986 for materials processing to enhance the material properties as well as economic advantages [168]. Microwave heating offers several potential advantages over the conventional heating for inducing or enhancing chemical reactions [169]. These includes direct microwave interaction with certain class of molecules, volumetric heating rather than heat flow through the vessel wall, less waste
heat, increased control over heating rates and the possibility of selective enhancement of desired reactions [170]. Microwave synthesis has been developed and widely used for the synthesis of zeolites and ceramic materials. Compared with conventional methods, microwave synthesis has advantages: 1) Production of small particles with a narrow size distribution with high purity and 2) within very short reaction time. These conveniences could be attributed to fast homogeneous nucleation and ready dissolution of the gel [171]. Microwave heating is in situ mode of energy conversion therefore it is very attractive for chemist due to its simplicity and cost effective technique.

A number of methods have been used for synthesizing ZnO nanopowders [172-178] and in recent years, a new method has been reported as microwave-assisted synthesis. Due to its unique features such as short reaction time, enhanced reaction selectivity, energy saving, and high reaction rate [179], the application of microwave-assisted synthesis of ZnO nanoparticles has been rapidly growing [179-183]. Many methods have been reported for the synthesis of ZnO nanoparticles, including the sol-gel [184], microwave method [185], evaporative decomposition of solution [186], template-assisted growth [187], wet chemical synthesis [188] and gas-phase reaction [189]. Some researchers have been highlighted the performance of ZnO for degradation of some organic compounds [190-191]. In addition, ZnO has more functions than TiO$_2$ [192] and recent researches have pointed out that ZnO can also be used in the acidic or alkaline conditions through the proper treatment [193-194].

Hong et al., [195] reported the synthesis of Zinc oxide (ZnO) nanoparticles using zinc nitrate and NaOH by ultrasonic irradiation technique at room temperature. The ZnO nanoparticles were heated individually in an electric furnace for two hours at 700°C. The morphology and optical properties of the C$_{60}$ and ZnO nanoparticles were characterized by X-ray diffraction, SEM, transmission electron microscopy and UV-Visible spectroscopy. The photocatalytic activity of the heated and unheated C$_{60}$ and ZnO nanoparticles were studied for the decomposition of Methylene blue, Methyl orange and Rhodamine B.
Comparison of dye degradation efficiency using ZnO powders with various sizes reported by Wang et al., [196]. ZnO powders with various size scales (mean diam.size: 10, 50, 200, and 1000 nm) were prepared by two different preparation methods, thermal evaporation method and chemical deposition method. The size 50 nm prepared by thermal evaporation method shows the highest photocatalytic activity. In addition the tetrapod ZnO nanopowders had the higher efficiency than irregular ZnO nanoparticles. However, the smallest 10 nm ZnO nanoparticles prepared by chemical deposition method and the degradation efficiency was discussed through the photocatalytic experiments using 50 nm ZnO nanoparticles as photocatalyst. Giraldi et al., [197] reported annealing effect on photocatalytic efficiency of ZnO nanoparticles prepared by chemical technique. The samples were annealed and effects on the photocatalytic properties, surface decontamination and the consequent particle change, in terms of crystallinity are studied. The as-prepared samples correspond to a metastable phase (oxy or hydroxy zinc acetate) and post annealing leads to ZnO crystals. The XRD patterns showing only the ZnO phase for heat treatment at 100°C, FTIR data shows that carboxylate group remains attached to the ZnO surface up to 300 °C. Up to 300 °C the presence of these carboxylate groups, provided by the synthesis method, showed to be more relevant to photoactivity than the specific surface area. At higher temperatures, crystallinity becomes the dominant factor and an increasing of crystallinity favors the photoactivity.

The study of photoconductivity and photoluminescence of ZnO nanoparticles is reported by Kripal et al., [198]. They studied the photoconductivity and photoluminescence properties of ZnO nanoparticles (NPs) prepared by using co-precipitation method and thioglycerol as a capping agent and annealed at 300°C. The TEM and XRD pattern confirm the hexagonal wurtzite structure of ZnO nanoparticles. The UV-Visible absorption spectrum of ZnO NPs shows blue shift of absorption peak as compared to bulk ZnO. The photoluminescence (PL) spectra of as-synthesized ZnO NPs show band edge emission as well as blue-green emission.
Growth and gas sensing properties of p and n-type ZnO nanostructures are reported by Ramgir et al.,[199]. ZnO nanoparticles (NPs) of 5 to 15 nm size and nanowires (NWs) of 50 to 100 nm diameter were prepared using simple chemical method, exhibiting p and n-type characteristics, respectively. ZnO NW-films show good sensitivity and selectivity towards H₂S in ppm range with fast response and recovery times. Interestingly, ZnO NP-films showed p-type conductor.

Sun et al.,[200] reported on bar-like nano ZnO prepared by hydrothermal method at 230°C using ZnSO₄ and CO(NH₂)₂ as the materials and CTAB as the surface active agent. The XRD shows that the nanoparticles of ZnO have hexagonal wurtzite structure. The observed results by SEM shows that the products showed rod-like morphology with average diameter of about 60-80 nm and length of about 260-580 nm. Methylene blue in aqueous solution could decompose rapidly under photocatalysis of bar-like nano ZnO when pH value of the solution was 8.0 and the degradation rate of Methylene Blue reached 100% after 90 minutes.

Dalai et al., reported [201], hollow ZnO microspheres with interior diameter of ∼10 µm were synthesized by a facile solution method using polymethyl methacrylate (PMMA) microspheres as template. The hollow microspheres are built by layers of nanoparticles with high crystallinity. The shell thicknesses are ∼100 nm. The XRD, SEM, TEM and XPS measurements, a possible formation mechanism for the hollow ZnO microspheres is discussed. As-synthesized hollow ZnO microspheres exhibit novel absorption band in the region of UV. Band gap of the hollow ZnO microsphere is 3.53 based on its UV-Visible absorption spectrum.

The study of photochemical properties of CeO₂-coated ZnO nanorods were carried out by Lau et al., [202]. Well-aligned ZnO nanorods were deposited by a mild hydrothermal process and coated with nanosized CeO2 particles (∼5 nm) by an oxidative-soak-coating method at 45° C. The low growth temperature proved useful in avoiding interfacial reaction between the two phases. Correlation of photoluminescence results indicated that the defects
responsible for the deep level emission (DLE) from ZnO were largely located at the surface. The CeO$_2$ coating reduced the DLE but also the photocatalytic activities as surface hydroxyl groups were involved in the nucleation of the CeO$_2$ phase. Wang et al., [203] reported the hydrothermal process for CeO$_2$-ZnO composite nanostructure, by using Zn(NO$_3$)$_2$·6H$_2$O, Ce(NO$_3$)$_3$·6H$_2$O and hexamethylenetetramine on Si substrate at 90°C. The structures, morphologies and the composite of CeO$_2$/ZnO samples have been investigated by XRD, TEM, SEM and EDX at room and it shows that the obtained CeO$_2$/ZnO composite nanostructures have different morphology for composite. The result shows that the uniform and dense CeO$_2$ nanoparticles cover the whole surface of single crystal ZnO rods when the Ce$^{3+}$/Zn$^{2+}$ molar ratio of reaction solution is 1/10. This kind of the CeO$_2$/ZnO composite nanostructure may find potential application in the selective detection of CO.

Wu et al., [204] developed a layer-by-layer (LBL) assembly approach to synthesize ZnO nanorod-based hybrid nanomaterials such as ZnO/CeO$_2$, ZnO/CdS and ZnO/Ag on ZnO nanorod templates at room temperature. The ZnO nanorod-based hybrid nanomaterials have been characterized by TEM, HRTEM, XRD and XPS. It is indicated that a uniform coating layer consisting of homogeneous nanoparticles is deposited on the surface of ZnO nanorods due to the strong electrostatic attraction between metal ions and polyelectrolyte modified ZnO nanorods. The general approach presented here can be extended to the synthesis of other one-dimensional (1D) nanostructure-based hybrid Nanomaterials.

CeO$_2$/ZnO nanostructured microspheres as catalysts for the oxidative coupling of CH$_4$ with CO$_2$, the conversion of CH$_4$ corresponded with that using the CeO$_2$/ZnO nanoparticles observed by Yongjun et al., [205]. CeO$_2$/ZnO nanostructured microspheres with an average diameter of $\approx$3.8 µm were synthesized by a solid-stabilized emulsion technique. The CeO$_2$/ZnO nanostructured microspheres were characterized with SEM, XRD, CO$_2$-TPD, BET measurement. Based on the oxidative coupling reaction of CH$_4$ with CO$_2$ as an oxidant, the catalytic performance of the CeO$_2$/ZnO nanostructured
microspheres was evaluated and compared with that of the CeO$_2$/ZnO nanoparticles. The surface of the CeO$_2$/ZnO nanostructured microspheres consisted of petal-like structures with a petal thickness of $\approx 90$ nm and a petal depth of 0.4-0.9 $\mu$m. Using CeO$_2$/ZnO nanostructured microspheres as catalysts for the oxidative coupling of CH$_4$ with CO$_2$, the conversion of CH$_4$ corresponded with that using the CeO$_2$/ZnO nanoparticles, while the CeO$_2$/ZnO nanostructured microspheres had much longer operating life.

ZnWO$_4$ as a kind of tungstate has received considerable attention due to its applications as an X-ray and $\gamma$-scintillator, photoanodes and solid-state laser host, as well as for acoustic and optical fibers reported by Montini et al. [206]. Tungstates of divalent transition metals (M$^{II}$WO$_4$, M=Co$^{II}$, Ni$^{II}$, Cu$^{II}$, Zn$^{II}$) were prepared by reaction of transition metal nitrates with sodium tungstate. The precipitates were then calcined at 500ºC. The materials were characterized by means of ICP-AES, UV, XRD, SEM and surface area analysis. The higher activity for the decolorization of Methylene Blue (MB) and Methyl Orange (MO) of ZnWO$_4$ compared to that of the other investigated tungstates was correlated with its strong tendency of excitons self-trapping.

The enhanced photocatalytic performance was observed by Huang et al., [207] ZnWO$_4$ nanoparticles prepared by hydrothermal technique with different annealing temperature and time. The high photocatalytic activity confirmed by degradation of formaldehyde and RhB in gaseous and water respectively. The highest photocatalytic activity both appeared at 450ºC for 1 h. The photocatalytic activity of ZnWO$_4$ was a little higher than that of P-25 (Degussa) in gaseous phase and lower in aqueous.

Jia et al., [208] reported the structural and optical properties of ZnWO$_4$ and CdWO$_4$ nanofilms by a novel route through the combination of reverse micelle system with dip-coating technology. Here collodion is used as a dispersant and film-forming agent to obtain nanofilm with a good quality films. The SEM and XRD results indicate ZnWO$_4$ and CdWO$_4$ nanoparticles with monoclinic system and wolframite structure. The nanofilm's PL bands shows blue shift compared with bulk materials where as red shift compared with
nanoparticles. FTIR absorption bands between 400 and 900 cm\(^{-1}\) prove the presence of ZnWO\(_4\).

Wang et al., [209] used a microwave assisted sol-gel method. The results indicate the cubic fluorite structure. TEM reveals that the size of crystalline particles of 4 to 6 nm. Preparation of monodisperse cerium oxide nanoparticles were carried out by Soucek et al. [210]. The products were characterized by Raman spectroscopy, XRD, UV-Visible spectroscopy and TEM. The TEM images and UV-Visible spectra show that the CeO\(_2\) particles prepared are uniform nanosized and absorb UV light in the range of 250 to 400 nm. The sizes of the nanoparticles were obtained about 5 to 20 nm.

Zhang et al. [211] synthesized hierarchical CeO\(_2\) nanocrystal microspheres by sol-gel method at of 120°C temperature. The product was characterized by XRD, TEM and clearly revealed the microstructure of the CeO\(_2\) nanospheres. These nanospheres are of porous structure and 50 to 100 nm in diameter. Photocatalytic degradation of various dyes with different chromophores such as Methyl Violet, Methylene Blue and Rhodamine B by using titanium oxide was reported by Hosseinnia et al. [58]. They have been synthesized single phase anatase titania powders by a simple precipitation method. The powders were characterized by XRD, TEM and surface area, after calcinations at 550°C for 3 hrs. TEM results show the particle size about 20 nm and surface area of 75 m\(^2\)/g. From the detailed literature survey it is seen that very few scientists have been given attention for the semiconductors like ZnO, ZnWO\(_4\), CeO\(_2\) and ZnO-CeO\(_2\) by using microwave assisted method. Therefore it has an advantage of very short reaction time, production of small particles with a narrow size distribution and high purity. These conveniences could be attributed to fast homogeneous nucleation and ready dissolution of the gel. Microwave heating is in situ mode of energy efficient method.

**1.16 Plan of the Research Work**

From the industrial point of view, it is of prime importance to use new materials as a photocatalyst. Metal oxide nanomaterials are the benign catalyst.
The metal oxide nanoparticles as a photocatalyst are supposed to modify the route of chemical reaction thereby reducing the cost of production. Photodegradation of hazardous organic compounds like dye and pesticides from industrial effluents is of prime importance and at ease can be done by metal oxide nanoparticles within shorter duration due to its large surface to volume ratio.

It is observed from the literature survey that mixed oxides are more favourable than single oxides due to its increase in surface area, tuning of the band gap of energy, which is required for photocatalyst.

The important task of the present work is to prepare ZnO and its mixed oxides such as ZnO-CeO$_2$ and ZnWO$_4$ by using very simple microwave assisted sol-gel method. The properties such as crystal structure, catalytic and spectral properties are greatly influenced by the metal ions present at two different sites. Therefore, to find out the effect of substitution of different metal ions on the properties of metal oxide, various techniques such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), electron dispersive X–ray analysis (EDS), X–ray diffraction analysis (XRD), thermogravimetric analysis (TGA), Differential thermal analysis (DTA), UV-Visible spectroscopy and IR spectroscopy are used. The microwave assisted method is employed for the synthesis of zinc oxide, ZnO-CeO$_2$, and ZnWO$_4$. The ZnO and mixed ZnO with CeO$_2$ and WO$_3$ are tested for the photodegradation of dyes such as Methyl Orange, Methylene Blue and Rhodamine B. The effect of catalyst loading, pH and initial concentration of dyes on the photocatalytic degradation efficiency using ZnO and mixed ZnO nanorods as a photocatalyst was tested.
1.17 References

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