2.1 Introduction

Numerous methods were reported for the synthesis of nanomaterials which depend on the nature of the materials, size regime and applications [1-7]. Whatever be the method, the attraction of the method depends on its capability for the reproduction of size, shape and the control of average size. Generally, the doping of bulk semiconductors are carried out by high temperature thermal diffusion or molecular deposition techniques which include chemical vapor deposition, atomic layer epitaxy, gas phase deposition, vacuum evaporation, etc. In case of nanoparticles, incorporation of impurities into quantum-confined systems which contain only few ten of atoms or molecules are the more difficult and complex because no conventional high temperature process can be applied. In this case, doping has carried out by low temperature process, mostly by wet-chemical synthesis routes. The substitution through wet-chemistry creates some new difficulties that are not encountered in the case of bulk materials. For example, the dopant ions used in the reaction may preferentially precipitate, as a stable phase, prior to the incorporation into the host lattice leading to very low or no doping at all. Further, even though dopant ions are incorporated into the lattice, these may tend to diffuse on to the nanoparticles surface or the surrounding matrix because the impurity ions are always only a few lattice constant away from the surface. Thus the preparation of effectively doped semiconductor nanocrystals and their application in the nanotechnology frontier still remain a challenging task.

There are two general approaches for the synthesis of nanomaterials; a) top-down and b) bottom-up techniques. a) The top-down technique, it starts with a large scale object and gradually reduces its dimensions, it covers mostly physical
methods such as e-beam lithography, which shines radiation through a templates onto a surface coated with a radiation sensitive resist, atomic force manipulation, gas-phase condensation, aerosol spray etc. b) bottom up approach, where individual atoms or molecules are placed or self assembled precisely at the required places, basically include all wet-chemical methods like, reverse-micelle, sol gel synthesis, colloidal. Generally, the bottom up approach is preferred for the synthesis of luminescent nanoparticles.

We can prepare nano grains either by allowing the atom to fuse together until the desired size is attained (construction) or by breaking a bulk material (deconstruction) to the predetermined size. The building up method is chosen for the preparation of nanomaterials rather than the breaking down process since, the former method allows better in the preparation of particles of desired size [8]. The various methods used for the preparation of nanomaterials are as under

1. Co-precipitation method  
2. Sol-gel method  
3. Solid state reaction method.  
4. Solvothermal method  
5. Sono-chemical co-precipitation  
6. Hydrothermal method

### 2.2 Preparation techniques of nanomaterials

Chemical methods were widely used for synthesis of multi component metal oxides. These are the most important solution chemistry methods used to prepare nanoparticles i.e. co-precipitation and sol-gel techniques. In recent years, attention is focussed on materials obtained by chemical precipitation route. The chemical method is characterized by a complete and homogeneous mixing of the solutions of the starting compounds to the molecular or atomic level. In comparison with other conventional methods, this method requires only low thermal treatment. Also, synthesis of materials by this method yield small particle size, high homogeneity and stoichiometry, which could not be achieved at high temperatures. Chemical methods are used for preparation of materials by several
groups to exploit the low-grade iron cores to prepare impurity-free fine particles of high surface area and hence oxides of desired crystal structures [9-11].

2.2.1 Co-precipitation method

The co-precipitation method, where metal ions are precipitated as organometallic compounds. Thermal treatment can also be seen as chemical grinding because during decomposition, the grow gases break the particles which decrease their sizes. The co-precipitation method is relatively easy to scale up. The main advantage of precipitation, in comparison to solid state reaction method is that it rejects most of the impurities to the solution during the formation of solid product.

a) Nucleation

The precipitation involves nucleation, where the driving force is the change in chemical potential between standing and equilibrium states. It is the most common method to generate supersaturation by reactive precipitation, when a chemical reaction produces insoluble species. The supersaturation in precipitation is often very high, giving high nucleation rates.

Nucleation is the least understood process in precipitation. Unlike in laser vaporization where homogeneous nucleation dominates, three main types of nucleation occur in chemical precipitation: Primary homogeneous or heterogeneous or secondary. Homogeneous nucleation occurs in the absence of solid interface while heterogeneous nucleation occurs in the presence of foreign seed surfaces and secondary nucleation in the presence of a solute particle interface. The dominance of each type of nucleation varies with the precipitation conditions.

In homogeneous nucleation of small clusters a large fraction of atoms are present at the surface of the particles thus having higher potential energy than in the interior of the particles due to fewer and weaker bonds. The free energy of
these small aggregates is the result of free energy due to the new surface and the formation of new solid.

In precipitation methods, nucleations in practice likely to be heterogeneous since contact with vessel, stirrer etc is difficult to avoid. Nucleation on a foreign surface has a lower surface energy leading to a lower critical supersaturation. Secondary nucleation results from the presence of crystals in solution and it can be divided into three classes: apparent, true and contact. Apparent refers to small fragments washed from the surface of seeds. True secondary nucleation occurs due to the presence of particles in solution. Contact secondary nucleation occurs when a growing particle contacts walls, stirrer, etc. producing new particles. Contact nucleation is often the most important nucleation mechanism and depends on rotation speed, particle mass density and saturation ratio.

b) Particle Growth

This can grow by several different mechanisms after a particle is nucleated. The kinetics of the growth mechanisms are determined the structure and particle size distribution. On a macroscopic level, mass transport usually limits the particle growth while heat transfer is so fast that it controls the growth only at a very high heat of crystallization. Diffusion controlled growth is described by diffusion of solvated ions to the surface and diffusion of solvent and other coordination ions away from the surface.

The supersaturation driving force can be written as $S - S(r^*)$ if the particles are small. If $S - S(r^*)$ is positive particle will precipitate from solution and when $S - S(r^*)$ is negative particles smaller than size $r$ will dissolve and particles larger than $r^*$ will grow. This dissolution of fine particles and re-precipitation of larger particles is called Ostwald ripening. Ripening occurs in batch reactors because the supersaturation ratio ‘$S$’ decreases with time. Large number of fine particles is produced at high supersaturation nucleation.

Impurities can change the crystal habit drastically, specially ionic surfactants by adsorbing on the surface of crystals can change the kinetics.
Impurities can reduce the supply of material to the surface, reduce the specific surface energy or block surface sites. Ionic surfactants absorb on the surfaces with opposite charge and control the growth of particles in some directions.

c) **Agglomeration**

In chemical methods, the agglomeration time is long compared to the confined growth zone in vaporization methods. Normally crystals do not occur as single discrete units but they form bigger clusters. There are two main classes of agglomeration; a primary agglomeration results from the faulty growth of crystals and secondary growth is due to crystal-crystal interactions. There are two cases of secondary aggregation. Particles can aggregate by Brownian motion or shear induced aggregation. In the first case, the diffusion of particles by Brownian motion causes collisions and in the latter case fluid movement causes particle collisions.

d) **Drying**

The precipitation methods involve separation of solid phase from the liquid reaction media. Drying requires simultaneous heat and mass transfer. These processes are dependent on temperature and partial pressure of the solvent in the atmosphere. It depends on the kinetics of the drying of the boundary layer surrounding the green body and the pores of different stresses are induced in the materials. The wet green body has a compressive capillarity force which holds it together. During drying, this capillary induced tension is present if flow keeps the surface wet. This flow arises from the rearrangement of particles in the green body. This capillarity force disappears as the liquid is evaporated. The green body is susceptible during drying to non-uniform stresses due to the pressure gradient of the flow of liquid during shrinkage and the escaping gases or the differential thermal expansion of the ceramic owing to temperature gradients in the green body.
2.2.2 Sol-gel Method

The sol-gel process is a wet chemical route used for the synthesis of colloidal dispersions (sols) of inorganic and organic hybrid materials, particularly oxides and oxide-based hybrid at relatively low temperatures. Sols are dispersions of colloidal particles in a liquid [12] and colloids are solid particles with diameters of 1-100 nm. The sols are converted into viscous gels (sol-gel transition) [13] by vigorous stirring at low temperatures. The solution or sol becomes a rigid at the transition, porous mass through destabilization, precipitation or supersaturation. The sol becomes a gel when it can support stress elastically. A gel is an interconnected rigid network with pores of submicrometer dimensions and polymeric chains whose average length is greater than a micrometer [14]. The gels can be dried at room temperature to form glass or they can be ground to make fine powders. In the sol-gel process the grain growth occurs at the same time as agglomeration such that it becomes difficult to differentiate between primary particles which consist of small grains or crystallites and secondary particles which agglomerate with primary particles [15].

The sol-gel processing is particularly useful in making complex metal oxide, temperature sensitive organic-inorganic hybrid materials, and thermodynamically unfavorable or metastable materials. The sol-gel method has attracted great scientific interest in the recent years for making advanced materials and for designing devices with very specific properties [16].

Sol-gel processing generally refers to the hydrolysis and condensation of alkoxide-based precursors. It can produce ceramic and glasses with better purity and homogeneity than high temperature conventional process. Sol-gel process can be used to produce wide range of metal oxides and mixed metal oxides in various forms, including powders, fibers, coatings with thin films, monoliths and porous membranes. The sol-gel method is a multi-step process which involves both chemical and physical processes such as hydrolysis, polymerization, drying and
densification. Appropriate drying and calcination leads to ultra-fine porous oxides [17-19].

Important features of the sol-gel techniques are as such better homogeneity, high purity, lower processing temperature, more uniform phase distribution in multicomponent system, better size and morphological control, the possibility of preparing new crystalline and non-crystalline materials, and lastly easy preparation of thin films and coatings. The sol-gel method is widely used in ceramic technology. The important steps of sol-gel synthesis are briefly outlined.

a) Hydrolysis

The process of hydrolysis may initiate with a mixture of a metal alkoxide and water in a solvent (usually alcohol) at the ambient or slightly elevated temperature. During this, the acid/base catalysts are added to speed up the reaction.

b) Polymerization (sol formation)

This step involves the condensation of adjacent molecules wherein H₂O and ROH are eliminated and metal oxide linkages are formed. Polymeric networks grow to colloidal dimensions in the liquid (sol) state.

c) Gelation

In this step, the polymeric network links up to form a three-dimensional network throughout the liquid. The system becomes somewhat rigid, characteristic of gel. The solvent as well as water and alcohol remain inside the pores of the gel. Aggregations of smaller polymeric units to the main network are continued progressively on aging the gel.

d) Drying

Here, water and alcohol are removed at moderate temperature (less than 470 K) which leaves behind a hydroxylated metal oxide with residual organic content. If the object is to prepare a high surface area of aerogel powder with low bulk density, the solvent is removed.
e) **Dehydration**

This step is carried out between 670 and 1070 K to drive off the organic residues and chemically bound water which yields a metal oxide with 20-30% micro porosity.

f) **Densification**

In this step, the elevated temperature is used above 1270 K to form the densed oxide product. Material synthesis procedure is depicted in figure 2.1 (a, b) and 2.2.

By this method metal oxide and mixed metal oxides are prepared with higher surface area, high purity and porous materials, but this method plugged by the limitations such as, time consuming, multistep process, starting precursors are generally used in alkoxide form.

### 2.2.3 Solid State Reaction Method (SSR)

Most widely used method for synthesizing the polycrystalline solids (powders) is the direct reaction, in this method, a mixture of oxides are used as starting materials. Oxides do not usually react together at room temperature over normal time scale so it is necessary to heat them at much higher temperature for long time duration for reaction to occur at an appreciable rate. Solid State Reaction (SSR) method provides large range of selection of starting materials like, oxides, carbonates, etc. Since, solids do not react with each other at room temperature (RT), it is necessary to heat them at elevated temperatures as for the proper reaction to take place at appreciable rate.

There are two factors namely thermodynamic and kinetic which are important in solid state reaction, the former determines the possibility of any chemical reaction to occur by the free energy considerations which are involved while the latter determines the rate at which the reaction occurs [20, 21]. The atoms diffuse through the material to form a stable compound of minimum free energy. Different compounds or phases might have the lowest free energy at
various temperatures or pressures or the composition of the gas atmosphere might affect the reaction. In order to prepare a single-phase sample, the conditions during any reaction are very important. During synthesis, the parameters such as temperature, pressure, gas flow and time for the reaction are needed to be varied according to the phase requirements in the sample. Mapping of all variables have made to find the conditions, which are best for each material and phase.

The factors on which the feasibility and rate of a solid state reaction include, reaction conditions, structural properties of the reactants, surface area of the solids, their reactivity and the thermodynamic free energy change associated with the reaction. Reagents are the solid reactants from which it is proposed to prepare a solid crystalline compound. The selection of reactant chemicals depends on the reaction conditions and expected nature of the product. The reactants are dried thoroughly prior to weighing. After the reactants have been weighed out in the required amounts, they are mixed together. For manual mixing of small quantities, usually an agate mortar by pestle are employed. Sufficient amount of some volatile organic liquid - preferably acetone or alcohol - is added to the mixture to aid homogenization. This forms a paste which is mixed thoroughly. During the process of grinding and mixing, the organic liquid gradually volatilizes and has usually evaporated completely after 10 to 15 minutes. For quantities much larger than ~20g, mechanical mixing is usually adopted using a ball mill and the process may take several hours. For the subsequent reaction at high temperatures, it is necessary to choose a suitable container material which is chemically inert to the reactants under the heating conditions used. The noble metals, platinum and gold, are usually suitable. Containers may be crucibles or boats made from foil. For low temperature reactions, other metals like Nickel (below 600-700 °C) can be used. The heating programme to be used depends very much on the form and reactivity of the reactants. In the control of either temperature or atmosphere, nature of the reactant chemicals is considered in detail. A good furnace is used for
heat treatment. Pelleting of samples is preferred prior to heating, since it increases the area of contact between the grains.

### 2.2.4 Solvothermal method

Solvothermal processes involve using water at elevated temperatures and pressures in a closed system, often in the vicinity of its critical point [22-25]. A more general term, “solvothermal” refers to a similar reaction in which a non-aqueous solvent (organic or inorganic) is used. Under solvo (hydro) thermal conditions, certain properties of the solvents, such as density, viscosity and diffusion coefficient change dramatically and the solvents behave much differently from what are expected under ambient conditions [21]. Consequently, the solubility, the diffusion process and the chemical reactivity of the reactants (usually solids) are highly increased or enhanced, enabling the reaction to take place at much lower temperature than normal. This method has been widely applied and adopted for crystal growth for many inorganic materials, such as zeolites, quartz, metal carbonates, phosphates and other oxides and halides.

Solvothermal techniques have been extensively developed for the synthesis of metal oxides [26-29]. Solvothermal synthesis concerns much soft and softer chemistry conducted at low temperatures. The mild and soft conditions make it possible to leave polychalcogen building blocks intact while they reorganize themselves to form various new structures, many of which might be promising for applications in catalysis, electronic, magnetic, optical and thermo electronic devices.

Although some solvothermal processes involve supercritical solvents, most simply take advantage of the increased solubility and reactivity of metal salts and complexes at elevated temperatures and pressures without bringing the solvent to its critical point. The metal complexes are decomposed thermally either by heating the contents in an inert atmosphere or by using an autoclave. A suitable capping agent or stabilizer such as a long-chain amine, thiol, trioctylphosphine oxide
(TOPO), etc are added to the reaction contents at a suitable point to hinder the growth of the particles and hence stabilize them against agglomeration. The stabilizers are also help in dissolution of the particles in different solvents. The cases of co-precipitation and sol–gel methods, solvothermal process also allow substantially reduced reaction temperatures and the products of such reactions are usually crystalline and do not require post-annealing treatments.

Using this method, Yin and coworkers produced 2-10 nm crystallites of monodispersed TiO$_2$ nano particles [30], Niederbetger and co-workers [31] reported the preparation of nanocrystalline iron, indium, gallium, and zinc oxide by solvothermal method and monodispersed CeO$_2$ with very narrow size distribution was also synthesized by solvothermal method [32].

2.2.5 Sono-chemical co-precipitation method

In recent years, ultrasound irradiation has extensively used for the preparation of novel materials with unusual properties. Ultrasound irradiation can induce the formation of particles with much smaller size and higher surface area. This method involved the precipitation of metals, which exits in solution was exposed to high intensity ultrasound irradiation under ambient air for a particular time period with a varying pulse of the order of one or two seconds. It was accomplished with a high intensity ultrasonic probe immersed directly in the solutions.

The principle of sonochemistry is breaking the chemical bond with the application of high power ultrasound waves, usually between 10 and 20 MHz. The physical phenomenon responsible for the sono-chemical process is acoustic cavitation. According to published theories for the formation of nanoparticles by sonochemistry, the main events that occur during the preparation are creation, growth and collapse of the solvent bubbles that are formed in the liquid. These bubbles are in the nanometer size range. Solute vapors diffuse into the solvent bubble and when the bubble reaches a certain size, it collapse. During the collapse,
very high temperature of the order of 500-2500 K [33] is reached which is enough to break chemical bonds in the solute. The collapse of the bubbles take place in less than nanosecond hence high cooling rate (1011 K/s) is required. This high cooling rate hinders the organization and crystallization of the products. Since the breakings of bonds in the precursor occur in the gas phase, amorphous nanoparticles are formed. Though the reason for the formation of amorphous product is well understood, not the formation of nanostructure. One possible explanation is that in each collapsing bubble a few nucleation centers are formed and while the fast kinetics does not stop the growth of nuclei that growth is limited by the collapse.

The sonochemical method has found useful in many areas of material science, for the preparation of amorphous products through the insertion of nanomaterials into mesoporous materials to deposition the nanoparticles on ceramic and polymeric surfaces [34-37]. The polycrystalline CeO$_2$ nanorods (5-10 nm in diameter and 50-150 nm in length) were synthesized via ultrasonication using polyethylene glycol (PEG) as structure directing agent at room temperature. The content of PEG, the molecular weight of PEG and sonication time was confirmed to be the crucial factors which determine the formation of one dimensional CeO$_2$ nanorods. A possible ultrasonic formation mechanism is shown in figure 2.3 [38].

2.2.6 Hydrothermal Method

The term hydrothermal is geologic in origin and many of the mechanisms were originally elucidated for mineral systems by Morey [39]. Hydrothermal synthesis is defined as an aqueous chemical reaction in a sealed container at a temperature that autogenously generates an elevated pressure [40]. Processing in this manner allows low temperature range 100 - 374°C which are the boiling and critical point for water, respectively, synthesis of fully crystalline oxide nanoparticles to be realized [41, 42].
There are several advantages to hydrothermal processing including high purity (> 99.5%) and chemical homogeneity, small particle size (< 5 nm possible), narrow particle size distribution, single step processing, low energy usage, fast reaction times, low cost equipment, the ability to generate metastable compounds, no calcinations are required for many materials since they are fully crystallized by the reaction [43]. Too many parameters the fact that nanomaterials including one, two and three dimensional structures can be synthesized to the fully crystalline state is one of the reasons for oxide nanostructures made via hydrothermal synthesis have grown in popularity during the past decade from under 100 publication in 1999 to over 1,600 in 2008 (data from Web of Science). Continued expansion of this field is expected as microwave, ultrasonic, electrochemical and mechanical systems are being combined with the hydrothermal processing to improve reaction kinetics and reduce processing time [43].

An example of how reaction time was reduced dramatically demonstrated by Jouhannauad et al [44] who used microwave hydrothermal synthesis to make 5nm SnO$_2$ nanoparticles with process times as short as 60 seconds. This is a huge improvement as most synthesis techniques require at least 6 hours of reaction time [45]. Driving reaction times down to minutes may enable combinational style nanomaterials research where literally hundreds of variants could be examined in a short period of time to help further understanding of the reaction mechanisms involved. Generally, the hydrothermal synthesis involves with the two major characteristics. One of the systems is always at a non-ideal and non-equilibrium state; and second the solvent is always at its near-critical, critical or supercritical state. The disadvantages of hydrothermal processing are such it includes expensive autoclaves, safety issues during the reaction process and it is not observing of the reaction process.
2.3 Characterization techniques

2.3.1 X-ray diffraction technique (XRD)

Many researchers have extensively used XRD to explore the structures of the materials which is a non-destructive technique. This technique can be used to determine the crystal structure of metals and alloys, minerals, inorganic compounds, polymers and organic materials. Also, this technique is applied to derive information on fine structure of materials like crystallite structure, lattice strain, chemical composition etc. Typical XRD pattern consists of a series of peaks, in which peak intensity is plotted on the Y-axis and diffraction angle (2θ) along X-axis. These peaks are called “reflections”. Each peak in the diffraction pattern corresponds to X-rays diffracted from a specific set of planes in the material, these peaks have different heights (intensities). The positions of the peaks in XRD patterns depend on the crystal structure of the material while intensities depend on many factors like atomic structure factor, incident intensity, slit width, number of grains etc. The particular advantage of X-ray diffraction analysis is that it discloses the presence of a substance, as that substance actually exists in the sample. Diffraction analysis is useful whenever it is necessary to know the state of chemical combination of the elements involved or the particular phase in which they are present. Compared with ordinary chemical analysis the diffraction method has the advantage that it is usually much faster, requires only very small quantity of sample and it is non-destructive [46, 47].

The basic law involved in the diffraction method of structural analysis is the Bragg’s law. When monochromatic X-rays impinge upon the atoms in a crystal lattice each atom acts as a source of scattering. The crystal lattice acts as series of parallel reflecting planes. The intensity of the reflected beam at certain angles will be maximum when the path difference between two reflected waves from two different planes is an integral multiple of \( \lambda \). This condition is called
Bragg’s law and it is given by the relation. The relation is shown schematically in figure 2.4.

\[ 2d \sin \theta = n\lambda \]  \hspace{1cm} (2.1)

Where \( n \) is the order of diffraction, \( \lambda \) is the wavelength of X-rays, \( d \) is the spacing between consecutive parallel planes and \( \theta \) is the glancing angle (or the complement of the angle of incidence) [48].

Experimentally obtained diffraction patterns of the materials are compared with Joint Council Powder Diffractions (JCPDS) data for standards. This gives information of different crystallographic phases, relative abundance and preferred orientation. From the width of the diffraction peak, average grain size can also be estimated. The block diagram of the experimental setup of XRD is shown in figure 2.5 using CuK\( \alpha \) radiation (with wavelength \( \lambda = 1.5406 \) Å).

The average grain size of the film can be calculated using the Scherrer’s formula [46],

\[ D = \frac{K\lambda}{\beta_{hkl} \cos \theta} \]  \hspace{1cm} (2.2)

Where, \( K \) is the shape factor, \( \lambda \) is the wavelength of X-ray and \( \beta \) is the full width at half maximum intensity in radians. The lattice parameter values for different crystallographic systems can be calculated from the following equations using the (hkl) parameters and the interplanar spacing \( d \).

For hexagonal system,

\[ \frac{1}{d_{hkl}^2} = \frac{4}{3} \left[ \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2} \right] \]  \hspace{1cm} (2.3)

For cubic system,

\[ \frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2} \]  \hspace{1cm} (2.4)
Where ‘a’ and ‘c’ are the lattice parameters and d is the lattice interplanar spacing.

2.3.2 Scanning electron microscopy (SEM)

Scanning Electron Microscopy (SEM) is used to study the surface morphology of the materials. The atomic arrangements are governed by the interatomic forces and chemical bonds. The ratio of the number of atoms on the surface to the total number of atoms on the surface to the total number of atoms in a nanoparticle (surface to volume ratio) is inversely proportional to particle size. Also the surface energy increases with decreasing particle size. So clearly a nanoparticle would prefer a shape which would minimize its surface energy [49]. In the nano world, since the properties of materials depend on the size and shape of the particles, morphology study has relevance. SEM can be effectively used to test the amorphous or crystalline texture of nano materials. This is also an effective tool to check the porosity and the presence of physically absorbed and chemically bound water. In the case of nano materials the amorphous raw powder reveals micrometer sized agglomerated particles with a highly porous structure while the calcined products show well faceted grains made up of several tiny crystallites. This interesting structural change can be easily visualized using SEM photograph.

The scanning electron microscope (SEM) is a microscope that uses electrons rather than light to form an image. There are many advantages for using the SEM instead of a light microscope [50, 51]. The SEM has a large depth of field which allows a large amount of the sample to be in focus at the same time. The SEM also produces image of high resolution which means that closely spaced features can be examined at a high magnification. Preparation of the samples is relatively easy since most SEMs only require that sample should be conductive. The combination of higher magnification, larger depth of focus, high resolution and ease of sample observation makes SEM one of the most heavily used
instrument in the research field. The electron beam comes from a filament which made up of various types of materials. The most common is the Tungsten hairpin gun. This filament is a loop of tungsten that functions as the cathode. A voltage is applied to the loop, causing it to heat up. The anode, which is positive with respect to the filament, forms powerful attractive forces for electrons. This causes electrons to accelerate toward the anode. The anode is arranged, as an orifice through which electrons would pass down to the column where the sample is held. Other examples of filaments are lanthanum hexaboride filaments and field emission guns.

A schematic diagram of a SEM is shown in figure 2.6. The electron gun consists of a cathode (a filament is made up of W wire), which is heated to emit electrons by thermionic emission. The electrons are accelerated towards an anode with a potential difference of several tens of kV (the maximum voltage is typically 40 kV). A series of electromagnetic lenses are focused the electron beam to a spot on the surface of the specimen. A variety of signals can be emitted as a result of interactions between the electron beam and the specimen. The beam is rastered over the surface of the specimen using electrostatic coils and the amplified signal collected by the chosen detector can be used to form a TV image. The signal from secondary electrons is the most commonly used for image.

2.3.3 Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) is an imaging technique whereby a beam of electrons is focused onto a specimen causing an enlarged version to appear on a fluorescent screen or layer of photographic film or to be detected by a CCD camera. The first practical transmission electron microscope was built by Albert Prebus and James Hillier at the University of Toronto in 1938 using concepts developed earlier by Max Knoll and Ernst Ruska. Electrons are generated by a process known as thermionic discharge in the same manner as the cathode in a cathode ray tube, or by field emission; they are then accelerated by an electric
field and focused by electrical and magnetic fields onto the sample. The electrons can be focused onto the sample providing a resolution far better than as possible as light microscopes and with improved depth of vision. Details of a sample can be enhanced in light microscopy by the use of marks. Similarly with electron microscopy, compounds of heavy metals such as osmium, lead or uranium can be used to selectively deposit in the sample to enhance structural details. The electrons that remain in the beam can be detected using a photographic film, or fluorescent screen [50]. So areas where electrons are scattered appear dark on the screen or on a positive image.

An additional class of these instruments is the electron cryomicroscope which includes a specimen stage capable of maintaining the specimen at liquid nitrogen or liquid helium temperatures. This allows imaging specimens prepared in vitreous ice, the preferred preparation technique for imaging individual molecules or macromolecular assemblies. Another type of TEM is the scanning transmission electron microscope (STEM), where the beam can be rastered across the sample to form the image. In analytical TEMs the elemental composition of the specimen can be determined by analysing its X-ray spectrum or the energy-loss spectrum of the transmitted electrons. Modern research TEMs may include aberration correctors to reduce the amount of distortion in the image which allows information on features on the scale of 0.1 nm to be obtained (resolutions down to 0.08 nm has been demonstrated, so far). Monochromators may also be used which reduce the energy spread of the incident electron beam which is less than 0.15 eV.

From TEM images, size of the nanoparticles can be determined. Parallel lines in the high resolution transmission electron micrograph (HRTEM) represent planes in the crystal lattice and distance between them corresponds to d spacing. By comparing these d spacing values with the JCPDS data, one can identify the orientation of the planes in the synthesized material. Selective area electron diffraction (SAED) is the map of the reciprocal lattice which will also give the signature of various planes in which material has been grown. Depending on the
crystalline nature of the material, the SAED pattern will be orderly arranged spots, distinguishable ring or fused rings. But in the case of quantum dots concentric rings were observed in the SAED. The d spacing of the planes corresponding to the rings can be determined by the following equation

\[ (Dd) = CL\lambda \]  \hspace{1cm} (2.5)

Where \( L \) is the effective camera length, \( \lambda \) is the de-Broglie wavelength of the accelerating electrons, \( D \) is the ring diameter of a standard electron diffraction pattern and \( d \) is the interplanar spacing [50].

One of the first applications of TEM is to study the particle size, shape and size distribution of particles from solutions such as colloidal preparation, soil fractions and precipitates and from dry origins such as airborne dusts, paint pigments, powders and fibers. A second application of TEM is the identification of crystal structure of the crystalline particles by electron diffraction. The diffraction pattern is in the form of concentric rings or series of spots. Each rings or series of spots correspond to a particular set of crystal planes. The block diagram of TEM is shown in figure 2.7 and TEM instrument photo graph is shown in figure 2.8.

### 2.2.4 Fourier transformation infrared spectroscopy (FTIR)

In order to understand the contribution of quantum size to the infrared transmittance, Fourier Transformation Infrared transmission studies have been carried out for materials.

Fourier Transformation Infrared Spectroscopy uses Michelson interferrometer to produce an interferrogram. The interferrogram is related to IR spectrum by the mathematical operation, the Fourier transformation. The fundamental part of the instrument is the so-called Michelson interferometer [52]. It consists of a beam splitter and two mirrors, one fixed and other movable. The infrared radiation emitted by a broad band source which is splited into two beams of equal intensity. Either one beam or both are passed through the sample, but one beam is made to traverse a longer path than the other. Depending on the movable
mirrors relative displacement, the beams are recombined either constructively or destructively. The recombination of the two beams produces an interference pattern. By changing the path difference the interference pattern changes to produce a detailed signal varying with optical path difference. This pattern is known as the interferrogram. The interferrogram is converted into a plot of absorption versus wavelength by the Fourier Transformation of the interferrogram using a computer built into the machine. There are several advantages of FTIR [52] over the traditional dispersive method, the most important being the much higher signal to noise ratio.

Harmonic oscillators-like states occur in solids where ions are in random translation motion [53]. The local potential of the moving ion will fluctuate on a very small time scale because of its interaction with the neighbors and hence the ions can be assumed to be behaving like a highly damped harmonic oscillator. Both the lattice vibration of the bound nuclei or the local motions of the moving ion are characterized by a characteristic frequency which can be seen in the far-IR region [53].

It has been shown that the optical absorption and scattering in the fundamental lattice absorption region are the size dependent [54]. As the crystal size decreases the surface band increases in intensity relative to the bulk band and shift to higher frequencies. In order to study the modifications in the IR spectra when the crystal size is reduced, far-IR transmission spectra of the nanoparticles were recorded.

In an infrared spectrum the absorption or transmittance peaks correspond to the frequencies of vibrations between the bonds of the atoms making up the material. From the characteristic peaks, different functional groups or chemical species present in the compound can be identified. This aspect makes infrared spectroscopy quite useful in material characterization. A schematic block diagram of an FTIR is shown in figure 2.9
2.3.5. UV-Vis-NIR Spectroscopy

Light from the source is made to fall on a grating. The grating is made to rotate about an axis in such a way that the angle of incidence of the light beam from the source gradually changes. The output beam from the grating will contain different wavelengths, which are spatially separated. At a particular angle of the grating, only one wavelength will pass through the slit such that the output from the slit will be monochromatic. Different wavelengths are obtained in accordance with different angles of incidence. This beam is split by means of a beam splitter. One of the beam passes through the reference and the other beam passes through the sample for which the absorption is to be recorded. The phase and intensity of the transmitted beams from both the reference and the sample are detected (Radiation in the UV-visible region is detected using a PMT and that in the NIR region by a PbS crystal detector). By comparing these data using a phase sensitive amplifier the absorption spectrum of the sample is displayed and recorded. A schematic block diagram of an UV-VIS-NIR – Spectrophotometer instrument is as shown in figure 2.10

The ultra-violet region is subdivided into two spectral regions. The range between 2000 and 4000 Å is referred to as the near ultra violet region. The region below 2000Å is called the far or vacuum ultra violet region.

There are two classes of spectra, namely emission and absorption spectra. An emission spectrum is obtained by analyzing the light emitted by a luminous source. An absorption spectrum is obtained by the spectroscopic analysis of the light transmitted by an absorbing medium which is placed between the light source and the detector. When light is incident on a sample, absorption takes place inside depending on the energy $h\nu$ of the incident light and energy band gap ($E_g$) of the material [55]. When $h\nu < E_g$, the light passes through the material with little absorption. As the energy of the irradiation increases such that $h\nu \sim E_g$, a sharp increase or a rise in the absorption takes place.
The most direct and simplest method for determination the band structure of semiconductors is by measuring the absorption spectrum. Absorption is expressed in terms of a coefficient \( \alpha(hv) \), which is related to the energy gap \( E_g \) according to the equation

\[
\alpha(hv) = A (hv - E_g)^n
\]  

(2.6)

where \( A \) is a constant, \( h \) is the planks constant, \( \nu \) is the frequency of the incident beam and \( n \) – is equal to \( \frac{1}{2} \) for a direct band gap and 2 for an indirect gap.

The absorption coefficient is calculated from spectrum by dividing the \( \alpha \) values. It is plotted against the photon energy for pure and Mn doped ZnO. The intercept of this plot on the photon energy axis gives band gap of the sample. The probable energy for the transitions was estimated from the Taue plot by plotting the \( \alpha(hv)^{1/2} \) vs \( hv \) graphs.

2.3.6. Vibrating sample magnetometer (VSM)

A vibrating sample magnetometer or VSM was invented in 1955 by Simon Foner at Lincoln Laboratory MIT. It is a scientific instrument that measures magnetic properties. The paper about his work was published in 1959 [56]. A sample is placed inside a uniform magnetic field to magnetize the sample. The sample is then physically vibrated sinusoidally, typically through the use of a piezoelectric material. Commercial systems use linear actuators of some form and historically the development of these systems was done using modified audio speakers, though this approach was dropped due to the interference through the in-phase magnetic noise produced as the magnetic flux through a nearby pickup coil varies sinusoidally. The induced voltage in the pickup coil is proportional to the samples magnetic moment but does not depend on the strength of the applied magnetic field. In a typical setup, the induced voltage is measured through the use of a lock-in amplifier using the piezoelectric signal as its reference signal. By measuring the field of an external electromagnet, it is possible to obtain the hysteresis curve of a material.
The VSM (Princeton measurements corporation, MicroMag™ 2900) is essentially a gradiometer, measuring the difference in magnetic induction between a region of space with and without the specimen. A schematic diagram of a VSM is shown in figure 2.11. The sample (S) is mounted on a small plastic cylinder using some silicon grease and it is attached to a glass rod which is then placed in the VSM. The sample is centrally located between four, stationary pick-up coils and oscillated vertically in a uniform magnetic field (sample is driven by a loudspeaker mechanism). At the upper end of the glass rod there is a reference in the form of a small permanent magnet (M) situated between a set of reference coils. Therefore the AC signal induced in the pick-up coils by the magnetic field of the sample is compared with the signal from the permanent magnet and which is converted to a number proportional to the magnetic moment. This means that the set-up is insensitive to change in the vibration amplitude and frequency.

The VSM has a high sensitivity and is capable for measuring magnetic moments in the range of µemu. Its accuracy is better than 2 %. However, the specimens used have to be rather short to fit between the pole pieces of the electromagnet and the hysteresis loops obtained are not intrinsic because of demagnetising effects associated with using short specimens. For quantitative work, the VSM was calibrated with a bulk sample of Ni of known saturation magnetization. This sample was small enough to assume that all flux produced will cut the sense coils. However, thin film samples are normally grown on 10×5 mm 2 substrates and so in certain orientations not all of the magnetic flux from these larger samples will cut the sense coils.
References


