CHAPTER 2

PREPARATION METHODS AND CHARACTERIZATION TECHNIQUES

2.1 INTRODUCTION

Over the past two decades, the synthesis of chalcogenides has attracted significant interest and is still the subject of intense investigations. Conventionally, metal chalcogenides can be prepared in a variety of ways, the most straightforward of which is the direct combination of the elements at elevated temperatures. Some of the important methods are purely physical, chemical, biological or hybrid. Irrespective of the method of synthesizing the nanoparticles it is essential to avoid the coalescence of particles into larger particles and achieve monodispersity and chemical stability over a long period. Herein, a review about the latest progress in the field of synthesis and characterization studies of semiconductor nanomaterials is presented. This review mainly focuses on some novel synthetic methods, experimental setup of some analytical techniques and measurements that are used to characterize the semiconductor nanomaterials.

2.2 METHODS OF SYNTHESIS OF NANOPARTICLES

Nanocrystalline materials can be synthesized either by consolidating atoms/molecules/clusters or breaking down the bulk material into smaller and smaller dimensions. The former is known as the ‘Bottom up’ approach whereas the latter is referred to as the ‘Top down’ method. Many
techniques including both Top-down and Bottom-up approaches have been
developed and applied for the synthesis of the nanoparticles. In the Top-down
approach a block of a bulk material is whittled or sculptured to get the
nanosized particle. The Top-down approaches include milling or attrition,
lithography etc. The main disadvantage of the Top-down approach is the
imperfection of the surface structure. The nanoparticles produced by the
attrition have a relatively broad size distribution and various particle shape or
geometry. In addition they may contain significant amount of impurities. In
the Bottom-up approach, the individual atoms and molecules are placed or
self assembled precisely where they are needed. Here the molecule or atomic
building blocks fit together to produce nanoparticles. Bottom-up approaches
are more favourable and popular in the synthesis of nanoparticles and many
preparation techniques of Bottom-up approach have been developed.

![Figure 2.1 Schematic representation of Bottom-up and Top-down
technique](image)

The nanostructured materials have been synthesized by different
methods including inert gas condensation, mechanical alloying, spray
conversion processing, plastic deformation, electro deposition, rapid
solidification from the melt, physical vapour deposition, chemical vapour
processing, co-precipitation, sol-gel processing, sliding wear, spark erosion,
plasma processing, auto-ignition, laser ablation, hydrothermal pyrolysis,
thermophoretic forced flux system, quenching the melt under high pressure and biological templating. Also, some novel synthetic methods for nanocrystalline metal chalchogenides that have been established in the past decade including microwave assisted heating, sonochemical method, sonoelectrochemical method, photochemical synthesis, \(\gamma\)-irradiation method, microemulsion route, low-temperature solid-state synthesis, solvothermal technique and electrochemical template synthesis. Table 2.1 lists some of the more common methods used to produce nanocrystalline materials and also the dimensionality of the product obtained.

**Table 2.1 Methods to synthesize nanocrystalline materials**

<table>
<thead>
<tr>
<th>Starting phase</th>
<th>Technique</th>
<th>Dimensionality of product</th>
</tr>
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<tbody>
<tr>
<td>Vapour</td>
<td>Inert gas condensation</td>
<td>3D</td>
</tr>
<tr>
<td></td>
<td>Physical vapour deposition –</td>
<td></td>
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<tr>
<td></td>
<td>Evaporation and sputtering</td>
<td>1D</td>
</tr>
<tr>
<td></td>
<td>Plasma processing</td>
<td>3D</td>
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<tr>
<td></td>
<td>Chemical vapour condensation</td>
<td>3D, 2D</td>
</tr>
<tr>
<td></td>
<td>Chemical reactions</td>
<td>3D</td>
</tr>
<tr>
<td>Liquid</td>
<td>Rapid solidification</td>
<td>3D</td>
</tr>
<tr>
<td></td>
<td>Electrodeposition</td>
<td>1D, 3D</td>
</tr>
<tr>
<td></td>
<td>Chemical reactions</td>
<td>3D</td>
</tr>
<tr>
<td>Solid</td>
<td>Mechanical alloying/milling</td>
<td>3D</td>
</tr>
<tr>
<td></td>
<td>Devitrification of amorphous phases</td>
<td>3D</td>
</tr>
<tr>
<td></td>
<td>Spark erosion</td>
<td>3D</td>
</tr>
<tr>
<td></td>
<td>Sliding wear</td>
<td>3D</td>
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In the present study the molecular precursor methods that involve thermal decomposition of a compound containing an M-S or M-Se bond as the chalcogenide source was adopted to obtain the sample in powder form. This method is cost effective and gives high yield with fine grains. This method has already been thoroughly investigated and is found to be reliable at relatively low temperature (200-350 °C). The grain size, morphology and texture can be varied by suitably modifying/controlling the process variables in these methods. Each of these methods has advantages and disadvantages and the appropriate method is chosen depending upon the requirements. The various aspects of the synthesis method are described right from the preparation of solutions till the sample recovery in brief.

2.2.1 Inert gas Condensation

Gleiter (1989) used the inert gas condensation technique to produce nanocrystalline powder particles and consolidated them in situ into small disks under ultra-high vacuum (UHV) conditions. Vapour condensation has been known to produce very fine-grained or amorphous alloys depending on the substrate temperature and other operating conditions. Thus, this technique was originally used to synthesize small quantities of nanostructured pure metals. The schematic diagram of inert gas condensation technique is shown in Figure 2.2. This involves evaporation of metal (by resistive heating, radio-frequency heating, sputtering, electron beam heating, laser/plasma heating, or ion sputtering) inside a chamber that was evacuated to a very high vacuum of about $10^{-7}$ torr and then backfilled with a low pressure inert gas, typically a few hundred pascals of helium. The evaporated atoms collide with the gas atoms inside the chamber, lose their kinetic energy and condense in the form of small, discrete crystals of loose powder. Convection currents, generated due to the heating of the inert gas by the evaporation source and cooled by the liquid nitrogen-filled collection device (cold finger), carry the condensed fine
powders to the collector device, from where they can be stripped off by moving an annular teflon ring down the length of the tube into a compaction device.

**Figure 2.2 Schematic diagram of inert gas condensation method**

The inert gas condensation method produces equiaxed (3D) crystallites. The crystal size of the powder is typically a few nanometers and the size distribution is narrow. The crystal size is dependent upon the inert gas pressure, the evaporation rate and the gas composition. Extremely fine particles can be produced by decreasing either the gas pressure in the chamber or the evaporation rate and by using light inert gasses (such as He) rather than heavy inert gases (such as Xe). The results from experiments using the inert gas condensation method to produce nanoparticles of Mn, AuPd and CoO were presented in the literatures (Ward et al 2006; Tijerina et al 2010; Ceylan et al 2007)
2.2.2 Chemical Vapour Deposition and Chemical Vapour Condensation

Chemical Vapour Deposition (CVD) is a well known process in which a solid is deposited on a heated surface via a chemical reaction from the vapour or gas phase. In thermal CVD the reaction is activated by a high temperature above 900 °C. A typical apparatus comprises of a gas supply system, a deposition chamber and an exhaust system.

In plasma CVD, the reaction is activated by plasma at temperatures between 300 and 700 °C. In laser CVD, pyrolysis occurs when laser thermal energy heats an absorbing substrate. In photo-laser CVD, the chemical reaction is induced by ultra violet radiation which has sufficient photon energy to break the chemical bond in the reactant molecules. In this process, the reaction is photon activated and deposition occurs at room temperature. Nano composite powders are also prepared by CVD method. For example, SiC/Si₃N composite powder was prepared using SiH₄, C₂H₂ and NH₃ as a source of gas at 1400 °C (Hong and Lai 1999). Chemical Vapour Condensation (CVC) process was developed in Germany in 1994. The schematic diagram of CVC is shown in Figure 2.3. It involves pyrolysis of vapours of metal organic precursors in a reduced pressure atmosphere. A metal organic precursor is introduced in the hot zone of the reactor using mass flow controller. The reactor allows synthesis of mixtures of nanoparticles of two phases or doped nanoparticles by supplying two precursors at the front end of reactor and coated nanoparticles by supplying a second precursor in a second stage of reactor. The process yields quantities in excess of 20 g/hr. The yield can be further improved by enlarging the diameter of hot wall reactor and mass of fluid through the reactor.
2.2.3 Mechanical Alloying

Mechanical alloying produces nanostructured materials by the structural disintegration of coarse-grained structure as a result of severe plastic deformation. Mechanical alloying consists of repeated welding, fracturing and rewelding of powder particles in a dry high-energy ball mill until the composition of the resultant powder corresponds to the percentages of the respective constituents in the initial charge. In this process, mixtures of elemental or pre alloyed powders are subjected to grinding under a protective atmosphere in equipment capable of high-energy compressive impact forces such as attrition mills, vibrating ball mills and shaker mills. A majority of the work on nanocrystalline materials has been carried out in highly energetic small shaker mills. The process is referred to as mechanical alloying when one starts with a blended mixture of elemental powders and as mechanical milling when one starts with single component powders such as elements or
intermetallic compounds. These processes have produced nanocrystalline structures in pure metals, intermetallic compounds and immiscible alloy systems. It has been shown that nanometer-sized grains can be obtained in almost any material after sufficient milling time. The grain sizes are found to decrease with milling time down to a minimum value that appeared to scale inversely with the melting temperature. Huller et al (2008) and Suryanarayana (2008) have recently summarized the process of mechanical alloying/milling and the characteristics and properties of the nanocrystalline materials thus obtained.

2.2.4 Electrodeposition

This is a simple and well-established process and can be easily adopted to produce nanocrystalline materials. Electrodeposition of multilayered (1-D) metals can be achieved by using either two separate electrolytes or much more conveniently from one electrolyte by appropriate control of agitation and the electrical conditions (particularly voltage). Also, 3D nanostructure crystallites can be prepared using this method by utilizing the interference of one ion with the deposition of the other. Recently many researchers extensively used this process to study the synthesis and properties of nanocrystalline materials (Gu and Suh 2010; Song et al 2009; Zhang et al 2008). It has been shown that electrodeposition yields grain sizes in the nanometer range when the electrodeposition variables (e.g., bath composition, pH, temperature, current density, etc.) are chosen such that nucleation of new grains are favoured rather than growth of existing grains. This is achieved by using high deposition rates, formation of appropriate complexes in the bath, addition of suitable surface-active elements to reduce surface diffusion of ad-atoms, etc. This technique can yield porosity-free finished products that do not require subsequent consolidation processing. Further, the process requires
low initial capital investment and provides high production rates with few shape and size limitations.

2.2.5 Chemical Precipitation and Co-precipitation

A chemical precipitation process consists of three main steps: chemical reaction, nucleation and crystal growth. Chemical precipitation is generally not a controlled process in terms of reaction kinetics and the solid phase nucleation and growth processes. Therefore, solids obtained by chemical precipitation have a wide particle size distribution plus uncontrolled particle morphology, along with agglomeration. To obtain nanoparticles with a narrow size distribution, the necessary requirements are (i) a high degree of supersaturation, (ii) a uniform spatial concentration distribution inside a reactor and (iii) a uniform growth time for all particles or crystals.

The other commonly used solution method for the synthesis of multi component oxide ceramics is co-precipitation method, which produces a “mixed” precipitate comprising two or more insoluble species that are simultaneously removed from solution. The precursors used in this method are mostly inorganic salts (nitrate, chloride, sulfate, etc.) that are dissolved in water or any other suitable medium to form a homogeneous solution with clusters of ions. The solution is then subjected to pH adjustment or evaporation to force those salts to precipitate as hydroxides, hydrous oxides, or oxalates. The crystal growth and their aggregation are influenced by the concentration of salt, temperature, the actual pH and the rate of pH change. After precipitation, the solid mass is collected, washed and gradually dried by heating to the boiling point of the medium. The washing and drying procedures applied for co-precipitated hydroxides affect the degree of agglomeration in the final powder and must be considered when nanosized powders are the intended product. Generally, a calcination step is necessary to transform the hydroxide into crystalline oxides. In most of the binary, ternary
and quaternary systems, a crystallization step is necessary, which is generally achieved by calcinations or, more elegantly, by a hydrothermal procedure in high-pressure autoclaves.

A large number of reports are available on the synthesis of ultrafine oxide powders (Bumb et al 2008; Li et al 2008; Tao et al 2006), oxide-oxide composites (Aifan et al 2006) and biomaterial (Wang et al 2011) by co-precipitation reactions. The advantages of co-precipitation reactions are (i) the homogeneity of component distribution, (ii) the relatively low reaction temperature, (iii) the fine and uniform particle size with weakly agglomerated particles and (iv) the low cost. However, these reactions are highly susceptible to the reaction conditions and because of incomplete precipitation of the metal ions, control over the stoichiometry of the precursors is rather difficult to achieve. In addition, the co-precipitation reactions are not suited for certain oxides/hydroxides, for instance, in the case of amphoteric systems.

2.2.6 Sol–gel Synthesis

Sol–gel processing is also a promising method for the preparation of nano dimensional materials. The reaction product of the sol–gel synthesis could be either colloidal powders or films. In addition to the sol–gel method precursor-based solution deposition routes can also be used for nanostructure formation. One of the advantages of this method is the ability to control the microstructure of final product by controlling chemical reaction parameters. It has been demonstrated that modification of the reaction conditions could significantly affect the structure of the sol–gel product. Reports on the sol–gel synthesis of nanosized sulfides, selenides, or tellurides are relatively much scarcer. There are two sol–gel routes that are used most commonly in preparation of metal sulfides. The first one involves a modified sol–gel route in which the conventional alcohol sol is exposed to a stream of H₂S or some other sulfur sources. The other one is the use of thiols in place of alcohol for
the formation of sulfides by a modification of the first sol–gel route. In the past few years, by using these two routes, a variety of nanocrystalline sulfides, either in powder form or films, have been successfully prepared by sol–gel method. Arachchige and Brock (2007) reported a sol–gel method for the preparation of metal sulfides. This method is widely used in the synthesis of inorganic and organic-inorganic hybrid materials and capable of producing nanoparticles, nanorods, thin films and monoliths.

2.2.7 Sonochemical Synthesis

Currently, ultrasound irradiation has become an important tool in chemistry. It provides an unusual mechanism for generating high-energy chemistry with extremely high local temperatures and pressures and an extraordinary heating and cooling rate. Sonochemistry drives principally from acoustic cavitations: the formation, growth and implosive collapse of bubbles in liquids. When solutions are exposed to strong ultrasound irradiation, bubbles are implosively collapsed by acoustic fields in the solution. High-temperature and high-pressure fields are produced at the centers of the bubbles. The implosive collapse of the bubbles generates a localized hotspot through adiabatic compression or shock wave formation within the gas phase of the collapsing bubbles. The conditions formed in these hotspots have been experimentally determined, with the transient temperature of ~5000 K, pressure of > 1800 atm and cooling rates in excess of 1010 K/s. These extreme conditions enable many chemical reactions to occur. The products are sometimes nano amorphous particles and, in other cases, nanocrystalline (Bang and Suslick 2010, Gedanken 2004). This depends on the temperature in the ring region where the reaction takes place.

Ultrasound irradiation differs from traditional energy sources (such as heat, light, or ionizing radiation) in duration, pressure and energy per molecule. Ultrasound irradiation has also been used to induce hydrolysis to
produce various metal oxide nanoparticles. Ultrasound irradiation also offers a very attractive method for the preparation of various nanosized metal chalcogenides (Praharaj et al 2006). They vary in size, shape, structure and in their solid phase (amorphous or crystalline), but they are always of nanometer size.

2.2.8 Photochemical Synthesis

Absorption of photo energy can change the structure of molecules and induce a variety of photochemical reactions. During recent years, a photochemical technique has emerged as an effective synthetic technique for the preparation of nanosized metal chalcogenides with various morphologies. This method has the advantages of mild reaction conditions and convenient operations and the equipments involved are simple and cheap. Generally speaking, a low-pressure mercury pillar lamp and a high-pressure column-like indium lamp are most commonly used as the ultraviolet irradiation and visible photo irradiation source, respectively.

Zhu’s (2001) group reported the photochemical synthesis of CdSe nanoparticles by employing a high-pressure indium lamp as the visible photo irradiation source. Wang et al (2000) established an ultraviolet irradiation method for in-situ synthesis of nanocrystalline CdS particles. CdS nanocrystallites with cubic or hexagonal phase structures were prepared at room temperature via precipitation of Cd\(^{2+}\) ions with homogeneously released S\(^{2-}\) ions, generated from the decomposition of thioacetamide by ultraviolet irradiation reduction. This technique may be extended to prepare other sulfide semiconductor nanoparticles, including ZnS, Ag\(_2\)S, PbS, NiS and CuS. This method can be extended to the preparation of nanocrystalline CdS with different morphologies. Mo et al (2001) established a morphology-controlled synthesis of CdS nanocrystallites by introducing poly vinyl alcohol (PVA) as the protecting agent, which self-assemble into desirable shapes. CdS spherical nanoparticles, nanodisks and nanowires have been obtained conveniently and
there are some CdS nanotubes that appeared in the CdS nanodisk sample. This method gives a mild chemical route to fabrication of semiconducting nanowires which may be applied in many fields.

### 2.2.9 γ-Irradiation Method

γ-Irradiation is one of the new and effective methods for synthesis of nanometer materials. It has been extensively used in the preparation of nanocrystalline metals, alloys, oxides and polymer/metal nanocomposites (Chen et al 2007; Pan et al 2004). Currently, inorganic/organic composites have been playing increasingly important roles in research and in numerous applications. They frequently have special properties, which are combinations of those of their original organic and inorganic components. Among these materials, semiconductive chalcogenide/polymer nanocomposites have aroused more and more attention. γ-irradiation offers an applicable means by which the polymerization of monomers and formation of inorganic nanoparticles take place simultaneously, leading to the fabrication of inorganic/polymer nanocomposites. However, it is only quite recently that the γ-irradiation has been applied to the synthesis of chalcogenide/polymer nanocomposites. The ease, reproductivity and versatility of this synthetic approach will facilitate development of functional nanomaterials and the examination of their structure-property relationships.

### 2.2.10 Microwave Synthesis

The interaction of dielectric materials, liquids or solids, with microwaves leads to what is generally known as dielectric heating. Electric dipoles present in such materials respond to the applied electric field. In liquids, constant reorientation leads to the friction between molecules, which subsequently generate heat. Claimed effects of microwave irradiation include thermal effects and nonthermal effects (Saskia 1997). Microwave irradiation
as a heating method has found a number of applications in chemistry. The frequencies allotted for microwave assisted heating are 918 MHz and 2.45 GHz, with the latter frequency being most often used. The microwave ovens used in microwave chemistry range from simple household multimode ovens to large-scale batch as well as continuous multimode ovens. Microwave-assisted synthesis for the production of inorganic compounds has been studied since 1986. As compared to conventional oven heating (with a slow heating rate and heat transfer), microwave “volumetric” heating of liquids is an alternative heating approach with specific advantages.

The microwave irradiation has been used in the synthesis of inorganic nanoparticles and keeps showing rapid growth in its application to materials science. Compared with conventional heating methods, microwave assisted heating presents a more rapid and simultaneous environment for the formation of nanoparticles due to the fast and homogeneous heating effects of microwave irradiation. Therefore, microwave assisted heating method has the advantages of short reaction time, high energy efficiency and the ability to induce the formation of particles with small size, narrow size distribution and high purity. In the past few years, microwave assisted heating has been applied in the soft chemical synthesis of various nanocrystalline metal chalcogenides and presents a promising trend in its future development (Hu et al 2010; Tai et al 2010; Zhu et al 2007). Liao et al (2001) extended this methodology to the microwave assisted preparation of various metal sulfide nanoparticles including CdS, ZnS, CuS, HgS and Bi₂S₃ by choosing formaldehyde aqueous solution as solvent. Zhu et al (2002) has successfully applied microwave irradiation, to induce the one-dimensional preferential growth of some II-VI and V-VI group semiconductors and prepared CdS nanoribbons by microwave-induced decomposition of single-source precursors.
2.2.11 Thermolysis of Metal Complexes

One of the simplest methods to prepare nanoparticles is the decomposition of organometallic precursors. This decomposition may be driven by heat (thermolysis), light (photolysis), or sound (sonolysis). Advantages of using organometallic compounds are that precursors can be decomposed at relatively low temperatures to form the final product. By controlling the decomposition temperature, the growth of the nanoparticles can be controlled. Since size and morphology have an effect on the properties of the nanoparticles, control of these properties is a primary goal. In many cases, polymers, organic capping agents, or structural hosts are used to limit the size of the nanoparticle growth.

Using bis(hexyl(methyl)dithio/-diselenocarbamato)-cadmium(II)/zinc(II) compounds as a single source precursor, nanoparticles of CdSe/CdS, CdSe/ZnS, CdSe/ZnSe core/shell and CdSe/CdS alloys have been prepared (Abdelhady et al 2011; Liu et al 2009; Mandal et al 2009; Malik et al 2001;). The biggest disadvantage of this approach is that most of the reactions involve air-sensitive reactants as well as the final precursor; therefore, glove box or schlenck line techniques must be used. The advantage of this method is the reaction does not need any additional reducing agents.

2.3 CHARACTERIZATION METHODS

In the present work, different methods have been employed to characterize the synthesized metal complexes and nanomaterials. The analysis of phase purity, surface morphology, elemental composition, magnetization nature, thermal properties and optical properties were carried out by powder X-ray diffractometry, Transmission and Scanning Electron Microscopy, Thermo Gravimetry, Infrared, UV-Visible and luminescence Spectroscopy, Electron Spin Resonance spectroscopy.
2.3.1 Powder X-ray Diffraction

Powder X-ray diffraction (XRD) is a powerful technique used to identify the crystalline phases present in materials and to measure the phase composition, preferred orientation, grain size, strain state and defect structure of these phases.

A beam of X-rays of wavelength $\lambda$ is directed to the crystal at an angle $\theta$ to the atomic planes. The interaction between X-rays and the electrons of the atoms is visualized as a process of X-ray reflections by the atomic planes. This is an equivalent description of the diffraction effects produced by a three dimensional grating. The atomic planes are considered to be semitransparent, that is, they allow a part of the X-ray to pass through and reflect the other part, the incident angle $\theta$ being equal to the reflected angle (called Bragg angle). Referring the Figure 2.4, there is a path difference between rays reflected from plane 1 and the adjacent plane 2 in the crystal.

The two reflected rays will reinforce each other, only when this path difference is equal to an integral multiple of the wavelength. If $d$ is the interplanar spacing, the path difference is twice the distance $d \sin \theta$, as indicated in Figure. 2.4. (Bragg’s Law)

$$2d \sin \theta = n\lambda$$

Where $n$ is an integer

$\lambda$ is the wavelength of the X-rays

d is the interplanar spacing generating the diffraction and

$\theta$ is the diffraction angle

$\lambda$ and $d$ are measured in the same unit, usually in angstrom unit (Å).
A generalized approach of powder diffractometry is given as follows: The characteristic X-rays from an X-ray generator are collimated and directed onto the sample. As the sample and detector are rotated, the intensity of the reflected X-rays is recorded. A detector records and processes the X-ray
signal and converts the signal into count rate which is then sent to a device such as a printer or computer monitor. The instrument used to maintain the angle and rotate the sample is termed as goniometer. XRD patterns of semiconductor nanocrystal powders were collected using a BRUKER D2 PHASER diffractometer (Figure 2.5) in Bragg-Brentano geometry with Ni filtered CuKα radiation (\(\lambda = 1.5406 \, \text{Å}\)) and LYNXEYE detector.

2.3.2 Electron Microscopy

2.3.2.1 Transmission Electron Microscopy

High Resolution Transmission electron microscopy (HRTEM) is a tool for carrying out structural and morphological characterization of materials in the micron, nanometer and sub nanometer regimes. HRTEM image offers information about: morphology (the size, shape and arrangement of the particles), crystallographic information such as the arrangement of atoms in the specimen and their degree of order, detection of atomic-scale defects in areas a few nanometers in diameter.

The ability to determine the positions of atoms within materials has made the HRTEM an indispensable tool for nanotechnology research and development in many fields, including heterogeneous catalysis and the development of semiconductor devices for electronics and photonics. The basic principle of electron diffraction in HRTEM: consider a very thin slice of crystal that has been tilted so that a low-index direction is exactly perpendicular to the electron beam. All lattice planes about parallel to the electron beam will be close enough to the Bragg position and will diffract the primary beam. The diffraction pattern is the Fourier transform of the periodic potential for the electrons in two dimensions. In the objective lens all diffracted beams and the primary beam are brought together again; their interference provides a back transformation and leads to an enlarged picture
of the periodic potential. The picture is magnified by the following electron-optical system and finally seen on the screen at magnifications of typically $10^6$. In this work a HITACHI (HF-2000) is used to study the morphology of the nanoparticles with a resolution of 0.5-3 Å. The samples were examined under the TEM after dispersing them in acetone and placing a few drops of the mixture in the Cu grid. The photographic image of transmission electron microscope is shown in Figure 2.6.

![HRTEM instrument](image)

**Figure 2.6 Photograph of HRTEM instrument**

### 2.3.2.2 Selected Area Electron Diffraction (SAED)

The diffraction pattern is made under broad parallel electron illumination. The SAED patterns can be used to identify the crystal structure and measure lattice parameter. The energy of the electrons used for selected area diffraction was 200 KeV. The de Broglie wavelength corresponding to the energy is 0.025 Å. With this short wavelength the electron diffraction for various planes in 123 like systems will give very small glancing angle ($\sim 0.4^\circ$). This will make the reflecting planes almost parallel to the incident
beam. The reciprocal vectors of various diffracting planes will be almost in a plane to the incident beam. The Bragg conditions that \( 2d \sin \theta = \lambda \) can be re-written as,

\[
d \cdot 2\theta = \lambda \tag{2.2}
\]

Where, \( \sin \theta = \theta \) for small value of \( \theta \).

\[
2\theta = \frac{r}{L} \tag{2.3}
\]

where \( r \) is the distance of the diffracted spot from the point where the incident beam falls on the screen and \( L \) is the distance between the screen (detector) and the sample \( L \) is also known as camera length. Camera length is usually kept constant for given set of experiments (20 cm here). Now the Bragg condition becomes

\[
d \cdot \frac{r}{L} = \lambda \tag{2.4}
\]

\[
d = \frac{L \lambda}{r} \tag{2.5}
\]

\( L \) and \( \lambda \) are constants of the experiment.

### 2.3.2.3 Scanning Electron Microscopy

The scanning electron microscope (SEM) is capable of producing high resolution images of a sample surface. Due to the manner in which the SEM images are created, they have characteristic three-dimensional appearance and are useful for judging the surface morphology of the sample. In a typical SEM, electrons are thermionically emitted from a tungsten or Lanthanum Hexaboride (LaB\(_6\)) cathode and fly towards an anode; alternatively, electrons can be emitted via field emission (FE). The whole setup is maintained under a very high vacuum. The electron beam which has an energy ranging from a few hundred eV to 50 keV is focused by one or two condenser lenses into a beam with very fine focal spot sized 1 nm to 5 nm.
The principal images produced in the SEM are of three types: secondary electron images, backscattered electron images and elemental X-ray maps. Secondary and backscattered electrons are conventionally separated according to their energies. When the energy of the emitted electron is less than about 50 eV, by convention it is referred to as a secondary electron (SE). Most of the emitted secondaries are produced within the first few nm of the surface and hence provide the information about the surface. X-rays which are also produced by the interaction of the electrons with the sample may also be detected in an SEM equipped for energy dispersive X-ray spectrometer (EDX) or wavelength dispersive X-ray spectrometer (WDX). In our experiments the SEM imaging was carried out using the HITACHI S-3400 (SEM) and FEI Quanta FEG 200 (HR-SEM) equipments (Figure 2.7).

2.3.3 Thermo Gravimetric and Differential Thermal Analysis

Thermo gravimetry analysis (TGA) is an analytical technique that in which the mass of a substance (and/or its reaction products) is measured as a function of temperature whilst the substance is subjected to a controlled temperature program. Thermo gravimetric analysis is used to monitor the
changes in weight of the sample with increasing temperature. Normally, this is done in air and at a ramp rate of 5 to 10 °C per minute.

![Figure 2.8 Photograph of TG DTA instrument](image)

In differential thermal analysis (DTA), the temperature difference that develops between a sample and an inert reference material is measured, when both are subjected to identical heat treatments. The DTA instruments record the difference in temperature between a substance and a reference material against either time or temperature as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate. The resultant endothermic and exothermic peaks give the information of the melting point and optimal sintering temperature of the samples.

### 2.3.4 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared spectroscopy (FTIR) provides information about the chemical bonding in a material. It is particularly useful for the nondestructive analysis of solids and thin films. The goal of the basic infrared experiment is to determine changes in the intensity of a beam of infrared radiation as a function of wavelength or frequency after it interacts
with the sample. The ratio of the intensity before and after the light interacts with the sample is determined. The plot of this ratio versus frequency is the infrared spectrum. The infrared spectrum originates from the vibrational motion of the molecule. The vibrational frequencies are a kind of fingerprint of the compounds and are used for characterizing of organic, inorganic and biological compounds. The band intensities are proportional to the concentration of the compound and hence qualitative estimations are also possible. The IR spectroscopy is also carried out by using Fourier transform technique. The interference pattern obtained from a two beam interferometer as the path difference between the two beams is altered, when Fourier transformed, gives rise to the spectrum. The transformation of the interferogram into spectrum is carried out mathematically with a dedicated on-line computer shown in Figure 2.9.

In our experiments, Mid-infrared spectra were recorded using a Perkin Elmer Spectrum1 FT-IR instrument by KBr pellet technique. About 4 mg of the sample was ground with 200 mg of special grade KBr to form a mixture, which was then made into a pellet by pressed pellet technique. The ground powder is finally introduced into a mini press and made into pellet. This pellet was used for recording the spectra in the range 4000-450 cm\(^{-1}\).
2.3.5 UV-Visible Absorption Spectroscopy

Optical spectroscopy has been widely used for the characterization of nanomaterials and the techniques can be generally categorized into two groups: absorption and emission spectroscopy and vibrational spectroscopy. The former determines the electronic structures of atoms, ions, molecules or crystals through exciting electrons from the ground to excited states (absorption) and relaxing from the excited to ground states (emission). The optical absorption is a result of interaction between the material and light. When a frequency of light is in resonance with the energy difference between states the transition allowed or partly allowed by selection rules, a photon is absorbed by the material. By measuring the absorption of the sample as a function of the frequency of light, a characteristic absorption spectrum of the material can be obtained.

The characteristic lines observed in the absorption spectra of nearly isolated atoms and ions due to transitions between quantum levels are extremely sharp. As a result, their wavelengths or photon energies can be determined with great accuracy. The lines are characteristic of a particular atom or ion and can be used for identification purposes. Molecular spectra, while usually less sharp than atomic spectra, are also relatively sharp. Positions of spectral lines can be determined with sufficient accuracy to verify the electronic structure of molecules. In solids, the large degeneracy of the atomic levels is split by interactions into quasi-continuous bands (valence and conduction bands) and makes their optical spectra rather broad. The energy difference between the highest lying valence (the highest occupied molecular orbital, HOMO) and the lowest lying conduction (the lowest unoccupied molecular orbital, LUMO) bands is designated as the fundamental gap. Penetration depths of electromagnetic radiation are on the order of 50 nm through most of the optical spectrum (visible light). Such small penetration depths limit the applications of optical absorption spectroscopy for the
characterization of bulk solids; however, this technique is readily applicable for the characterization of nanostructures and nanomaterials.

In present study, a SHIMADZU UV-2450 spectrophotometer is used for recording the absorption spectra in the range of 200-800 nm at room temperature. This contains double beam and double pass monochromator system with good resolving power and photometric efficiency in the UV and visible regions. The light beam from Deuterium lamp passing through the filter is focused onto the grating by a concave mirror. The beam is again reflected by grating and is directed to the partial reflecting mirror which in turn splits the pulsating beam into two paths, one through the sample under investigation and the other through the reference sample. These two beams of light are directed onto a detector. The photograph of SHIMADZU UV-2450 Spectrophotometer is shown in Figure 2.10.

![Photograph of UV-Visible Spectrophotometer](image)

**Figure 2.10 Photograph of UV-Visible Spectrophotometer**

### 2.3.6 Photoluminescence Spectroscopy

Luminescence refers to the emission of light by a material through any process other than blackbody radiation. The emission of light can result
from a variety of stimulations. In photo luminescence (PL) the physical and chemical properties of materials are measured by using photons to induce excited electronic states in the material system and analyzing the optical emission as these states relax. Typically, light is directed onto the sample for excitation and the emitted luminescence is collected by a lens and passed through an optical spectrometer onto a photon detector. The spectral distribution and time dependence of the emission are related to electronic transition probabilities within the sample and can be used to provide qualitative and, sometimes, quantitative information about chemical composition, structure, impurities, kinetic process and energy transfer. Sensitivity is one of the strengths of the PL technique, allowing very small quantities (nanograms) or low concentrations (parts-per-trillion) of material to be analyzed. Precise quantitative concentration determinations are difficult unless conditions can be carefully controlled and many applications of PL are primarily qualitative.

In PL, a material gains energy by absorbing photon at some wavelength by promoting an electron from a low to a higher energy level. This may be described as making a transition from the ground state to an excited state of an atom or molecule, or from the valence band to the conduction band of a semiconductor crystal or polymer (electron-hole creation). The system then undergoes a non-radiative internal relaxation involving interaction with crystalline or molecular vibrational and rotational modes and the excited electron moves to a more stable excited level, such as the bottom of the conduction band or the lowest vibrational molecular state. After a characteristic lifetime in the excited state, electron will return to the ground state. In the luminescent materials some or all of the energy released during this final transition is in the form of light, in which case the relaxation is called radiative. The wavelength of the emitted light is longer than that of the incident light. It should be noted that depending on the characteristic life-
time of emission, fast PL with life-time of sub microsecond is also called “fluorescence”, whereas slow ones, $10^{-4}$ to 10 s, are referred to as “phosphorescence”. Optical absorption and photoluminescence spectra are commonly used in the characterization of the size of nanocrystals of semiconductor.

The photoluminescence spectra of the powder samples of the present system were recorded in the wavelength range 400-800 nm using a HORIBA Jobin Yvan iHR 550 photoluminescence system shown in Figure 2.11. The light emitted from the UV laser (405 nm) enters the excitation monochromator. The beam splitter splits the light emerging from the excitation monochromator and a fraction of it is directed to the CCD detector. A shutter is provided between the excitation monochromator and the sample, which is placed in the optical path as commanded from the operation panel. All the driving components, i.e., the wavelength drive motors, slit control motors and rotary solenoid for shutter is operated by signals sent from the computer.

Figure 2.11 Photograph of Photoluminescence Spectrometer
2.3.7 Electron Paramagnetic Resonance

Microwave absorption is measured as a function of the magnetic field by Electron Paramagnetic Resonance (EPR) spectroscopy. The unpaired electrons are excited to a high energy state under the magnetic field by the absorption of microwave. The excited electron changes its direction of spin and relaxes into the ground state by emitting phonons.

In principle, EPR spectra can be generated by either varying the photon frequency incident on a sample while holding the magnetic field constant, or doing the reverse. Commercial EPR spectrometers typically vary the magnetic field and holding the frequency constant. The majority of EPR spectrometers are in the range of 8-10 GHz (X-band), though there are spectrometers which work at lower and higher fields: 1-2 GHz (L-band) and 2-4 GHz (S-band), 35 GHz (Q-band) and 95 GHz (W-band).

EPR spectrometers work by generating microwaves from a source (typically a klystron), sending them through an attenuator and passing them onto the sample, which is located in a microwave cavity. Microwaves reflected back from the cavity are routed to the detector diode and the signal comes out as a decrease in current at the detector analogous to absorption of microwaves by the sample.

EPR spectra are generally presented as the first derivative of the absorption spectra for ease of interpretation. Magnetic field strength is generally reported in units of Gauss or mTesla. In the current investigation an X-band CW EPR facility (EMX 102.7) is used for taking EPR spectra. Magnetic moments for the samples are calculated from g factor obtained from the EPR spectra. The effective g-factor is determined from the following equation
\[ g = \frac{hv}{\beta H} \] (2.6)

where \( h \) is the Planck’s constant, \( v \) is the frequency of the microwave, \( H \) is the magnetic field occurring at the maximum resonance and \( \beta \) is the Bohr magneton. This analysis is used to confirm the successful incorporation of magnetic ions into host materials.