Chapter 2

Preparation and Characterization Techniques
Chapter-2  Preparation and characterization techniques

2.1  Introduction

Most of the diluted magnetic semiconductors (DMS) nanoparticles can be synthesized by a variety of methods. Some of the important methods are purely physical, chemical, biological or hybrid. Whatever be the method of synthesizing the nanoparticles, it is essential to avoid the coalescence of particles in to larger particles and achieve monodispersity and chemical stability over a long period. Therefore, the synthesis routes, which protect or passivate the particles, have become attractive compared to those, which do not take care of long term stability or monodispersity. Different ways to synthesize nanoparticles are chemical deposition [1-16], Sol-gen [17], gas evaporation [18-20], electrostatic deposition [21], magnetron sputtering [22-23] and electro chemical deposition [24-25]. In the present study, the chemical co-precipitation method has been adopted to obtain CdS and CdS:Ni samples in nanocrystalline form. Thiophenol is used as a capping agent to passivate the particles. Chemical method is very cost effective and can yield fine grains [26]. This chapter while outlining the relevant theory on grain growth describes some of the methods in vogue for synthesizing nanomaterials with special emphasis on the chemical methods. Finally step by step details of the method (chemical co-precipitation) used in the present work are given in this chapter.

2.2  Various Methods of Synthesis of Nanoparticles

In general, nanocrystalline materials can be synthesized either by consolidating atoms/molecules or breaking down the bulk material into smaller and smaller dimensions. The former is known as ‘bottom up’ approach whereas the latter is referred to as the ‘top down’ method. A number of techniques have been developed to prepare nanostructured materials starting from the vapour, liquid, or solid states. If any phase transformation is involved, e.g., liquid to solid, steps have to be taken to increase the nucleation rate and decrease the growth rate during the formation of the product phase.

In recent years nanostructured materials have been synthesized by methods including inert gas condensation [27], mechanical alloying [28], spray conversion processing [29], sputtering [30], electro-deposition [31], spark erosion [32], rapidly quenching, the complete crystallization of amorphous solids [33], sonochemical method [34]. Nanocrystalline ceramic powders have been prepared by means of co-precipitation and sol-gel techniques [35,36]. Normally chemical co-precipitation technique is relatively less expensive and convenient to prepare large area semiconductors. At moderate temperature materials can easily be obtained in the
colloidal form, which can subsequently be precipitated to give dry and stable powders. The growth process involves controllable chemical reactions. Adjusting pH, temperature and the relative concentrations of various reactants in the solution yields a product with controlled particle size, size distributions and degree of agglomeration [37].

The co-precipitation (CPT) is the carrying down by a precipitate of substances normally soluble under the conditions employed. There are three main mechanisms of co-precipitation: inclusion, occlusion and adsorption. An inclusion occurs when the impurity occupies a lattice site in the crystal structure of the carrier, resulting in a crystallographic defect. This can happen when the ionic radius and charge of the impurity are similar to those of the carrier. An adsorbate is an impurity that is weakly bound (adsorbed) to the surface of the precipitate. An occlusion occurs when an adsorbed impurity gets physically trapped inside the crystal as it grows. Besides its applications in chemical analysis and in radiochemistry, co-precipitation is potentially important to many environmental issues closely related to water resources, including acid mine drainage, radionuclide migration in fouled waste repositories, metal contaminant transport at industrial and defense sites, metal concentrations in aquatic systems and waste water treatment technology.

Among the above techniques, the chemical co-precipitation method has been used in the present work and discussed as follows.

2.3 General Procedure for DMS Nanoparticles

(a) Starting Materials

In the preparation of DMS nanoparticles through chemical method, the choice of starting materials is very important, because the by-products formed in the reaction should be easily removable by way of peptization (washing with pure water). Also, the starting materials should not get coated within the heating flask during hydrolysis, this may not yield the described product in the precipitate. Hence, the selection of proper starting materials is very vital.

(b) The Apparatus

The solutions prepared from the starting materials in double distilled water are taken in a round-bottomed flask fitted with a reflex-cooling tube. The contents are heated a heating mantle, the vapours rise in the inner tube of the reflex, while the cooling water a chiller circulated in the outer jacket reflect the vapours back to the flask by considensing them. Hence, the quantity taken in the flask is invariable even after heating for hours together.
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(c) The Experiment

The stoichiometric solution is heated for required duration (say 20 hours), so that it is dissociated completely into ions. As the hydrolysis hour is increased, the grain size decreased. The hydrolyzed solution is cooled and aqueous ammonium hydroxide solution is added in drops using burette with constant stirring. The pH of the hydrolyzed solution and the pH after precipitation on adding NH₄OH is also noted down. The solution usually goes from acidic to base, i.e., the pH increases on adding the precipitating reagent. The precipitating reagent is added in excess till precipitation is complete and the particles settle down, with the mother liquor staying at the top.

(d) Sample Recovery and Calcination

The precipitates are allowed to settle down for a reasonable time and by-products are removed by washing with pure water (peptization). This is repeated till the entire mother liquor is separated out and the solution with settled precipitates is clear. Now, the precipitates are filtered out using filter paper of fine pore size and the spongy content in the filter cone is allowed to dry as such. When the moisture content is reduced, the sample can also be dried (Calcination) in a ceramic pan at about 50°C to help the remnant moisture and traces of by-products to evolve out of the sample completely. Now the sample is ready for further treatments and studies.

2.4 Synthesis of CdS: Ni Nanoparticles in the Present Study

The principle and the various steps involved in the synthesis of CdS: Ni nanoparticles are mentioned in the following sections. Finally the actual procedure followed to produce CdS: Ni nanopowders is described.

(a) Starting Materials

In the preparation of CdS: Ni DMS nanoparticles through chemical method, the choice of starting materials is very important, because the by-products formed in the reaction should be easily removable by way of peptization (washing with pure water). Also, the starting materials should not get coated within the heating flask during hydrolysis, this may not yield the desired product in the precipitate. Hence, the selection of proper starting material is very vital. In the present work cadmium acetate, sodium sulphide and manganese acetate were used as precursors for Cd, S, and Ni respectively. Thiophenol was used as the capping agent, for synthesizing CdS: Ni nanoparticles with different manganese concentrations.

(b) The Apparatus

The solutions prepared from the starting materials in double distilled water are taken in a round-bottomed flask fitted with a reflex- cooling tube. The contents are
heated by a heating mantle, the vapours rise in the inner tube of the reflex, while the cooling water from a chiller is circulated in the outer jacket reflect the vapours back to the flask by condensing them. Hence, the quantity taken in the flask is invariable even after heating for hours together.

(c) The Experiment

The stoichiometric solution is heated for required duration (say 20 hours), so that it is dissociated completely into ions. As the hydrolysis time is increased, the grain size decreased. The hydrolyzed solution is cooled and aqueous ammonium hydroxide solution is added in drops using burette with constant stirring.

The pH of the hydrolyzed solution and the pH after precipitation on adding NH₄OH is also noted down. The solution usually goes from acidic to base, i.e., the pH increases on adding the precipitating reagent. The precipitating reagent is added in excess till precipitation is complete and the particles settle down, with the mother liquor staying at the top.

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The precipitates are allowed to settle down for a reasonable time and by-products are removed by washing with pure water (Peptization). This is repeated till the entire mother liquor is separated out and the solution with settled precipitates is clear. Now, the precipitates are filtered out using filter paper of fine pore size and the spongy content in the filter cone is allowed to dry. When the moisture content is reduced, the sample can also be dried (Calcination) in a ceramic pan at about 50 °C to help the remnant moisture and traces of by-products to evolve out of the sample completely. Now the sample is ready for further treatments and studies.

(e) The Procedure Followed in the Present Work

In the present work, DMS nanoparticles of CdS and CdS: Ni were prepared by the colloidal chemical co-precipitation method using cadmium acetate, sodium sulphide and copper acetate as starting compounds. Appropriate quantities of these are weighed in a microbalance (M/s SICO, India) according to the stoichiometry to obtain 2, 4, 6, 8 and 10 at% of Ni target dopant concentrations and are dissolved in 100 ml of methanol to make 0.1M solutions. The stoichiometric solution is taken in a burette and added in drops with continuous stirring to a mixture of Na₂S (0.1M) + 50 ml of H₂O + 1.1 ml of thiophenol + 100 ml of methanol until fine precipitate of CdS: Ni is formed. After complete precipitation, the solution in conical flask is constantly stirred for about 20 h. A single step chemical reaction is given below for the precipitation of the Ni doped CdS nanoparticles. Then the precipitates are filtered out separately and
washed thoroughly with de-ionized water. Finally these samples are subjected to sintering process. The dark yellow colored nanocrystalline CdS or CdS: Ni powders are obtained. The experimental setup for preparing the samples is shown in the Fig. 2.1. The various steps involved in preparation method are shown in the Fig. 2.2 as a flow chart. The samples are calcined at 300 °C / 2h in vacuum. The furnace used for calcinating the samples are shown in the Fig. 2.3

$$(1-x)\text{CdCH}_2\text{COOH}+x\text{CuCH}_3\text{COOH}+\text{Na}_2\text{S} \rightarrow \text{CdS: Ni} + 2\text{NaCH}_3\text{COOH}$$

Chemical precipitation gives high purity materials with good chemical homogeneity as this offers mixing at the molecular level. Further, size control can be achieved by controlling the reaction kinetics by adding suitable capping agents. In the present investigations, as already mentioned, thiophenol is used as the capping agent to prepare nanoparticles of Ni doped CdS.

Figure 2.1. Experimental setup for preparation of CdS and Ni doped CdS nanopowders by chemical co-precipitation method.

Figure 2.2. Photograph of the setup used for the calcinations at 300 °C.
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The as-deposited powder samples are subjected to preliminary XRD studies to confirm their crystallinity. In the present investigation the as-prepared samples are found to be amorphous in nature and hence further heat treatment become necessary to induce the desired nanocrystallinity. The powdered samples are calcined in a vacuum furnace at 100 °C, 200 °C and 300 °C followed by XRD. The samples calcined at 300 °C are found to be nanocrystalline in nature, whereas the samples calcined at 100 °C and 200 °C are amorphous. The nanocrystalline CdS:Ni samples (calcined at 300 °C) only characterized in this work.

Figure 2.3. Flowchart for the synthesis of Ni doped CdS nanoparticles.

2.5 Characterization Techniques

2.5.1 X-ray Diffraction (XRD)

X-ray diffraction (XRD) is a versatile, non-destructive analytical tool for identification and quantitative determination of the various crystalline forms known as phases of compounds present in the powdered and solid samples [38]. Identification is achieved by comparing the X-ray diffraction pattern obtained from an unknown sample with an internationally recognized database containing reference patterns for more than 70,000 phases.

A crystal lattice is a regular array of atoms in space. These are arranged in space to form a series of parallel planes separated from each other by distance \( d \),
which varies according to the nature of materials. For crystal planes oriented in different directions have different ‘d’ spacing. When a monochromatic X-ray beam with wavelength \( \lambda \) is incident on the lattice planes in the crystal at an angle, \( \theta \), diffraction occurs only when the distance traveled by rays reflected from successive phases differs by a complete number ‘n’ times of \( \lambda \). That is, when it satisfies the Bragg’s condition given by [38].

\[
n \lambda = 2d \sin \theta
\]

By varying \( \theta \), the Bragg’s law can be satisfied by different ‘d’ spacing in a polycrystalline material. Plotting angle position and intensity of the resultant diffraction peaks produces a pattern, which is characteristic of the sample. For a sample containing a mixture of phases, the XRD pattern is formed by addition of individual patterns.

The three basic components of an X-ray diffractometer are: X-ray source, specimen and X-ray detector. They all lie on the circumference of a circle, which is known as the focusing circle. The angle between the plane of the specimen and the X-ray source and \( \theta \) is the Bragg angle. The angle between the projection of the X-ray source and the detector is \( 2\theta \). For this reason the X-ray diffraction patterns produced with such geometry are often known as 0-20 scan.

The shift in peak angles with the addition of dopant in the host and also with the change in dopant concentration gives valuable information about dopant atoms which are substitutional in the lattice. The patterns thus obtained are used as input to a powder pattern indexing programme “Powdin”. This software has the capability of least square fitting and other routine refinements. The programme directly outputs the lattice parameter data. Unmatched lines if any are separated from matched lines and are separately indexed for different phase / structure. For zinc blende, inter planar spacing d is given by

\[
1/d^2 = 1/ a^2 (h^2 + k^2 + l^2)
\]

where \( h, k, l \) are miller indices and ‘a’ is cubic lattice parameter. For wurtzite structure, the relation is

\[
1/d^2 = (4/3a^2) (h^2 + k^2 + l^2) + l^2 / c^2
\]

where \( c \) and \( a \) are the lattice parameters, and \( h, k, l \) are the miller indices of the diffracting planes [39-40]. The grain size \( L \) for all the compositions of the samples are obtained [41] using the relation

\[
L = n\lambda / \beta \cos \theta
\]
where \( n \) is a constant equal to 0.91, \( \lambda \) is the wavelength of x-rays used, \( \beta \) is the angular full width at half maximum intensity in radiations and \( \theta \) is the diffraction angle. Siefert X-ray diffractometer (Model: 3003TT) with Cu k\textsubscript{a} radiation source (wavelength (\( \lambda \)) =1.5420 Å) is used in the present work to find for studying the structure of the as- prepared and calcined CdS:N\textsuperscript{2+} samples (Fig.2.4). The x-rays scan over the samples in the 2\( \theta \) range of 20\(^\circ\)- 80\(^\circ\) with a scan rate of 1\(^\circ\)/min. The x-ray generator is operated at 40 kV and 30 mA.

![Figure 2.4. Photograph of Siefert 3003 TT X-ray diffractometer.](image)

2.5.2 Scanning Electron Microscopy (SEM)

Electron microscopes are instruments that use a beam of high energetic electrons to examine very small objects. This examination can yield information on morphology, topography and crystallography. In a SEM shown in Fig. 2.5, an electron gun emits a beam of electrons, which passes through a condenser lens (objective lens) and is refined into a thin stream. The objective lens contains a set of coils, which are energized with varying voltages. The coils create an electromagnetic field that exerts a force upon the electrons in the electron beam, which in turn redirects the electrons to scan the specimen in a controlled pattern called a raster. The electromagnetic field of the coils also causes a spot of light on a cathode-ray tube to move along at the same rate as the scanning electron beam. When the electrons from the beam hit the...
specimen, a series of interactions deflect secondary particles to a detector, which then converts the signal to voltage and amplifies it. This voltage is then applied to a cathode-ray tube and converted to an image.

As shown in Fig 2.6, SEM has six modes of operation ((i) X-ray mode (ii) emissive mode (iii) transmissive mode (iv) cathode luminescence mode (v) acoustic mode and (vi) current/voltage induced mode. Back scattered electrons and Auger electrons from the first 10 Å layer and secondary electrons from 50 Å-500 Å layer of specimen surface are the major electron emissions. Characteristic X-rays, continuous X-rays and secondary fluorescence are the important photon emissions from the deep surface.

**Figure 2.5.** Highly simplified view of a SEM microscope.

The SEM X-ray mode gives elemental analysis, transmissive mode gives structure; cathode luminescence gives electron trap characteristics; acoustic mode gives mechanical defects, and electron induced current/voltage gives semi conducting band structure parameters of the materials. Hence, SEM analysis is the most sophisticated and efficient tool in the characterization of materials.

In the present investigation, the SEM images are taken by JEOL JSM-840A instrument. For this purpose the nanocrystalline CdS:Ni powders are sprayed on a cylindrical metal rod and were capped with gold layer by sputtering method using ion sputtering device (Model: JEOL JFC-1100E).
Figure 2.6. Principle of SEM.

2.5.3 Energy Dispersive Analysis of X-rays (EDAX)

The basic principle involved in EDAX is the bombardment of the sample by the electrons. As a result of this X-rays are emitted. The X-rays emitted from the 'tear drop' volume of the surface of the material consist of easily analyzable photons of different energies, and by sorting and counting them, identification and quantification of chemical species is achieved. It is very difficult to achieve higher resolutions in energy / wavelength analysis of X-rays than those achieved in analyzing the electron velocities in photoelectron spectroscopy. Energy dispersive spectrometer (EDS) or wavelength dispersive spectrometer (WDS) is used for sorting X-rays. In EDS technique, lithium drifted silicon/germanium detector with multichannel analyzer is used. Though there is a chance of assigning two X-rays each having energy 'E' coming from different atoms (Z, Z') to identical levels, such occurrences are rare. In WDS, single crystals are used for resolving wavelengths before counting intensity. Though WDS has higher sensitivity, EDS is fast and economical. The resolving power of X-rays is low when compared to that of photoelectron spectroscopy techniques such as Auger spectroscopy.

The electron beam is scanned on a single line or selected area for any specific element. The detector also could be fixed for specific characteristic X-ray for mapping specific species over scanned area/line. The detector used does not need continuous liquid nitrogen cooling. Samples as many as 10 could be loaded simultaneously for scanning analysis. One drawback of SEM is that it cannot be used
to analyze specimens that give off any type of vapour. This vapour would interact with the electrons. This disadvantage can be overcome by using cryogenic SEM, where the specimen is frozen and coated with gold so that the vacuum tube can remain relatively free of vapour. As said earlier in the present study JEOL JFC-1100E ion sputtering device is used for gold coating.

In the present work Scanning Electron Microscopy, with EDAX attachment camera (Model: JSM 840A) and scintillation counter detector, was used for both physical observations of the sample surfaces as well as chemical mapping. Fig. 2.7 shows the photograph of scanning electron microscope (Model: JSM 840A) used in the present study.

Figure 2.7. Photograph of SEM with EDAX (Model: JSM 840A).

2.5.4 Transmission Electron Microscopy (TEM)

Transmission electron microscopy is a unique tool in characterization of materials. Crystal structure and microstructure are simultaneously obtained by diffraction and imaging techniques. In the present investigation, High resolution Transmission electron Microscopy (HRTEM) (Model JEOL JEM 3010) is used for studying the structure and average particle size of the CdS:Ni\(^{2+}\) samples respectively. Samples for HRTEM are prepared by placing a drop of the ethanol suspension of the nanopowders on a carbon coated Cu TEM grid. Before placing the drop, the solution was sonicated for about 2 minutes so that the particles are well dispersed in the suspension. The ray diagram of a conventional TEM is shown in Fig. 2.8.
(a) Working Principle of TEM

In a conventional transmission electron microscope, a thin specimen is irradiated with an electron beam of uniform current density. Electrons emitted from the electron gun illuminate the specimen through a two or three stage condenser lens system. Objective lens provides the formation of image/diffraction pattern of the specimen. The electron intensity distribution behind the specimen is magnified with a three or four stage lens system and viewed on a fluorescent screen. The image can be recorded by direct exposure of a photographic emulsion or an image plate or digitally by a CCD camera.

The acceleration voltage in conventional instruments is 120 to 200 kV. Medium-voltage instrument work at 200-500 kV to provide a better transmission and resolution and in high voltage electron microscopy (HVEM) the acceleration voltage is in the range 500 kV to 3 MV. Acceleration voltage determines the velocity, wavelength and hence the resolution (ability to distinguish the neighboring micro structural features) of the microscope [42].

(b) Diffraction and Imaging Techniques

(i) Diffraction

Electrons of wavelength 0.025 Å at 200 kV are transmitted through the specimen are diffracted according to Bragg’s law, forming a diffraction pattern (consisting of a transmitted and diffracted beam spots) on the display screen of the microscope. A diffraction pattern gives us information on the periodicities in the lattice, and hence the atomic positions. It also provides valuable information regarding the ‘d’ spacing of the hkl planes. The formula used to calculate the same is

\[ R_{d_{hkl}} = \lambda L \]  

(2.6)

where \( R \) = measured radius of the rings or spots, \( d_{hkl} \) = desired ‘d’ value of the (hkl) plane, \( \lambda \) = Wavelength of the electron beam used and \( L \) = focal length of the camera. Knowing the ‘d’ spacing value, cell parameter ‘a’ can be obtained by the formula.

\[ d = a / (h^2 + k^2 + l^2)^{1/2} \]  

(2.7)
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The diffraction patterns produced in transmission electron microscope can be of three different types

- Ring pattern.
- Selected area diffraction pattern.
- Convergent-beam electron diffraction pattern.

In the present study the diffraction pattern is obtained through selected area diffraction. In this method, the electron beam passing through a small area limited by the intermediate lens aperture forms the pattern.

(ii) Imaging

There are two kinds of imaging (a) bright field imaging and (b) dark field imaging.

When the incident electron beam passes through the specimen, it splits chiefly into unscattered and scattered electron beams. The former forms a bright field image and the latter a dark field image. Fig. 2.9 shows the ray diagram for bright field imaging.

Depending on the aim of the investigation and configuration of the microscope, transmission electron microscopy can be categorized as:

- Conventional transmission electron microscopy
- High resolution electron microscopy
- Analytical electron microscopy
- Energy-filtering electron microscopy
- High voltage electron microscopy

(iii) Uses of TEM

- Identifying the phases and crystal structures present in the material.
- Characterizing and identifying defects (antiphase boundaries, dislocations, stacking faults) in the crystal structure and to determine modes of deformation (identifying the slip systems of a material or mode of failure).
- Determining site occupancy preferences of the atoms in the crystal structures.
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- Imaging atomic planes and defects in packing associated with dislocations or interfaces compositional analysis of individual phases.
- Determining the growth directions of precipitates or lamella in the material and the type of interfaces between different phases (i.e. coherent, semi-coherent and incoherent).

![Ray diagram for bright field imaging.](image)

**Figure 2.9.** Ray diagram for bright field imaging.

### 2.5.5 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) provides information about molecular vibrations that cause a change in the dipole moment of molecules. It offers a fingerprint of the chemical bonds present within materials. FTIR is a very powerful analytical tool for examining both inorganic and organic materials.

FTIR spectrometry uses the technique of Michelson interferometry, as illustrated in Fig. 2.10. A beam of radiation from the source is focused on a beam splitter, where half the beam is reflected to a fixed mirror and the other half of the beam is transmitted to a moving mirror, which reflects the beam back to the beam splitter. From there it travels, recombined with the original half beam, to the detector. The IR intensity variation with optical path difference (interferogram) is the Fourier transform of the (broadband) incident radiation. The IR absorption spectrum can be obtained by measuring an interferogram with and without a sample in the beam and transforming the interferograms into spectra [43].

Fig. 2.11 illustrates the working principle of MIR 8300™. The scanner modulates the radiation from the source or from sample and the A/D board digitalises the analog signals from the detection system and sends them to a computer. The data
acquisition and scanner control system controls the scanner as well as acquires and manipulates data.

![Figure 2.10. Schematic diagram of a generic Michelson interferometer used in FTIR.](image)

![Figure 2.11. The MIR 8300™ FTIR spectrometer system at the optical characterisation facility.](image)

The scanner is the heart of MIR 8300™. Two corner cubes and a retro-reflector make the system immune to tilt and shift with a minimum of realignment required. Moreover, the scanning mirror control system of MIR 8300™ is based on two in-quadrature He-Ne laser interferograms that provide position and direction of information. Fine-tuning is available to position the ZPD, zero path difference, exactly in the centre of the scan. Modular IR Fourier spectrometer 8300 provides
FTIR transmission and reflection spectra in the range of 1.7-28 μm. Normal FTIR suits liquid and solid bulk materials and requires some sample preparation. The attenuated total reflection (ATR) is a versatile and powerful technique for infrared sampling. Materials are either too thick or too strongly absorbing to be analysed by transmission spectroscopy can be routinely analysed using ATR spectroscopy. ATR is also useful for layered sample when only the surface of the material needs to be analysed. The 2 mm spot size can produce high quality spectra from a small amount of samples. In the present work, KBr is used as the solvent and the powdered samples are made into pellets. The output spectrum is obtained by subtracting the background due to the solvent.

Table 2.1. Specifications for MIR 8300™ in the optical characterisation facility.

<table>
<thead>
<tr>
<th>Model</th>
<th>FTIR - 8300</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interferometer</td>
<td>Michelson types with 30 degree Incident Angle, Dynamic Alignment, Sealed and Desiccated.</td>
</tr>
<tr>
<td>Optical System</td>
<td>Single Beam Optics</td>
</tr>
<tr>
<td>Beam Splitter</td>
<td>Germanium Coated KBr plate</td>
</tr>
<tr>
<td>Light Source</td>
<td>Ceramic</td>
</tr>
<tr>
<td>Detector</td>
<td>Temperature Controlled High Sensitivity Detector (DLATGS Detector)</td>
</tr>
<tr>
<td>S/N</td>
<td>Above 3200:1 (KBr-5 plate, 4cm⁻¹, for 4 seconds, around 2200 cm⁻¹, P-P Note 1)</td>
</tr>
<tr>
<td>Wave Number range</td>
<td>7800 cm⁻¹ - 350 cm⁻¹</td>
</tr>
<tr>
<td>Resolution</td>
<td>0.5, 1, 2, 4, 8, 16 cm⁻¹</td>
</tr>
<tr>
<td>Mirror Speed</td>
<td>1, 2, 4, 8, 16 cm⁻¹</td>
</tr>
<tr>
<td>Data Sampling</td>
<td>3 steps: 2.8 mm/sec, 5 mm/sec, 9 mm/sec</td>
</tr>
<tr>
<td></td>
<td>By He-Ne laser</td>
</tr>
</tbody>
</table>

### 2.5.6 Optical Absorption Spectroscopy

The electronic band structure of semiconductors and metals are determined by their optical properties. 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 then the transition is allowed or partly allowed by selection rules, and a photon is absorbed by the material, leading to a decrease of transmission or an increase in absorbance of the light passing through the sample. By measuring
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the transmission or absorbance of sample as a function of the frequency/wavelength of the light, one can obtain a spectrum characteristic of the material.

The light beam from either a tungsten or deuterium lamp (after passing through the filter (F) and slit (S)) is focused onto the grating by a concave mirror. The beam is chopped by chopper (BC) three times per second and is converted into a pulse beam. The pulsating beam can easily be differentiated from the background radiation for accurate optical measurements. This beam is again reflected by the 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 a reference sample. These two beams of light are directed onto a detector. Lockin amplifier measures the light intensity by eliminating background and unwanted intensities of light. At the detector the relative beam intensities of reference and experimental samples alternately striking, facilitate accurate measurements of the radiation. A photomultiplier tube is used as a detector in UV and VIS regions where as lead sulphide photosensitive element is used in IR region. In this spectrometer the detector is selected by means of automatic test function.

In the present study, Carey – 5E spectrophotometer is used for recording the absorption spectra of the CdS: Ni nanocrystalline samples in the range of 200-2000 nm at room temperature. This contains double beam and double pass monochromator system with good resolving power and photometric efficiency in the UV, VIS and IR regions. It is possible to carry out accurate spectral measurements due to its sensitive dual microprocessor based system. The block diagram of optical Carey -5E spectrophotometer is shown in Fig. 2.12. A photograph of Carey-5E spectrophotometer is shown in Fig. 2.13.

![Figure 2.12. Shows the block diagram of optical carey 5E-spectrophotometer.](image-url)
2.5.7 Photoluminescence (PL) Studies

The light emitted from the Xe-lamp enters the excitation monochromator. The beam splitter splits the light emerging from the excitation monochromator and a fraction of it is directed to the monitor 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.

The radiation coming from the Xe-lamp is converged at the entrance slit $S_1$ of the excitation monochromator through lenses $L_1$ and $L_2$. Only the light dispersed by the excitation concave grating (excitation beam) enters the exit slit $S_2$. The excitation beam from the exit slit $S_2$ is split by a beam splitter $BS$ and a part of the split beam is diverted to the monitor detector via lens $L_3$ and diffusion plate for measurement of its intensity. On the other hand, most of the split beam after $BS$ is reflected by the mirror $M_1$ and converges at the sample cell through lens $L_4$. The fluorescence coming out of the sample is restricted into the entrance slit $S_1$ of the emission monochromator through lenses $L_5$ and $L_6$. The fluorescence dispersed by the emission concave grating passes through the exit slit $S_4$ and is converged at the photomultiplier via concave mirror $M_2$ for intensity measurements. The emission shutter is provided in order to protect the photomultiplier. The photoluminescence spectra of the present CdS:Ni nanocrystalline samples were recorded in the wavelength range 400-700 nm, using Fluorescence Spectrophotometer (Model; Hitachi F-3010). The block diagram of the fluorescence spectrophotometer is shown in Fig. 2.14.
Figure 2.14. Functional block diagram of Hitachi F-3010 fluorescence spectrophotometer.

The configuration of the optical system of Model F-3010 fluorescence spectrophotometer is shown in Fig. 2.15.

Figure 2.15. Optical system configuration of Hitachi F–3010 fluorescence spectrophotometer.

2.5.8 Electron Paramagnetic Resonance (EPR)

When an unpaired electron subsystem of any material is subjected to a magnetic field, all the spins precess about the magnetic field. Though initially all the spins have the same energy, the crystal field and the mutual interactions of spins lift the degeneracy. A transverse microwave power drives these spins into a resonant state and the corresponding transitions provide information regarding the crystal field and mutual interactions [44]. JEOL FE 1X spectrometer operating at X- band microwave
frequency (8.8 to 9.6 GHz) is used for recording the EPR spectra. The block diagram of the EPR spectrometer with its construction details is shown in Fig. 2.16.

![Block Diagram of EPR Spectrometer](image)

**Figure 2.16.** Schematic block diagram of JEOL-FE 1X EPR.

A photograph of JEOL-FE 1X EPR spectrometer is shown in Fig. 2.17. The main parts of spectrometer are (a) source (b) sample cavity (c) microwave bridge (d) magnet (e) detector and (f) recorder /oscilloscope.

![Photograph of JEOL FE 1X EPR spectrometer](image)

**Figure 2.17.** Photograph of JEOL FE 1X EPR spectrometer.

(i) **Source**

Most of the ESR spectrometers are operated by the Klystron oscillator or Gunn diode oscillator. In JEOL FE spectrometer, the microwave generator is a Gunn diode oscillator, which is operated in the X-band region at power variable from 0.1 to 200 mW. Power may be withdrawn from the oscillator through a wave guide by a loop of wires, which couples with the oscillating magnetic field and sets up a corresponding field in the wave guide. A wave guide consists of hollow rectangular (copper or brass) tubing, 2.2 x 10 cm, with silver or gold plating inside to produce a
highly conducting, flat surface. An isolator prevents reflection of the microwave power back into the oscillator.

(ii) Sample Cavity

The sample placed in a cylindrical quartz tube is held in a cavity between the poles of the magnet. A standing wave is set up in the cavity. The standing wave is composed of both magnetic and electric field at right angles to each other. In case the sample material possesses a large dielectric constant, to minimize its influence on the sensitivity of the measurements, the sample tube is to be located in the cavity at a position corresponding to maximum r.f magnetic field.

(iii) Microwave Bridge

The microwave system is to be operated as balance bridge with all the advantages of null methods in electrical circuits. The microwave bridge will not allow microwave power to pass in a straight line from one arm to the opposite arm. A set of coils mounted on the walls of the sample cavity and fed by 0.1 MHz sweep generator provides modulation of dc magnetic field at the sample position.

(iv) Magnets

In JEOL FE 1X spectrometer, the homogeneous magnetic field varies from 0 to 6000 G. The field can be swept in different rates from 360 mm /0.5 min to 360 mm /28 min. The Hall element supplies a.c voltage to the magnetic field control unit that is proportional to the field so that linear field sweep can be carried out. Excitation power supply supplies a highly stabilized excitation current to the electromagnet.

(v) Detector

All the modern spectrometers use semi conducting crystal diode rectifiers as the basis of the detecting system.

(vi) Oscilloscope and Pen Recorder

After detection of the signal, the signal is amplified. But the amplified signal contains a lot of noise. The reduction of noise is achieved by sending the signal through a phase sensitive detector. Finally, the signal from phase sensitive detector and sweep unit is recorded by the DYT type recorder, which records the ESR signal on a chart of width 250x360 mm. The oscilloscope screen (133 mm) provides a facility for mode check before recording. The sample is fixed to one end of a quartz rod with epoxy and is placed in the sample cavity with the help of goniometer. If the sample is in powder form, 100 mg powder is taken in quartz tube.
Chapter-2 Preparation and characterization techniques

The ESR spectra can be recorded either by first differential curve or second differential curve of the absorption signal. The instrument has high sensitivity (2x10^10 – 3x10^11 spins/gauss), a high resolution (1x10^5), and frequency stability of 1x10^6. The high Q of cavity and hot carrier diode enables to accomplish high sensitivity in ESR measurements. The polycrystalline Di Phenyl Picryl Hydrazyl (DPPH) with a ‘g’ value of 2.0036 ± 0.002 is used as a standard field marker. In the ESR spectrometer, in practice, adjusting the frequency (ν) is kept constant and the field H is varied. The values of ‘g’ have been calculated using the resonance condition

\[ hv = g\beta H \]  

where h is the Planck’s constant, \( \beta \) is the Bohr magneton, ν is the microwave frequency applied to the sample and H is the applied magnetic field.

2.5.9 Vibrating Sample Magnetometer (VSM)

The vibrating sample magnetometer (VSM) is the basic instrument for characterizing magnetic materials. Since its invention (forty years ago), it has become the workhorse in both laboratory and production environments for measuring the basic magnetic properties of materials as a function of magnetic field and temperature. Computer control and automation were introduced to the VSM two decades ago, but otherwise there have been no major advances in performance until quite recently. This quantum improvement in performance has been imposed by the advancements in magnetic recording storage systems and, more specifically, by the advanced magneto-resistive and spin valve heads and the high coercivity and low remanence thickness product media employed in these systems. The magnetic layer(s) in these advanced heads and media have very low magnetic moment per unit area, requiring significantly improved sensitivity and high signal- to-noise ratio. The VSM employs an electromagnet, which provides the magnetizing field (DC), a vibrator mechanism to vibrate the sample in the magnetic field, and detection coils, which generate the signal voltage due to the changing flux emanating from the vibrating sample. The output measurement displays the magnetic moment M as a function of the field H.

Vibrating sample magnetometer [45-46] works on the principle of Faraday’s laws of induction. When a magnetic sample is placed in a uniform magnetic field \( ‘H’ \), the sample acquires a magnetic moment M. If the sample is made to undergo sinusoidal motion, an electric signal is induced in suitably located pick up coils. This signal is proportional to the magnetic moment, vibrational amplitude and vibrational
frequency. To eliminate signal dependence on amplitude and frequency, the pick up signal and a signal derived from a vibrating capacitor are fed to a difference amplifier. When a synchronous detector is used between this signal and the oscillator signal, a d.c signal proportional to the magnetization alone is obtained. This signal is further used as a feedback signal for stabilizing the transducer circuit.

VSM (Model No. PAR 4500 manufactured by EC&G Princeton Applied Research, USA) based on Foner's design is used for carrying out magnetization measurements. The block diagram of the vibrating sample magnetometer is shown in Fig. 2.18. A photograph of the vibrating sample magnetometer is shown in Fig. 2.19.

Figure 2.18. Block diagram of vibrating sample magnetometer.

Figure 2.19. Photograph of vibrating sample magnetometer (Model No. EC & G 4).
2.5.10 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) measurements [47] are carried out to identify the thermal behavior of samples (endothermic or exothermic reaction) accompanied by the change in temperature. The samples are subjected to thermal analysis using Perkin Elmer 7. The fine powdered sample of about ~3 mg is placed in the aluminum pan with lid and pressed to form a micro pellet. This pellet is used to study the chemical behavior at a heating rate of 10 °C/min from 50 °C to 650 °C under flowing nitrogen atmosphere.

2.5.11 Thermo Gravimetric Analysis (TGA)

The thermal measurements are employed to determine the various phenomena like phase transition, melting crystallization glass transition and decomposition occurring in a material [47]. The thermo gravimetric analyzer is used to find the weight loss and Curie transition in a sample.

In thermo gravimetric analysis, the mass of a simple in a controlled atmosphere is recorded continuously as a function of temperature or time as the temperature of the samples is increased. The thermo gravimetric analyzer consists of a sensitive analytical balance to measure the weight accurately, a micro-high furnace to change the temperature in a controlled fashion at a specified rate, a pure gas system for providing an inert atmosphere and a microcomputer for the instrument control. The author has used in Perkin Elmer TGA 7 PC Series thermo gravimetric analyzer for measuring the Curie temperature of the samples by placing a small magnetic around the micro-furnace producing a field of 4 mT. Before starting the experiment, the instrument was calibrated with standard Ni and Fe with the known Curie transition [48].
References

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