Chapter 2

Experimental techniques: Hydrothermal synthesis and characterization tools

2.1 Introduction

This chapter describes the experimental set up for the low temperature hydrothermal growth of nanostructures. The different measurements and analysis techniques employed to characterize the as synthesized materials are also included in this chapter. The schematic diagrams, photographs and working principles of the experimental set up and characterization tools are also presented.

2.2 Synthesis of nanostructures

There are a variety of synthesis techniques used for the synthesize of nanostructures. These methods are basically based on top-down and bottom-up
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Some of the bottom-up approaches such as thermal evaporation, chemical vapor deposition, pulsed laser deposition, atomic layer deposition and sputtering etc., require vacuum for the synthesis process which add up with the cost. The chemical method, sol-gel method, spin coating, spray pyrolysis technique and hydrothermal method are low cost bottom up approaches for the synthesize of nanostructures and these techniques do not require vacuum. Among the non vacuum technologies, hydrothermal process is a very useful cost effective technique to synthesize high quality one dimensional nanostructures.

2.2.1 Hydrothermal technique

Hydrothermal synthesis method is one of the important tools used for the advanced level material processing of nanostructured materials which has applications in the field of electronics, optoelectronics, catalysis, ceramics, magnetic data storage, biomedical, biophotonics, etc [99]. Hydrothermal processing helps to synthesis monodispersed homogeneous nanoparticles as well nano-composite materials. The term ‘hydrothermal’ is derived from the Greek words ‘hydros’ means water and ‘thermos’ means heat [153]. The word ‘hydrothermal’ was first put forward by the British geologist, Sir Roderick Murchison to describe the reaction of water at higher temperature and pressure [154]. Hydrothermal synthesis method can be defined as the heterogeneous chemical reaction in the presence of water, which is aqueous or non-aqueous above the room temperature and at pressure greater than 1 atm in a closed container [154].

Now a days, any chemical reaction in the presence of water or mineralizes under pressure and temperature conditions are generally called as hydrothermal reaction process. Hydrothermal method give numerous advantages over
other conventional methods for the synthesis of nanomaterials. It offers the synthesis of different dimensional nanomaterials with respect to the low costs for instrumentation, energy and precursors salt used. It is an eco-friendly process than many other methods, since the reactions occur inside a sealed container. The stoichiometric control is less for the materials synthesized at high temperature reaction processes due to volatilization of components and stress-induced defects caused by phase transformations. But, relatively low temperature hydrothermal process can avoid such undesirable problems and the capability to precipitate the powders directly from solution regulates the rate and uniformity of nucleation, growth and aging, which influence the size, morphology and aggregation control etc. Hydrothermal method have the capability of synthesizing materials with various morphologies and particle sizes, that can be achieved by changing different growth parameters.

Pressure-temperature interaction is one of the important physical process in hydrothermal solution because of that it is very difficult to synthesize different phases of the materials. Materials synthesized under hydrothermal method often shows variation in population of point defects when compared to materials synthesized by high temperature synthesis [155]. The main consideration of researchers about hydrothermal experiment is that, the system should operate reliably under extreme pressure-temperature conditions [153]. Temperature fluctuations of the oven causes the rise in temperature of the growth medium which leads to a higher dissolution rate. This method is also beneficial to industrial production of morphologically controlled materials with desired size and shape.

2.2.2 Hydrothermal technique:-Instrumentation

A vessel/container which withstand highly corrosive solvent at high temperature and pressure is the main part of a hydrothermal set up which is known as
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autoclave. Some researchers used to call hydrothermal autoclave as hydrothermal bomb since there occur high pressure inside the reaction system during experiments. Nevertheless, an ideal hydrothermal autoclave should have the following features [153] such as,

- Inertness to acids, bases and oxidizing agents other reactants used for the experiment.
- Apart from that it is easy to handle especially during assembling and disassembling.
- The autoclave should have sufficient length to obtain a desired temperature gradient.
- It should be a perfect leak-proof mechanism to maintain temperature and pressure range during reaction process.
- It should bear high pressure and temperature experiments for longer periods without any damage. Further, it should not need any treatment after each experimental run.

The autoclaves can be fabricated with any of the following materials a thick glass cylinder or a thick quartz cylinder with high strength alloys, such as stainless steel, iron, nickel, cobalt-based super alloys, etc. The experimental temperature, pressure conditions and its corrosion resistance of a given solvent or chemicals is the primary concern related to selection of materials for the synthesis of autoclave. Teflon lining or beakers, platinum, gold, silver tubes or lining etc., are used to protect the autoclave main part from highly corrosive media and extreme pH conditions. In the present, study we used sealed stainless steel autoclaves and Teflon beaker as the reaction container. The Teflon
The precursor solution mainly made of water is transferred into the Teflon beaker. The Teflon beaker containing precursor solution was kept inside the stainless steel autoclave. This system is sealed well in order to avoid any solvent leakage during heating of the system. The sealed autoclave is kept into the electrically heated oven for providing desired temperature. On application of the desired hydrothermal synthesis temperature, an autogenous pressure is generated within the autoclave. The hydrothermal growth advances by the presence of applied temperature and the autogenous pressure developed in the autoclave.

2.3 Characterization tools

2.3.1 X-ray diffraction technique

X-ray diffraction technique is a widely used non destructive characterization tool in materials science. It is a qualitative and quantitative phase identification technique. X-ray diffraction technique give crystalline structure of the
materials at the atomic level. It is a fingerprint characterization method for the determination of structure of crystalline materials. Every solid crystalline materials can have a unique characteristic X-ray diffraction pattern which can be used for the identification of that material. The major information obtained from the diffraction technique are crystal structure, packing of atoms together in the crystalline state, interatomic distance and angle between the atomic bonding [156, 157]. X-diffraction analysis is useful to know the state of chemical combination of the elements in a particular phase. The information obtained from the material is basically related to its crystalline structure rather than other factors. X-ray diffraction studies gives a whole range of information about the crystal structure, orientation, average crystalline size and stress in the material.

When a beam of X-rays hit on a crystalline material, the electrons around the atoms in the material oscillate with the same frequency of the incoming X-ray beam. In a crystal lattice, the atoms are arranged in a regular pattern, constructive interference occur along a few directions. A well defined X-ray beams leaving from the sample to various directions and the waves are in the same phase. A diffracted beam which composed of scattered rays are mutually reinforcing one another [157]. Scattering from the periodic arrays of atoms that leads to the diffraction effect. Scattering represented in term of simple expression which is known as Bragg’s law. It is the basic law involved in the diffraction method of structural analysis between the scattering angle, the wavelength of the radiation and the spacings between the planes of atoms [157]. Since the distances between the atomic planes are dependent on the size and distribution of atoms, the structure of the material [156, 157].

In the present study, Powder X-ray diffraction (XRD) characterization were carried out to study the crystallographic structure of the hydrothermally grown ZnO and transition metal doped ZnO (ZnO:TM). The structural characteri-
zation of as synthesized samples were done by Rigaku D-max C X-ray diffrac-
tometer with CuKα radiation (λ = 1.5414 Å) varying 2θ from 20° to 80° at
scanning rate 5°/min (Figure 2.2). X-ray tube voltage and current were set at
30 kV and 20 mA respectively.

In crystalline material, atoms are arranged regularly in three-dimensional
ways called crystal lattices. A crystal can be assumed to be made up of a
number of crystal planes [158]. When X-ray beam is incident on a crystal
surface, the atoms of the crystal occupying definite positions in the crystal
lattices act as scattering centers of X-rays. X-rays getting scattered from
different atoms reinforce each other under certain conditions and scattered X-
rays come out in certain directions. These scattered waves can be considered
as reflected waves or diffracted waves. Certain crystal planes will be rich in
atoms and from these crystal planes we get scattered waves of large intensities
[158].
Consider a crystal in which the crystal planes are at a distance ‘d’ apart as shown in the figure 2.3. Parallel beam of X-rays are incident on the crystal surface at an angle ‘$\theta$’. We get scattered wave BC corresponding to the incident wave AB. Where ‘$\lambda$’ is the wavelength of X-ray and ‘d’ is the interplanar distance.

\[ \text{Figure 2.3: Illustration of Bragg’s diffraction} \]

Another wave along $A'B'$ is incident on the next layer of atoms and scattered along $B'C'$. The two reflected waves BC and $B'C'$ will reinforce each other to produce a strong reflected X-ray if the path difference between them is equal to the product of wavelength of X-ray and an integer ‘n’ (n$\lambda$). To find the path difference draw the normal BM and BN. Therefore path difference between BC and $B'C'$ is $MB' + B'N$ [159].

For triangle $BB'M$,

\[ \frac{MB'}{BB'} = \sin \theta \]

i.e., $MB' = BB' \sin \theta$
Similarly from triangle $BB'N$,

$$B'N = d \sin \theta$$

Therefore for reinforcement or to produce a reflected X-ray beam,

$$d \sin \theta + d \sin \theta = n\lambda, \text{ or}$$

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

This is known as Bragg's Law.

Experimentally obtained diffraction patterns of the sample are compared with the standard powder diffraction files (JCPDS). The XRD data of present samples were processed with the Rietveld refinement analysis in order to extract the lattice parameters using the FullProf program [160].

### 2.3.2 Scanning electron microscope (SEM)

Scanning electron microscope (SEM) is one of the sophisticated devices for the morphological analysis of the nano or microstructures, mainly morphological imaging of the sample surfaces. When the sample is irradiated with an electron beam, secondary electrons are emitted from the specimen surface. These secondary electrons will create the image of the material surface [161]. The major components of SEM are electron system to produce an electron probe, a sample stage for placing the sample, a secondary-electron detector to collect secondary electrons, an image display unit, and an operation system to perform various operations.

The electron optical system is made of an electron gun, a condenser lens and an objective lens, a scanning coil to scan the electron probe [161]. The electron
optical system (inside of the microscope column) and a space surrounding the specimen are kept at vacuum. Electron beam generation system is usually fixed at the top of the microscope column. This system generates the illuminating beam of electrons known as the primary electron beam for imaging purpose. The electron gun is made of tungsten filament by heating the filament at high temperature about 2800 K which produces electron beam. These thermo-electrons are focused as an electron beam, flowing into the metal plate (anode) by applying a positive voltage to the anode. The electron beam is finely focused by the action of the Wehnelt electrode. Generally, Field-emission electron gun (FE gun) or the Schottky-emission electron gun (SE gun) are also used for the generation of electron beam in order to get better resolution of images [161].

If we apply an electric current passing through a coil wound over electric wire, a rotationally-symmetric magnetic field is formed and it will act as a magnetic lens [161]. Detection system usually consist of different types of detectors, each sensitive to different energy per particle emissions that occur on the sample. A fluorescent material is coated on the tip of the detector. A high voltage of about 10 kV is applied to it and the secondary electrons from the sample are attracted by this high voltage. These secondary electrons generate photon by hitting the scintillator. These photons are transmitted to a photo-multiplier tube (PMT) through a light guide and these light is converted to electrons and amplified as an electrical signal. A supplementary electrode, called the collector, is also placed before the scintillator in order to help the scintillator to acquire secondary electrons and number of secondary electrons which is collected by it can be controlled by changing this applied voltage [161].

Electrons have the tendency to disperse or scatter due to collisions with other molecules. Therefore, SEM instrument required a good vacuum system. The electron optical system and the sample chamber should be kept at high
Transmission electron microscope (TEM) is used for the imaging of ultra fine particles with high magnification. Transmission electron microscope have three
major components which are electron gun, image producing system and image recording system. The electron gun is the source of electrons similar to that of electron gun in SEM described previously. V-shaped tungsten filament (cathode) is used for the production of electrons, and these beams are focused by the condenser system onto the sample. Lanthanum hexaboride nanowires are also used for the production of electron beams in high resolution TEM instrument. The filament is surrounded by a control grid (Wehnelt cylinder) and negative potential is applied to the cathode and the control grid which is equal to the accelerating voltage of electrons. A disk shaped structure with an axial hole is used as anode. The electrons ejected from the cathode is accelerated toward the anode [164].

The image producing system constitute an objective lens, movable specimen stage, and intermediate and projector lenses. This system helps to focus the electrons passing through the sample to form a real and magnified image. The condenser lens controls the beam intensity [164]. The objective lens is having short focal length of the order of 1-5 nm which produces a real intermediate image. Image recording system is used to convert the electron image into visual image which is achieved by means of a fluorescent screen, gauges, etc.

The quality of the final image in the transmission electron microscope depends largely upon the accuracy of electromagnetic lenses. These lenses are aligned to one another to the illuminating system. The lenses need power supplies with high accuracy in order to get highest standard of resolution as well as electronic stabilization. Transmission electron microscope also need high vacuum system which is maintained by diffusion, turbo pumps similar to that in scanning electron microscope [164]. The operational control of transmission electron microscope is done by means of computer controlled system with software. The TEM characterization of the samples used in the present study
were carried out using a JEOL JEM-2100 transmission electron microscope which is shown in figure 2.5.

![JEOL JEM-2100 transmission electron microscope](image)

**Figure 2.5:** JEOL JEM-2100 transmission electron microscope

[165]

### 2.3.4 Energy dispersive X-ray analysis (EDX)

Energy dispersive X-ray (EDX) is an analytical method for identifying the elemental composition of the materials. The interaction between the electron beam with a sample target leads to the emission of X-rays with various range of energy [166]. The characteristic X-rays of different elements in the energy spectrum can be known by analyzing the energy of the emitted X-rays [167]. In EDX measurements, the sample is bombarded with an electron beam, these electron beam collide with the electrons of the sample atoms resulted the X-ray emission. Every element releases X-rays with unique nature which is characteristic of that particular element. By measuring the amounts of energy present in the X-rays being emitted by a sample during electron beam bombardment,
the identity of the atom from which the X-ray was emitted can be established [168].

An EDX spectrum identifies the element corresponding to each of its peaks and also the type of X-ray. A peak corresponding to the amount of energy possessed by X-rays emitted by an electron in the L-shell going down to the K-shell is identified as a $K_{\alpha}$ peak [169]. The peak corresponding to X-rays emitted by M-shell electrons going to the K-shell is identified as a $K_{\beta}$ peak shown in the figure 2.6. The EDX measuring arrangement is usually housed inside the scanning electron microscope or transmission electron microscope.

### 2.3.5 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy is a quantitative spectroscopic surface chemical analysis method used to estimate the chemical composition and electronic state of elements on the surface of materials or ultra thin layers of materials [170, 171]. XPS usually collect quantitative information from the top most atomic layer of the solid surface [170]. Further more, XPS can be used to determine the thickness of materials made one or more thin layers (1-8 nm)
X-ray photoelectron spectroscopy (XPS) with different materials. X-ray photoelectron spectroscopy operates on the principle of photoelectric effect postulated by Albert Einstein. It operates under ultra vacuum conditions. XPS can give information about the empirical formula of the sample and the chemical state of elements present in a material [171]. When a photon (X-rays) of suitable energy is incident on a material, it will emit photoelectrons. If we know the quantity i.e, energy of the particular X-ray wavelength used to excite an electron from a core orbital of an atom, we can determine the electron binding energy of each of the emitted electrons by using the following equation.

\[ E_{\text{binding}} = E_{\text{photon}} - E_{\text{kinetic}} - \phi \]

Where \( E_{\text{binding}} \) is the energy of electron emitted from one electron configuration within the atom, \( E_{\text{photon}} \) is the energy of the X-ray photons being emitted, \( E_{\text{kinetic}} \) is the kinetic energy of the emitted electron as measured by the instrument and \( \phi \) is the work function of the spectrometer and not of the material. Measuring the kinetic energy and the binding energy of the electron gives an idea about the oxidation state of the elements present on the materials. The number of electron reflects the proportion of the specific elements on the surface [171].

The major limitation of XPS is that it could not detect light elements like Hydrogen or Helium because these elements have only valance orbitals. The elemental composition of the samples used in the present study were carried out using a Kratos AXIS Ultra spectrometer which is shown in figure 2.7.
Figure 2.7: Kratos AXIS Ultra spectrometer

2.3.6 UV-Vis diffuse reflectance spectra (DRS)

Diffuse reflectance is an important tool for the optical characterization of powdered sample in the UV-Vis-NIR spectral ranges [173]. The DRS measures the spectral change between incident and back scattered light intensity related to absorption and scattering processes. DRS technique is used mostly in the case of samples with poor optical transmission. The reflectance from the sample at particular wavelength consist of the sum of two components: regular or specular (mirror) reflectance and diffuse (volume or nondirectional) reflectance.

DRS basically depend on the projection focus of the spectrometer beam into the sample where it is reflected, scattered and transmitted through the sample material. The diffusely scattered light and the back reflected light is then collected by the accessory and directed to the detector of the spectrometer. Sometimes the sample may absorb a portion of the incident light [173]. A portion of the incident beam undergoes scattering within the sample and returned to the surface of the sample and is called diffuse reflection. The
specular reflectance component in diffused reflectance light may contribute to
cmp changes in band shapes and its relative intensity These process follows laws
of geometric optics. When a light beam is absorbed by a sample it follows
Lambert absorption law [173].

\[ I = I_0 e^{-\alpha t} \]

In which ‘I’ is the radiation flux transmitted from an initial flux ‘I_0’ follow-
mping passage through a layer of thickness ‘t’ of a sample with an absorption (or
extinction) coefficient ‘\alpha’ measured in transmission [173].

If the size of the sample is small with respect to beam cross section but large
relative to the wavelength of light, there is probability of optical diffraction.
Randomly distributed particles with such a small size are seen in powdered
sample. As a result, a portion of the incident radiation goes back at all an-
gles into the hemisphere of origin of the radiation. This reflection process
contributed to reflection, refraction, diffraction, and absorption by particles
oriented in all directions is called diffuse reflection [167, 173].
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When light falls on a powder sample, it is reflected in all directions because of variation in shape of the sample. A part of the light is refracted as it enters the powder, and is scattered due to internal reflection, reflection from the surfaces of other grains, or repeated refraction. Some of this scattered light is returned back into the air medium. As the diffuse reflected light is reflected or passes through the powder, it becomes weaker if it is absorbed by the powder [173]. This results in a diffuse reflected spectrum, similar to the transmission spectrum. K-M function (F(R_{\infty})) derived by Kubelka-Munk is used for comparison to transmission spectra or quantitative analysis [174].

$$F(R_{\infty}) = \frac{(1-R_{\infty})^2}{2R_{\infty}} = \frac{K}{S}$$

Where F(R_{\infty}) is usually termed the remission function or Kubelka-Munk (KM) function. R_{\infty} is the absolute reflectance, ‘K’ is the absorption coefficient, and ‘S’ is the scattering coefficient. However, due to the difficulty in measuring the absolute reflectance R_{\infty}, in practice, the comparative reflectance r_{\infty} with respect to a standard BaSO_{4}, of which ‘K’ is nearly zero in the actual measurement range.

The comparative reflectance r_{\infty} is calculated from the equation,

$$r_{\infty} = \frac{R_{\infty}(Sample)}{R_{\infty}(Standard)}$$

In the present study, we are used Jasco V 570 spectrophotometer for DRS measurement and BaSO_{4} as standard (Figure 2.8). R_{\infty}(Standard) is taken as unity and is taken as unity and R_{\infty}(Sample) is the diffuse reflectance of the sample. Therefore F(r_{\infty}) become,

$$F(r_{\infty}) = \frac{(1-r_{\infty})^2}{2r_{\infty}} = \frac{K}{S}$$

The band gap of the material is estimated from the plot of $[(k/s)h\nu]^2$ versus h\nu (where h\nu is the photon energy) by extrapolating the graph to the x-axis.
2.3.7 Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared (FTIR) spectroscopy is a versatile analytical method used to analyze organic or inorganic solid, liquid or gas samples which gives both qualitative and quantitative information from the sample. It is a relatively cost effective method for the analysis of crystalline or amorphous samples [175, 176]. When an electromagnetic radiation in the IR region passes through a material, molecules in the material will vibrate which result in absorption of IR radiation corresponds to the vibration of the molecule. Each molecule has its own characteristic vibrational frequency which gives unique information about the molecular structure and functional groups present in the material.

In FTIR spectrometers, the interference of radiation between two rays gives an interferogram [177]. The interferogram is measured for all frequencies in the corresponding frequency range simultaneously and a time domain spectrum is obtained from the sample. The time domain spectrum is converted to frequency domain spectrum with Fourier transformation. A spectrum consist of intensity vs individual frequency and this makes the interpretation of data much more easier. The Fourier transformation operation is carried out with a computer program [178]. The FTIR instrument consists of a moving mirror, fixed mirror, beam splitter, IR radiation source and detector. Michelson interferometer like optical arrangement is used to generate interferogram from the sample.

The resolution for an FTIR instrument is limited by the maximum path difference between the two beams. The limiting resolution in wave numbers (cm\(^{-1}\)) is the reciprocal of the path length difference (cm) and it is usually gives high resolution [177]. Optical slits and other restricting devices are not using in FTIR spectrometer so the total source output can be passed through the sample continuously. This results in a substantial gain in energy at the detector [177]. The optical components of the IR spectrometer are made of
hygroscopic alkali halide materials like KBr which limits the efficiency of this machine in highly humid environment. Further, the sample will be damaged, because it requires to make pellet with IR transmitting material like KBr for the measurement. Majority of the FTIR spectrometer operates in the mid IR frequency region which is from 400-4000 cm$^{-1}$. In the present study we have used Shimadzu Prestige spectrometer for FTIR measurements (Figure 2.9).

![Shimadzu Prestige FTIR spectrometer](image)

**Figure 2.9:** Shimadzu Prestige FTIR spectrometer

### 2.3.8 Raman Spectra

The Raman spectroscopy is complimentary method to infrared spectroscopy which measures the molecular vibrations, rotations, lattice vibrations etc., of a molecule. Raman spectroscopic technique can be used to study solid, liquid and gaseous samples [179]. The physical phenomenon involved in Raman spectroscopy is different from the infrared spectroscopy. Raman spectroscopy is based on the scattering of light while the infrared spectroscopy is based on absorption of photons. The basic phenomenon Raman effect was experimentally observed by C.V. Raman in the year 1928 and is popularly known as Raman effect [180]. Raman scattering measurement technique is based on
the phenomenon of Raman Effect. Raman spectra occurs due to the inelastic scattering of incident radiation through its interaction with molecules of the sample [181].

The Raman effect is based on molecular deformations in the electric field ‘E’ determined by molecular polarizability ‘\(\alpha\)’. An electromagnetic radiation especially laser beam can be considered as an oscillating electromagnetic wave with electrical vector ‘E’. The interaction of this radiation with the sample induces electric dipole moment \(P = \alpha E\) which deforms molecules. Because of periodical deformation, molecules start vibrating with its characteristic frequency of the molecules present in a material ‘\(\nu_m\)’. A change in polarizability during molecular vibration is an essential requirement to obtain Raman spectrum of the sample [181, 182].

When a monochromatic light beam strikes on the sample, it scatters and the scattered radiation split up into three components. Among these, one has a frequency equal to frequency of incident radiation called the Rayleigh scattering [181]. Only a small fraction of scattered radiation have frequency less than that of incident radiation gives stokes lines in the Raman spectrum. But when the frequency of scattered radiation is higher than frequency of incident radiation, anti-stokes lines originate in the Raman spectrum [182]. Stokes Raman bands involve the transitions from lower to higher virtual energy vibrational levels which are more intense than anti-stokes bands. Stokes Raman bands are measured in conventional Raman spectrometer and anti-stokes bands are measured especially from the fluorescing samples [181, 182]. The magnitude of Raman shifts does not depend on wavelength of incident radiation, but it depends on frequencies of vibration of molecules.

The most important advantages of Raman spectroscopy over other analytical techniques are the easiness of sample handling and the rich information gathering in the frequency range 50-4000 cm\(^{-1}\) [183]. Moreover, no two
molecules give exactly the same Raman spectrum, so the Raman spectrum of each sample gives unique information. The intensity of the scattered light is related to the amount of material present in the sample. Raman spectra gives both qualitative and quantitative information about the sample.

Raman spectroscopy is an important non-destructive technique, extensively for analysis of crystallinity of materials, phase transitions and polymorphs [183]. In the present study, Raman spectrum of the sample was recorded with a Horiba Jobin Yvon LabRam HR system with Ar-ion laser (514.5 nm) as the excitation source (Figure 2.10).

2.3.9 Photoluminescence

Photoluminescence (PL) is a physical process in which spontaneous emission of light from a material will occur under optical excitation. Photoluminescence spectroscopy is a nondestructive sensitive analytic method for probing
Photoluminescence

the discrete electronic structure of materials without any electrical contact [185]. PL investigations of a material will provide a lot of information related to material parameters. The PL emission spectrum can be used to identify surface, interface, and impurity levels in a material. The intensity of the PL signal provides information on the quality of surfaces and interfaces. By using pulsed excitation sources, the transient PL intensity gives knowledge about lifetime of non-equilibrium interface and bulk states. Thermally activated physical phenomenons in a material will also leads to variation in PL intensity with respect to the temperature [185]. When light incident on a sample, it is absorbed by the sample and the excess energy is used for photo-excitation. The sample will dissipate this excess energy through the emission of light, or luminescence [186]. Photo-excitation leads to the lifting of electrons within a material to move into permissible excited states and these excited electrons return to their equilibrium states, by giving out the excess energy in the form of photons. The relaxation process of electrons from excited state to normal state are either radiative process or a non-radiative process (Figure 2.11). In a radiative process, the energy of the emitted light relates to the difference in energy levels between the two electronic states. The quantity of the emitted light is related to the relative contribution of the radiative process. Resonant radiation, fluorescence and phosphorescence are the major photoluminescence process, the phenomina of each emission process is different [186].

A photon of a particular wavelength is absorbed and an equivalent photon is immediately emitted in resonant radiation process which occur within a time of 10 nanoseconds. When a material undergoes internal energy transitions before relaxing to its ground state by emitting photons, some of the absorbed energy is dissipated so that the emitted light photons are of lower energy than those absorbed is fluorescence, which has a short lifetime \(10^{-8} \text{ to } 10^{-4} \text{ s}\) [186].

If the energy of a photon is greater than the band gap energy, then it
can be absorbed and thereby raise an electron from the valence band to the conduction band across the forbidden energy gap in a semiconductor material [187]. After this photo-excitation process, the electron may falls down, the energy it loses is converted back into a luminescent photon which is emitted from the material. This the energy of the emitted photon is a direct measure of the band gap energy (\(E_g\)) [187].

PL technique can be provide a detailed information on discrete electronic states involving both intrinsic optical processes and the wide variety of defect present in material. In practical semiconductor materials, an extrinsic optical processes by applying an external light with energy \(h\nu \geq E_g\); where \(E_g\) denotes the energy band gap, and observing the re-emitted photons. The major features of photoluminescence measurements are given below [185],
• Study the recombination mechanisms and identification of surface, interface, and impurity levels.

• Common radiative transitions in semiconductors occur between states in the conduction and valence bands, which has an energy difference equivalent to its band gap, $E_g$. As a result the band gap of the semiconducting materials can be easily determine with PL technique.

• Further, material quality can be measured by quantifying the amount radiative recombination. Since most of the non-radiative recombination is associated to localized defect levels that are detrimental to material quality and subsequently to device performance.

• Sometimes, radiative transitions also contributes to the involvement of localized defects, the photoluminescence energy associated to these levels can be used to identify specific defects.

• It gives information about deep energy states in a material, because radiative transitions give very broad spectra due to strong phonon coupling.

In the present work, room temperature photoluminescence (PL) of the samples was measured on a Horiba Jobin Yvon LabRam HR system with the He-Cd laser (325 nm) as excitation source (Figure 2.10).

2.3.10 Diamond anvil cell (DAC) technique

The diamond anvil cell (DAC) can be used to create very high pressures of the order of 100 GPa for high-pressure physical measurements. The major feature of DAC is its adaptability for different experimental setups due to its
smaller size [188]. The experimental sample is kept between flat parallel faces of two diamond anvils which are termed as called cutlet faces of the diamond. A modest force applied across the wide face of the diamond (table face) which can generate high pressure on the small ‘cutlet face’ [188]. The applied force pushes one anvil diamond against the other. The diamond anvils should be perfectly aligned axially and set parallel to each other which is required for pressure generation [188]. Solid and liquid samples can be put in between the cutlet faces of the diamonds because diamond is very hard and inert [188]. Especially, powder samples can be easily investigated with DAC because powder sample will be trapped between the two anvils smoothly. Once compressed, it will become a circular film approximately 30 µm thick. There pressure gradient within the sample since the center of the sample will be at high pressure and the edges it is about 1 atmosphere [188]. Pressures within the diamond anvil cell can be made about 100 GPa (1 GPa = ~ 9869.23 atmospheres). Figure 2.12 shows the typical schematic representation of diamond anvil cell.

The major parts of the diamond anvil cell are given below [188],

• **Diamond anvil**

Two diamonds having $\frac{1}{2}$ - 1 carat in size can cut like small ‘cutlet face’ which helps the diamond anvils sit on ‘seats’. The seats are usually made of strong material so that they can transmit the load from rest of the cell to the diamonds [188].

• **Gasket**

The gasket which used to contain the sample is a thin sheet which has a small hole about $\frac{1}{2}$ diameter of the cutlet face of the diamond - typically <500 µm. The steep pressure gradient is contained in the gasket which spares with the sample. Rhenium, Kapton Cu, Be etc. are commonly used material for making gasket [188].
Figure 2.12: Schematic representation of diamond anvil cell

- **Pressure media**

Gases such as Ne, Ar, or N₂ etc. are used to transmit pressure (Pressure transmitting medium) on the sample. The pressure inside the DAC can be adjusted by simply changing distance between the diamonds and keeping them in that position. Pressure transmitting medium in the liquid form due to compression provide hydrostatic environment inside the DAC [188].

- **Pressure Measurement**

Ruby crystal exhibit fluorescent emission consists of two well defined peaks at wavelengths of 6942 Å (R₁ line) and 6927 Å (R₂ line). The position of these fluorescent emission will change with respect to pressure and can be used to
monitor the pressure inside a DAC [188]. The ruby scale shows almost linear behavior up to 300 kbar [189]. The pressures dependence of ruby fluorescence lines shows the following relationship [190].

\[
P = \left( \frac{1094}{B} \left( 1 + \frac{\Delta \lambda}{694.24} \right)^B - 1 \right)
\]

Where ‘P’ is the pressure in GPa, ‘\(\Delta \lambda\)’ is the ruby R1 line shift in nm, and parameter ‘B’ is 7.665 for quasi-hydrostatic conditions and is 5 for non-hydrostatic conditions.

2.3.11 Superconducting quantum interference device magnetometer (SQUID)

Superconducting quantum interference device (SQUID) consists of ring of superconductor worked on the principle of Josephson effect [191]. It can be used to detects very small variations in magnetic flux. The SQUID is used to study the magnetic properties of materials especially materials showing weak magnetic properties because of its size. It is also used to detect small quantities of paramagnetic ions, and quantitative determination of the number of unpaired electrons in samples [192]. Apart from that it can be used to measure the small magnetic field, current, magnetic susceptibility, etc. of materials [193]. In the present study, the magnetic properties of the samples were studied with a SQUID magnetometer (QUANTUM DESIGN).

The Magnetic property measurement system (MPMS) in the SQUID device is the source of the instrument sensitivity, which does not measure the magnetic field from the sample directly. The experimental specimen is allowed to move through a superconducting coils. The current from the detection coils are inductively coupled to the SQUID sensor [191]. The change in magnetic flux leads to the variations in the current in the detection coils which produce
corresponding variation in the SQUID output voltage which are proportional to the magnetic moment of the sample [191]. These systems are extremely sensitive to magnetic properties of materials and it can be measured in different temperatures especially in the low temperature up to liquid He temperature.

2.3.12 Vibrating sample magnetometer (VSM)

Vibrating sample magnetometer (VSM) systems are usually used to study the magnetic properties of materials and its sensitivity less with respect to that of SQUID. It can used to measure the magnetic properties of materials as a function of magnetic field, temperature, and time. Samples in different forms such as powders, solids, and thin films can be used in the sample holder set-up [193]. It can measure magnetic properties of materials such as hysteresis, saturation, coercivity, and anisotropy [194].

Based on Faraday's law of induction, the VSM relies on the detection of the emf induced in a coil of wire which is given by [194],

\[
e = -N \frac{d}{dt} (BA \cos \theta)
\]

where ‘N’ is the number of wire turns in the coil, ‘A’ is the coil turn area, and ‘\( \theta \)’ is the angle between the field B and the direction normal to the coil surface. In VSM, the magnetic sample is placed on a long rod which is driven by a mechanical vibrator. This rod is placed between the pole pieces of an electromagnet which is attached with detection coils. The motion of the magnetized sample will induce a voltage in the detection coils which is proportional to the magnetization of the sample [194, 195]. The room temperature magnetic properties of the present samples were studied by using a Lakeshore VSM-7410 vibrating sample magnetometer.
Experimental techniques