Chapter 3

Experimental Techniques

3.1 Introduction

The experimental techniques used for the characterization and study of the physical properties of the grown crystals include XRD analysis, Infrared spectroscopy, UV-visible absorption studies, thermal analysis, Energy-Dispersive Analysis by X-rays, optical microscopy, microhardness measurement, microwave dielectric studies and magnetic studies. A brief description of the principles involved and procedures followed in these studies is given in this chapter.

3.2. X-ray diffraction analysis

X-ray powder diffraction technique is extensively used for the structural characterization of crystals[1-3]. In this technique, monochromatic X-rays are allowed to fall on a powdered specimen of the crystalline substance. The basic principle underlying this method is that since a very large number of tiny crystals in the powder sample have random orientations, all possible diffraction planes will be available for Bragg reflection to take place. Such reflections will take place from many sets of parallel planes lying at different angles to the incident X-ray beam. Moreover, each set will give not only first order reflections, but those of higher orders. Since all orientations are equally likely, the reflected rays will form a cone whose axis lies along the direction of the incident beam and whose semi-vertical angle is twice the glancing angle for that particular set of planes. For each set of planes and for each order there will be such a cone of diffracted X-rays.
The basic relations used in X-ray diffraction studies was derived by Bragg \[4\] and is expressed as

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

where \(d\) is the distance between the atomic planes of the crystal, \(\theta\) is the angle of diffraction, \(\lambda\) is the wavelength of the X-ray beam and \(n\) is the order of diffraction.

In an X-ray diffractometer a monochromatic beam of X-rays is incident on a powdered specimen C.

![Figure 3.1 X-ray diffractometer (schematic)](general_features.png)

The specimen, in the form of a flat plate, is supported on a table \(H\), which can be rotated about an axis \(O\) perpendicular to the plane of the drawing. The X-ray source \(S\) is normal to the plane of the drawing and therefore parallel to the diffractometer axis \(O\). X-rays diverge from the source and are diffracted by the specimen to form a convergent diffracted beam which comes to a focus at the slit \(F\) and then enters the counter \(G\). A and B are special slits which define and estimate the incident and diffracted beams.
The receiving slits and counter are supported on the carriage E which may be rotated about the axis O and whose angular position $2\theta$ may be read on the graduated scale K. The supports E and H are mechanically coupled so that a rotation of the counter through $2\theta$ degrees is automatically accompanied by rotation of the specimen through $\theta$ degrees. The diffracted intensities from the various planes of the powder sample are measured directly using the counter. The angular distribution of the diffracted intensities can be recorded in terms of a series of peaks corresponding to the different Bragg reflections from various planes. The heights of the peaks will be directly proportional to the intensities of the lines. This graphical record of the diffraction pattern is called a diffractogram.

In the present investigation, the diffraction patterns were recorded using a Bruker AXS Advanced X-ray diffractometer with nickel filtered CuK$_\alpha$ radiations ($\lambda = 1.5418$ Å).

The arrangement of atoms within a crystalline specimen can be determined using the analytical technique of single crystal X-ray diffraction. The molecular structure, atomic coordinates, bond lengths, bond angles, molecular orientation and packing of molecules in single crystals can be determined by X-ray crystallography. Single crystal X-ray diffractometer collects intensity data required for structure determination. To find the structure, accurate measurement of intensities of reflections of all Miller indices within a specified reciprocal radius (usually $25^0$ for MoK$_\alpha$ and $68^0$ for CuK$_\alpha$) is required to find the structure. But unit cell parameters depend only on the direction of reflections. For single crystal analysis, the specimen should be smaller than the cross section diameter of the beam. Larger crystals are to be cut into proper size and smaller crystals may be suitable if they contain strongly diffracting elements.
When monochromatic X-rays suffer Bragg diffraction at a crystal plane, the intensity of the diffracted beam depends on the nature and arrangement of atoms in the crystal. Collection of intensities of a full set of planes in the crystal contains the complete structural information of the molecule. Fourier transformation techniques are used to determine the exact coordinates of atoms in the unit cell from this data. Using the X-ray diffraction data, unit cell parameters, space groups, molecular structure of the crystalline solids and Miller indexing of the different faces of the crystal are possible. Unit cell parameter is actually the dimension of the basic molecular unit with which the crystal is built. Space group gives the symmetry with which the molecules are arranged within the unit cell. All the geometrical features of molecules (bond distance, bond angles etc.) may be obtained from coordinates.

In the present work, single crystal X-ray diffraction analysis was performed using an ENRAF (Bruker) Nonius CAD 4 single crystal X-ray diffractometer. The shield was equipped with graphite monochromated MoKα radiation. Reflections were collected from different zones of the reciprocal lattice using random search procedure. The reflections were indexed using the method of short vectors followed by least square refinements and unit cell parameters were obtained.

3.3 Infrared spectroscopy

The infrared spectrum is formed as a consequence of the absorption of electromagnetic radiation at frequencies that correlate to the vibration of specific sets of chemical bonds from within a molecule. The fundamental vibrational frequency of a molecular ensemble can be expressed as

\[ \nu = \frac{1}{2 \pi c} \sqrt{\frac{k}{\mu}} \]

Where \( \nu \) = fundamental vibration frequency, \( k \) = force constant, and \( \mu \) is the reduced mass. The reduced mass \( \mu = m_1 m_2 / (m_1 + m_2) \) where \( m_1 \) and
m_2 are the component masses for the chemical bond under consideration. This equation provides a link between the strength of the covalent bond between two atoms (or molecular fragments), the mass of the interacting atoms (molecular fragments) and the frequency of vibration [5].

Infrared spectroscopic studies help to identify the functional units, internal structure of molecules and the nature of chemical bonds of the sample [6]. This is achieved by recognizing characteristic shapes and patterns within the spectrum and using the information obtained from published group of frequency data, along with other chemical and physical data. The IR absorption bands are related to the motion of individual atoms in a polyatomic molecule. The frequency of the incident radiation is varied and the quantity of radiation absorbed or transmitted by the sample is obtained. When the frequency of the incident radiation coincides with the vibrational frequency of some part of the molecule, resonance occurs and absorption of energy takes place. When the molecules return from the excited state to the original ground state, the absorbed energy is released giving rise to distinct peaks in the IR spectrum. Hence a unique fingerprint of the molecules in the sample is obtained. The IR absorption is due to the change in dipole moment during the vibration cycle. IR spectroscopy includes the twisting, bending, rotational and vibrational motion of atoms in a molecule.

The IR spectral range is subdivided into three regions

i) near IR (12000-4000 cm⁻¹)

ii) mid IR (4000 – 200 cm⁻¹)

iii) far IR (200 – 10 cm⁻¹)

Most of the standard IR spectrophotometers cover the mid IR region as this range is of great practical significance.

Fourier Transform Infrared (FTIR) Spectroscopy has been employed in the present work. Fourier Transform Spectroscopy is a
simple mathematical technique to resolve a complex wave into its frequency components. Conventional spectroscopy called the frequency domain spectroscopy records the radiant power as a function of frequency. In the time domain spectroscopy the change in radiant power is recorded as a function of time. In the FTIR Spectrometer, IR radiation is analysed using a scanning interferometer. Radiations containing the IR wavelength is split into two beams. After reflection the two beams recombine at the beam splitter and for any particular wavelength, constructive or destructive interference takes place depending on the optical paths. The resulting interferogram which contains all the information is reconstructed into the spectrum by the mathematical programming of Fourier transformation.

The schematic diagram of FTIR Spectrometer is shown in Fig. 3.2

![FTIR spectrometer (schematic)](image-url)
It consists of an infrared source, a sample chamber with a provision for holding solids, liquids, and gases, a monochromator, a detector, and a recorder, which are integrated with a computer. The interference pattern is obtained from a two-beam interferometer as the path difference between the two beams is altered, then Fourier transformed output gives rise to the spectrum. The transformation of the interferogram into spectrum is carried out mathematically using a computer. The spectrometer works under vacuum condition.

For a solid sample, recording of IR spectra is difficult since the particles reflect and scatter the incident radiation and hence transmittance is always low. The pressed-pellet technique is employed to record the IR spectra of solid compounds that are insoluble in the usual solvents. A few milligrams of the sample are ground together in an agate mortar with about 100 times the quantity of a material transparent to the infrared. The usual material is KBr. The ground powder is pressed to form a pellet suitable for infrared transmission work.

Using KBr pellet method, IR absorption bands in the range 400 cm\(^{-1}\) to 4000 cm\(^{-1}\) are recorded.

3.4 UV – visible – near infrared spectroscopy

By the absorption of electromagnetic radiation of sufficient frequency, electronic transitions within the atom may occur from one energy level to another. For electronic transitions involving outer (valence) shells, the associated energy usually lies in the visible and ultraviolet regions; however, for inner shell transitions, much larger energies are involved and fall in the X-ray region. Optical absorption studies in the UV-visible-near IR region are widely used for the qualitative and quantitative determination of the molecular species present in the sample [7]. The energy absorbed in this region corresponds to the excitation of the valence electron from an occupied molecular orbit. The spectrum
obtained in this case is a plot of wavelength of absorption versus the absorption intensity. The position of the absorption peaks corresponds to the wavelength of radiation whose energy is equal to that required for an electronic transition.

In the present work, the UV-visible absorption spectra of the samples were recorded using Shimadzu UV-2401 PC spectrophotometer.

### 3.5 Thermal analysis

Thermogravimetric analysis (TGA) gives a quantitative measurement of any weight change associated with transition. TGA can directly record the loss of weight with time or temperature due to dehydration or decomposition \[8\text{-}10\]. TGA curves are characteristic for a given compound or system because of the unique sequence of physicochemical reactions which occur at definite temperature ranges and at rates governed by the molecular structure. Changes in weight of the sample occur as a result of the rupture and/or formation of various physical and chemical bonds at elevated temperatures that lead to the evolution of volatile products or formation of reaction products. Hence the TGA curve gives information about the thermodynamics and kinetics of various chemical reactions, reaction mechanisms and the intermediate and final reaction products.

Modern TG instruments consist of the following.

(i) a sensitive analytical balance.

(ii) a temperature programmable furnace.

(iii) a pure gas system for providing suitable gas atmosphere.

(iv) a microprocessor for instrument control, data acquisition and display.

In differential thermal analysis (DTA), the temperature of the sample and a thermally inert reference material are measured and the chemical changes involved are studied as a function to temperature.
When the sample is heated or cooled it will absorb or liberate energy depending on the transitions taking place. The corresponding deviation of the sample temperature from that of the reference (ΔT) versus the programmed temperature (T) is recorded and it explains whether the transition is endothermic or exothermic. The differential thermal curve would be parallel to the temperature axis till the sample undergoes any physical or chemical change of state. However, as soon as the sample has reached the temperature of this change of state, the additional heat flux reaching the sample will not increase the sample temperature at the same rate as that of the reference and the differential signal appears as a peak. The differential signal would return to the base line only after the change of state of the sample is completed and the temperature becomes equal to that of the reference material. The thermal effects are observed as peaks whose sequence (on the temperature scale), sign (endothermic or exothermic), magnitude and shape reflect the physical and chemical changes taking place. Generally, phase transitions, dehydration, reduction and some decomposition reactions produce endothermic effects whereas crystallization, oxidation and some decomposition reactions produce exothermic effects. The TGA studies along with DTA provide detailed information regarding the dehydration, decomposition and phase transitions of the sample during heating.

The thermal characteristics of the grown crystals were analysed using Shimadzu thermal analyser DT-40 in the temperature range 30 - 800°C at a scan rate of 10°C per minute.

3.6 Energy dispersive analysis by X-rays (EDAX)

Energy dispersive analysis by X-rays is an analytic technique to determine the chemical composition of a material. When a beam of high energy electrons is incident on the specimen its atoms are excited and while returning to the ground state they emit X-rays. The energy of these
X-rays is strictly related to the atomic number of the elements excited. Hence the constituents of the specimen can be determined. The intensity of the emitted X-rays is proportional to the concentration of the elements in the sample. This method is a non-destructive one and gives simultaneous record of all elements having $Z \geq 11$.

The main components of an energy dispersive spectrophotometer consists of a polychromatic source, a sample holder and a detector. A lithium drifted silicon p-i-n diode held at liquid nitrogen temperature is used as the detector of the emitted X-rays. The cooled detector is covered by a beryllium window [usually a beryllium sheet about 10 µm thick]. Because of X-ray absorption in the detector window and in the lithium drifted silicon chip itself, elements with atomic number less than ten are not usually identified or analysed energy dispersively. The output pulses are stored in a multichannel analyzer.

3.7 Optical microscopy

Structural and geometrical investigation of the surface features of a crystal is the most fundamental step in characterizing a crystal [11, 12]. The surface studies also provide information regarding the nature and distribution of imperfections in a crystal.

The surface features and etch patterns of the grown crystals were studied using a Leitz Metallux - 3 optical microscope. It is a large binocular polarizing microscope with versatile functions. The modulpack AF can be used for the bright field, dark field, polarizing light and phase contrast. It has a FSA 20 binocular photo tube with $30^\circ$ viewing angle of adjustable interpapillary distance. In the vertical photo port of the microscope, a camera is attached. The lamp housing can be adjusted for reflected or transmitted position along with the filter. Magnifications of 50, 100, 200 and 1000 times are possible with the adjustable objectives.
3.8 Microhardness measurement

The suitability of materials for device applications depends to a large extent on their mechanical properties. Measurement of hardness provides information about the elastic, plastic, viscous and fracture properties of a great variety of both isotropic and anisotropic materials [13]. The hardness properties are basically related to the structural properties of a crystal. Hardness values obtained from high purity, good quality and well annealed crystals can be correlated with the strength of the interatomic binding in these crystals [14]. Plendl and Gielisse [15] correlated the hardness of several crystals with their lattice energy.

The microhardness of the grown crystal samples was measured using Vicker’s indentation method.

Figure 3.3  Schematic diagram of Vicker’s diamond pyramidal indentor and an indentation mark.

A hardness tester (Leitz Mini load 2) fitted with a diamond pyramidal indentor attached to an incident light microscope was used for the study. The diamond indentor is in the form of a square pyramid, opposite faces of which make an angle 136° with one another. Indentation can be done with different loads from 5 g to 250 g. The impression is of a
square pyramid and has a superficial area of $d^2/2 \sin 68^0$ where $d$ is the length of the diagonal of the indentation square in micrometers. The area of impression is related to hardness as Vicker’s Hardness number $H_v$.

$$H_v = \frac{\text{load}}{\text{area of impression}}$$

$$= \frac{2p \sin 68^0}{d^2} \text{g.}\mu\text{m}^{-2}$$

$$= \frac{1.8544p}{d^2} \text{Kg/mm}^2$$

Where $P$ is in Kilograms and $d$ is in millimeters.

### 3.9 Microwave dielectric studies

The cavity perturbation technique is an accurate and precise method for complex permittivity measurements. This technique proposed for the first time by Bethe and Schwinger [16] considered the cases in which the perturbation is caused (i) by insertion of a small dielectric sample into a cavity (ii) by a small deformation of the boundary surface of the cavity. They showed that the real and imaginary parts of complex permittivity/ permeability are quantities measurable in terms of the real and imaginary parts of complex frequency shift.

Birnbaum and Franeau [17] developed the method of measurement of complex permittivity based on cavity perturbation technique. A small cylindrical sample was placed in a rectangular cavity, operating in the $\text{TE}_{10p}$ mode in X-band. The assumption that the electric field in the perturbing sample is equal to the electric field of the empty cavity was made in their calculation. The technique was further modified by Casimir [18] to include the determination of the magnetic property of a small sphere. Chao [19] reviewed the theory and technique of cavity perturbation method for measuring the conductivity and dielectric constant of materials.

There are two methods for the determination of the dielectric parameters of an unknown sample using cavity perturbation technique (i) from the perturbation equation of the cavity and (ii) from the calibration of the cavity against some materials whose dielectric constant is known very
The fundamental idea of cavity perturbation is that the change in the geometrical configuration of the electromagnetic fields on the introduction of the sample must be small. The computation of the relative dielectric constant from the perturbation equations of the cavity is an absolute method that does not rely on any reference data.

The waveguide cavity resonator in the cavity perturbation technique [20] consists of a closed section of a waveguide. A transmission type cavity resonator is used in which electromagnetic energy is coupled to the cavity through coupling holes at the end of the cavity. A non-radiating slot is provided at the broad wall of the cavity for the introduction of the sample. Depending on its dimensions, the resonator resonates at different frequencies.

The principle of cavity perturbation technique is that the field within the cavity resonator is perturbed by the introduction of the dielectric sample through the non-radiating slot. The resonant frequency and the quality factor of the cavity get shifted by the perturbation. The shift in the frequency is the measure of dielectric constant and that in quality factor gives the loss factor.

![Figure 3.4 Schematic diagram of the transmission type cavity resonator](image-url)
The experimental set up consists of a transmission type S-band rectangular cavity resonator, HP 8714 ET network analyzer and an interfacing computer (Figure 3.4; 3.5). The cavity resonator is excited in the TE\textsubscript{$10_0$} mode. The dielectric measurements of the grown samples of crystals in the powdered form were done and recorded.

![Experimental set up](image)

**Figure 3.5** Experimental set up

### 3.10 Magnetic studies

The measurement of magnetization of magnetic samples can be done by induction method, force method and methods based on the detection of the dipole field of a magnetized specimen. A convenient way for measuring the magnetization of a specimen by induction method is by using a vibrating sample magnetometer (VSM) [21,22].

A VSM is a gradiometer measuring the differences in magnetic induction between a region of space with and without the specimen. Hence it gives a direct measure of magnetization of the specimen. The specimen is made to vibrate sinusoidally in a uniform magnetic field and the alternating electric signals generated due to the flux changes are induced to the surrounding stationary pick up coils. The pick up coils are placed with their axes perpendicular to the main magnetizing field so as to minimize error signals arising from field fluctuations. The electrical signal is proportional to the magnetic moment, the vibrational amplitudes and the vibrational frequency. The electronic system is so designed that the amplitude and frequency of vibrations are accounted for such that the electrical signal is proportional only to the magnetization of the sample.

The magnetic moments of the given samples were measured using Lakeshore Model 736 VSM.
References


