CHAPTER 2
CHARACTERISATION TECHNIQUES

2.1 INTRODUCTION

Characterization is a tool for the measurement of physical and chemical properties of materials. Characterization provides a basis for understanding and improving the characteristics of material for specific applications. Characterization of a material essentially depends on the characterization and experimental techniques involved with tools of sophisticated technology. Today scientists and researchers have powerful and elegant tools for obtaining qualitative and quantitative information about the composition and structure of matter. The development of these tools began over two centuries ago and the search still continues. The use of instrumentation is an exciting and fascinating part of any analysis that interacts with all the areas of chemistry and with many other fields of pure and applied science.

Characterization of a crystal essentially consists of determination of chemical composition, structure, defects and study of their optical properties. Crystal studies such as structural analysis, investigation of growth defects, and measurement of linear and nonlinear optical properties are essential in understanding the nature and properties of the grown crystals. In order to obtain good quality single crystals pertaining to specific applications enhancement of the desired properties must be done. In the present investigation, the grown crystals are subjected to various characterizations to study their structure from single crystal XRD, powder XRD,
FTIR and Raman spectral analysis. The optical transmittance and UV cut-off wavelength of the grown materials were evaluated by recording optical transmission spectra. The Fourier transform nuclear magnetic resonance (FT-NMR) spectrum confirms the presence of organic compounds in the grown crystal. Thermal characteristics of the crystals were analyzed using TG-DTA and DSC spectrum. Etching studies carried out revealed the defects and growth pattern of the crystals. The surface morphology and dislocation on the surface of the grown crystal was analyzed using scanning electron microscope (SEM). The second harmonic generation (SHG) of the crystal is checked with Nd$^{3+}$:YAG laser operating at 1.06 μm by Kurtz-Perry powder method (Kurtz and Perry 1968). Also the mechanical hardness of the crystals is studied using hardness measurement. Hence a basic description of the various characterization techniques used in the present work is discussed in this section.

2.2 X-RAY DIFFRACTION STUDIES

X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. X-rays are partially scattered by atoms when they strike the surface of a crystal. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg’s Law ($n\lambda = 2d_{hkl}\sin\theta$) (Figure 2.1), where $\lambda$ is the wavelength of the radiation used, $n$ is an integer, $d_{hkl}$ is the perpendicular spacing between the lattice planes in the crystal and $\theta$ is the complement of the angle of incidence of X ray beam. This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample.
Figure 2.1 Bragg’s law
2.2.1 Single crystal X-ray diffraction

Single-crystal X-ray Diffraction is a non-destructive analytical technique commonly used for the study of crystal structures including unit cell dimensions, bond-lengths and bond-angles. X-ray diffractometer consists of three basic elements, an X-ray tube, a sample holder, and an X-ray detector. X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons toward a target by applying a voltage and impact of the electrons with the target material. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced. These X-rays are collimated and directed onto the sample.

When the geometry of the incident X-rays impinging the sample satisfies the Bragg Equation, constructive interference occurs. A detector records and processes this X-ray signal and converts the signal to a count rate which is then output to a device such as a printer or computer monitor. Figure 2.2 shows a schematic of a single-crystal diffractometer. This diffractometer can use either 3- or 4-circle goniometers. Samples are mounted on thin glass fibres which are attached to brass pins and mounted onto goniometer heads.

Adjustment of the X, Y and Z orthogonal directions allows centering of the crystal within the X-ray beam. X-rays leave the collimator and are directed at the crystal. Rays are either transmitted through the crystal, reflected off the surface, or diffracted by the crystal lattice. A beam stop is located directly opposite the collimator to block transmitted rays and prevent burn-out of the detector. Reflected rays are not picked up by the detector due to the angles involved. Diffracted rays at the correct orientation for the configuration are then collected by the detector.
Figure 2.2 Schematic diagram of single crystal diffractometer
2.2.2 Powder X-ray diffraction method

In powder X-ray diffraction, the diffraction pattern is obtained from a powder of the material, rather than an individual crystal. Most materials have unique diffraction patterns, compounds can be identified by using a database of diffraction patterns. The purity of a sample can also be determined from its diffraction pattern, as well as the composition of any impurities present. A diffraction pattern can also be used to determine and refine the lattice parameters of a crystal structure. A powder X-ray diffractometer consists of an X-ray source (usually an X-ray tube), a sample stage, a detector and a way to vary angle $\theta$. The X-ray is focused on the sample at some angle $\theta$, while the detector opposite the source reads the intensity of the X-ray it receives at 20 away from the source path. The incident angle is than increased over time while the detector angle always remains 20 above the source path. The experimental setup for the powder X-ray diffraction is shown in the Figure 2.3 (Buerger 1965).

2.3 INFRARED SPECTROSCOPY

Infrared spectrum is an important record which gives information about the structure of a compound. The most important region in which most of the molecular absorptions observed are 400 to 4000 cm$^{-1}$. The IR region of electromagnetic spectrum can be divided into three regions namely near, mid and far infrared region. The region from 4000–12500 cm$^{-1}$ is called the near IR region, from 4000–400 cm$^{-1}$ is called the mid IR region and that from 400 to 50 cm$^{-1}$ is called far infra red region. The absorption in the infra red region is due to the changes in the vibrational and rotational levels.
Figure 2.3 Experimental setup for powder X-ray diffraction
The various stretching and bending vibrations of bond occur at certain quantized frequencies. When IR radiation is passed through the sample, energy is absorbed and the amplitude of that vibration is increased. From the excited state, the molecule returns to the ground state by the release of extra energy by rotational, collision or translational processes. Thus the infra red spectrum of a molecule results due to the transitions between two different energy levels. The various regions in the IR will give rise to useful information about the molecule. The near IR spectrum is a very useful tool for structural analysis of protein, fat, sugar etc. The mid IR spectrum is very useful tool to confirm the presence of functional group in the molecule. The region range from 700 – 1500 cm\(^{-1}\) is called the finger print region which is very unique for every molecule. The far IR spectrum is useful for finding out the metal ligand bonding. Thus IR spectrum is a very useful tool for confirming the presence of the functional group in the material and also the presence of hydrogen bonding with the molecule can be identified using the spectrum.

The instrumentation of the IR spectroscopy is shown in the Figure 2.4. Light from the source is split into two beams. One of the beams is passed through the sample under examination and is called the sample beam. The other beam is called the reference beam. When the beam passes through the sample, it becomes less intense due to the absorption of certain frequencies. Let Io be the intensity of the reference beam and I be the intensity of the beam after interaction with the sample respectively. The absorbance and the transmittance of the sample at a particular frequency can be calculated using the formula \(A=\log_{10} \left( \frac{1}{T} \right)\); \(T=\frac{I}{Io}\). Intensity of the bands can be recorded as a linear function T against the corresponding wave
number. Intensities of the two beams are converted into and measured as electrical energies with the help of detector thermopile (Sharma 2000).

### 2.4 RAMAN SPECTROSCOPY

In Raman studies, light is scattered from a sample after irradiation from a high intensity monochromatic source—typically a laser. Most of the radiation collected in a Raman measurement results from elastic scattering, and this remains unchanged with respect to frequency or wavelength compared to the original incident beam. This is known as Rayleigh scattering. An extremely small fraction of the scattered radiation results from inelastic scattering. The Raman effect is the result of the molecule undergoing vibrational transitions, usually from the ground state, to the first vibrational energy level, giving rise to the Stokes lines, observed as spectral lines occurring at lower frequency (longer wavelength) than the incident beam. The main advantage of this Raman spectroscopy is ease of sample preparation, non-destructive nature and rich information content. The exact characteristics of Raman radiation depend on the chemical composition of the sample and each molecule has a unique spectral fingerprint.

The FT-Raman spectroscopy uses an interferometer to produce an interferogram, which “encodes” the unique frequencies of the Raman scattering into a single signal. The signal is measured very quickly, making signal averaging fast and accurate. The interferometer employs a beam splitter optimized for near-infrared (NIR) radiation, which divides the incoming Raman scatter into two optical beams, one transmitted and one reflected. The reflected beam travels to and reflects off a flat fixed mirror. The transmitted beam travels to and reflects off a flat moving mirror, which has a constant frequency and fixed motion. The two beams recombine
Figure 2.4 Instrumentation of IR spectroscopy
at the beam splitter. Depending on their path difference, the two beams constructively and destructively interfere with each other. Constant frequency and fixed motion of the moving mirror modulates the interference pattern. The resulting interferogram has the unique property that every data point (a function of the moving mirror position) has information about every frequency of the Raman scatter collected from the sample (Willard et al., 2012). Figure 2.5 represents the instrumentation of the FT-Raman spectroscopy.

2.5 UV-Visible Spectroscopy

UV visible spectrometer is a device which detects the percentage of transmittance of light radiation when light of certain intensity and frequency range is passed through the sample. It involves the promotion of electrons from a bonding to an antibonding orbital. The various transitions involved in the ultraviolet spectroscopy are excitation of sigma electrons to antibonding sigma orbital, non bonding electron to antibonding sigma ($\sigma^*$) orbital, $\pi$ electrons to an antibonding $\pi$ orbital ($\pi^*$) and the promotion of non bonding electron to antibonding $\pi$ orbital. The energy required for the various transitions obey the order of transitions obey the order of $\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$.

The UV-visible spectrometer consists of light source, monochromator, detector, amplifier and the recording devices. The most suitable light sources are tungsten filament lamp and hydrogen-deuterium discharge lamp which covers over the entire UV-visible region. Most spectrometers are double beam instruments. The schematic representation of the UV-visible spectroscopy is shown in the Figure 2.6. The incident beam is first dispersed with the help of a rotating prism and then the source is divided into two beams of equal intensity.
Figure 2.5 Instrumentation of FT- Raman spectroscopy
The light from the first dispersion is passed through a slit and then sent to the second dispersion. After the second dispersion, light passes through the exit slit. One of the beams of the selected monochromatic light is passed through the sample and the other beam through the reference. After the beams pass through the sample as well as the reference, the intensities of the respective transmitted beams are then compared over the whole wavelength range of the instrument. The spectrometer electronically subtracts the absorption of the solvent from the absorption of the sample. The signal for the intensity of absorbance versus corresponding wavelength is automatically recorded on the graph. The spectrum is plotted as absorbance against wavelength (Sharma 2000).

2.6 THERMAL ANALYSIS

Thermal analysis comprises of several techniques in which physical property of a substance is measured as a function of temperature while the substance is subjected to a controlled temperature programme. When a material is heated it undergo changes such as fusion, melting, crystallization, oxidation, decomposition, reaction, transition, expansion and sintering. Thus from thermal analysis it is possible to know the thermal stability, melting point and the mechanism involved in the decomposition process of the material.

2.6.1 Thermogravimetry analysis and differential thermal analysis

Thermo gravimetric analysis (TGA) provides a quantitative measurement of any weight changes associated with thermally induced transitions. The TGA curve of a given compound is due to the unique sequence of physical transitions and chemical reactions that occur over definite temperature ranges. The weight loss observed during the process give us a complete idea about the sequence in which the molecule decompose and also the melting point of the material can be easily known.
Figure 2.6 Instrumental set up for UV-Visible spectroscopy
from the TGA data. The usual temperature range for TGA is from ambient to 1200°C in either inert or reactive atmospheres.

Differential thermal analysis (DTA) measures the temperature, direction and magnitude of thermally induced transitions in a material by heating a sample and comparing its temperature to the temperature of an inert reference material under similar conditions. This difference in temperature is determined as a function of time or temperature in a controlled atmosphere and provides useful information about the temperatures, thermodynamics and kinetics of reactions. This technique is sensitive to endothermic or exothermic processes including phase transitions, dehydration, decomposition and solid state reactions. A plot of the differential temperature versus the programmed temperature indicates the transition temperature and whether the transition is exothermic or endothermic.

The powder form of the sample is placed in a crucible that is positioned in a furnace on a quartz beam attached to an automatic recording balance. The horizontal quartz beam is maintained in the null position by the current flowing through the transducer coil of an electromagnetic balance. A pair of photosensitive diodes acts as a position sensor to determine the movement of the beam. Any change in the weight of the sample causes a deflection of the beam which is sensed by one of the photodiodes. The beam is then restored to the original null position by a feedback current sent from the photodiodes to the coil of the balance. The current is proportional to the change in weight of the sample. The block diagram of the thermal analysis setup is shown in the Figure 2.7.
2.6.2 Differential scanning calorimeter

Differential scanning calorimeter (DSC) is the most widely used thermal analysis technique. In this technique the sample and reference materials are subjected to a precisely programmed temperature change. When a thermal transition occurs in the sample, thermal energy is added to either the sample or the reference container to maintain both the sample and the reference at the same temperature. The sample and the reference are placed in separate pans that are kept on a raised platform of a constantan disk (Cu-Ni). This constantan disk is used as the primary means of transferring heat to the sample and reference positions and it is also used as one of the element in the temperature sensing thermoelectric junction. The differential heat flow to the sample and the reference is monitored by the chromel/constantan thermocouples formed by the junction of the constantan disk and the alumel wires connected to the underside of each platform. The chromel and alumel wires connected to the underside of the wafers form a chromel/alumel thermocouple, which is used to directly monitor the sample temperature. Constant calorimetric sensitivity is maintained by the computer software, which linearizes the cell calibration coefficient. DSC provides maximum calorimetric accuracy from -170 to 750 °C and the sample size ranges from 0.1 to 100 mg (Willard et al., 2012). Figure 2.8 shows the block diagram of the DSC setup.

2.7 KURTZ POWDER METHOD

The second harmonic generation efficiency of a material can be studied using Kurtz powder method. The basic configuration used for the study of second harmonic generation in powder is shown in the Figure 2.9. The material under study is finely grind and packed in between two glass plates. The instrument consists of
Figure 2.7 Block diagram of thermal analysis instrument
Figure 2.8 Block diagram of DSC instrument
a Q-switched laser whose beam falls unfocused on to a thin section of powder of the material under study. After the fundamental beam is removed by a series of short wavelength passing filters, the second harmonic generated is detected by a photomultiplier and displayed on an oscilloscope. A reference beam is obtained by the use of beam splitter placed ahead of the sample. This enables the intensity of the fundamental beam generated in a reference sample to be monitored by displaying both signals simultaneously on dual beam scope. The system also permitted the insertion of narrow pass filters at the second harmonic wavelength between the short filters and the photomultiplier to eliminate spurious signals (Kurtz 1968).

2.8 ETCHING STUDIES

The study of the identification, origin and characteristic of crystalline defects such as boundaries, slip planes, dislocation and plastic flow relies heavily on etching phenomena (Sangwal 1989). Etching is the selective dissolution of the crystal, a reverse phenomenon of growth. When a crystal phase is exposed to a solvent, dissolution begins by the nucleation of unit pits of one molecular depth which then grows in the size by the retreating steps across the crystal surface.

Etching is however a surface technique and care must be exercised in the interpretation of etching studies, since defect densities and properties in the surface and bulk regions of crystals frequently show a marked difference. For any defect etchant, it is essential to assess the extent to which a correspondence exists between etch features and dislocations. In general, it should be noted that not all etch pits are necessarily formed at emergent dislocations and that not all dislocations give rise to etch features.
Figure 2.9 Setup used for the measurement of second harmonic generation for Kurtz powder technique.
An etchant is a solvent of the testing sample. But all the solvents are not the best etchants for the same sample. An etchant should satisfy the following requirement: continued etching of a surface should, in general result in no net change in the number of pits other than where pits are associated with, for example, dislocation loops. In such cases, the pits should appear or disappear in pairs. The occurrence of etch pits is an illustration of the enhanced chemical reactivity of dislocation, while in this case the different etch pit shapes on the same crystal face demonstrate the dependence of this behaviour upon dislocation character. This technique requires only very basic equipment and yields much valuable information, particularly about mechanical properties.

There are different methods to obtain preferential dislocation on a crystal surface such as Chemical etching, Thermal etching, Ionic etching and Electrolytic etching. In chemical etching the growth spiral could be removed by observing the impressions of the depressions that are left behind.

The three important parameters for performing chemical etching of a material are:

(i) Etchant
(ii) Temperature of Etching
(iii) Time of Etching

2.9 CONCLUSIONS

Single crystals grown by the various methods need to be characterized to assess the suitability of crystals for various applications. By instruments used for the characterization such as spectral, optical, thermal, electrical, SEM, etching and hardness and techniques used have been discussed in this chapter.