CHAPTER 2

CHARACTERIZATION TECHNIQUES

2.1 INTRODUCTION

Assessment of the structural, chemical and physical properties of the grown crystals has become an essential part of the crystal growth research. This enables to decide on a suitable material for a specific application and device fabrication. Also, one can find ways to improve the required qualities of the material.

Generally, characterization of a NLO crystal involves,

(i) Investigation of its crystal and molecular structures.
(ii) Confirmation of the molecular structure by identifying various functional groups in the sample.
(iii) Testing of its NLO property
(iv) Determination of the optical and electrical properties to test its suitability for possible NLO applications.
(v) Determination of the mechanical strength, thermal and other properties to check its suitability for device fabrication.

This chapter presents a comprehensive description on the techniques that have been employed to characterize the grown crystals in the present research work. The instrumentation used in each case is described briefly.
The grown crystals have been characterized using single crystal X - Ray Diffraction (XRD), powder XRD, CHN analysis, FTIR, FTIRaman, FTNMR, UV - Visible spectroscopy, PL spectroscopy, NLO studies (Kurtz Perry powder method for SHG and Z - scan technique for THG), thermal (TG - DTA and DSC), dielectric, chemical etching and hardness studies.

2.2 X - RAY DIFFRACTION ANALYSES

X - ray diffraction is one of the important techniques for material characterization. The diffraction experiments using X - rays help to study the structural properties of materials on atomic scale. The technique is also used to measure crystallite size and to calculate lattice strain, chemical composition, state of ordering and to determine phase diagrams as well.

2.2.1 Basic Principle

Crystalline substances act as three - dimensional diffraction gratings for X - ray wavelengths comparable to the spacing of crystal planes in the lattice.

![Diagram of X-ray diffraction at a crystal lattice](image)

**Figure 2.1 Diffraction of X - rays at crystal lattice**

X - rays interact with electrons in atoms and elastically get scattered. The scattered waves from many atoms in the atomic plane can interfere with each other
and if the waves are in phase they interfere constructively. These diffracted X-rays contain information regarding the electron distribution in materials. The diffracted beams are in specific directions ($\theta$), governed by the Bragg’s law which relates the wavelength of the incident X-rays ($\lambda$) and the spacings of the atomic planes ($d$) as,

$$2d \sin \theta = n\lambda \quad (2.1)$$

There are three main diffraction methods in which either $\theta$ or $\lambda$ is varied.

<table>
<thead>
<tr>
<th>Method</th>
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<tr>
<td>Laue method</td>
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<tr>
<td>Rotating crystal method</td>
<td>Fixed</td>
<td>Variable</td>
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<tr>
<td>Powder method</td>
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In practice, the widely employed techniques for characterization of crystalline materials are Single crystal (Rotating crystal) X-ray diffraction and Powder X-ray diffraction.

### 2.2.2 Single Crystal X-ray Diffraction

Single crystal X-ray diffraction is a powerful technique for the precise determination of crystallographic information such as lattice parameters, crystal system and space group of a crystalline material. As well as the molecular structure, atomic coordinates, bond lengths, bond angles, molecular orientation and packing of molecules in crystal lattice can be determined.

#### 2.2.2.1 Instrumentation and sample selection

A fully automated single crystal X-ray diffractometer consists of an X-ray generator, a goniometer, an X-ray detector and an interface to the computer.

A suitable crystal is selected (ideal dimensions are approximately $0.3 \times 0.3 \times 0.3 \text{ mm}^3$) and is fixed on the tip of a thin glass fibre using epoxy or cement, or in a loop including specific oil, which fits into the goniometer head in the diffractometer. The crystal is then aligned along the beam direction. The
monochromatic X-rays (Mo K\textsubscript{a} radiation of \(\lambda = 0.71073\text{Å}\)) are generated and directed on to the crystal plane at an angle \(\theta\). The incident rays are diffracted upon satisfaction of Bragg's relation. The detector (usually a scintillation counter) collects the diffracted rays. The intensity data of diffracted X-rays from all possible crystalline planes are collected with the help of a four circle instrument set up in the goniometer which are then used for structure determination.

![Schematic diagram of 4-circle diffractometer](http://serc.carleton.edu)

The intensity of the diffracted rays depends on the arrangement and nature of atoms in the crystal. Collection of intensities of a full set of planes in the crystal provides the complete structural information about the material. The data generated from the X-ray analysis is then processed and refined to obtain the crystal structure using certain available programs. Generally, Fourier transformation techniques are employed to determine the exact coordinates of atoms in the unit cell from this data.

The refinement cycles include positional atomic parameters and anisotropic vibration parameters. Finally, the hydrogen atom positions, if present, are determined or calculated. The structural refinement is evaluated from the agreement between the calculated and the measured structure factors. The
refinement is considered finished when the following essential conditions are fulfilled:

- The agreement factors are small enough.
- The structural model is chemically appropriate
- The estimated standard deviations of all geometrical parameters are as small as possible
- The peaks remaining in the electron density map are as small as possible.

In the present study, all the grown crystals were characterized by Enraf-Nonius CAD4 - MV31 single crystal X-ray diffractometer, a fully automated four circle instrument controlled by a computer installed at SAIF, IIT Madras, Chennai, Tamil Nadu, India and the crystal structures were solved by direct method using SHELXS - 97 program [107]; the structures were refined by full matrix least square using SHELXL - 97 program [108].

2.2.3 Powder X-Ray Diffraction

Powder X-ray diffraction analysis has a wide range of applications [109, 110] from the basic distinction between amorphous and crystalline materials through phase analysis to full profile analysis (with possibilities of microstructural characterization and refinement and solution of crystalline structures). It provides a convenient and practical means for the qualitative identification of crystalline compounds. This application is based upon the fact that an X-ray diffraction pattern is unique for each crystalline substance. Thus, if an exact match can be found between the pattern of an unknown and an authentic sample, chemical identity can be assumed.

2.2.3.1 Instrumentation and sample selection

In powder XRD, finely ground and homogenized sample is used. The sample may be held in thin walled glass or cellophane capillary tubes. The X-rays
(usually, $K_α$ radiation of wavelength $1.5418\text{Å}$ emitted from copper) required for diffraction are monochromatized by filtering with the help of foils or crystal monochrometers. These X-rays are collimated and directed onto the sample. In powder form a significant number of the crystallites can be expected to be oriented to fulfill the Bragg condition for reflection from every possible interplanar spacing. Thus, the sample and detector are rotated and the intensity of the reflected X-rays is recorded. A detector records and processes this X-ray signal and converts the signal to a count rate which is then output to a printer or computer monitor. The goniometer is designed such that the sample rotates in the path of the collimated X-ray beam at an angle $\theta$ while the X-ray detector on an arm to collect the diffracted X-rays rotates at an angle of $2\theta$. For typical powder patterns, data is collected for a $2\theta$ range of $5^\circ$ to $70^\circ$ at scan speed of $2^\circ\text{ min}^{-1}$. The position of a diffraction peak is dependent only on the size and shape of the unit cell. Each peak represents a certain lattice plane and can therefore be characterized by a Miller index.

![Figure 2.3 X-ray diffraction from a powder sample](image)

In the present study, the powder XRD patterns of the samples were recorded using PANalytical X’pert PRO diffractometer, at Nanotechnology Research Centre, SRM University, Kattankulathur, Tamil Nadu, India. The peaks in the patterns have been indexed using CELREF program.
2.3 CHN ANALYSES

CHN analysis is the most common form of elemental analyses. It used for the rapid determination of carbon, hydrogen, and nitrogen content in organic and other types of materials. It has the capability of handling a wide variety of sample types in the field of pharmaceuticals, polymers, chemicals, environmental and energy, including solids, liquids, volatile and viscous samples.

2.3.1 Basic Principle

CHN analyzer works on the principle of "Dumas method" which involves the complete and instantaneous oxidation of the sample by "flash combustion".

2.3.2 Instrumentation and sample preparation

The system is comprised of four major zones: combustion, gas control, separation and detection. In the combustion zone, samples encapsulated in tin or aluminum vials are inserted automatically or manually. The combusted sample then goes through a reduction chamber to a homogenization chamber. The resultant gases such as NO₂, CO₂, SO₂ and H₂O are separated using Frontal Chromatography, then elute through a thermal conductivity detector. This gives an output signal proportional to the concentration of individual components of the mixture.

These experimental results are analyzed by comparing them with the percentages of elements according to the chemical formula. The examined sample can be decided as the expected compound if the deviation of elemental analysis results from the calculated is less than 0.4%.

In the present study, the CHN analysis of the grown crystals were carried out using Perkin - Elmer 2400 Series II CHNS/O Analyzer operated in CHN mode. This facility is available in the Department of Chemistry, IIT Madras, Chennai, Tamil Nadu, India.
2.4 FOURIER TRANSFORM INFRA RED ANALYSIS

Infrared (IR) spectroscopy is one of the most common spectroscopic techniques used for identification of functional groups present in the molecule, both organic and inorganic. Among various practical instrumentations to obtain IR spectra, the Fourier Transform Infrared (FTIR) spectrophotometer is most widely used. This uses Michelson interferometers to create an interferogram, from which all resolution elements are determined simultaneously.

An IR spectrophotometer measures the absorption of IR radiations by a sample at various IR frequencies. Generally, the spectral data are presented as a graph of IR intensity versus IR frequency. The preferred format for qualitative analysis is in the percentage transmittance format which provides the best dynamic range for both weak and intense bands. The peaks in the spectrum give information about molecular structure with which the compound can be identified. The modern infrared instruments record spectra from an upper limit of around 4000 cm\(^{-1}\) down to 400 cm\(^{-1}\).

2.4.1 Basic Principle

The principle approach is the fact that structural features of a molecule produce characteristic and reproducible absorptions in the spectrum. The absorption of electromagnetic radiation at frequencies is correlated to the vibration of specific sets of chemical bonds within the molecule.

The fundamental requirement for absorption of infrared radiations is that there must be a net change in dipole moment during the vibration of the molecule or the functional group in the molecule.

2.4.2 Instrumentation and Sample Preparation

The FTIR spectrometer consists of an infrared source, a sample chamber with a provision for holding the sample, a monochromator, a detector and a recorder, which are integrated with a computer. Interferometric multiplex instruments make
use of the Fourier transform. At present, all commercially available infrared spectrophotometers employ reflection gratings rather than prisms as dispersing elements.

Using various sampling accessories, IR spectrometers can accept a wide range of samples in all types of gases, liquids and solids. A common method for handling solid samples is the compressed alkali metal halide pellet method (KBr pellet or disk method). With liquids, it is always beneficial to examine the sample as it is received.

For the present work, FTIR spectra were recorded using Perkin Elmer Spectrum1 FT - IR Spectrometer at SAIF, IIT Madras. The instrument can cover a region between 450 cm⁻¹ and 4000 cm⁻¹ with a resolution of 1 cm⁻¹.

2.5 FOURIER TRANSFORM RAMAN ANALYSIS

Raman spectroscopy is an invaluable technique for characterization of materials. It is a complementary technique to infrared spectroscopy. While IR is sensitive to functional groups and to highly polar bonds, Raman is more sensitive to backbone structures and symmetric bonds. Using both techniques, twice the information about the vibrational structure can be obtained than by using either alone. Fourier Transform Raman (FTRaman) spectrometer is one of the instrumentation techniques of recording Raman spectrum which makes use of Michelson interferometers.

2.5.1 Basic Principle

Raman spectroscopy is based on inelastic scattering (Raman scattering) of monochromatic light, usually from a laser source. The Raman effect is observed due to molecular deformations in electric field E determined by molecular polarizability, $\alpha$.

2.5.2 Instrumentation and Sample Preparation

An FTRaman spectrometer uses a laser of wavelength 1064 nm as an excitation source. As the spectrometer accepts various kinds of sample (bulk solids, powders, liquids, tablets, polymers, paper, etc) only a very little or no sample
preparation is required. An interferometer converts the Raman signal from the sample into an interferogram, permitting a detector to collect the entire Raman spectrum simultaneously. Usually, indium gallium arsenide or liquid nitrogen-cooled germanium detectors are used signal detectors. Application of the Fourier transform algorithm to the interferogram converts the results into a conventional Raman spectrum.

In the present investigation, FTRaman spectra of grown crystals were recorded using BRUKER RFS 27: Stand alone FTRaman Spectrometer, at SAIF, IIT Madras.

![Schematic representation of a FTRaman spectrometer](image)

**Figure 2.4 Schematic representation of a FTRaman spectrometer**

2.6 NUCLEAR MAGNETIC RESONANCE STUDIES

Nuclear magnetic resonance (NMR) can be used for structural and purity confirmation of an organic compound. By means of NMR, it is possible to study the environment of all commonly occurring functional groups as well as fragments such as hydrogen atoms attached to carbon. NMR may also be utilized for quantitative determination of compounds in mixtures.
2.6.1 Basic Principle and Instrumentation

NMR spectroscopy involves the change of the spin state of a nuclear magnetic moment when the nucleus absorbs electromagnetic radiation in a strong magnetic field [111, 112].

NMR is based on the fact that many atomic nuclei such as $^1$H, $^{13}$C, $^{15}$N, etc., oscillate like tiny gyroscopes when they are in a magnetic field. In NMR, a sample is placed in a powerful magnetic field (1 - 14 tesla), which forces the nuclei into alignment. The sample is bombarded with radio waves and, as the nuclei absorb the radio waves, they topple out of alignment with the magnetic field. Hence, the nuclei lose the energy absorbed from the radio waves and re-align themselves again to the magnetic field. By measuring the specific radio frequencies (RF) that are emitted by the nuclei and the rate at which the realignment occurs, detailed information about the molecular structure can be obtained and the molecular motion within the sample can be studied. It has proven much more efficient to excite all the proton / carbon nuclei in a molecule at the same time, followed by mathematical analysis of the complex RF resonance frequencies emitted as they relax back to the equilibrium state. This is the principle on which a pulse Fourier transform spectrometer operates.

NMR imaging is a technique to create maps, which relies on placing the sample in a spatially inhomogeneous magnetic field whose nuclear resonance frequency is matched to the radio frequency signal in a small region [113]. In general, the RF field is fixed and the magnetic field is varied over a range of a few gauss until the resonance is observed. The resonance depends on the chemical environment of the protons. The intensity of an ensemble of protons is directly proportional to the number of protons in it. The frequency, at which a proton resonates with respect to a standard sample is called chemical shift.

Chemical shifts expressed in ppm versus the standard are usually given in a dimensionless unit called delta ($\delta$). Since the chemical shift reflects the molecular structure, it can be used to determine the structures of unknown compounds and
since hydrogen is an almost universal constituent of organic compounds, the proton NMR is widely applicable along with carbon NMR.

A typical instrumentation for this technique includes a powerful magnet, radio-frequency signal generator, amplifier, detector, etc. Figure 2.10 shows the instrumentation for proton NMR from a solution. To record spectra owing to more than one elemental type of nucleus (for example $^1\text{H}$, $^{13}\text{C}$), a separate transmitter and set of coils is required for each nuclear type [114]. Usually, NMR solvents are deuterated to provide the field frequency lock signal. Most commonly used solvent for organic compounds is deuterated chloroform (CDCl$_3$). For polar compounds, acetone - d$_6$ and (Dimethyl Sulfoxide - d$_6$) DMSO - d$_6$ are often used. For highly polar and ionic compounds, D$_2$O can be used. The standard reference that was chosen is tetramethylsilane (TMS).

![Figure 2.5 Functional block diagram of a FTNMR spectrometer](image)

2.7 UV - VISIBLE - NIR SPECTROSCOPY

UV - visible - NIR spectroscopy alternatively known as electronic absorption spectroscopy is a non-destructive characterization technique which measures absorption of radiation by the material as a function of wavelengths in ultraviolet, visible and near infrared regions. The spectrometer is well suited for samples in the dissolved (solution) form. The spectral range with appropriate solvent is 200 nm to 2500 nm and also it can be used to study single crystals and powder samples.
2.7.1 Basic Principle

Absorption of UV - Visible photons by a molecule results in electronic excitation of the molecule which is characteristic of a compound. The electronic transition involves promotion of valence electrons from an electronic ground state to higher energy state, usually from a molecular orbital called HOMO to LUMO. These electronic transitions can be,

1. Transitions involving \( \pi, \sigma, \) and \( n \) electrons
2. Transitions involving charge - transfer electrons
3. Transitions involving \( d \) and \( f \) electrons

2.7.2 Instrumentation and Sample Preparation

A typical double beam UV - visible - NIR spectrophotometer is shown in Figure 2.6. In the spectrophotometer, a light source (combination of deuterium lamp for the UV region and tungsten or halogen lamp for the visible region) emits continuous radiation. The beam of light is separated into its component wavelengths by a diffraction grating. A slit positioned next to grating sends a narrow monochromatic beam into the next section of the spectrophotometer.

Light from the slit then falls onto a rotating disc which directs the light towards a sample cell and reference cell alternatively with the help of different segments in the disc. The sample cell is filled with the solution in which the sample is dispersed or dissolved while the reference cell is filled with the pure solvent. (The instrumentation for solid state UV - visible absorption spectroscopy is slightly different from the solution phase experiments). After passing through the cells the second rotating disc transmits light intensities to a detector. The detector converts the intensities into corresponding current signals which are read by a computer. The computer compares the transmitted intensities from the sample cell and reference cell and then calculates the absorbance using,

\[
A = \log_{10} \left( \frac{I_0}{I} \right) \tag{2.2}
\]
where, \( A \) denotes absorbance, \( I \) is sample cell intensity and \( I_o \) is the reference cell intensity.

The output is a plot of absorbance against wavelength. For transmission study the plot is between percentage of transmission and the wavelength.

For the present work, the UV - Visible absorption spectra were recorded at SAIF, IIT Madras using CARY 5E UV - VIS - NIR SPECTROPHOTOMETER.

![Schematic representation of a UV - Visible - NIR spectrophotometer](image)

**Figure 2.6 Schematic representation of a UV - Visible - NIR spectrophotometer**

### 2.8 PHOTOLUMINESCENCE SPECTROSCOPY

Photoluminescence (PL) analysis is widely used in science and industry to evaluate the properties of a material such as band gap energy, *impurity levels and recombination mechanisms.* Photoluminescence is the direct emission of light from an excited medium.

#### 2.8.1 Basic Principle

When a material is treated with an optical source having energy greater than the band gap of the material, electrons are pumped to excited states. After a relaxation period these electrons fall back to lower states through radiative recombination pathways. Because of the thermal relaxation, the emitted photons have no correlation with the excitation process.
2.8.2 Instrumentation and sample preparation

In a typical PL Spectrofluorimeter (Figure 2.7), a light source (usually, Xenon lamp) emits light typically in the range between 180 nm and 1550 nm. A monochromator (grating) selectively transmits the light in a narrow range centered about the specified excitation wavelength. The transmitted light passes through adjustable slits that control magnitude and resolution by further limiting the range of transmitted light. The filtered light is then made to fall on the sample kept in its compartment which results in light emission at characteristic wavelengths. An emission monochromator positioned next to the sample cell helps to narrow down the emission wavelength. The emission monochromator is placed at 90° with respect to the excitation light path in order to eliminate back ground signal and minimize noise due to stray light. Finally the monochromatized light exits through adjustable slits and falls on a detector. The detector generates a voltage proportional to intensity of emitted light. The intensity and spectral content of this photoluminescence is a direct measure of various important material properties [115].

In the present study the PL spectra were recorded at SAIF, IIT Madras using JY Flurolog - 3 - 11 Spectrofluorimeter which has a maximum resolution of 0.2 nm.

![Functional block diagram of a Spectrofluorometer](image-url)
2.9 THERMAL ANALYSES

The thermal analysis technique comprises of a series of methods, which detect the changes in the physical properties such as mass, temperature, enthalpy, dimension, dynamic characteristics, etc. of the given substance by the application of heat. It finds its application in finding the purity, crystallinity and thermal stability of the chemical substances under study. Sometimes it is used in the determination of the composition of complex mixtures. The following are the popular methods under this technique:

2.9.1 Thermogravimetric Analysis (TGA)

In this technique the change in sample weight is measured while the sample is heated at a constant rate (or at constant temperature), under air (oxidative) or nitrogen (inert) atmosphere. This technique is effective for quantitative analysis of thermal reactions that are accompanied by mass changes, such as evaporation, decomposition, gas absorption, desorption and dehydration.

A TGA consists of a sample pan that is supported by a precision balance. That pan resides in a furnace and is heated during the experiment. The mass of the sample is monitored during the experiment. A sample purge gas controls the sample environment. This gas may be inert or a reactive gas that flows over the sample and exits through an exhaust. The micro - balance plays a significant role; during measurement the change in sample mass affects the equilibrium of the balance. This imbalance is fed back to a force coil, which generates additional electromagnetic force to recover equilibrium. The amount of additional electromagnetic force is proportional to the mass change. During the heating process the temperature may go as high as 1600 °C inside the furnace.
2.9.2 Differential Thermal Analysis (DTA)

This technique measures the temperature difference between a sample and an inert reference material as a function of temperature as they are subjected to identical thermal cycles. Here the heat flow to the sample and reference remain the same rather than the temperature. It provides vital information of the materials regarding their endothermic and exothermic behaviour at high temperatures.

2.9.3 Differential Scanning Caloriemeter (DSC)

This technique is more or less similar to DTA except that it measures the amount of heat absorbed or released by a sample as it is heated or cooled or kept at constant temperature (isothermal). Here the sample and reference material are simultaneously heated or cooled at a constant rate. The difference in temperature between them is proportional to the difference in heat flow (from the heating source i.e. furnace), between the two materials. This technique determines the heat of melting and melting point, glass transition temperature (Tg.), endothermic & exothermic behaviour. The instrumentation is exactly similar to that of DTA except for the difference in obtaining the results.
In the present work, the combined TGA and DTA of the grown crystals were carried out using SDT Q 600 V8.3 BUILD 101 and DSC using NETZSCH at CECRI, Karaikudi, Tamil Nadu, India.

2.10 DIELECTRIC STUDIES

Dielectric studies help to analyze the optical quality of the sample and presence of defects. These parameters greatly influence the performance of nonlinear optical materials in their applications. The dielectric studies involve determination of dielectric constant ($\varepsilon_r$) and dielectric loss (proportional to dissipation factor, $D$). Dielectric loss quantifies a dielectric material's inherent dissipation of electromagnetic energy into heat. It can be parameterized in terms of either the loss angle ($\delta$) or the corresponding loss tangent ($\tan \delta$).

2.10.1 Basic Principle

The measurement is based on the fact that a dielectric medium gets polarized when it is inserted between the charged plates of a capacitor. The dielectric constant can be determined by measuring the capacitance, $C$ of the dielectric enclosed between the plates. If $A$ is the area of the plate and $d$ is the separation between the plates then the dielectric constant,
\[ \varepsilon_r = \frac{Cd}{\varepsilon_0 A} \]

(2.3)

Usually, the dielectric loss is presented in terms of dissipation factor, \( D \) and the dissipation factor is given in terms of reactance, \( R \) as,

\[ D = \tan \delta = \frac{I}{\omega RC} \]

(2.4)

\[ 2.10.2 \quad \text{Instrumentation And Measurement} \]

In the measurement, a parallel plate capacitor is formed by placing a silver coated sample between two copper electrodes. A special care should be taken to ensure that the silver paint does not spread to the sides of the crystal. The capacitance of the parallel plate capacitor is measured for frequencies from 50 Hz to 5 MHz at room temperature using which the capacitance, \( C \) of the sample is calculated. The dielectric loss is also calculated as a function of frequency. The measurements can also be done at different temperatures using the four-probe sample holder housing the chromel-alumel thermocouple for temperature measurements.

In the present study, the measurement of capacitance and dissipation factors of all the grown crystals were made using HP 4275 Multi frequency LCR meter and HIOKI 3532-50 LCR HITESTER present in the Department of Physics, Loyola College, Chennai, Tamil Nadu, India.

\[ 2.11 \quad \text{CHEMICAL ETCHING STUDIES} \]

Etch pitting is the simplest, most widely employed method to detect crystal symmetry, dislocations and dislocation density. Investigations of the properties of single crystals have relied upon the measurement of density and distribution of dislocations. Since dislocations are regions of disorder, they can be revealed through the use of an etchant that preferentially attacks these locations.
Etching is the selective dissolution of the crystal, a reverse phenomenon of growth. The basis of etching technique is the fact that the region where dislocations intersect the surface of the crystal is energetically different from the surrounding area. This is reflected as difference in chemical or physical “reactivity”. In chemical etching process, a suitably prepared crystal is immersed into a specific liquid or gas at ambient or elevated temperatures for a certain time period. The etch pits are formed on the surface of the crystal where dislocations are present (which can be examined using a suitable optical microscope). On a freshly cleaved surface, newly formed (fresh) dislocations as well as grown - in (old) dislocation can be revealed. Some etching solutions attack only the fresh dislocations while other etchants attack only old dislocations. In general, fresh dislocations are more easily revealed, probably because of the strain field associated with the fresh dislocation. Depending on the etch composition, surface quality and orientation there can be a one - to - one correlation between etch pit density and dislocation density. However, etch pits can also occur at precipitates and inclusions. Thus, care is required in interpreting the results of etching process.

In the present work, etching studies were carried out at Nuclear Physics Department, University of Madras, Chennai, India. To analyze the etch patterns, optical microscopy (Reichert Polyvar 2 MET Microscope) has been used.

2.12 VICKER’S MICROHARDNESS STUDIES

The mechanical property plays a vital role in device fabrication. The applicability of a crystal depends on its mechanical strength. Harder crystals do not pose much problem while cutting and polishing whereas the soft crystals need great care while handling. The mechanical strength of a crystal can be judged by measuring its hardness.

The hardness of a crystal is primarily concerned with the response of the crystal to forces or loads depending on its plastic and elastic properties.
In Vicker’s hardness test an indentation is made on the smooth surface of the test material, by means of applying a load \( (P) \) on the surface for fixed duration (about 10 seconds), through a pyramid - shaped diamond - indentor of top angle 136°. Then the diagonal length \( (d) \) of the indentation is measured of the hardness \([116, 117]\). The hardness is proportional to Vicker’s hardness number,

\[
H_v = \frac{1.8544P}{d^2} \text{kg/mm}^2
\]  

\[\text{(2.5)}\]

![Diagram of pyramid-shaped diamond indentor](image)

**Figure 2.10 Schematic of diagram pyramid - shaped diamond indentor**

In microhardness measurement a microscope with a calibrated eyepiece is used to observe the indentation mark on the crystal surface and measure the diagonal length (in \( \mu \text{m} \)) of the indentation mark.

In the present work, Vickers hardness measurement was carried out on the grown crystals at the Department of Nuclear Physics, University of Madras, Chennai, Tamil Nadu, India, using a Reichert Polyvar 2 MET Microscope with a Microduromat 4000E hardness controller.
2.13 NONLINEAR OPTICAL STUDIES

Among various nonlinear optical (NLO) processes, the present work mainly focuses on Second Harmonic Generation (SHG) and Third Harmonic Generation (THG). The noncentrosymmetric crystals grown in the present work have been characterized for SHG by Kurtz Perry powder technique while the centrosymmetric crystals have been characterized for THG by Z - scan technique.

2.13.1 Kurtz Perry Powder Method

The Kurtz Perry powder technique is extremely valuable tool for initial screening of materials for frequency doubling activity. It is a convenient method for both qualitative and quantitative Second Harmonic Generation (SHG) measurements [3]. This method measures an average SHG efficiency of microcrystalline powders and predicts the phase matching direction in crystals.

2.13.1.1 Basic Principle

For a single crystal, only certain orientations (phase matching angles) in respect to incoming photons will produce SHG. However, by grinding the single crystal into powder, one arrives at a large number of randomly oriented small crystallites whose SHG does not depend on the incoming light direction.

2.13.1.2 Instrumentation and Measurement

The experimental setup for measuring SHG efficiency is shown in the Figure 2.11. The crystals are powdered and graded with standard sieves to obtain a uniform particle size. Then, they are uniformly packed in a capillary tube. A fundamental laser beam from a Q - switched, mode locked Nd:YAG laser (of wavelength 1064 nm, pulse width 8 ns at a repetition rate of 10 Hz) is made to fall normally on the powder sample. The power of the incident beam is measured using a powermeter. When the monochromatic light passes through the sample, a beam of green light (of wavelength 532 nm) is generated due to SHG process. Filters behind the samples are used to remove the fundamental and leave only the second harmonic
signal. The assembly of an oscilloscope and photomultiplier tube (PMT) is employed to measure the light emitted by the sample. The measured intensity is compared with that emitted by a reference material measured under similar condition. The reference materials are usually, KDP and Urea.

![Functional block diagram of SHG Measurement](image)

**Figure 2.11 Functional block diagram of SHG Measurement**

The SHG measurements using Kurtz Perry powder technique of the noncentrosymmetric crystals grown in the present work were carried out at Inorganic and Physical Chemistry Department, Indian Institute of Science (IISc), Bangalore, India.

### 2.13.2 Z-Scan Technique

In the present investigation, the centrosymmetric crystals grown in the work have been subjected to Z-scan technique to study their intensity dependent nonlinear optical properties.

Z-scan technique is a sensitive and popular measurement technique for characterizing third order nonlinear optical materials in solids, liquids and liquid solutions [118, 119]. The basic principle of Z-scan technique is the spatial beam distortion which arises from an optically induced nonlinear refractive index.

This technique is particularly useful when the optical nonlinearity in a material is caused by both nonlinear absorption and nonlinear refraction. This
technique enables simultaneous measurement of nonlinear index of refraction, $n_2$ and nonlinear absorption coefficient, $\beta$. Only these quantities decide the third order NLO susceptibility $\chi^{(3)}$ as are related to the real and imaginary parts of $\chi^{(3)}$, respectively.

Figure 2.12 illustrates the experimental arrangement for $Z$-scan measurements. In this technique, a single Gaussian laser beam is tightly focused using a lens on the sample. By translating the sample through the focus, the change in the far-field intensity is monitored. Here, the sample is translated along the axis of the laser beam, (taken to be the $Z$-axis) from the left to the right of the focal point. The transmitted intensity is first measured keeping an aperture in front of the detector thus obtaining closed aperture $Z$-scan data. Next, the transmittance is measured without aperture as the sample is translated along the $Z$-direction in order to obtain the open aperture $Z$-scan data. The sample itself behaves as a thin lens for the laser beam propagating through it. When the sample is translated along the beam path, its effective focal length changes depending on the intensity of the converging laser beam. This results in a change in the intensity distribution in the far-field zone and is measured by the closed aperture $Z$-scan technique. In addition to this refraction due to nonlinearity, the medium also possesses nonlinear absorption, which is significant in the open aperture measurement. Thus, collectively, the closed and the open aperture data allow us to calculate values of both $n_2$ and $\beta$.

Figure 2.12 Experimental set up for $Z$-scan technique
2.13.2.1 Measurement of NLO Parameters

In third order NLO materials, index of refraction, $n$ and nonlinear absorption $\alpha (I)$ can be expressed as,

$$n = n_0 + n_2 I \quad (2.6)$$

$$\alpha (I) = \alpha_0 + \beta I \quad (2.7)$$

where $n_0$ is the linear refractive index, $n_2$ (cm$^2$/W) is the nonlinear part of the index (optical Kerr coefficient), $\alpha_0$ is the linear absorption coefficient and $\beta$ is the nonlinear absorption coefficient.

![Figure 2.13 Model Transmittance in closed aperture Z - scan](image)

The peak followed by a valley in the closed aperture Z - scan curve (dotted line in Figure 2.13) is the signature for negative index of refraction (self-defocusing) while valley followed by a peak (solid line in Figure 2.12) is for positive index of refraction (self-focusing). The local variation of refractive index with temperature results in phase distortion of the propagating beam.
In an open aperture Z - scan plot, the enhanced transmission near the focus is indicative of the saturation of absorption at high intensity. Absorption saturation in the sample enhances the peak and decreases the valley in the closed aperture Z - scan thus distorting the symmetry of Z - scan curve about Z = 0. The value of $\beta$ can be obtained from a theoretical fit performed on the experimental data of the open aperture measurement and the value of $n_2$ can be obtained from a closed aperture Z - scan measurement.

The on - axis phase shift at the focus $|\Delta \phi_0|$ is related to the difference in the peak and valley transmission $\Delta T_{p,v}$ as,

$$\Delta T_{p,v} = 0.406(1 - S)^{0.25} |\Delta \phi_0|$$

(2.8)

where $S$ is the aperture linear transmittance and is given as,

$$S = 1 - \exp\left(-2r_0^2/\omega_0^2\right)$$

(2.9)

with $r_0$ denoting the aperture radius and $\omega_0$ denoting the beam radius at the aperture in the linear regime. The nonlinear refractive index is given by, [120, 121]

$$n_2 = |\Delta \phi_0|\lambda / 2\pi I_0 L_{\text{eff}}$$

(2.10)

where $\lambda$ is the laser wavelength, $I_0$ the intensity of the laser beam at focus $Z = 0$, The effective sample length, $L_{\text{eff}}$ ($L_{\text{eff}} = [1-\exp(-\alpha L)/\alpha]$ ), takes the linear absorption coefficient $\alpha$ and sample thickness $L$ into account.

The nonlinear absorption coefficient, $\beta$ is given as,

$$\beta = 2\sqrt{2\Delta T / I_0 L_{\text{eff}}}$$

(2.11)

where $\Delta T$ is the one valley value at the open aperture Z - scan curve. The value of $\beta$ will be negative for saturable absorption and positive for two photon absorption. The real and imaginary parts of the third order nonlinear optical susceptibility $\chi^{(3)}$ are defined as,
\[ \text{Re} \chi^{(3)} (\text{esu}) = 10^{-4} (\varepsilon_0 C^2 n_0^2 n_2) / \pi \ (\text{cm}^2/\text{W}), \]  
(2.12)

\[ \text{Im} \chi^{(3)} (\text{esu}) = 10^{-2} (\varepsilon_0 C^2 n_0^2 \lambda \beta) / 4\pi^2 \ (\text{cm}^2/\text{W}), \]  
(2.13)

where \( \varepsilon_0 \) is the vacuum permittivity, \( n_0 \) is the linear refractive index of the sample and \( c \) is the velocity of light in vacuum.

In the present work, the Z - scan measurements were carried out using a laser of wavelength 632.8 nm in the Department of Physics, National Institute of Technology, Tiruchirappalli, Tamil Nadu, India

2.14 CONCLUSION

In this Chapter, the basic principles of characterization techniques, such as X - ray diffraction (Single Crystal XRD and Powder XRD), Fourier transform infrared, Fourier transform Raman, Nuclear Magnetic Resonance, UV - Visible and Photoluminescence spectroscopic techniques, Dielectric, Chemical Etching and Vicker’s Microhardness studies, Kurtz Perry Powder and Z - scan Measurement techniques are discussed.