CHAPTER - 2
TOOLS AND TECHNIQUES FOR CHARACTERIZATION

2.1 INTRODUCTION

Characterization of materials outlined as complete description of its physical and chemical properties. Hence characterization renders a basis for realizing and enhancing the characteristics of materials towards their applications. In crystal growth to analyse the nature and properties of the grown crystal, it should be subjected to various characterization techniques, in which characterization comprises of an evaluation of the chemical composition, structure, defects, thermal stability, conductivity and optical properties. The measurement of optical properties admits the study of optical transmission and absorption of the crystal. SHG conversion efficiency coefficient, electro-optical coefficient and structural dependence of these properties lead to the complete understanding of the optical behaviour of the crystal. This chapter discusses the principles of various experimental techniques employed in the characterization of the grown crystals.

2.2 X-RAY DIFFRACTION ANALYSIS

2.2.1 Single Crystal X-ray diffraction and Morphological Studies

Single crystal X-ray diffraction is a powerful technique, used to study the structure of solids (organic, inorganic or metallorganic) which provides accurate and precise measurements of atomic and molecular dimension. In particular the detailed information about the internal lattice of crystalline
substances, including unit cell dimensions, bond-lengths, bond-angles, molecular orientation, morphology and packing of molecules in single crystals can be determined by X-ray crystallography analysis. Single crystal X-ray diffractometer collects intensity data required for structure determination.

According to Max von Laue (1912), the crystalline substances act as three dimensional diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice. Constructive interference of monochromatic X-ray is the basis for X-ray diffraction, in which the interaction of X-rays with the sample brings out the constructive interference and a diffracted ray, when conditions satisfy the Bragg’s Law. The Bragg’s condition for reflection can be written as, \(2d \sin \theta = n\lambda\), where ‘d’ is the interplanar spacing of the incident plane, ‘\(\lambda\)’ is the wavelength of X-rays and ‘n’ is a positive integer. Intensities of reflections of all Miller indices within a specified reciprocal radius (usually 25° for MoK\(_\alpha\) and 68° for CuK\(_\alpha\)) is necessitated in crystal structure determination, while unit cell parameters depend only on direction of reflections. In single crystal studies, the specimen should be smaller than the cross section diameter of the beam. The crystal can be broken off to get a larger sample and the best fragment be selected from it. The intensity of the diffracted rays depends on the arrangement and nature of atoms in the crystal. The collection of intensities on a full set of planes in the crystal contains the complete structural information about the molecule.

Fourier transformation techniques are used to determine the exact coordinates of atoms in the unit cell from this data. With the set of X-ray diffraction data collected, the measurement of unit cell parameter, space groups, molecular structure of the crystalline solids and Miller indexing for the
different faces of the crystal are possible. The cell parameter is simply the dimension of the basic molecular brick with which the crystal is built and the space group tells us the symmetry with which the molecules are arranged within the unit cell. All the geometrical features of molecules (bond distance, bond angles, torsion angles between bonds, dihedral angles between planes etc.) may be obtained from the coordinates.

The unit cell parameters and crystal structure of the grown crystals were determined from single crystal X-ray diffraction data. The single crystal data were obtained using ENRAF NONIUS CAD-4 diffractometer with MoKα (0.71073Å) radiation. The unit cell parameters of the grown crystals were measured at 295 K. The crystal data were integrated using Bruker SAINT; corrections for absorption and decay were applied using Bruker SAINT. The crystal structure was solved by the direct method using the SHELXS-97 program and refined by the SHELXL97 program.

Morphology predicts the external morphology of a crystalline material from its internal crystal structure. The studies of crystal growth morphology are important for its device applications, in which only some particular facet is usable towards desired applications.

Bravais-Friedel-Donnay-Harker has made the first attempt to relate crystal morphology to internal structure at the molecular level. The relationship between the crystal morphology and the internal arrangement of atoms allows the prediction of crystal shapes, the development of tailor-made additives, and the control of solvent and impurity effects.
Morphology allows researchers both in the study of particle shape and considers the effects of altering the growth rate of particular faces on crystal morphology. In the present work, measurements of morphological planes were located using ENRAF NONIUS CAD4 single crystal X-ray diffractometer.

2.2.2 X-ray powder diffraction Studies

The powder X-ray method is useful for samples that are difficult to obtain in single crystal form. The powder X-ray diffraction method is used for exploration of the internal arrangement of atoms in a crystal. In particular, this method is used to determine the value of lattice parameters accurately. Lattice parameters are the magnitudes of the unit vectors \(a\), \(b\) and \(c\) and the angles, \(\alpha\), \(\beta\) and \(\gamma\) which define the unit cell of the crystal. The powder diffraction method involves the diffraction of monochromatic X-rays by a powder specimen. Monochromatic usually means a strong \(K_\alpha\) characteristic component of the filtered radiation from an X-ray tube operated above the \(K_\alpha\) excitation potential of the target material.

Selection of \(K_\alpha\) renders the incident beam to be a highly monochromatised one. The focusing on monochromatic geometry results in narrower diffracted peaks and low background at low angles.

The sample is mounted vertically to the Seemann-Bohlin focusing circle with the scintillation counter tube moving along the circumference of it. It is possible to record the diffracted beam from 2 to 160°. The diffractometer is connected to a computer for data collection and analysis.
The scintillation counter tube can be moved in steps of 0.01° by means of a stepper motor and any diffracted beam can be closely scanned to study the peak profile. This arrangement is achieved practically in the Debye-Scherrer camera. A very small amount of powdered material is taken into a fine capillary tube made from glass that is accurately aligned to be in the centre of the camera. X-rays enter the camera through a collimator. The powder diffracts the x-rays in accordance with Bragg’s law to produce cones of diffracted beams. These cones intersect a strip of photographic film located in the cylindrical camera to produce a characteristic set of arcs for the film. When the film is removed from the camera, flattened and processed, it shows the diffraction lines and the holes for the incident and transmitted beams. There are always two arcs in the X-ray beams, $K_α$ and $K_β$, this causes the highest angle back reflected arcs to be doubled. The results of the procedure are commonly presented as peak positions at $2θ$ and X-ray counts (intensity) in the form of a table or an x-y plot, known as diffractogram. For determination of unit cell parameters, each reflection must be indexed to specific Miller indices $(h, k, l)$. Nowadays, many types of software are available in market for powder XRD data analysis.

A Rich Seifert X-ray powder diffractometer with CuK$_{α1}$ radiation of $λ = 1.5406$ Å was used to measure the cell parameters of the grown crystal. The diffraction pattern was recorded within Bragg’s angle ranges $5° < 2θ < 70°$. The detector used to be a scintillation counter. The sample was scanned at a rate of $1° \text{min}^{-1}$. 
The powder sample was mounted on a quartz support to minimize background. The various planes of reflection were indexed using XRDA 3.1 program and the lattice parameters were evaluated.

2.2.3 High-Resolution X-ray diffraction Study

Crystals grown from solution are usually having defects due to the variation in growth rate, temperature fluctuation and solvent inclusions. It induces different types of effects such as; interstitial, line and vacancy. Hence crystals are influenced by such defects towards its applications. For this purpose, high resolution X-ray diffraction (HRXRD) is a suitable method to analyse the crystalline perfection. Lal et al (1989) developed the multicrystal X-ray diffractometer to analyse the crystalline perfection of crystals by high resolution X-ray diffraction at the National Physical Laboratory, New Delhi, India. There are two instrumental configurations (double & triple axes) for HRXRD. In the double-axes experiment, the detector does not discriminate between different diffraction angles 2\(\theta\). In the triple-axes experiment, a slit or analyzer crystal determines the angular acceptance of the detector. In the present work, PANalytical X’Pert PRO MRD high-resolution XRD system, with CuK\(\alpha\) radiation, was employed to assess the crystalline perfection the crystals. The rocking curves of the crystals for the (200) diffraction planes were recorded in symmetrical Bragg geometry using the (100) natural facets performing at \(\omega\) scan [Bhagavannarayana et al (2010)] with a triple-axis geometry.

The monochromated X-ray beam incident on the specimen was obtained using a hybrid two-bounce Ge (220) monochromator with a parabolic
multilayer mirror assembly. The diffracted beam from the specimen was detected using a scintillation detector with a triple-axes three bounce Ge (220) analyser. The specimen crystal was aligned in the (+, −, −, +) configuration. Due to the dispersive configuration, though the lattice constant of the monochromator crystal(s) and the specimen is different, the unwanted dispersion broadening in the diffraction curve (DC) of the specimen crystal is insignificant. The specimen was rotated about the vertical axis, which is perpendicular to the plane of diffraction, with a minimum angular interval of 0.4″. The rocking or diffraction curve was recorded by changing the glancing angle (angle between the incident X-ray beam and the surface of the specimen) around the Bragg diffraction peak position θ_B (taken as zero for the sake of convenience) starting from a suitable arbitrary glancing angle and ending at a glancing angle after the peak so that all the meaningful scattered intensities on both sides of the peak include in the diffraction curve.

Diffraction curves (DC) can be obtained using Lorentz fit which depicts the internal structural very low (tilt angle ≤ 1 arc min) and low angle (tilt angle > 1 arc min but less than a degree) boundaries [Bhagavannarayana et al (2005)]. The DC was recorded by the so-called ω scan wherein the detector was kept in the same angular position 2θ_B with wide opening for its slit.

This arrangement is very appropriate to record the short range order scattering caused by the defects or by the scattering from local Bragg diffractions from agglomerated point defects or due to low angle and very low angle structural grain boundaries [Bhagavannarayana et al (2010)]. The specimen was first lapped and chemically etched in a non-preferential
etchant of water and acetone mixture in 1:2 volume ratio in order to remove the non-crystallized solute atoms remained on the surface of the crystal and the possible layers which may sometimes form on the surfaces of crystals grown by solution methods [Bhagavannarayana et al (2006)] and also to ensure the surface planarity.

2.3 FOURIER TRANSFORM INFRARED (FT-IR) ANALYSIS

To examine the chemical applications, Fourier Transform Spectroscopy of both the far-infrared and infrared regions was introduced in the late 1960s. Fourier Transform Spectroscopy is a simple mathematical technique to resolve a complex wave into its frequency components. It is an easy way to identify the presence of certain functional groups in a molecule. The conventional IR spectrometers are not of much use for the far IR region, as the sources are weak and the detectors are insensitive.

FT-IR has made this energy-limited region more accessible. It has also made the mid–infrared (4000-400 cm\(^{-1}\)) more useful. Conventional spectroscopy, called the frequency domain spectroscopy, records the radiant power as a function of frequency. In the time domain spectroscopy, the change in radiated power is recorded as a function of time.

Fourier Transform Spectrometer, a time domain plot is converted into a frequency domain spectrum. The actual calculation of the Fourier transforms of such systems is done by means of high - speed computers.
2.3.1 Experimental procedure

The FT-IR spectrometer consists of an infrared source, a sample chamber with a provision for holding solids, liquids and gases, monochromator, a detector and a recorder, which are integrated with a computer. At present, all commercially available infrared spectrophotometers employ reflection gratings rather than prisms as dispersing elements. Interferometric multiplex instruments employing the Fourier transform are now finding more general applications in both qualitative and quantitative infrared measurements. 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 a spectrum is carried out mathematically with a dedicated online computer.

The spectrometer consists of global and mercury vapor lamp as sources. An interferometer chamber comprising of KBr and Mylar beam splitters is followed by a sample chamber and a detector. The spectrometer works under vacuum condition. Solid samples are dispersed in KBr or polyethylene pellets depending on the region of interest. This instrument has a resolution of 0.1 cm$^{-1}$. Signal averaging, signal enhancement, baseline correction and other spectra manipulations are possible with multitasking OPUS software on the dedicated PC/AT 486. Spectra are plotted on an HP plotter and data can be printed.

Recording of the IR spectrum for solid sample is more difficult because the particles reflect and scatter the incident radiation and therefore
transmittance is always low. Three different techniques are employed commonly in recording such spectra. For solid compounds that are insoluble in the usual solvents, a convenient sampling method is the Pressed–Pellet Technique. A few milligrams of the sample are ground together in an agate or a mullet mortar with about 100 times the quantity of a material (the matrix) transparent to the infrared. The usual material is KBr, although other compounds such as CsI, TIBr and Polyethylene are used in special circumstances. The ground powder is finally introduced into a mini pressing arrangement made from two half-inch diameter stainless steel bolts and a stainless steel nut.

The FT-IR spectrum was recorded using Perkin Elmer spectrum one FT-IR spectrometer in the region 4000–400 cm\(^{-1}\) at room temperature by KBr pellet technique and each IR spectrum was acquired in 10 scans at 0.5 cm\(^{-1}\) resolution. The band intensities are expressed in transmittance (%).

2.4 FOURIER TRANSFORM RAMAN (FT-RAMAN) ANALYSIS

FT-Raman technique is predominantly applicable to the qualitative and quantitative analysis of covalently bonded molecules. It is a non-destructive technique used for molecular vibration modes. The various functional groups present in the molecule can be assigned by comparison of the spectra with characteristic functional group frequencies.

As the positions of the bands are directly related to the strength of the chemical bond, a large number of investigations including intermolecular interactions, phase transitions and chemical kinetics can be carried out using this branch of spectroscopy. It is applicable for high temperature studies. In this
technique, low wave number regions can also examine. Raman Spectroscopy is based on the inelastic (Raman) scattering of radiation by the molecules. The different selection rules for the processes make these techniques mutually complimentary and together they provide the complete vibrational structure of the molecule. Fourier Transform method increases the signal to noise ratio and reduces the measurement time. In Raman spectroscopy, usually a laser is the excitation source in the visible spectral region (Argon or Krypton laser as the excitation source). However, in the FT-Raman technique Nd: YAG laser, 1064 nm is used as a source. FT-Raman is particularly useful in the case of coloured samples that absorb light in the visible range and undergo fluorescence.

In the present work the Raman spectral measurements were made using FT-Raman Bruker RFS 27: S Raman module. An air cooled diode pumped Nd: YAG laser, operated at 1064 nm and a power output of 100 mW was used as a source. The spectra were traced in the range 3500–50 cm\(^{-1}\) with 500 scans at 0.1 cm\(^{-1}\) resolution.

### 2.5 NMR SPECTROSCOPY

Nuclear Magnetic resonance (NMR) is a powerful and versatile spectroscopic technique for investigating the molecular structure and dynamics. It involves reorientations of nuclear spins with respect to an applied static magnetic field.

The overall process can be understood by using classical arguments, but quantum treatment is needed in order to comprehend the details of the technique, especially those related to spin–spin interactions. While the proton is the most frequently studied nucleus, almost every element has an isotope active
in NMR. Multipulse and multidimensional Fourier Transform NMR techniques provide an unlimited diversity of possibilities for simplifying and interpreting complicated spectra, thus allowing resolution of the three dimensional structure of macromolecules.

As a non–destructive analytical technique, it is used in chemistry, agriculture, food science and the characterization of materials. Transient magnetic–field gradients applied across a sample allow the acquisition of images of great value for medical diagnosis.

2.5. 1 Instrumentation

NMR is a spectroscopic technique which provides information about the structure and some dynamic properties of a sample from the analysis of the interaction between the magnetic moments of sample nuclei and an applied electromagnetic wave by subjecting the sample to a static magnetic field. Nuclear magnetic moments will be introduced before proceeding to analyse their interaction with electromagnetic radiation. The nuclear magnetic moments interact with an applied magnetic field as a magnet does; its energy depends on the moduli and relative orientation of the magnetic moment and magnetic field vectors.

The commonly used NMR spectrometer is the Continuous wave (CW) NMR spectrometer which detects the resonance frequencies of nuclei in a sample placed in a magnetic field by sweeping the frequency of RF radiation through a given range and directly recording the intensity of absorption as a function of frequency. The essential features of the same are CW–NMR spectrometer (i) Powerful magnetic annexed by a sweep generator.
The magnets used here are large permanent or electromagnets, capable of producing strong, stable and homogenous magnetic field over the area occupied by the sample.

These magnets owe their remarkable strength to the superconducting properties of certain metals when cooled to extremely low temperature. The magnet is cryostically controlled although the sample is held at the room temperature by being thermally isolated. (ii) The sample probe holds the sample between the poles of the magnet in the strongest homogeneous part of the magnetic field.

The probe permits the sample tube to be spun, usually by an air jet directed towards a spinner turbine. (iii) Radio frequency oscillator generates radio frequency waves by electronic multiplication of the natural frequency of quartz crystal contained in a thermostatic block. Different crystal sources and transmitters are used for different resonance frequencies. The Radio frequency oscillator coil is installed perpendicular to the magnetic field and transmits radio waves of fixed frequency to a small coil that encircles the sample in the probe. The radio frequency source is associated with a power controlling device so that the level of RF power can be varied and adjusted empirically to get the best response. (iv) Radio frequency receiver and detector is installed perpendicular to both the magnetic field and oscillator coil. The sample in the NMR probe gives information or data which has been detected as an analog signal or voltage. Multiple amplification of the signal is done before they are fed to the output devices. The coil of RF receiver or detector is tuned to the same frequency as the transmitter. When the precessional frequency is in
unison with the radio frequency, the nuclei induce an emf in the detector coil by virtue of the change in the magnetic flux following flip over.

The signal is amplified and sent to the recorder (v) Recorder and Integrator forms the final part of the NMR spectrometer. The signal is usually sent directly to the recorder or oscilloscope. The oscilloscope is useful for fast scanning of the spectrum and allows preliminary adjustments to be made, like setting optimum sensitivity or gain and electronic filtering of the signal.

The recorder records the spectrum as a plot of the resonance signal versus the strength of the magnetic field. The strength of the resonance signal is directly proportional to the number of the nuclei resonating at the field strength. Most spectrometers are equipped with automatic integrators to measure the area under the observed signal. Such an area is proportional to the number of resonating nuclei giving the signal. Sample preparation for recording NMR spectra requires complete dissolution of required amount of the sample in the appropriate volume of NMR solvent. Carbon tetra chloride, D₂O and Chloroform (CDCl₃) are commonly used solvent. CDCl₃ is the most commonly used solvent as it dissolves compounds of reasonably varying polarity. If a compound is only sparingly soluble in this solvent, DMSO–d₆ may be added dropwise to increase the polarity of the solvent. Bruker AVANCE III 500 MHz spectrometers are used to record the ¹H NMR and ¹³C NMR spectra for the present investigation.
2.6 UV-VIS-NIR SPECTROSCOPY

UV-Vis-NIR spectroscopy is useful to characterize the absorption, transmission, and reflectivity of a variety of compounds associated with changes in the spatial distribution of electrons in atoms and molecules. In practice, the electrons involved are usually the valence or bonding electrons, which can be excited by absorption of UV or visible or near IR radiation.

Excitation of a bound electron from the highest occupied molecular orbital increases the spatial extent of the electron distribution, making the total electron density larger and more diffuse, and often more polarisable. A vibrationally excited state of the molecule contains rotational excitation and electronically excited state of a molecule also contains vibrational excitation.

The probability of electronic transitions determines the intensity of spectral lines. There must be a large overlap between the vibrational states in the initial and the final electronic states to have a large absorption cross-section, or high probability that the molecule will absorb/emit radiations. Electronic transitions are possible for a wide range of vibrational levels within the initial and final electronic states. Ultraviolet and visible light are energetic enough to promote outer (valence) electrons to higher energy levels. There are three types of valence electrons that are found in electron orbital namely \( \sigma \)- bonding orbitals, \( \pi \)- bonding orbital and non-bonding orbitals (n-lone pair electrons). Sigma (\( \sigma \)) bonding orbits tend to be lower in energy than \( \pi \)- bonding orbital, which in turn are lower in energy than non-bonding orbital. The unoccupied or anti- bonding orbital (\( \pi^* \) and \( \sigma^* \)) are the orbits of highest energy. The UV spectrum consists of far or vacuum ultraviolet region, near or
ultraviolet region and visible region. The region between 10-200 nm is termed as vacuum ultraviolet region, which can be studied in evacuated systems. The region between 200-380 nm is called quartz ultraviolet region, normally termed as ultraviolet region. The region or spectral range most accessible from 200 to 800 nm includes the visible region lying between 380-780 nm.

In the present work, UV-Vis-NIR studies were carried out using Perkin Elmer Lambda35 spectrophotometer.

2.7 PHOTOLUMINESCENCE STUDIES

Photoluminescence spectroscopy is a non-destructive technique to examine the electronic structure of the material. The process of temporary light absorption and subsequent light emission is called Photoluminescence, in which the period between absorption and emission is extremely short in the range of femto second-regime to milliseconds; however, it can also be extended into minutes or hours under special circumstances. The process of emission is a release of energy in the form of photons. If the photon has energy greater than the band gap energy, then it can be absorbed and thereby raise an electron from the valence band up to the conduction band across the forbidden energy gap. Direct measurement of the energy levels can be achieved from a peak observed by spectra with a spectrometer. Thus the energy of the emitted photon is a direct measure of the band gap energy, \( E_g \). The amount of energy carried by a photon is proportional to its frequency. Generally semiconductor material, GaAs is used in electronic devices due to its higher electron mobility than Si. In addition, GaAs termed as direct band-gap and Si known as an indirect band-gap. The identification of different recombination mechanisms is
based on excitation intensity- and temperature-dependent PL measurements. In order to understand the concept of the energy gap in a solid are not firmly attached to the atoms, as they are for single atoms, but can skip from one atom to another. These loosely attached electrons are bound in the solid by differing amounts and thus have much different energy.

Electrons having energies above a certain value are referred to as conduction electrons, while electrons having energies below a certain value are referred to as valence electrons. Furthermore, there is an energy gap between the conduction and valence electron states. Under the normal conditions electrons are forbidden to have energies between the valence and conduction bands. In the process of photoluminescence, photons are excited to follow by emission. Spectrometers usually contain a diffraction grating (or prism) to disperse the light, thereby spreading out the light of differing wavelengths into different positions. The spectrometer unit used here has an internal CCD (charged coupled device) silicon detector, essentially a digital camera detector, to measure the light intensity at various positions along its length. In the present study photoluminescence spectra of the grown crystalline powder samples were carried out using Varian Cary Eclipse Fluorescence spectrophotometer with a xenon flash lamp as the excitation source at a scan speed of 600 nm /min, having filter size 5 nm.

2.8 BIREFRINGENCE STUDIES

Birefringence is the optical property of a material having a refractive index that depends on the polarization and the propagation direction of light. Birefringence is an intrinsic material property. The channel spectrum method
(CS) has been employed for quantitative assessment of the optical quality of the grown specimens. This method can be adopted even if the crystal area is as small as 0.004 m$^2$ (Nagarajan et al 2007). A constant deviation spectrometer (CDS) was first calibrated using the standard procedure. A 1000W tungsten halogen lamp was used as a source(S), which is collimated by collimator. This provides a collimating beam for studying the single crystals. The optically polished single crystal is placed on a rotary stage between crossed polarizer’s in the path of polarized light.

The arrangement should be in such a way that, the direction of the optic axis of the crystal slab is perpendicular to the direction of the collimated light transmitted by the polarizer (P). Due to the effect of crystal, there are two linearly polarized component rays whose vibration planes are polarized perpendicular to each other (Morgan, 1953). These two waves have amplitude 1/$\sqrt{2}$ equal to that of the incoming wave (neglecting surface reflections). Inside the crystal both the extraordinary and ordinary waves have a wavelength of $\lambda/n_e$ and $\lambda/n_o$ respectively. The light from the exit surface of the crystal has 180° phase difference between two polarized components (Zernike et al 1930). Finally the light was passed through the analyser (A), and emerging light waves were examined by the microscope (M).

The values of birefringence have been calculated using the formula $\nabla n = k\lambda/t$ (Zernike et al 1930), where $\lambda$ is the wavelength, $t$ is the thickness of the crystal and $k$ is the fringe order.
2.9 LASER DAMAGE THRESHOLD (LDT) STUDIES

The development of higher damage threshold optics is an important task, as it would result in less expensive laser components for high power lasers and overall smaller systems. It leads to research groups to develop such a system which benefits scientific progress in the field of laser-matter interaction. Laser damage threshold is a significant parameter, the knowledge of which is essential for using the crystal as an NLO element in various applications involving large laser input power like frequency doubling, optical parametric processes, etc.

Optical damage may be caused by several mechanisms and can be of various types. The predominant type is irreversible damage, which can take the form of surface or bulk damage. It can be caused by thermal heating, induced absorption, self-focusing and dielectric breakdown. When performing LDT testing, the sample is irradiated numerous times using a small beam over the whole clear aperture of the sample (Boling et al 1973). The laser damage threshold value was measured using a Q-switched Nd: YAG laser source of pulse width 10 ns and repetition rate of 10 Hz operating in TEM$_{00}$ mode.

The energy per pulse of 1064 nm laser radiation attenuated using appropriate neutral density filters was measured using an energy meter (Coherent EPM 200). For both single and multiple shots experiments, the sample was mounted on an X–Y translator which facilitates in bringing different areas of the sample. For surface damage observation, the sample was placed at the focus of a planoconvex lens with focal length of 20 cm. The laser damage threshold was calculated using the relation,
where \( P \) is the Laser damage threshold in \( \text{GW/cm}^2 \), \( E \) is the energy required to break the crystal, \( \tau \) is the response time in ns and \( A \) represents the beam area. It is extremely important as the surface damage of the crystal by high-power lasers limits its performance in NLO applications. The laser beam of diameter 4 mm was focused on the crystal sample. The pulse energy of each shot was measured using the combination of a phototube and an oscilloscope. During laser irradiation, the power meter records the energy density of the input laser beam by which the crystal gets damaged. For both single and multiple shot experiments, the sample was mounted on a translator which facilities in bringing different areas of the sample for exposure precisely.

2.10 KURTZ POWDER SHG METHOD

Interests have been made on nonlinear optical properties due to its applications rely on the manifestation of the molecular hyperpolarisability of the material.

A number of research efforts are underway to improve their performance and to optimize their efficiency in new device geometry. Thus researchers focused their interest to find the materials which have suitable nonlinear optical properties for use as the active media in efficient second harmonic generators, tunable parametric oscillators and broadband electro-optic modulators.

The growth of large single crystals is a slow and difficult process. The existence or absence of second harmonic generation in materials is
determined by two factors. Formerly, and fundamentally, the material should crystallize in a noncentrosymmetric crystal structure. Latterly material should possess phase matching properties i.e. the propagation speeds of the fundamental and harmonic waves should be identical with the material. Kurtz and Perry (1968) proposed a powder SHG method for comprehensive analysis of the second order nonlinearity. Employing this technique, Kurtz (1968) surveyed a very large number of compounds.

The nonlinear optical behaviour of the sample can be examined by parsing the output of Nd: YAG Quanta ray laser through the crystalline powder sample. A Q-switched, mode locked Nd: YAG laser was used to generate about 6 mJ/pulse at the 1064 nm fundamental radiation. This laser can be operated in two modes. In the single shot mode, the laser emits a single 8 ns pulse. In the multishot mode the laser produces a continuous train of 8 ns pulses at a repetition rate of 10 Hz. In the present study, a single shot mode of 8 ns laser pulse with a spot radius of 1mm has been used. This experimental setup used a mirror and a 50/50 beam splitter (BS) to generate a beam with pulse energies about 6 mJ.

The input laser beam was passed through an IR reflector and then directed on the microcrystalline powdered sample packed in a capillary tube of a diameter 0.154 mm. The photodiode detector and oscilloscope assembly measured the light emitted by the sample. The SHG was confirmed by the emission of green radiation (532 nm) and the optical signal was collected by a photomultiplier tube (PMT). The optical signal incident on the PMT was converted into voltage output at the CRO. Microcrystalline powder of Urea or
KDP is taken in a similar capillary tube sealed at one end for comparison. The intensity of the second harmonic output from the sample is compared with that of either KDP or Urea.

2.11 THERMAL STUDIES

Thermal analysis (TA) is termed as a group of techniques in which the physical property of a substance is measured as a function of temperature whiles the substance is subjected to a controlled temperature program. The importance of thermal analysis in quality control, failure analysis and material research and development is well established. Thermal analysis is a general term, which covers a group of related techniques in which the temperature dependence of the parameters of any physical property of a substance can be measured. Among the thermal methods, the most widely used techniques are thermogravimetry analysis (TGA), differential thermal analysis (DTA) and Differential scanning calorimetry (DSC).

2.11.1 Thermogravimetric analysis (TGA)

Thermogravimetry analysis involves monitoring the weight while varying temperature. The curve obtained in a thermogravimetric analysis is called a thermogram (TG) and its first derivative is called as a derivative thermogram (DTG). The inflection point in the program corresponds to the peak point in the derivation thermogram. Modern commercial TGA instruments consist of the following:

(i) A sensitive analytical balance
(ii) A temperature programmable furnace
(iii) A pure gas system for providing a suitable gaseous atmosphere and
(iv) A microprocessor for instrument control, data acquisition and display.

Even though different types of balance mechanism are available today, those employing null-point-weighing mechanism are favoured as the sample remains in the same zone of furnace irrespective of changes in mass. The furnace is normally an electrical resistive heater and the temperature range for most of the furnace is from ambient to 1000-2000°C. Thermogravimetry analysis is used to study the thermal degradation / decomposition / dehydration and to check the sample purity, temperature of desorption and drying, oxidative stability, etc.

The kinetic parameters of solid state reaction involving weight loss have been investigated by many workers using TG data [Coats et al 1997, Joshi et al 2003, Dabhi et al 2003]. The shape of the curve depends on the kinetic parameters of pyrolysis, such as the order of reaction, the frequency factor and the energy of activation. Coats and Redfern [Coats et al 1997] developed a method for the calculation of activation energy from nonisothermal TG data at a constant heating rate. The general correlation equation used in Coats and Redfern method is given below

$$
\log_{10} \left( \frac{1 - (1 - \alpha)^{-n} - T}{T^2 (1 - n)} \right) = \log_{10} \left\{ \frac{AR}{\alpha E} \left( 1 - \frac{2RT}{E} \right) - \frac{E}{2.303RT} \right\}
$$

(2.2)

where, $\alpha = (W_0 - W)/(W_0 - W_f)$, $W_0$ is the initial weight, $W$ is the weight at time $t$, $W_f$ is the final weight, $n$ is the order of the reaction, $A$ is the frequency factor, $E$ is the activation energy of the reaction, $R$ is the Gas constant, $\alpha$ is heating rate in K min$^{-1}$. The Coats–Redfern formula used to calculate the kinetic parameters for the first-order reactions is as follows:
\[
\log_{10} \left[ -\log \left( \frac{1 - \alpha}{T^2} \right) \right] = \log_{10} \left[ \left( \frac{AR}{\alpha E} \right) \left( 1 - \frac{2RT}{E} \right) \right] - \left( \frac{E}{2.303RT} \right) \quad (2.3)
\]

The other kinetic parameters such as enthalpy of activation (\(\Delta H\)), the entropy of activation (\(\Delta S\)) and free energy change of decomposition (\(\Delta G\)) were evaluated [Yakuphanoglu et al 2004] using equations,

\[
\Delta H = E - \Delta n \, RT \quad (2.4)
\]

where \(\Delta n = \text{number of moles of product} - \text{number of moles of reactant in the reaction.}\)

\[
\Delta S = 2.303 \times R \times \log_{10} \left[ \frac{Ah}{k_B T_m} \right] \quad (2.5)
\]

\[
\Delta G = \Delta H - T \Delta S \quad (2.6)
\]

where \(A\) is (Arrhenius constant) determined from the intercept, \(k_B\) is the Boltzmann constant \((1.3807 \times 10^{-23} \text{ J K}^{-1})\) and \(h\) is the Planck constant \((6.626 \times 10^{-34} \text{ J s})\).

### 2.11.2 Differential thermal analysis (DTA)

Differential thermal analysis (DTA) technique is primarily used for the detection of transition temperature. DTA is involved in the measurement of temperature difference between the sample and inert reference materials, as both are subjected to identical thermal regimes, in an environment heated or cooled at a constant rate. The origin of the temperature difference in the sample lies in the energy difference between the products and the reactants or between...
the two phases of a substance. This energy difference is manifested as enthalpy changes, either exothermic or endothermic.

The differential thermal curve would be parallel to the temperature (time) 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 appear as a peak. The differential signal would return to the baseline 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 or chemical changes taking place.

Since any change in the chemical or physical state of a substance is accompanied by changes in energy that are manifested as heat changes, the DTA method is applicable to all studies listed for TG and also to phase transformations including polymerization, phase equilibrium and chemical reactions.

2.11.3 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry analysis involves in the direct measurement of energy changes. DSC has become 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 (chemical or physical change that results in the emission or
absorption of heat) occurs in the sample, thermal energy is added to either the sample or the reference containers in order to maintain both the sample and reference at the same temperature. Because the energy transferred is exactly equivalent in magnitude to the energy absorbed or evolved in the transition, the balancing energy yields a direct calorimetric measurement of the transition energy. Since DSC can directly measure both the temperature and enthalpy of a transition or the heat of a reaction, it is often substituted for differential thermal analysis as a means of determining these quantities except in certain high temperature applications. In general, each substance gives a DSC curve in which the number, shape, and position of the various endothermic and exothermic features serve as a means of qualitative identification of the substance. Endotherms generally represent physical rather than chemical changes.

Sharp endotherms are an indication of crystalline rearrangements, fusions, or solid-state transitions for relatively pure materials. Exothermic behaviour (without decomposition) is associated with the decrease in entropy of a phase or chemical system. Narrow exotherms indicate the crystallization of a metastable system. Exotherms with decomposition can be either narrow or broad depending on the kinetics of the behaviour.

2.11.4 Thermal measurement

In the present investigation, thermal analysis was performed in a simultaneous TG–DTA instrument (SDT Q 6000 V 8.2 Built 100 thermal analyzer). The experimental conditions were: (i) continuous heating from room temperature to 1000°C at a heating rate of 20°C/min, (ii) N₂-gas dynamic
atmosphere (90 cm³ min⁻¹), (iii) alumina, as reference material and (iv) sample: without pressing. The temperature was detected with a Pt–Pt 13% Rh thermocouple fixed in a position near the sample pan. Analytical model developed by Coats and Redfern was used to analyse the TGA data and to determine the activation energy as well as various thermodynamic parameters. The DSC curve was recorded using a Netzsch DSC 204 instrument. The measurements were carried out in nitrogen atmosphere.

2.12 MICROHARDNESS STUDIES

Hardness measurement is an important factor which enables to resist plastic deformation, usually by penetration and also refer to resistance to bending, scratching, abrasion or cutting. In particular, hardness is a measure of resistance against lattice destruction or the resistance offered to permanent deformation or damage. It is a non-destructive method to determine the mechanical behaviour of the materials. For hard and brittle materials, the hardness test has proved to be a valuable technique in the general study of plastic deformation (Westbrook and Conrad 1971). Hardness properties are basically related to the crystal structure of the material and the bond strength; microhardness studies have been applied to understand the plasticity of the crystals. Hardness tests are commonly carried out to determine the mechanical strength of materials and it correlates with other mechanical properties like elastic constants and yield stress. Hardness measurements can be defined as
macro, micro and nano according to the forces applied and displacement obtained.

The hardness of the materials is strongly influenced by the conditions of measurements than properties of the material. The microhardness method is widely used for studying the individual structural constituent elements of metallic alloys, minerals, glasses, enamels and artificial abrasives.

2.12.1 Methods of hardness testing

Various methods adopted for the measurement of hardness classified as

✓ Static indentation test
✓ Dynamic indentation test
✓ Scratch test
✓ Rebound test and
✓ Abrasion test

Among the different methods, static indentation test preferred for the hardness measurement due to its popularity and simple, in which an indenter of specific geometry is pressed onto the surface of a test specimen under a known load. The indenter may be a ball or diamond cone or diamond pyramid. A permanent impression is retained in the specimen after removal of the indenter.

The hardness is calculated from the area or the depth of indentation produced. The variable is the type of indenter or load. The indenter is made up of a very hard material to prevent its deformation by the test piece, so that it can cover materials over a wide range of hardness. For this reason, either an
intender of steel sphere or a diamond pyramid or cone is employed. A pyramid indenter is preferred as geometrically similar impressions which are obtained at different loads. In this static indentation test, the indenter is pressed perpendicularly to the surface of the sample by means of an applied load. By measuring the cross sectional area or the depth of the indentation and knowing the applied load, empirical hardness number may be calculated. This method is followed by Brinell, Meyer, Vickers, Knoop and Rockwell tests (Wyatt and Dew Hughes 1974; Taber 1951; Neil 1967).

In the dynamic indentation test, a ball or a cone (or a number of small spheres) is allowed to fall from a definite height and the hardness number is obtained from the dimensions of the indentation and the energy of impact. In the rebound test, an object of standard mass and dimension is bounced from the test surface and the height of rebound is taken as the measure of hardness. In the abrasion test, a specimen is loaded against a rotating disk and the rate of wear is taken as a measure of hardness.

The Vickers pyramid indenter whose opposite faces contained an angle ($\alpha = 136^\circ$) is the most widely accepted pyramid indenter. A pyramid indenter is suited for hardness tests due to the following reasons (Batta et al 1980).

- The contact pressure for a pyramid indenter is independent of indent size and
- Pyramid indenters are less affected by the elastic release than other indenters.

The base of the Vickers pyramid is a square and the depth of indentation corresponds to $1/7^{th}$ of the indentation diagonal. Hardness is generally defined as the ratio of the load applied to the surface area of the indentation.
The Vickers hardness number (HV) of Diamond Pyramid Number (DPN) is defined as

\[ H_V = \frac{2P \sin (\alpha/2)}{d^2} \]  

(2.7)

where \( \alpha \) is the apex angle of the indenter (\( \alpha = 136^\circ \)). The Vickers hardness number is thus calculated using the relation

\[ H_V = 1.8544 \frac{P}{d^2} \text{ kg-mm}^{-2} \]  

(2.8)

where \( P \) is the applied load in kg and \( d \) is the diagonal length of the indentation mark in mm. Hardness values are always measured from the observed size of the impression remaining after a loaded indenter has penetrated and has been removed from the surface. Thus, the observed hardness behaviour is the summation of a number of effects involved in the material’s response to the indentation pressure during loading, in the final measurement of the residual impression. The load variation can be interpreted by using Meyer’s law:

\[ P = K_1 d^n \]  

(2.9)

\[ \log P = \log k + n \log d \]  

(2.10)

where \( k \) is the material constant and \( n \) is the Meyer’s index. In order to calculate the value of \( n \), the graph was plotted against \( \log P \) vs \( \log d \) which gives a straight line and the slope of this straight line gives the value of \( n \). The simplest way to describe the indentation size effect (ISE) is Meyer’s law. For the normal ISE behaviour, the exponent has \( n < 2 \). When \( n > 2 \), there is reverse
ISE behaviour. Hence the title crystal exhibits reverse ISE behaviour. According to Onitsch (1947), $n$ should lie between 1 and 1.6 for harder materials and above 1.6 for softer materials. Hays and Kendall’s theory of resistance pressure, explains a relationship between indentation test load ($P$) and indentation size ($d$) by assuming the following equation:

$$P - W = k_2 d^2$$ \hspace{1cm} (2.11)

where $W$ is the sample resistance pressure (or Newtonian resultant pressure) and represents the minimum load that causes an indentation, $k_2$ is an another constant. Substituting the expression of equation (2.9) for $P$ in equation (2.11),

$$W = k_1 d^n - k_2 d^2$$ \hspace{1cm} (2.12)

or

$$d^n = \frac{W}{k_1} + \left(\frac{k_2}{k_1}\right) d^2$$ \hspace{1cm} (2.13)

The plot of $d^n$ against $d^2$ is a straight line having a slope of $k_2/k_1$ and intercept of $W/k_1$. From these, the material resistance to the initiation of plastic flow ($W$) has been calculated. Also the elastic stiffness constant was calculated using Wooster’s empirical formula,

$$C_{11} = Hv^{7/4}$$ \hspace{1cm} (2.14)

which gives an idea about the tightness of bonding between the neighbouring atoms. From the hardness value, the yield strength ($\sigma_y$) can be calculated (Cahoon et al 1971). For Meyer’s index $n > 2$:  

50
when $n \leq 2$, the equation (2.15) is reduced to $\sigma_y = Hv/3$ (Wyatt 1974).

The brittleness gives information about the fracture induced in a material without any appreciable deformation and is an important property that affects the mechanical behaviour of a material. The brittle index for different loads, was calculated using the formula,

$$B_i = \frac{H_v}{K_c}$$

(2.16)

where $K_c$ is fracture toughness and it can be calculated from the relation,

$$K_c = \frac{P}{\beta_0 C^{3/2}}$$

(2.17)

where $P$ is the applied load in N, $C$ is the crack length measured from the centre of indentation mark to crack end, $d$ is the diagonal length of the indenter impression in $\mu$m, and $\beta_0$ is taken as 7 for the Vickers indenter.

In the present study microhardness studies were carried out at room temperature using Leitz–Wetzler hardness tester fitted with a Vickers’ diamond pyramidal indenter at a dwell time of 10 s. The diagonal length of the indentation impression was measured using a microscope. The indentation marks were made on the surfaces of varying the load from 25 to 100 g. For a particular load, at least five well-defined impressions were considered and the average of the all the diagonals ($d$) was considered.
2.13 DIELECTRIC STUDIES

Dielectric measurement plays a vital role to examine the electrical response of solids. Since every material has a unique set of electrical characteristics, such as dielectric properties, like permittivity, permeability, resistivity, conductivity, etc. Thus dielectric properties of solids give information about the electric field distribution within the solid. If the materials are having the ability to store energy, when the electric field is applied termed as dielectric. The dielectric characteristics of the material are important to study the lattice dynamics in the crystal. It is important to note that permittivity and permeability are not constant.

They can change with frequency, temperature, orientation, mixture, pressure, and molecular structure of the material. The frequency dependence of these properties gives a great insight into the materials applications. In general, if electrode effects are neglected, the four major contributions to the dielectric permittivity would be the

- extrinsic nature of the material
- electronic polarizability
- ionic polarizability and
- deformation of the ions.

The different polarization mechanisms in solids can be understood from the study of dielectric constant as a function of frequency and temperature. Dielectric loss is a measure of the energy absorbed by dielectric. The ratio of the imaginary part to the real part of the permittivity is known as dielectric loss or the dissipation factor $D$. 
\[ D = \tan \delta \]  

(2.18)

In the present investigation, the dielectric measurement was carried out by measuring different parameters such as capacitance and dielectric loss of the pressed pellets of samples of known dimension at room temperature using HIOKI 3532-50 LCR HITESTER meter. The samples were made as electrode on either side with a silver coating to make it behave like a parallel plate capacitor. The experiment was carried out in the frequency range 100 Hz–5 MHz at room temperature.

The real and imaginary parts of dielectric permittivity of the crystal have been calculated using the relations,

\[ \varepsilon' = \frac{cd}{\varepsilon_o A} \]  

(2.19)

and

\[ \varepsilon'' = \varepsilon' \tan \delta \]  

(2.20)

respectively. \( C \) is the capacitance, \( d \) is the thickness, \( A \) is the area of the sample, \( \varepsilon_o \) is the absolute permittivity of the free space and \( \tan \delta \) is the dielectric loss.

The a.c conductivity is one of the studies done on solids in order to characterize the bulk resistance of the crystalline sample. The a.c. conductivity is given by:

\[ \sigma_{ac} = 2\pi f \varepsilon_o \varepsilon' \tan \delta \]  

(2.21)

where \( f \) is the frequency. Using the above equation, the a.c conductivity at different temperatures was calculated and the graph between log \( \sigma_{ac} \) and \( 1/T \) is
plotted. The total conductivity, \( \sigma (\omega) \) may be expressed as the sum of dc and ac components according to the Jonscher's universal power law equation (Jonscher et al 1977),

\[
\sigma_{ac} = \sigma_{dc}(0) + A\omega^s
\]  

where \( \sigma_{dc}(0) \) is frequency independent conductivity at low frequencies and \( A\omega^s \) represents the frequency dependent conductivity at high frequencies. \( A \), is a frequency independent and temperature dependent parameter, \( \omega=2\pi f \), is the angular frequency and the temperature dependent frequency exponent which represents the frequency dependent conductivity. A better way of displaying the frequency and temperature dependence of ac conductivity is to present the ac conductivity data in the form of Arrhenius plots at different frequencies. The dependence of conductivity with temperature allows evaluating the activation energy of the sample at a particular frequency. The activation energy \( (E_a) \) of the electrical process was calculated from the plot between \( \ln \sigma_{ac} \) and inverse of temperature using the relation (Verwey et al 1947):

\[
\sigma = \sigma_o \exp \left( \frac{-E_a}{kT} \right)
\]  

where \( \sigma_{ac} \) is the conductivity at temperature \( T \), \( E_a \) the activation energy for the electrical process and \( k \) is the Boltzmann constant.

The dc conductivity values for different temperatures were measured by extrapolating the low frequency plateau regions of the log \( \sigma_{ac} \)–log \( f \) graph and were obtained from their intercepts at zero frequency. To further confirm, the
process going on with the curve, it is fitted with the Arrhenius equation for conduction given by

\[ \sigma_{dc} = \sigma_0 \exp \left( \frac{E_a}{k_B T} \right) \]  

(2.24)

Where \( \sigma_0 \) is a constant, \( E_a \) is the activation energy, \( k_B \) is the Boltzmann constant and \( T \) is the absolute temperature. From the slope of the fitted straight line, the activation energy value was calculated.

### 2.14 CONCLUSION

To evaluate the suitability of the grown crystals for various applications including NLO device applications crystals should be subjected to different characterizations. The structural characterization plays an important role to realize the behaviour of solid material. In order to examine the optical properties, transparency window and cut-off wavelength of the crystal were performed. Since the entire thrust is with respect to NLO application, the SHG property was estimated. In addition, the mechanical, thermal, dielectric, laser damage threshold of the grown crystal was also investigated.