2.1 Structural characterization

The structural characterization of the materials under study is envisaged using single crystal X-ray diffractometer, powder X-ray diffractometer, transmission electron microscope and FTIR and Raman spectrometers. The elemental analysis has been carried out using CHN analyzer and Energy Dispersive X-ray spectroscopy.
2.1.1 Single crystal X-ray crystallography

The oldest and most precise method of X-ray crystallography is single-crystal X-ray diffraction. It is the most elucidative method of determining the arrangement of atoms within a crystal, in which a beam of X-rays strikes a crystal and gets diffracted into many specific directions and a three-dimensional picture of the density of electrons within the crystal is obtained. From this electron density distribution, information about the mean positions of the atoms, their chemical bonds, and the extent of disorder can be obtained.

Crystals are formed by regular periodic arrangement of atoms. Atoms scatter X-rays. X-ray diffraction results from an electromagnetic wave impinging on a regular array of scatterers, determined by Bragg's law:

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

(2.1)

Here \( d \) is the spacing between diffracting planes, \( \theta \) is the glancing angle, \( n \) is any integer, and \( \lambda \) is the wavelength of the X-ray beam. These specific directions appear as spots on the diffraction pattern.

X-rays are used to produce the diffraction pattern because their wavelength \( \lambda \) is typically of the same order of magnitude as the spacing \( d \) between planes in the crystal. These scattered beams make a diffraction pattern of spots as the crystal is gradually rotated and the diffraction patterns can be recorded. X-ray diffraction data can be used to determine the mean chemical bond lengths and bond angles to within a few thousandths of an angstrom and to within a few tenths of a degree, respectively.

The technique of single-crystal X-ray crystallography has three basic steps. The first step is to obtain a large and regular crystal with no significant internal imperfections such as cracks or twinning. In the second step, the crystal is placed in an intense beam of monochromatic X-rays, to produce
regular pattern of reflections. The crystal is gradually rotated and the intensity of every spot is recorded at every orientation of the crystal. When a crystal is mounted and exposed to an intense beam of X-rays, it scatters the X-rays into a pattern of spots or reflections and the relative intensities of these spots provide the information to determine the arrangement of atoms/molecules within the crystal. To collect all the necessary information, the crystal must be rotated step-by-step through 180°, with an image recorded at every step. The intensities of these reflections may be recorded with photographic film, an area detector or with a charge-coupled device (CCD) image sensor. The recorded series of two-dimensional diffraction patterns, each corresponding to a different crystal orientation, is converted into a three dimensional model of the electron density, using Fourier transform. In the third step, these data are combined computationally with complementary chemical information to produce and refine a model of the arrangement of atoms within the crystal. Finally, refined model of the atomic arrangement called the crystal structure is stored in a database.

Data processing begins with indexing the reflections by identifying the dimensions of the unit cell and which image peak corresponds to which position in reciprocal space. A byproduct of indexing is to determine the symmetry of the crystal, i.e., its space group. Having assigned symmetry, the data is then integrated. This converts the hundreds of images containing the thousands of reflections into a single file, consisting of records of the Miller indices of each reflection, and intensity for each reflection. Structure analysis by single crystal X-Ray diffraction is the most powerful technique for structural characterization of crystals. In the present work single crystal X-ray diffraction was carried out using Enraf Nonius CAD-4 diffractometer to study the structure and morphology of the grown crystals. The molecular structure is solved by direct method and refined by SHELXL program [1]
2.1.2 Powder X-ray diffraction

Powder diffraction is a key analytical method to analyze qualitatively the phase purity, particle size, strain etc. of the samples and also to establish the molecular structure of the samples, whose crystal structure has already been determined. Powder X-ray diffractometer utilizes the sample in the powdered form. It consists of a goniometer and a fixed detector to detect the diffracted X-rays. The monochromator provides a specific wavelength and the resulting trace is recorded in intensity for different diffracting angles ($2\theta$). The powdered sample provides all possible orientations of the crystal lattice and the diffracted patterns from all planes are recorded. The powder X-ray diffraction method is useful for qualitative rather than quantitative analysis.

In the present study, powder X-ray diffraction has been carried out using Bruker D8 advance diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å). The crystal structure has been refined by Pawley method [2] using the TOPAZ version 3 program[3]. The Rigaku X-ray diffractometer with Cu Kα radiation of wavelength $\lambda = 0.15496$ nm has also been used for the structural analysis in the present work.

2.1.3 Transmission Electron Microscope

Transmission electron microscopy (TEM) is a high resolution microscopy technique whereby a beam of electrons is transmitted through an ultra thin specimen and an image is formed by the interaction of the electrons with the specimen. The image is magnified and focused onto an imaging device, such as a fluorescent screen, or a layer of photographic film, or detected by a sensor such as a CCD camera. The transmitted beam which is
used to form the image contains information about electron density, phase and periodicity.

The first TEM was built by Max Knoll and Ernst Ruska in 1931[4]. It has the same principle as that of an optical microscope. The maximum resolution, $d$, obtained with a light microscope is limited by the wavelength of the photons that are being used to probe the sample $\lambda$, and the numerical aperture (NA) of the system, given by

$$d = \frac{\lambda}{2n \sin \alpha} \approx \frac{\lambda}{2NA} \quad (2.2)$$

In TEM imaging technique, electrons play the role as that of photons in an optical microscope. A beam of electrons behave like a beam of electromagnetic radiation whose wavelength is given by

$$\lambda_e \approx \frac{h}{\sqrt{2m_0E \left(1 + \frac{E}{2m_0c^2}\right)}} \quad (2.3)$$

where, $h$ is Planck's constant, $m_0$ is the rest mass of an electron and $E$ is the energy of the accelerated electron. Electrons are generated by an electron gun or by field emission and are accelerated by an electric field. The beam can be focused by electric and magnetic fields on to the sample. The beam is restricted by the condenser aperture, knocking out high angle electrons. The beam strikes the specimen and part of it is transmitted which is focused by the objective lens into an image. Optional objective and selected area metal apertures can restrict the beam. The objective aperture enhances contrast by blocking out high-angle diffracted electrons and the selected area aperture examines the periodic diffraction of electrons by ordered arrangements of
atoms in the sample. The image is passed through the intermediate and projector lenses and directed on to the image screen. The beam transmitted by the sample contains electrons that have not undergone scattering and that have lost energy by inelastic scattering and also electrons reflected by various crystallographic hkl planes. A bright field image is produced when an aperture is inserted and a dark field image when the aperture is positioned to select only beams reflected from a particular hkl plane. The schematic diagram of TEM is shown in Fig: 2.1.

![Schematic diagram of Transmission Electron Microscope](image)

**Fig: 2.1 Schematic diagram of Transmission Electron Microscope**

### 2.2 Elemental Analysis

The elemental composition of the samples investigated in the present study has been determined using CHN analysis, EDX and ICP AES.
2.2.1 CHN analysis

This is a very elucidative technique to determine the empirical formula of a compound. The empirical formula is the formula for the compound that contains the smallest set of integer ratios, which gives the correct elemental composition by mass for the elements present in the compound. The CHN analysis is basically a combustion process, where the sample is burnt in an excess of oxygen. The various traps collect the combustion products like carbon dioxide, nitric oxide, water etc. From the weights of these combustion products, the composition of the unknown sample can be calculated.

The analysis is performed by working out a chemical formula that fits with the ratio of the elements of the sample. This technique is important as it helps to determine the composition of the sample and also to confirm the purity of the compound. VarioEL III CHNS analyzer has been used to study the chemical composition of the samples in the present study.

2.2.2 Energy Dispersive Analysis by X-rays (EDX)

This is a technique to identify the elements present in a compound. The system works as an integrated feature of a scanning electron microscope [5]. The principle of EDX is that the electron beam generates X-rays within the specimen. The electron beam incident on the sample excites an electron in an inner shell and ejects it. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower energy shell may be released in the form of an X-ray. The number and energy of the X-rays emitted from a specimen can be measured by an energy-dispersive spectrometer. The energy of the X-rays are characteristic of the difference in energy between the two shells, and of the atomic structure of
the element from which they are emitted. This helps in determining the elemental composition of the specimen. The EDX system consists of an X-ray detector, a pulse processor and a computer. The X-ray detector intercepts X-rays emitted from the specimen. On entering the detector, X-rays generate a small current, which is then converted into a voltage pulse. The size of the voltage pulse is proportional to the energy of the X-rays. A computer measures the voltage pulses and plots them as a histogram. The histogram shows a spectrum of the X-ray energies and by examining the spectrum, the elements present can be determined. The EDX spectrum displays peaks and each peak is unique to an atom and corresponds to a single element. The higher the peak, the more concentrated is the element present in the specimen.

2.2.3 Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP AES)

It is an analytical technique used for the detection of trace metals. It is a type of emission spectroscopy that uses the inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element. The intensity of this emission indicates the concentration of the element within the sample.

2.3 Vibrational Spectral Analysis

This is a method of characterization of materials to get information about the composition and the structure of molecules. The techniques used are Fourier Transform Infra red (FTIR) Spectroscopy and Raman Spectroscopy.
2.3.1 Fourier transform infra red spectroscopy (FTIR)

It is a vibrational spectroscopy that records absorptions of IR light by chemical bonds in all molecules. Different bonds absorb IR light at characteristic but different wavelengths and hence FTIR spectroscopy is often referred to as fingerprint spectroscopy. As a consequence pure compounds have characteristic and unique FTIR spectra. Spectra are collected based on measurements of the coherence of a radiative source, using time-domain measurements of the electromagnetic radiation. FT-IR is a method of obtaining infrared spectra by first collecting an interferogram of a sample signal using an interferometer, and then performing a Fourier Transform (FT) on the interferogram to obtain the spectrum. An FT-IR Spectrometer collects and digitizes the interferogram, performs the FT function, and displays the spectrum.

An FT-IR spectrometer is based on a Michelson Interferometer. The interferometer consists of a beam splitter, a fixed mirror, and a moving mirror that translates back and forth. The beam splitter transmits half of the radiation striking it and reflects the other half as shown in Fig: 2.2. Radiation from the source strikes the beam splitter and gets separated into two beams. One of the beams is transmitted through the beam splitter to the fixed mirror and the second is reflected off the beam splitter to the moving mirror. The fixed and moving mirrors reflect the radiation back to the beam splitter. Half of this reflected radiation is transmitted and half is reflected at the beam splitter, resulting in one beam passing to the detector and the second back to the source. In FTIR spectrometer, the sample is placed between the output of the interferometer and the detector. The sample absorbs the radiation of a particular wavelength. An interferogram of a reference (sample cell and
solvent) is required to revive the spectrum of the sample. After the collection of the data, a fourier transform is performed using a computer program which results in a frequency domain trace.

![Schematic diagram of FTIR spectrometer](image)

**Fig: 2.2 Schematic diagram of FTIR spectrometer**

The process of conversion of the interferogram into a spectrum is through the Fast Fourier Transform algorithm introduced by J.W. Cooley and J.W. Tukey in 1965. A number of steps are involved in the conversion process. The advantages of infra red spectroscopy include wide applicability, possibility of measurement under ambient conditions and the capability of providing detailed structural information. The merits of FT technique are higher sensitivity, higher precision, better speed of measurement and better efficiency of data processing [6, 7].

Infra red spectra originate due to the transitions between two vibrational levels of a molecule in the electronic ground state and are observed as absorption bands in the infrared region. For a molecule to have infrared absorption bands, it should have a permanent dipole moment. The dipole interacts with the oscillating electric field of the incident infrared radiation. There must be a change in the dipole moment of the molecule during the vibration of the molecule to be infrared active or to give rise to an observable infrared band.
The vibrational frequency is determined by the force constant and reduced mass and hence the frequency of the fundamental vibration will be higher, if the bond strength is higher. The frequency will be lower when the masses of the atoms attached to the bond increases.

The infrared spectrum can be divided into the functional group region and the fingerprint region. The region ranging from 1500 cm$^{-1}$ to 4000 cm$^{-1}$ is called the functional group region and that below 1500 cm$^{-1}$ corresponds to the fingerprint region. The functional group region includes stretching vibrations which are localized and gives information about the nature of the components that make up the molecule. The fingerprint region includes molecular bending vibrations characteristic of the entire molecule [8].

2.3.2 Raman spectroscopy

This spectroscopic technique is named after Sir. C.V. Raman. It is used to study vibrational, rotational, and other low-frequency modes in a system. It relies on the inelastic scattering of monochromatic light in the visible, near infrared, or near ultraviolet range by molecular vibrations, phonons or other excitations in the system, called Raman scattering, resulting in the energy of the photons being shifted up or down. The shift in energy gives information about the phonon modes in the system. Infrared spectroscopy yields similar, but complementary, information.

A Raman spectrometer consists of an illumination source, typically a laser source, a sample chamber, a double monochromator and a spectrometer, a multichannel detector and a photomultiplier tube.

When a molecule is placed in an electromagnetic field, a transfer of energy between the molecule and the field takes place resulting in spectra
which have frequencies higher and lesser than the frequency of the incident field. Raman spectra originate due to the polarization caused by the incident radiation which interacts with a pulsating electron cloud. This interaction is modulated by the molecular vibrations which in turn depend on the chemical structure of the molecules that scatter the radiation.

Raman spectroscopy has become a very powerful tool for the analysis of solids, liquids and solutions and can even provide information on physical characteristics such as crystalline phase and orientation, polymorphic forms, and intrinsic stress [9, 10]. Fig: 2.3 depicts the experimental set up for Raman spectroscopic studies.

![Experimental setup for Raman spectroscopic studies](image)

**Fig: 2.3** Experimental set up for Raman spectroscopic studies.

### 2.4 Optical characterization

Optical characterization includes both linear and nonlinear optical properties of the specimen. Linear optical properties are investigated by UV-Vis absorption and photoluminescence studies and the nonlinear optical properties, by employing Kurtz Perry powder technique for estimating the second harmonic generation efficiency and the open aperture Z scan technique for investigating the third order nonlinear effects.
2.4.1 UV-Vis absorption spectroscopic studies

UV/Vis absorption spectroscopy is based on the Beer-Lambert law which is useful in the quantitative analysis of samples and the absorption spectrum is recorded using a spectrophotometer. Different molecules absorb radiation of different wavelengths. An absorption spectrum will show a number of absorption bands corresponding to structural groups within the molecule [11,12]. The absorption of UV or visible radiation corresponds to the excitation of outer electrons.

When an atom or molecule absorbs energy, electrons are promoted from their ground state to an excited state. In a molecule, the atoms can rotate and vibrate with respect to each other. Possible electronic transitions of $\pi$, $\sigma$, and $n$ electrons are –

1. $\sigma \rightarrow \sigma^*$ transition
2. $n \rightarrow \sigma^*$ transitions.
3. $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ Transitions

The UV-Vis absorption spectrophotometer consists of the following components:

1. Source (UV and visible)
2. Wavelength selector (monochromator)
3. Sample container
4. Detector
5. Signal processor and readout
Chapter 2

Source of UV radiation is the radiation generated by electrical excitation of deuterium or hydrogen at low pressures which produces a continuous spectrum. The tungsten filament lamp is commonly employed as a source of visible light.

Monochromators contain 1) an entrance slit, 2) a collimating lens, 3) a dispersing device (a prism or a grating), 4) focusing lens and (5) an exit slit.

The containers or cuvettes for the sample and reference solutions must be transparent to the radiation and hence the material used for cuvettes is quartz.

The detector commonly used is a photomultiplier tube which consists of a photoemissive cathode, several dynodes, and an anode. The schematic diagram of the UV-Vis spectrophotometer is shown in Fig: 2.4.

![Schematic diagram of a double-beam UV-Vis. Spectrophotometer](image)

**Fig: 2.4** Schematic diagram of a double-beam UV-Vis. Spectrophotometer

The absorbance of an absorbing species in solution, using the Beer-Lambert law is given by

\[
A = \log_{10}(I_0/I) = \epsilon \cdot c \cdot L
\]  

(2.4)
where $A$ is the measured absorbance, $I_0$ is the intensity of the incident radiation at a given wavelength, $I$ is the transmitted intensity, $L$ the path length through the sample, and $c$ the concentration of the absorbing species.

The photon absorption for crystalline materials is found to obey the Tauc relation given by

$$(\alpha hv) = A (hv-E)^n$$

(2.5)

where $\alpha$ is the absorption coefficient, $hv$ the photon energy, $A$ is a constant and the index $n$ is related to the distribution of density of states. The value for $n$ is equal to $1/2$ for direct allowed transition, and $n$ is equal to 2 for indirect allowed transition. The linear portion of the plot of $(\alpha hv)^2$ versus $hv$, when extrapolated to the energy axis, gives the band gap. In the present work, Jasco V 570 UV-Vis-NIR spectrophotometer has been employed for the absorption studies.

2.4.2 Photoluminescence studies

Photoluminescence (PL) is a process in which a substance absorbs electromagnetic radiation and gets excited to a higher energy state, from where it returns to a lower state accompanied by the emission of radiation and the process takes place in a very short duration of the order of a few nanoseconds. Photoluminescence is an important technique for estimating the purity and crystalline quality of semiconductors. Radiative transitions in semiconductors involve localized defect levels. The photoluminescence energy associated with these levels can be used to identify specific defects, and also to determine their concentration [13]. In the present study, the instrument Fluoromax 3 spectrofluorimeter has been used to carry out the PL studies.
2.5 Characterization of Nonlinear optical properties

The second and third order nonlinear optical properties of the samples of the present work have been investigated by determining the second harmonic generation efficiency (SHG), employing Kurtz Perry powder technique and by measuring the nonlinear absorption coefficient by the open aperture Z scan technique respectively.

2.5.1 Second harmonic efficiency (SHG)

Quantitative measurement of the relative second harmonic generation efficiency (SHG) of the sample can be assessed by the Kurtz Perry powder technique [14]. It is a simple method to determine the second order optical nonlinearity of a crystalline material. The crystal is powdered and filled densely in a capillary tube. High intensity laser radiation, like Nd-YAG laser of 1064nm wavelength, 10ns pulse width and 10 Hz pulse rate is made to fall on the sample. The transmitted wave is passed through a monochromator which separates the second harmonic signal from the fundamental. It is again passed successively through filters to remove any residual fundamental beam. The beam is finally focused to a photomultiplier tube which amplifies the second harmonic wave generated by the crystal. The SHG efficiency is determined by comparing the output with that of the reference such as KDP, powdered to the same size, using the formula 2.6. A schematic diagram of the set up is shown in Fig: 2.5

\[
\text{SHG efficiency} = \frac{I_{2\omega, \text{sample}}}{I_{2\omega, \text{KDP}}} \quad (2.6)
\]
2.5.2 Open aperture Z scan method

Z scan technique is a method used to determine the nonlinear absorption coefficient in the open aperture mode and nonlinear refraction in the closed aperture mode of liquids, films, crystals etc.[15,16].

In a typical Z scan experimental set up, a mode locked Nd-YAG laser beam is focused by a lens. A detector is placed at the far field. The sample is moved along the axial direction of the focused beam. The transmitted intensity is measured as a function of the position of the sample. A laser beam propagating through a nonlinear medium will experience both amplitude and phase variations.

If transmitted light intensity is measured without an aperture, the mode of measurement is referred to as open aperture z-scan. The technique is employed to measure nonlinear absorption in the sample.
When the intensity $I$ of the incident beam is sufficiently high, the response of the nonlinear medium will be such that the absorption becomes intensity dependent, given by

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

where $\beta$ is the absorption coefficient.

At sufficiently high intensities, the probability of a material absorbing more than one photon before relaxing to the ground state is greatly enhanced. The different phenomena manifested are

i. Saturable or reduced absorption
ii. Reverse saturable or increased absorption
iii. Two photon absorption (TPA)
iv. Multiphoton absorption
v. Free carrier absorption (FCA)

Two photon absorption (TPA) is a third order NLO process. It refers to the simultaneous absorption of two photons from an incident radiation field. The transmitted beam energy, reference beam energy and their ratio can be measured simultaneously by an energy ratio meter. The open aperture $z$ scan technique is employed to measure nonlinear absorption in the sample.

If $I(z)$ is the irradiance, $L$, the optical length and $\tau$, the time

$$I(z) = I/(\sqrt{\pi} Q(z)) \int \ln[1 + Q(z)] e^{-\tau^2} d\tau \quad (2.8)$$

where $Q(z) = \beta I(z) [(1 - e^{-\alpha L})/\alpha]$ 

$$Q(z) = \beta I(z) [(1 - e^{-\alpha L})/\alpha] \quad (2.9)$$

$$e^{-\alpha L}/\alpha = L_{\text{eff}}$$

the effective path length
In open aperture z scan the phase variations of the beam are not taken into consideration. Equation 2.9 yields the nonlinear absorption coefficient ($\beta$).

If the sample is a reverse saturable absorber, it is manifested in the measurement as a transmission minimum at the focal point. If the sample is a saturable absorber, transmission increases with increase in incident intensity and results in a transmission maximum at the focal region. Schematic representation of the experimental setup for z-scan technique is shown in Fig: 2.6

**Fig: 2.6 Schematic representation of the experimental setup for z-scan technique**

### 2.6 Thermal Characterization

The thermal characterization is carried out with the help of Thermogravimetric analysis (TGA).

This method basically measures weight changes in a material when subjected to variation in temperature in a controlled atmosphere. From the TGA analysis, the thermal stability and degradation temperature of the material, moisture content in the material, the amount of organic and inorganic...
components in the specimen, the decomposition temperature of explosive materials etc can be estimated [17].

The thermal analyzer consists of a high-precision balance with a pan made of platinum which is loaded with the sample. The sample is placed in a small electrically heated oven with a thermocouple to accurately measure the temperature. The atmosphere may be purged with an inert gas to prevent oxidation or other undesired reactions. A computer is used to control the instrument. A graph of the percentage of weight loss versus temperature is plotted from which the different thermal processes can be analysed.

2.7 Dielectric studies

An impedance analyzer is used to study the dielectric properties of the samples in the present study. Dielectrics are substances which do not have free electrons, but in the presence of an electric field E, the material gets polarized and a net dipole moment is induced in the substance. The polarization is given by

\[ P = \varepsilon_0 \chi_e E \]  

(2.10)

Where \( \varepsilon_0 \) is the permittivity of free space and \( \chi_e \) is the electrical susceptibility.

The dielectric constant \( \varepsilon_r \) is also called the relative permittivity and can be calculated using the relation:

\[ \varepsilon_r = \frac{Ct}{(\varepsilon_0 A)} \]  

(2.11)

where C is the capacitance, t, the thickness of the sample, \( \varepsilon_0 \), the permittivity of free space and A, the area of cross section.
2.8 Etching studies

Etching is a reverse growth process. When a crystal is placed in contact with a solvent, it dissolves chemically in such a way that the dissolution is consistent with the symmetry of the crystal. Due to the anisotropy of the crystal, the dissolution rates are different in different directions giving rise to depressions known as etch pits [18,19]. The dislocations can also be revealed in the form of etch pits. The shape of the etch pit is consistent with the symmetry of the crystal. There is also the possibility that the etch pits formed may be due to impurity inclusions, point defects etc.

Etching process is a very complex process and the etching study is based on qualitative or empirical aspects. It can mainly be used to reveal the history of growth of the crystals, to determine the density of dislocations and to estimate the impurity distribution in crystalline bodies.

2.9 References


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