CHAPTER- 2

EXPERIMENTAL

2.1. UV-vis-NIR spectroscopy

UV-vis spectra were recorded using CARY 5E UV-vis-NIR spectrophotometer.

![CARY 5E UV-vis-NIR spectrophotometer](image1.png)

Fig. 2.1. CARY 5E UV-vis-NIR spectrophotometer

2.2. Fourier transform infrared spectroscopy (FT-IR)

Fourier transform infrared spectra were recorded using AVATAR 330 FT-IR spectrometer.

![AVATAR 330 FT-IR spectrometer](image2.png)

Fig. 2.2. AVATAR 330 FT-IR spectrometer
2.3. **Powder X-ray diffraction**

Powder XRD can provide information about crystalline structure (or lack thereof) in a sample even when the crystal size is too small for single crystal X-ray diffraction. Data were analyzed with the PANalytical X’pert PRO X-ray diffractometer at room temperature using graphite monochromated CuKα radiation (1.54060 Å).

![PANalytical X’pert PRO diffractometer](image)

**Fig. 2.3. PANalytical X’pert PRO diffractometer**

2.4. **Single crystal X-ray diffraction**

Single crystal X-ray diffraction studies were carried out using Bruker AXS (Kappa APEX II) X-ray diffractometer. Data were collected on a diffraction system, which employs graphite monochromated MoKα radiation (λ = 0.71073 Å). The structures were solved and refined by full matrix least squares on F² with WinGX software package utilizing SHELXS97 and SHELXL97 modules. The plots for the
structures were created with *DIAMOND* software\(^2\). All non-hydrogen atoms were refined anisotropically.

![Bruker AXS (Kappa APEXII) X-ray diffractometer](image)

**Fig. 2.4.** Bruker AXS (Kappa APEXII) X-ray diffractometer

2.5. **Inductively coupled plasma emission spectroscopy (ICP)**

ICP studies were recorded by using Optima 5000 DV series spectrometer. ICP is a fast multi-element technique with a dynamic linear range and moderate-low detection limits (~0.2-100 ppb). The instrument uses an ICP source to dissociate the sample into its constituent atoms or ions, exciting them to a level where they emit light of a characteristic wavelength. Up to 60 elements can be screened per single sample run of less than one minute and the samples can be analyzed in a variety of aqueous or organic matrices. There is less chemical interference than with flame atomic absorption spectroscopy, but some spectral interference are possible and there are some element limitations.
Fig. 2.5. Optima 5000 DV ICP spectrometer

2.6. Thermal analysis

Thermogravimetry (TG)/differentical thermal analysis (DTA) curves were recorded by using SDT Q600 (TA instrument) thermal analyzer.

Fig. 2.6. SDT Q600 thermal analyzer

2.7. Scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS)

The surface morphology was observed using a JEOL JSM 5610 LV scanning electron microscope which has a resolution of
3.0 nm and an acceleration voltage of 0.3 to 30 kV having the maximum magnification of 2,00,000 times.

![SEM Image](image.jpg)

**Fig. 2.7. JEOL JSM 5610 LV scanning electron microscope**

SEM is an incredible tool for revealing the unseen world of micro space. It shows very detailed three-dimensional images at much higher magnification than is possible with an optical microscope. An electron gun (at the top) emits a beam of high-energy electrons. This beam travels downward through a series of magnetic lenses designed to focus the electrons to a very fine spot. As the electron beam hits each spot on the sample, secondary electrons are knocked loose from its surface. A detector counts these electrons and sends the signals to an amplifier. The final image is built up from the number of electrons emitted from each spot on the sample.

EDS is a chemical microanalysis technique performed in conjunction with a SEM. The technique utilizes X-rays that are emitted from the sample during bombardment by the electron beam to characterize the elemental composition of the analyzed volume. When the sample is bombarded by the electron beam of the SEM, electrons
are ejected from the atoms comprising the sample’s surface. A resulting electron vacancy is filled by an electron from a higher shell, and an X-ray is emitted to balance the energy difference between the two electrons. The EDS X-ray detector measures the number of emitted X-ray photons and their energy. The energy of the X-ray is characteristic of the element from which it was emitted. A spectrum of the energy versus relative counts of the detected X-rays is obtained and evaluated for qualitative and quantitative determination of the elements present in the sampled volume. Cobalt is used as the standard to study the EDS and this method can detect elements with atomic numbers ranging from 11 to 92.

**2.8. Kurtz and Perry powder SHG measurement**

The second harmonic generation test was performed by the Kurtz powder SHG method. An Nd:YAG laser with a modulated radiation of 1064 nm was used as the optical source and directed on the powdered sample through a filter. The grown crystals were ground to a uniform particle size of 125-150 µm and then packed in a micro capillary of uniform bore and exposed to laser radiation. The output from the sample was monochromated to collect the intensity of the 532 nm component and to eliminate the fundamental. Second harmonic radiation generated by the randomly oriented micro crystals was focused by a lens and detected by a photomultiplier tube. The doubling of frequency was confirmed by green radiation of 532 nm.
Fig. 2.8. Schematic representation of the experimental set-up for study of second harmonic generation in powders

2.9. High-resolution multicrystal X-ray diffractometry

Fig. 2.9 shows a schematic line diagram of the multicrystal (four crystal) X-ray diffractometer designed, developed and fabricated at National Physical Laboratory (NPL). This system is specially designed for high-resolution X-ray diffractometry and diffuse X-ray scattering studies. In this system, a fine focus ($0.4 \times 8$ mm; 2 kW Mo) X-ray source energized by a well-stabilized Philips X-ray generator (PW 1743) was employed. The X-ray source is combined with a long collimator, fitted with a pair of fine slit assemblies and a set of three plane (111) silicon crystals for monochromating and collimating the exploring X-ray beam. The specimen forms the fourth crystal stage. The white X-ray beam first passes through a collimator and is then diffracted from two plane (111) silicon Bonse-Hart type monochromator crystals. Well resolved Mo$K\alpha_1$ and Mo$K\alpha_2$ beams are obtained after
diffraction from the crystals and a well collimated Mo$K\alpha_1$ beam is isolated and further diffracted from the third plane (111) silicon monochromator crystal, set in dispersive symmetrical Bragg geometry in (+, −, −). This arrangement improves the spectral purity ($\Delta\lambda/\lambda < 10^{-5}$) of the Mo$K\alpha_1$ beam. Such an arrangement disperses the divergent part of the Mo$K\alpha_1$ beam away from the Bragg diffraction peak and there by gives a good collimated and monochromatic Mo$K\alpha_1$ beam at the Bragg diffraction angle, which is used as an incident, or exploring beam for the specimen crystal. The dispersion phenomenon is well described by comparing the diffraction curves recorded in dispersive (+, −, −) and non-dispersive (+, −, +) configurations$^6$. From the diffraction curves of these two configurations, one can see that due to dispersive nature, the X-rays which are slightly away from the exact Bragg peak position are dispersed away from the center and one can get highly collimated and monochromatic $K\alpha_1$ beam from the peak position as seen in the topograph. When such a dispersive configuration is used, though the lattice constant of the monochromator crystal(s) and the specimen are different, the dispersion-broadening in the diffraction curve of the specimen crystal does not arise. The specimen occupies the fourth crystal stage and is oriented for diffraction in (+, −, −, +) configuration. The height of the X-ray beam can be adjustable which is $\sim 6$ mm is at the specimen stage with vertical divergence of $\sim 10$ arc min in these experiments. The divergence of the exploring beam in the horizontal
plane (plane of diffraction) was estimated to be < 3 arc sec. The specimen can be rotated about a vertical axis, which is perpendicular to the plane of diffraction, with minimum angular interval of 0.5 arc sec. The diffracted intensity is measured by using a scintillator counter, whose output is fed to a counting system (Philips, PW1749) built in a microprocessor-controlled unit used to give step wise rotations to the specimen through a stepping motor.

![Diagram of multicrystal X-ray diffractometer](image)

**Fig. 2.9. Schematic line diagram of multicrystal X-ray diffractometer**

**2.10. Microhardness**

Microhardness measurements were carried out using Reichert 4000E Ultramicrohardness tester.
Fig. 2.10. Reichert 4000E Ultramicrohardness tester

2.11. Dielectric measurements

Dielectric measurements were carried out by the parallel plate capacitor method as a function of temperature for various frequencies using a Precision LCR meter (AGILENT 4284 A model).

Fig. 2.11. Precision LCR meter (AGILENT 4284 A model)

2.12. Crystal growth apparatus

The schematic diagram of the growth apparatus used for the low temperature solution growth technique is shown as Fig. 2.12. It consists of a large tank (constant temperature bath) heated at the base
using an infrared lamp. The IR lamps are energized through a relay switch. The control is effected by a jumo contact thermometer coupled to an on-off controller, which has a controlling accuracy of ± 0.01°C. A typical on-off controller circuit is shown in Fig. 2.13. The temperature of the constant temperature bath is converted into a signal by a suitable sensor. The controller is contacted with an on-off switch. It gets activated when the process variable (bath temperature) crosses the set point. There are only two stable states in an on-off controller. “On” state is enabled when the temperature is below the set point. As the desired set point is arrived, the controller goes to the “off” state. To get change in the state, the temperature must cross the set point. Set point variations, which occur due to electrical noise interference and process disturbances, seriously affect the practical applications of the controller. Contrary to this, a proportional controller continuously manipulates the process variable so that the heat input is in balance with the heat demand. The controller consists of a power supply, processor, booster and proportional controllers. In the present investigation, the growth instrument was modified by replacing the infrared lamp using a programmable temperature controller Eurotherm. The constant temperature bath used in the present study is shown in Fig. 2.14.
Fig. 2.12. Basic apparatus used for solution crystal growth

Fig. 2.13. A typical ON-OFF controller
Fig. 2.14. Constant temperature bath used for growth of crystal from aqueous solution

2.13. Computational details

Density functional theory (DFT) calculations were performed using the GAUSSIAN 09W program package on a personal computer without any constraints on the geometry, using B3LYP,9 levels with LANL2DZ as the basis set. By the use of the GAUSSVIEW 5.0 molecular visualization program the optimized structure of the molecule has been visualized. The Hirshfeld surface analysis was done using HF method with 3-21G as basis set, using single crystal XRD data.
REFERENCES


