EXPERIMENTAL TECHNIQUES

2 INTRODUCTION

This chapter presents a comprehensive description on the techniques that are followed to characterize the samples in this work. The advent of sophisticated equipments has improved its way in analyzing compounds for their chemical and physical properties. The technique of Fourier Transform Infrared (FTIR) spectroscopy has been employed to assess the functional groups present in the compounds. To corroborate the placement of protons in the compounds, proton NMR spectroscopy has been utilized. Single crystal X-ray diffraction technique was used to validate the structure of the grown crystals. The transparency of the crystal was tested using UV-Vis spectrophotometer. Mechanical properties of the crystals were investigated using Vickers microhardness tester fitted with diamond indentator. Thermogravimetric and differential thermal analysis technique have been applied to study the thermal stability of the crystal. Second harmonic generation test was studied to focus nonlinear optical character of the material.

2.1 SINGLE CRYSTAL X-RAY METHOD

Single crystal X-ray diffraction method is mainly concerned with the excitation of atoms by the removal of an electron from an inner shell. The excitation is followed by transferring an electron from an outer shell to inner shell with consequent emission of energy as X-rays; that is, photons of high energy and short wavelengths in the order of tenths of angstroms to several angstroms. There are three methods to determine the structure of compounds. One method uses
the fact that X-rays emitted by an excited element have a wavelength characteristic of that element and its intensity is proportional to the number of excited atoms. The excitation can be carried out in several ways either by direct bombardment of the material with electron (direct emission X-ray) or by irradiation of material with X-rays (fluorescent analysis). The second method of X-rays utilizes the differing absorption of X-rays by different materials (absorption analysis). A third method makes use of X-rays in analytical work by the diffraction of X-rays from the planes of a crystal (diffraction analysis) [1].

2.1.1 DESCRIPTION OF INSTRUMENT

X - Ray generating equipment consists of X-ray tube, which is kept at high vacuum. They are operated at 50 or 60 kV. Copper or molybdenum target is used. The schematic diagram of X-ray instrumentation is presented in Fig. 2.1.

2.1.1.1 COLLIMATORS

Radiation from an X - ray tube is collimated either by a series of closely spaced parallel metal plates by a bundle of tubes 0.5 mm or less in diameter. Increased resolution can be obtained by decreasing the separation between the metal plates of the collimator or by increasing the length of the unit but this is achieved at the expense of intensity [1].
Fig. 2.1 Schematic representation of X-ray spectroscopy
2.1.1.2 FILTERS

When the wavelengths of two spectral lines are nearly the same and there is an element with an absorption edge at a wavelength between the lines, the element may be used as filter to reduce the intensity of line of shorter wavelength. Filter for common targets of X-ray tubes are listed as Mo, Cu, Cr, Pt and W.

2.1.1.3 ANALYZING CRYSTAL

Virtually monochromatic radiation is obtained by reflecting X-rays from crystal planes. The relationship between the wavelength of X-ray beam, the angle of diffraction θ, and the distance between each set of planes of the crystal lattice, d, is given by Bragg condition

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

where \( n \) represents the order of diffraction.

2.2 INFRARED SPECTROPHOTOMETRY

The infrared (IR) spectroscopy is mainly concerned with the absorption of energy by a molecule, ion or radical from a continuum or with the study of emission of infrared radiation by species of excited states. It is one of the influential tools for recognition of organic, inorganic, polymeric, crystalline and co-ordination compounds. The IR region of the electromagnetic spectrum is considered to cover the range from 50 to 12,500 cm\(^{-1}\) approximately. It is generally subdivided into three regions – near IR (12,500 - 4000 cm\(^{-1}\)), middle IR (4000 - 400 cm\(^{-1}\)) and the far IR (400 - 50 cm\(^{-1}\)) [1]. The middle IR is the
region, most commonly employed for laboratory investigations as it covers most of the vibrational transitions.

The selection rule involved in infrared spectroscopy states that for vibration to be active in the infrared region there must be change in the dipole moment of the bond. When a molecule absorbs infrared radiation, the usual vibrational transition is from the ground state to the first excited state, but other transitions can also occur although not common, giving rise to weaker bands than the fundamentals and are called overtones and combinations. If two fundamental vibrations are simultaneously excited, then these are called combination bands.

2.2.1 FOURIER TRANSFORM INFRARED SPECTROSCOPY

Fourier transform spectroscopy is a simple mathematical technique to resolve a complex wave into its frequency components. Fourier Transform Infrared (FTIR) has made the mid IR region more useful. Conventional spectroscopy called the frequency domain spectroscopy, records the changes in radiant power as a function of frequency. In the time domain spectroscopy the changes in radiant power is recorded as a function of time. In the Fourier transform spectrometer a time domain plot is converted into frequency domain spectrum. The actual calculation of the Fourier transform of such systems is done by means of high speed computers [1].

2.2.1.1 DESCRIPTION OF FTIR SPECTROMETER

FTIR spectrometer consists of an infrared lamp as 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. Interferometric multiplex instruments employing the Fourier transform are now finding more general applications for both qualitative and quantitative infrared measurements. The schematic diagram of a FTIR spectrometer is shown in Fig. 2.2.

### 2.2.1.2 SAMPLE HANDLING TECHNIQUES

Recording of IR spectra of solid sample is more difficult because the particles reflect and scatter the incident radiation and therefore transmittance is always low. Three different techniques are commonly employed in recording such spectra.

#### 2.2.1.3 MULLING TECHNIQUE

A small amount of the sample is ground using mortar and pestle. Then a drop of nujol or paraffin oil is added and the grinding continued till the mixture attains the consistency of a thin paste. It is transferred to an infrared window and a second window is lowered onto it. A thick film free of air bubbles should be produced. The two plates with a mull between them are placed in a cell holder and the spectrum is recorded. There will be strong bands at 2900, 1470, 1370 cm⁻¹ and a weak band at 720 cm⁻¹ due to nujol [2].

#### 2.2.1.4 PRESSED - PELLET TECHNIQUE

A convenient method for solid compounds that are insoluble in the usual solvents, the pressed pellet technique can be employed. The pellet technique involves mixing the finely ground sample (1-100 μg) and potassium bromide powder and pressing the mixture in a
Fig. 2.2  Schematic representation of FTIR spectrometer
evacuated die at sufficient pressure to produce a transparent disk. Other alkali halides may also be used, particularly CsI or CsBr for measurements at longer wavelength. The ground powder is finally introduced into a mini press made from two half inch diameter stainless steel bolts and a stainless steel nut. The end of the bolt must be polished flat and parallel. One bolt is inserted about half way into the nut and the KBr plus sample mixture added. The second bolt is then screwed into the nut and pressure applied by tightening the bolts together. When the bolts are carefully withdrawn a pellet suitable of infrared transmission work remains. The pellet is not removed from the nut, which acts as a holder in the spectrometer [1, 3].

2.2.1.5 LIQUIDS AND SOLUTIONS

The easiest method to obtain a qualitative infrared spectrum of liquid is to place one drop of the liquid onto a disc of NaCl, KBr etc., cover the drop with a second disc and mount the pair in holder. Teflon spacers may be used to give various path lengths. Alternatively liquid samples can be run either as a pure liquid if a cell of suitable thickness is available (0.02 mm) or a solution in a longer cell if a suitable solvent can be found. The best solvents are nonpolar, nonhydrogen liquids such as CS₂ or CCl₄ [4].

2.3 RAMAN SPECTROMETRY

Raman spectroscopy is a complementary technique to infrared spectroscopy and provides information about the vibrational energy levels of molecules. In Raman spectroscopy, the radiation from a powerful monochromatic source such as a laser is focused on the
sample under study. The radiation scattered by the samples consist of the wavelength of the incident radiation (known as Rayleigh line) plus a number of other lines characteristic of the molecular vibrations (Raman lines). The Raman lines at frequencies higher than that of the Rayleigh lines are known as anti – Stokes lines and those at lower frequencies are known as Stokes lines. The Raman scattering of photons by a molecule corresponds to the vibrational and rotational transition of the scattering molecule. On interaction with molecules, the photons are inelastically scattered making the molecules move to a higher energy level, and as a result the photons lose energy and are scattered with a lower energy. If the molecules are in the higher vibrational energy level on interaction with the photons, they may undergo a transition to a lower energy level in which case the photons are scattered with increased frequency. Thus the Raman shifts are equivalent to the energy changes involved in the transitions of the scattering species and hence characteristic of the sample [1, 5].

2.3.1 DESCRIPTION OF LASER RAMAN SPECTROMETER

DILOR - Z 24 spectrometer consists of a triple additive monochromator, a macro sample chamber, a photomultiplier tube and a recorder. The monochromator consists of three holographic gratings of 1800 lines/mm. The photomultiplier tube is of Hamanau R943 type. Argon ion laser (5145 Å, 4880 Å), Helium Ne laser (6328 Å) and krypton ion laser (6471 Å), serve as sources. The spectra can be scanned in the region 10 – 4000 cm⁻¹ with resolution of 0.05 cm⁻¹ sequential and continuous scans are possible. Sample may be prepared in sealed glass tubes of 1-5 mm diameter. Fig. 2.3 shows the schematic representation of Laser Raman spectrometer [1, 5].
2.3.2 SAMPLE HANDLING TECHNIQUES

Samples in the form of liquids and solids can be handled by a standard instrument; gases however require a more sophisticated arrangement involving a higher power laser, multiple reflection cells and a specially cooled photomultiplier.

2.3.2.1 SOLIDS

Solids may be examined as powders, lumps, pellets or crystals. Powders are best handled in capillary tubes or tamped into a conical depression in the end of a metal rod. Irregular pieces of solid material may be glued to a glass rod and held in the laser beam. Powders may be pressed into pellets and examined in the same way. Water sensitive
solids samples can be loaded into capillary tubes in a dry box and sealed. Single crystals can be carefully positioned so that the laser beam passes along one of the axes of crystal [5].

2.3.2.2 LIQUIDS

A small volume quartz cell can be used as a Raman liquid sample container. Raman spectroscopy is ideally suited for micro sampling. The laser beam can be focused to a very small area and samples contained in melting point capillaries yield virtually the same spectra as much larger samples. It is important however to align the sample exactly with the slit of the monochromator [4].

2.4 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

In nuclear magnetic resonance (NMR) spectroscopy, the characteristic absorption of energy by certain spinning nuclei in a strong magnetic field, when irradiated by a second and weaker field perpendicular to it, permits identification of atomic configurations in molecules. Absorption occurs when these nuclei undergo transitions from one alignment in the applied field to an opposite one.

2.4.1 PULSED (FOURIER TRANSFORM) NMR SPECTROMETER

An NMR spectrometer capable of pulsed Fourier transform measurements is a combination of a continuous – wave circuit, as found in conventional NMR spectrometers, a computer controllable pulse generator, and a small digital computer of core memory size 8 - 20K. A simplified block diagram of a pulsed Fourier transform unit is
shown in Fig. 2.4. The computer controllable pulse programmer generates dc pulses. For $^{13}$C NMR resonance, the output of a 25 MHz rf oscillator in the Fourier transform unit is fed to an rf gate and sent to the power amplifier units only when the gate is open. The digital pulse programmer controls gate on/off and determines the pulse width, interval, and repetition rate. The timing of each pulse train is controlled by the clock pulse from the built-in, highly stable, crystal-controlled oscillator to assure high resettablility. For $^{13}$C experiments, the $^2$H signal of the deuterated solvent is used for the internal lock of the magnetic field. The lock signal is observed on the oscilloscope to adjust the magnetic homogeneity during signal accumulation. The oscilloscope can also be used for monitoring the free induction decay signal and quick display of accumulated signals and the Fourier transformed spectra to determine if the signal-to-noise ratio is satisfactory. The rest of the operation is under computer control. The operator can set the values of the spectral width, acquisition time, number of transients, and pulse width [1].

![Block diagram of pulsed Fourier Transform NMR Spectrometer](image)

**Fig. 2.4** Block diagram of pulsed Fourier Transform NMR Spectrometer
2.5 THERMAL ANALYSIS

2.5.1 THERMOGRAVIMETRIC ANALYSIS (TGA)

Thermal analysis includes a group of techniques in which the physical property of the substance is measured as a function of temperature while the substance is subjected to a controlled temperature program. When a sample is heated or cooled at a controlled rate, the weight of a substance in an environment is recorded and the change of weight (loss or gain) is measured as a function of temperature or time [1, 5]. The main parts of TGA are

- High sensitive thermobalance
- Micro - furnace
- Furnace temperature programmer or controller
- Recorder or Computer with plotter

The thermobalance is used to measure the weight accurately and the microfurnace to change the temperature in a controlled manner at a specific rate. A schematic diagram of TGA is presented in Fig. 2.5a. The thermobalance chamber consists of a servo controlled balance arm. At one end of the balance arm, a tare weight is suspended and at the other end, sample pan is hung down by means of a nichrome wire through a quartz link. This pan extends down to micro-furnace chamber through a metallic anti static tube. The thermobalance uses a servo operated balance system in which the electrical signal from an optical null detector is applied directly to control the current in a torque motor. The weight loss as a function of temperature is measured by the principle of null deflection method using a light source and photosensitive diode. Here the torque exerted by the servo motor to restore the balance arm to its null position, is directly
proportional to the weight of the sample which was calibrated using a standard 100 mg weight [1, 5].

The ultra microwave furnace and the sample holder are shown in Fig. 2.5b. A unique feature of this instrument is the small thermal mass furnace, consists of an alumina cylinder which is 0.5 inch in diameter and 0.75 inch in length, wound with platinum wire. The furnace is constructed with bifilarly wound platinum wire and plasma sprayed with alumina at high temperature. It is covered with ceramic cement and cured. This coating protects platinum winding from the attack of the corrosive gases evolved during analysis. The platinum wire functions both as a heater and also as a temperature sensor. A platinum sleeve is placed around the platinum wire wound around the mandrel to provide uniform distribution in the furnace. The maximum temperature of the furnace is 1000° C. This mandrel is held by a mullite stem, which is about four inches long. The mullite stem is supported by short posts at its base and fits into a stainless steel assembly. The whole assembly is enclosed by a pyrex tube provided with a gas outlet. Due to the low thermal inertia of the microfurnace, a controlled heating or cooling rate as high as 200° C/min is achieved. An automated furnace lift mechanism ensures the reproducible positioning of the sample [1, 5].

An automated temperature calibration programme is built into the system wherein the system is calibrated. The temperature of the furnace was calibrated with Ni and Fe (Curie point standards) along with a small horse shoe magnet placed around the microfurnace. A two point calibration is run to calibrate the TGA PC-7 series analyzer.
It takes care of the reaction kinetics and also detects the melting point of the compound, which is to be investigated.

Fig. 2.5a Schematic diagram of TGA
Fig. 2.5b Schematic diagram of ultra micro-furnace and sample holder
2.5.2 DIFFERENTIAL THERMAL ANALYSIS

In differential thermal analysis (DTA) the temperature of a sample and a thermally inert reference material are measured as a function of temperature (usually sample temperature). Any transition which the sample undergoes will result in the liberation or absorption of the energy by the sample with corresponding deviation of its temperature from that of the reference [1].

2.5.3 DIFFERENTIAL SCANNING CALORIMETRY

In differential scanning calorimetry (DSC), the sample and reference material are also subjected to a closely controlled programmed temperature. In the event that a transition occurs in the sample, however, thermal energy is added to or subtracted from the sample or reference containers in order to maintain both sample and reference at the same temperature [1]

2.6 MICROHARDNESS

Hardness of a material is the resistance it offers to indentation by a much harder body. It may be termed as a measure of the resistance against lattice destruction or the destruction or the resistance offered to permanent deformation or damage [6]. The term "hardness" means in different ways. It is the resistance to penetration to a metallurgist, resistance to wear to a lubrication engineer, resistance to scratching to a mineralogist and resistance to cutting to a machinist. All these are related to the plastic flow stress of the material. The hardness properties are basically related to the crystal
structure of the material. Microhardness study on the crystals brings out an understanding of the plasticity of the crystal [7].

Hardness is a technique, in which a crystal is subjected to a relatively high pressure within a localized area. By suitable choice of indenter material and relatively simple equipment construction, hardness tests can be easily carried out on all crystalline materials under various conditions of temperature and pressure. Deformation is local, so that a number of trials can be made on a single specimen of small dimensions and can be reproduced by maintaining the specimen indenter orientation relationship. Specimen of flat relatively smooth surface is required.

2.6.1 METHODS OF HARDNESS TEST

Hardness measurement can be carried out by various methods. They are classified as follows.

1. Static indentation test
2. Dynamic indentation test
3. Scratch test
4. Rebound test
5. Abrasion test

The most popular and simplest form is the static indentation test wherein the specific geometry is pressed into the surface of a test specimen under a known load. The indenter may be ball or diamond cone or diamond pyramid. Upon removal of the indenter, a permanent impression is retained in the specimen. The hardness is calculated from the area or depth of indentation produced. The variables are the
type of the 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 a hardened steel sphere or a diamond pyramid or cone is employed. A pyramid also has advantage that geometrically similar impressions are obtained at different loads. So naturally a pyramid indenter is preferred. In this static indentation test the indenter is pressed perpendicularly in the surface of the sample by means of an applied load. Then by measuring the cross sectional area or the depth of the indentation and knowing the applied load an empirical hardness number may be calculated. This procedure followed by Brinell, Meyer, Knoop and Rockwell test [8-10].

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.

The scratch test can be classified into two types:

a. Comparison test in which one material is said to be harder than another if the second material is scratched by the first.

b. A scratch test with a diamond indenter on the surface at a steady rate and under a definite load. The hardness number is expressed in terms of the width of depth of the groove formed.
In the rebound test an object of standard mass and dimensions is bounced from the test surface and the height of rebound is taken as the measure of hardness. In abrasion test, a specimen is loaded against a rotating disk and the rate of wear is taken as a measure of hardness.

### 2.6.2 VIC\textsuperscript{ERS TEST}

Among the various methods of hardness measurements discussed above, the most common and reliable method is the Vickers hardness test method. In this method, microindentation is made on the surface of a specimen with the help of diamond indenter (Fig. 2.6). Smith and Sandland [11] have proposed that a pyramid be substituted for a ball in order to provide geometrical similitude under different values of load. The Vickers pyramid indenter where opposite faces contain an angle ($\alpha = 136^\circ$) is most widely accepted pyramid indenter. A pyramid is suited for hardness tests due to the following two reasons [12]

- a. The contact pressure for a pyramid indenter is independent of indent size.
- b. Pyramid indenters are less affected by 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 $H_V$ of Diamond Pyramid Number (DPN) is defined as
where $\alpha$ is the apex angle of the indenter ($\alpha = 136^\circ$). The Vickers hardness number is therefore calculated from the relation

$$H_v = \frac{2P \sin \alpha / 2}{d^2} \text{ kg/mm}^2$$  \hspace{1cm} (2.2)$$

where $P$ is the applied load in kg and $d$ is the diagonal length of the indentation mark in mm. Hardness values are 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 behavior in the final measurement of the residual impression is the summation of a number of effects involved in the materials response to the indentation pressure during loading.

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Fig. 2.6  Schematic diagram of Vickers diamond pyramid indenter and indentation produced.
2.7 UV-VIS SPECTROPHOTOMETRY

Spectrophotometers include promotion of electrons from the ground state to higher energy state. In the ground state the spins of the electrons in each molecular orbital are essentially paired. In the higher state, if the spins of the electrons are paired then it is called an excited singlet state. On the other hand, if the spins of the electrons in the excited state are parallel, it is called excited triplet state.

2.7.1 DESCRIPTION OF THE INSTRUMENT

A spectrophotometer is a device which detects the percentage transmittance of light of certain intensity and frequency range is passed through the sample. Thus the instrument compares the intensity of the transmitted light with that of incident light. It consists of a source, focusing optics, standard sample cuvette, wavelength isolation device, and a detector with amplifier and readout system. Fig. 2.7 shows the schematic representation of double beam UV-Vis spectrophotometer.

2.7.2 SCANNING DOUBLE BEAM SPECTROPHOTOMETER

Spectrophotometers of this type feature a continuous change in wavelength. One beam permanently accommodates a reference or blank, and the other the sample. An automatic comparison of transmittance of sample and reference is made while scanning through the wavelength region. The ratio of sample to reference after conversion to absorbance values is plotted as a function of wavelength on a recorder.
Fig. 2.7 UV-Vis Spectrophotometer
In an optical arrangement light from either visible or ultraviolet source enters the grating monochromator. Broad band filters contained in a filter wheel are automatically indexed into position at a required wavelength to reduce the amount of stray light and unwanted orders from diffraction grating. The optical beam is then directed alternatively through the sample and reference cells by a system of rotating sector mirrors (choppers) and corner mirrors. Each beam, a pulse of light separated in time by a dark interval, is then directed onto a photomultiplier tube in a time sharing procedure. After amplification, the reference signal is used to provide a signal to dynode voltage regulator. The dynode voltage is varied to maintain a constant reference signal and keep all amplifiers within required operating limits. The sample signal is either processed through a logarithmic converter for absorbance measurements or is used directly for transmittance measurements. The result is fed to recorder, meter or digital indicator [1].

2.8 FLUORESCENCE SPECTROPHOTOMETRY

Fluorescence spectroscopy has assumed a major role in analysis, particularly in the determination of trace contaminants in our environment, industries, and bodies, because for applicable compounds fluorescence gives high sensitivity (in the low parts per trillion) and high specificity. High sensitivity results from the difference in wavelength between the exciting and fluorescence radiation. This results in a signal contrasted with essentially zero background; it is always easier to measure a small signal directly than as a small difference between two large signals as is done in absorption spectrophotometry. High specificity results from depend-
ance on two spectra; the excitation and the emission spectrum. Two compounds that are excited at the same wavelength but emit at different wavelengths are readily differentiated without the use of chemical separation techniques. Also, a fluorescent compound in the presence of one or more nonfluorescent compounds is readily analyzed fluorometrically even when the compounds have overlapping absorption spectra.

Fluorescence may be expected generally in molecules that are aromatic or contain multiple-conjugated double bonds with a high degree of resonance stability. Both classes of substances have delocalized π-electrons that can be placed in low lying excited singlet states. In polycyclic aromatic systems where the number of π-electrons available is greater than in benzene, these compounds and their derivatives are usually much more fluorescent than benzene and its derivatives.

A generalized luminescence instrument is illustrated in Fig. 2.8 It contains of (1) a source of light, (2) a primary filter or excitation monochromator, (3) a sample cell, (4) a secondary filter or emission monochromator, (5) a photodetector and (6) a data readout device. The primary filter or excitation monochromator selects specific bands or wavelengths of radiation from the light source and directs them through the sample in the sample cell. The resultant luminescence is isolated by the secondary filter or emission monochromator and directed to the photodetector which measures the intensity of the emitted radiation. For the observation of phosphorescence a repetitive shutter mechanism will be required.
Fig. 2.8 Basic components of fluorescence instrumentation

2.9 NONLINEAR OPTICAL MEASUREMENT TECHNIQUE

2.9.1 SECOND HARMONIC POWDER TEST

The basic configuration used for the study of second harmonic generation in powders is shown in Fig. 2.9. It consists of a Q-switched laser whose beam falls unfocused onto a thin section (~0.2 mm) of powder of the material under study. After the fundamental beam is removed by a series of short wavelength passing filters, the second harmonic is detected by a photomultiplier and displayed on an oscilloscope. A reference beam is obtained by use of beam splitter placed ahead of the sample. This enables the intensity of the fundamental or second harmonics generated in a reference sample [13] to be monitored by displaying both signals simultaneously on a dual-beam scope. The system also permitted the insertion of narrow-
Fig. 2.9. Apparatus used for study of second harmonic generation in powders

pass filters at the second-harmonic wavelength between the shott filters and the photomultiplier to eliminate spurious signals. In order to improve the efficiency of second harmonic collection at the detector, a parabolic reflector was placed directly in front of the sample (i.e., between the laser and the sample) with a small access hole for the laser beam. Nd:YAG laser of 1064 nm was used. It was Q-switched by a rotating mirror at a rate of 400 Hz. Peak powers in this case were ~1kW with pulsewidths of ~200 nsec [14].
2.9.2 SAMPLE PREPARATION AND MOUNTING

Samples were prepared and mounted using several techniques. For qualitative results and for most initial survey work, a thin layer (~0.2 mm) of upgraded powder was placed on a microscope slide and held in place with transparent tape. For quantitative work, powders were graded by use of standard sieves to the desired range of particle sizes (usually 75-150 μm) and loaded into a quartz cell of known thickness (0.2 mm, 0.1 mm, etc.) with the aid of a vibrator to assure uniform packing. Particle sizes were checked by standard optical microscopy techniques. In the case of materials such as quartz, zinc oxide, and other materials having known nonlinear coefficients and available in single-crystal form, powders were made from single crystals using a Spex vibrating ball mill, and then graded using standard sieves. A similar procedure was followed in the case of minerals of polycrystalline or single-crystalline character [14].

2.9.3 EXPERIMENTAL RESULTS

In order to determine the essential features of second-harmonic generation in thin powder layers, a series of experiments were performed to measure the dependence of second-harmonic intensity on the following parameters (1) angle between detector and direction of incident light beam (=θ), (2) powder-layer thickness (=L), (3) average particle size (=R), and (4) laser-beam diameter (=D).

Within certain ranges of layer thickness and particle size it was found that a fairly simple and reproducible dependence on each of the above parameters could be obtained. The following discussion is limited basically to a domain in which \( R \ll L \ll D \). This ordering insures that the fundamental beam strikes large number particles of
random orientation. There by performing a significant statistical average. In addition a planar geometry is retained.

2.9.4 ANGULAR DISTRIBUTION

When the average particle size, layer thickness, and beam diameter satisfy the inequality as \( \bar{r} << L << D \), it is found that the angular distribution of second-harmonic intensity for the powder in air is nearly cosinusoidal in \( \theta \) for both the forward and backward scattering directions. Thus, the sample considered as a source of second-harmonic radiation behaves like an isotropic planner radiator obeying Lambert’s (cos) law [15]

\[
I(\theta, \Phi) = I_o \cos \theta
\]  

(2.4)

Where \( \theta \) and \( \Phi \) are spherical polar angles and the photometric intensity \( I_o \) (energy/sec/sr) is defined as

\[
I_o = \int B dS
\]  

(2.5)

Where B is the photometric brightness and dS is a surface element.

2.9.5 DEPENDENCE OF \( I^{2o} \) ON LAYER THICKNESS L

The second-harmonic signal was found to vary linearly with layer with layer thickness L for fixed particle size r after integrating over the \( 4\pi \) solid angle. This implies that the second-harmonic intensity is proportional to the total number of particles present. A linear
dependence on $L$ was also found in the case of immersion of the powder in an index-matching liquid.

**2.9.6 DEPENDENCE OF $I^{2\omega}$ ON AVERAGE PARTICLE SIZE**

The important features of the particle-size dependence are: (1) a peak in the intensity when the particle size is close to the average coherence length $l_c$, (2) an approximately linear increase in intensity with increasing particle size $\tilde{r}$ for $\tilde{r} \ll l_c$ and (3) an inversion relation between intensity and particle size (i.e., $I^{2\omega} \propto 1/\tilde{r}$) for $\tilde{r} \gg l_c$.

This technique allows only a rough estimate of nonlinear optical response. The powder sample is irradiated by a fundamental laser beam and the generated second harmonic light is detected by a photomultiplier tube. A reference sample with well known nonlinearity is also used to calibrate the second harmonic light.

**REFERENCES:**


Chapter 2 Experimental techniques


