

## **CHAPTER II**

### **CHARACTERIZATION TECHNIQUES**

#### **2.1 INTRODUCTION**

The working principle and instrumentation of various techniques used for the characterization of a sample is discussed briefly in this chapter. The use of instrumentation is an exciting and fascinating part of any analysis that interacts with all the areas of chemistry and with many other fields of pure and applied science. Characterization of a crystal essentially consists of determination of chemical composition, structure, defects and study of their optical properties (Elwell and Scheel 1975).

#### **2.2 POWDER X-RAY DIFFRACTION (XRD) STUDIES**

Powder X-ray diffraction is a tool for accurate determination of lattice parameters of known crystal structure and for the identification of elements and compounds.

##### **2.2.1 X-ray Powder Diffractometer**

The powder diffraction method was devised independently by Debye and Scherrer. It is the most useful of all diffraction methods and when properly employed, can yield a great deal of structural information about the material under investigation. 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 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 degrees. The diffractometer is connected to a computer for data collection and analysis. The scintillation counter tube can be moved in step of 0.01 degree by means of a stepper motor and any diffracted beam can be closely scanned to study the peak profile. A high resolution powder diffractometer - RICH SIEFERT with Guinier geometry is employed for characterization and grain size determination.

### **2.2.2 Identification of the material**

The powder diffraction of a substance is characteristic of the substance and forms a sort of fingerprint of the substance to be identified. The peaks of the X-ray diffraction pattern can be compared with the standard available data for the confirmation of the structure.

### **2.3 FOURIER TRANSFORM INFRARED (FT-IR) ANALYSIS**

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.

### **2.3.1 Preparation of sample for FT-IR spectroscopy**

**Liquid:** A drop of a liquid organic compound is placed between a pair of polished sodium chloride or potassium bromide plates, referred to as salt plates. When the plates are squeezed gently, a thin liquid film forms between them. A spectrum determined by this method is referred to as a neat spectrum since no solvent is used. Salt plates break easily and are water soluble. Organic compounds analyzed by this technique must be free of water. The pair of plates is inserted into a holder which fits into the spectrometer.

**Solid:** All our samples were characterized by KBr pellet method, which involves mixing the finely ground solid sample with powdered potassium bromide and pressing the mixture under high pressure. Under pressure, the potassium bromide melts and seals the compound into a matrix. The result is a KBr pellet which can be inserted into a holder in the Spectrometer. The main disadvantage of this method is that potassium bromide absorbs water, which may interfere with the spectrum that is obtained. If a good pellet is prepared, the spectrum obtained will have no interfering bands since potassium bromide is transparent down to  $400\text{ cm}^{-1}$ .

## **2.4 FT-RAMAN VIBRATIONAL SPECTROSCOPY**

Vibrational spectroscopy is an extremely useful tool in the elucidation of molecular structure. The spectral bands can be assigned to different vibrational

modes of the molecule. The various functional groups present in the molecule can be assigned by comparison of the spectra with characteristic functional group frequencies. As the position 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.

Infrared and Raman spectroscopy are two complimentary techniques. In IR spectroscopy, the resonance absorption is made possible by the change in dipole moment accompanying the vibrational transition. Since the band intensity is directly proportional to the concentration of the sample, the technique can be very well used for quantitative estimation.

Raman spectroscopy results from the inelastic scattering (Raman scattering) of radiation by molecules. The difference in frequencies of the incident and scattered light corresponds to the vibrational and rotational energies of the molecule. It is the change in the polarizability of the molecule that is responsible for the transitions. Symmetry selection rules predict that for centro-symmetric molecules, the Raman active vibrations will be IR inactive and vice versa (mutual exclusion principle).

Raman spectroscopy has greatly advanced in the last two decades, thanks to the advancement in lasers and multichannel detection techniques. Specific techniques like Surface Enhanced Raman Spectroscopy (SERS), Resonance Raman Spectroscopy (RRS), Coherent Anti-stokes Raman

Scattering (CARS), Micro Raman, Time-Resolved Raman spectroscopy etc., have opened up a wide area of research. The advancement of optical fibers has made it a powerful pollution detection technique. The recent development, Fourier Transform (FT) Raman technique has simplified the detection of even weak bands and also ensures fluorescence-free spectra.

The FRA 106 module attached to IFS 66V FT-IR spectrometer provides the FT-Raman spectral measurements. The source of excitation used here is Nd:YAG Laser (1064 nm). In NIR excited FT-Raman, the fluorescence encountered in 90% of samples is essentially eliminated. Also absorption effects and photochemical degradation of the molecules are greatly reduced. The sample compartment is equipped with a reference source and all necessary optics for collecting radiation scattered at 90° and 180°. The interferometer consists of a CaF<sub>2</sub> beam splitter. Liquid nitrogen pre-cooled Ge-diode is used as the detector. The region covered by the instrument is 3500 cm<sup>-1</sup> - 50 cm<sup>-1</sup>. Vibrational spectroscopy can be used for:

- Characterization of functional group
- Determination of composition of mixtures
- Quantitative estimation
- Quality control of pharmaceutical products, petroleum products, etc.
- Study of ceramic material, glass, cement and other industrial products

- Study of blood and other biological systems in aqueous solutions and
- Studies of phase transitions

## **2.5 UV-Vis-NIR SPECTRAL STUDIES**

UV-Vis-NIR spectroscopy is helpful for the measurement of absorption or emission of radiation 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 radiations. 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, more diffuse and often more polarizable. A vibrational excited state of the molecule contains rotational excitation and electronically excited state of a molecule also contains vibrational excitation.

Ultraviolet spectrum of a molecule results from transitions between electronic energy levels accompanied by changes both in vibrational and rotational states. The probability for electronic transitions determines the intensity of spectral lines. There must be 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 radiation. Electronic transitions are possible for a wide range of vibrational levels within

the initial and final electronic states. Saturated hydrocarbons and compounds containing only alkyl groups, alcohol groups and ether groups are transparent (i.e., they show no absorption) in the region 200-1000 nm. Such compounds are useful as solvents for spectral determination, using solutions of the specimen in this region.

An isolated functional group not in conjugation with any other group is said to be a chromophore, if it exhibits absorption of a characteristic nature in the ultraviolet or visible region. If a series of compounds have the same functional group and no complicating factors are present, all of them will generally absorb at very nearly the same wavelength. Thus, it is readily seen that the spectrum of a compound, when correlated with data from the literature for known compounds, can be a very valuable aid in determining the functional groups present in the molecule. The absorption ( $A$ ) of a solution at a particular wavelength is given by Beer-Lambert's law  $ect = A$ , where  $c$  is the concentration of the compound,  $t$  is the thickness of the cell and  $e$  is the molar extinction coefficient characteristic of the compound at a given wavelength. This principle is used for quantitative measurements.

The UV spectrum consists of far or vacuum ultraviolet region, near or quartz 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 for the instruments, is 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 a Varian carry 5E model dual beam spectrophotometer. This is a high resolution spectrophotometer controlled by a microprocessor, which is used to study the electronic spectrum of solution, single crystals and powder samples in the range 3150 – 185 nm. Baseline correction, repetitive scan, kinetics, derivative and concentration modes are possible. Diffuse reflectance is available for solid samples.

## **2.6 NLO TEST – KURTZ POWDER SHG METHOD**

### **2.6.1 Introduction**

Growth of large single crystal is a slow and difficult process. Hence, it is highly desirable to have some technique of screening crystal structures to determine whether they are noncentrosymmetric and it is also equally important to know whether they are better than those currently known. Such a preliminary test should enable us to carry out the activity without requiring oriented samples. 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.

### **2.6.2 Experimental**

The nonlinear optical property of the grown single crystal is tested by passing 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 10.8 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 was used. This experimental setup used a mirror and a 50/50 beam splitter (BS) to generate a beam with pulse energies about 10.8 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 diameter 0.154 mm.

The photodiode detector and oscilloscope assembly measure the light emitted by the sample. 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. Thus, the figure of merit of SHG of the sample is estimated.

## **2.7 LASER DAMAGE THRESHOLD MEASUREMENT**

Laser induced breakdown is a common phenomenon observed in the crystals when subjected to high intensities of laser light. Hence, it is important to know the threshold intensities of the crystal that can withstand without getting damaged. Laser damage threshold measurements are usually carried out by pulsed irradiation. However, a direct comparison of results with the

literature values becomes impossible as the testing conditions, such as, wavelength and pulse widths are different.

The laser damage threshold of the grown crystal was measured using a Q-switched Nd:YAG laser. The damage was observed and the energy of the laser beam was measured by the power meter (Scientech Model No. ACX5004). The laser beam was focused using a focal spot size was nearly 130  $\mu\text{m}$  ( $1/e^2$  radius).

It is known that SHG output is increased on increasing the incident energy and reaches a maximum until damage occurs and decreases after damage for further increases of incident energy. The corresponding energy for maximum SHG output was taken for calculation.

$$M^2 = \theta_0 \pi D_0 / 4\lambda \quad (2.1)$$

Where, M is the laser quality and  $\theta_0$  is the beam divergence (0.5 m rad)

The diameter of the spot and the surface damage threshold of the crystals were calculated using the equations.

$$d = M^2 f 4\lambda / \pi D_0 \quad (2.2)$$

$$P = E / \tau \pi r^2 \quad (2.3)$$

Where, d is diameter of the spot (mm),  $\tau$  is the pulse width (ns), f is the focal length,  $\lambda$  is 1064 nm,  $D_0$  is the beam divergence length (1 cm), r is the radius of the spot (mm) and E is the energy (mJ).

## **2.8 THERMAL STUDIES**

Thermoanalytical methods involve the measurement of various properties of materials subjected to dynamically changing environments under predetermined conditions of heating rate, temperature range and gaseous atmosphere or vacuum.

In many cases, the use of a single thermoanalytical technique may not provide sufficient information to solve the problem on hand and hence the use of other thermal techniques, either independently or simultaneously for complementary information becomes necessary. For example, both differential Thermal analysis (DTA) and thermogravimetry analysis (TGA) are widely used in studies involving physicochemical changes accompanied by variation in the heat content and the weight of the material.

Among the thermal methods, the most widely used techniques are TGA, DTA and DSC which find extensive use in all fields of inorganic and organic chemistry, metallurgy, mineralogy and many other areas.

### **2.8.1 Differential Thermal Analysis**

Differential thermal analysis (DTA) though, often considered an adjunct to TGA is, in fact, far more versatile and yields data of a considerably more fundamental nature. The technique is simple as it involves the measurement of the temperature difference between the sample and an 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 enthalpic 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 appears as a peak. The differential signal would return to the base line 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 which are manifested as heat changes, the DTA method is applicable to all the studies listed for TGA and also to phase transformations including polymerization, phase equilibrium and chemical reactions. The DTA apparatus consists of a furnace for heating the sample and reference in an identical environment-both thermal and chemical-which may be varied, linear temperature-programmer controller, sample holder, differential temperature detector with preamplifier if required and a recorder.

### **2.8.2 Thermogravimetry**

Thermogravimetry is a technique in which the mass of a substance is measured as a function of temperature or time while the substance is subjected to a controlled temperature program. The curve obtained in a thermogravimetric analysis is called a thermogram (TG) and its first derivative is called a derivative thermogram (DTG). The inflection point in the program corresponds to the peak point in the derivative thermogram. It is important to note that the term “thermogravimetric analysis” and the abbreviation TGA are in common use.

The objective of TGA and DTA is to delineate as accurately as possible the various temperatures associated with the thermal behaviour of a given substance, i.e., temperature of decomposition, stability range of an intermediate compound and the temperature at which the reaction is complete.

## **2.9 MICROHARDNESS STUDIES**

Hardness is a measure of resistance against lattice destruction or the resistance offered to permanent deformation or damage. Measurement of hardness is a non-destructive testing method to determine the mechanical behaviour of the materials. As pointed out by Shaw (1973), the term hardness is having different meanings to different people depending upon their area of interest. For example, it is the resistance to penetration for a metallurgist, the resistance to cutting for a machinist, the resistance to wear for a lubrication engineer and a measure of flow stress for a design engineer. All these actions are related to the plastic stress of the material. 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).

The hardness depends not only on the properties of the materials under test but also largely on the conditions of measurement. Microhardness tests have been applied to fine components of clock and instrument mechanisms, thin metal strip, foils, wires, metallic fibers, thin galvanic coatings, artificial oxide films etc., as well as the thin surface layers of metals which change their properties as a result of mechanical treatment (machining), rolling, friction and other effects. The microhardness method is widely used for studying the individual structural constituent elements of metallic alloys, minerals, glasses, enamels and artificial abrasives.

### **2.9.1 Methods of hardness testing**

The various methods using which hardness measurement can be carried out are classified as follows

- (i) Static indentation test
- (ii) Dynamic indentation test
- (iii) Scratch test
- (iv) Rebound test and
- (v) Abrasion test

The most popular and simplest test is the static indentation test, wherein an indenter of specific geometry is pressed into 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 indenter of steel sphere or a diamond pyramid or cone is employed. A pyramid indenter is preferred as geometrically similar impressions 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 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; Tabor 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.

The scratch test can be classified into two types

- (i) Comparison test, in which one material is said to be harder than another, if the second material is scratched by the first.
- (ii) A scratch test is made with a diamond or steel indenter on the surface at a steady rate and under a definite load. The hardness number is expressed in terms of the width or depth of the groove formed.

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.

### 2.9.2 Vickers test

Vickers hardness method is the reliable and most common among the various methods of hardness measurement discussed above. In this method, micro-indentation is made on the surface of a specimen with the help of diamond pyramidal indenter.

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).

- (i) The contact pressure for a pyramid indenter is independent of indent size and
- (ii) 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  $1/7^{\text{th}}$  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  $H_v$  or Diamond Pyramid Number (DPN) is defined as

$$H_v = \frac{2P \sin(\alpha/2)}{d^2} \quad (2.1)$$

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

$$H_v = 1.8544p / d^2 \text{ kg-mm}^{-2} \quad (2.2)$$

where  $p$  is the applied load in kg and  $d$  is the diagonal length of the indentation mark in mm. Hardness values are 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.

### **2.9.3 Correlation of microhardness with other properties**

The importance of microhardness study lies in the possibilities of making an indirect estimate of mechanical characteristics of materials such as yield strength and toughness having a specific correlation with the hardness. Several workers have investigated the correlation of the indentation hardness with other physical properties. Even though the mechanism of deformation during indentation is clearly not understood, hardness testing provides useful information concerning the mechanical behavior of solids.

As an example, the hardness  $H_v$  is related to the yield strength  $Y$  (in  $\text{kg/mm}^2$ ) by

$$H_v = 2.8 Y \quad (2.3)$$

The best fit that was found experimentally by Wyatt and Dew Hughes (1974) is given by

$$H_v = 3Y \quad (2.4)$$

By analyzing the hardness results, Meyer related applied load  $p$  and indentation length  $d$  as

$$p = ad^n \quad (2.5)$$

where the exponent  $n$ , the Meyer number (or index), is a measure of the indentation size effect (ISE) and  $a$  is a constant for a given material.

If 'n' is less than 2, the hardness number decreases with increasing load and if 'n' is greater than 2, it increases with increasing load. The constant  $n$  is usually called work hardening coefficient ( $n$ ). For the normal indentation size effect, the exponent  $n < 2$ . When  $n > 2$ , there is the reverse indentation size effect (Sangwal 2000). The value of  $n$  can be determined from the slope of  $\log p$  versus  $\log d$  plot (Onitsch 1956).

## **2.10. DIELECTRIC STUDIES**

Study of the dielectric properties of solids gives information about the electric field distribution within the solid. The frequency dependence of these properties gives a great insight into the material's applications. The different polarization mechanisms in solids can be understood from the study of dielectric constant as a function of frequency and temperature.

Polarization  $\mathbf{P}$  of a dielectric is the numerical magnitude, which describes the phenomenon of polarization of a dielectric in an external electric

field. In the absence of an external electric field, each element in the volume of a dielectric has no electric moment.

The action of an electric field brings the charges of the molecules of the dielectric into a certain ordered arrangement in space. The study of the electrical and other properties of dielectrics in relation to their chemical composition and structure will lay the basis for obtaining new materials with new properties.

### **2.10.1 Theory**

#### **Dielectric constant**

The dielectric displacement or the charge density  $\mathbf{D}$  produced in a dielectric medium is directly proportional to the applied electric field  $\mathbf{E}$ .

$$D = \varepsilon \mathbf{E} \quad (2.6)$$

where  $\varepsilon$  is the dielectric constant or permittivity of the material placed between the electrodes.

If the same field is used in vacuum the relation will be

$$\mathbf{D} = \varepsilon_0 \mathbf{E} \quad (2.7)$$

where  $\varepsilon_0$  is called the absolute permittivity and is equal to  $8.854 \times 10^{-12}$  farad/metre. The relative permittivity or the relative dielectric constant  $\varepsilon_r$  may therefore be defined as

- (i) The ratio of the electric field density produced in the medium to that produced in vacuum by the same electric field strength.

- (ii) The ratio of the capacitance of a condenser containing a given dielectric to the same condenser with vacuum as the dielectric.

Therefore the relative dielectric constant  $\epsilon_r$  is

$$\epsilon_r = \frac{\epsilon}{\epsilon_0} \quad (2.8)$$

it is known that

$$\epsilon = \frac{Cd}{A} \quad (2.9)$$

$$\epsilon_r = \frac{Cd}{\epsilon_0 A} \quad (2.10)$$

where  $A$  is the area of the sample and  $d$  is the thickness of the sample. The relative permittivity ( $\epsilon_r$ ) is usually known as permittivity. It is always greater than unity. Suppose a parallel plate condenser has a capacitance of  $C_0$  in air, then its capacitance when the space between the plates is filled by a medium of permittivity  $\epsilon_r$  is given by

$$C = \epsilon_r C_0 \quad (2.11)$$

$\epsilon_r$  can be found out from the measurement of the capacitance.

The dielectric constant of a substance is a property of the constituent ions. In general, if electrode effects are neglected the four major contributions to the dielectric constant would be

- (i) the extrinsic nature of the material
- (ii) the electronic polarizability

- (iii) the ionic polarizability and
- (iv) the deformation of the ions.

### **Dielectric loss**

The dielectric loss is a measure of the energy absorbed by a dielectric. It is known that in a capacitor, the dielectric usually has a resistance  $R$  and impedance  $Z$  which are related to the phase angle.

Assuming  $R$  to be very large

$$\tan \delta = \frac{1}{\omega RC} \quad (2.12)$$

$\tan \delta$  is referred to as the dielectric loss. The dielectric loss depends very much on temperature and frequency.

### **Experimental**

Suitably cut and polished samples (with known dimensions) are subjected to dielectric studies using HIOKI 3532-50 HITESTER LCR meter with a conventional four terminal sample holder for investigations involving temperature variations and a conventional two terminal sample holder for only ambient condition. The samples are prepared and mounted between the copper platforms and electrodes. In order to ensure good electrical contact between the crystal and the electrodes, the crystal faces are coated with silver paint. Proper care is taken to ensure that the silver paint does not spread to the sides of the crystal. The capacitance and the dissipation factor of the parallel plate capacitor

formed by the copper plate and electrode having the sample as a dielectric medium were measured. The dielectric constant and dielectric loss were calculated using the equations 2.10 and 2.12 respectively. The measurements were made at frequencies ranging from 50 Hz to 5 MHz at different temperatures.

## **2.11 PHOTOCONDUCTIVITY STUDIES**

Photo detection technology is becoming more and more important in military applications, particularly in guided weapons and communication through fiber optics. Infrared developments are based on solid-state photonic devices. Further developments in these fields demand a good understanding of the basic principles of photoconductivity processes. Photoconductivity is an important property of solids by means of which the bulk conductivity of the sample changes due to incident radiation. Photoconductivity is not an elementary process in solids. Photoconduction, as the name suggests, includes the generation and recombination of charge carriers and their transport to the electrodes. Obviously, the thermal and hot carrier relaxation process, charge carrier statistics, effect of electrodes, and several mechanisms of recombination are involved in photoconduction. Above all, every mechanism mentioned is a complicated one, and therefore photoconductivity in general is a very complex process. In spite of the complexity of the photoconductivity process, it provides useful and valuable information about physical properties of materials and offers applications in photo detection and radiation measurements. Historically,

the first photoconductivity effect was recorded in 1873 by W. Smith, who observed that the resistivity of selenium was decreased by the radiation falling on it. According to the literature, this is the very first experimental detection of photoconductivity (Joshi 1990).

Einstein's explanation on the photoelectric effect opened the way to interpreting the interaction of radiation with matter, particularly optical absorption, photoconductivity, the photovoltaic effect and other related phenomena.

The basic principle involved in photoconductivity is often stated in a very simple way. When photons of energy greater than that of the band gap of the material are incident upon a photoconductive material, electrons and holes are created in the conduction and valence bands, respectively increasing the conductivity of the sample. But this statement is only partially true. In a doped material, for example, the impurity atom absorbs the photon of slightly less energy than that of the band gap and free electron is created in the conduction band (Bube 1960).

### **2.11.1 Photo conduction**

In short, photoconductivity is due to the absorption of photons (either by an intrinsic process or by impurities with or without phonons), leading to the creation of free charge particles in the conduction band and/or in the valence band. Photo absorption and hence photo conduction takes place by one of the following mechanisms.

- (i) Band-to-band transitions
- (ii) Impurity levels to band edge transitions
- (iii) Ionization of donors and
- (iv) Deep level (located in the valence band) to conduction band transitions.

### **2.11.2 Dark conduction**

Dark current (dark conduction),  $I_d$ , is the amount of current that flows through the material or device when no radiation is incident on it. It changes with operating temperature and applied voltage, and therefore these parameters should always be mentioned. Dark current is not a constant background current but also has fluctuations or noise. The average *dc* value of the current is generally mentioned as dark current.

### **2.11.3 Experimental**

The crystal sample is well-polished and surfaces are cleaned with acetone. This is attached to a microscope slide and two electrodes of thin copper wire are fixed on to the specimen at some distance apart using silver paint. After this, it is annealed at a temperature of 100 °C to perfect dryness. A dc power supply, a Keithley 485 picoammeter and the prepared sample are connected in series. The applied field is increased in steps of 20 V. The sample is covered with a black cloth to avoid exposure to any radiation. The current

(dark) is measured. To measure the photoconductivity, light from a 100 W halogen lamp is focused onto the sample. The current is noted for varying applied fields as before.

## **2.12 CONCLUSION**

Single crystals grown by the various methods need to be characterized to assess the suitability of the crystal for various applications including NLO device application. In order to understand the behaviour of any solid material, the structural characterization was carried out first. This is followed by the optical characterization, which helps to check the transparency window and cut-off frequency of the crystal. Since the entire thrust is with respect to NLO application, the SHG property was estimated. In addition to the above studies, the mechanical, thermal, dielectric and photoconductive behaviour of the grown crystal have also been investigated. The tools and techniques used in the present study are discussed in this chapter.