CHAPTER - III
CHARACTERIZATION TECHNIQUES

3.0. INTRODUCTION

This section presents a complete description on the techniques that are followed to characterize the samples in this research work. The advent of sophisticated equipments has improved the quality in analyzing the compounds chemical and physical properties.

3.1. ELEMENTAL ANALYSIS

3.1.1. Introduction

Elemental analysis is an experiment that determines the amount (typically a weight percent) of an element in a compound. Just as there are many different elements, there are many different experimental methods for determining elemental composition. The most common type of elemental analysis is for carbon, hydrogen, and nitrogen (CHN analysis). This type of analysis is especially useful for organic compounds (compounds containing carbon-carbon bonds). The elemental analysis of a compound enables one to determine the empirical formula of the compound. The empirical formula is a compound that contains the smallest set of integer ratios for the elements in the compound that gives the correct elemental composition by mass. Fig. 3.1 and 3.2 show the block diagram and photograph of elemental analyzer respectively.

3.1.2. Instrumentation

![Fig. 3.1 Block diagram of Elemental analyzer](image-url)
The Elementar vario EL III Analyzer allows fully automatic individual or simultaneous quantitative determination of carbon, hydrogen, nitrogen, oxygen, and sulfur content of samples based on the classical Dumas combustion method. The basic principle is high temperature combustion of organic and inorganic solid samples, separation of the gaseous products and analysis with a suitable detector. Solid samples are ranging from 0.02 mg to 1 g. Samples are dropped into the combustion tube automatically at user-selected temperatures up to 1200 °C, and the use of tin vessels elevates the sample temperature up to 1800 °C. Complete combustion without special or expensive catalysts occurs by use of a unique program for each sample matrix. Oxygen content of a sample is determined by converting O to CO at 1150 °C on a carbon black contact. The helium carrier gas transfers the gaseous combustion products into the copper tube. Nitrogen oxides are reduced to nitrogen, and the gaseous mixture enters the dynamic separation system. The N₂ travels directly to the thermal conductivity detector (TCD) while the CO₂, H₂O, and SO₂ are retarded in specific adsorption traps. Variations in concentrations and measuring modes are carried out by changing the adsorption traps available modes of the basic vario EL III unit include CN, CNS, CHN, CHNS, trace N, trace S, and trace S/N. Optional CHNS and oxygen modes are also available (Meyers 1994).

Applications

Elemental analysis or "EA" almost always refers to CHNX analysis the determination of the mass fractions of carbon, hydrogen, nitrogen, and heteroatoms (X) (halogens, sulfur) of a sample. This information is important to help determine the structure of an unknown compound, as well as to help ascertain the structure and purity of a synthesized compound.
Other applications include fine chemicals, medicines, fertilizers, organo-metallics, catalysts, polymers, plastics, rubber, leather, building and insulating materials, coal, oil, gasoline, sediments, soils, rocks and minerals, plants, wood, leaves, milk, sludges, compost, solid and liquid waste.

3.2. POWDER X-RAY DIFFRACTION

3.2.1. Introduction

X-rays are electromagnetic radiation of wavelength about 1 Å, which is about the same size as an atom. They occur in that portion of the electromagnetic spectrum between gamma-rays and the ultraviolet. The discovery of X-rays in 1895 enabled scientists to probe crystalline structure at the atomic level. X-ray diffraction has been in used for the crystalline materials and the determination of their structure. Each crystalline solid has its unique characteristic X-ray powder pattern which may be used as a "fingerprint" for its identification. Once the material has been identified, X-ray crystallography may be used to determine its structure, i.e. how the atoms pack together in the crystalline state and what the interatomic distance and angle are etc. X-ray diffraction is one of the most important characterization tools used in solid state chemistry and materials science. We can determine the size and the shape of the unit cell for any compound most easily using the diffraction of X-rays. The path difference between two waves:

\[ 2 \times \text{wavelength (} \lambda \text{)} = 2d \sin \theta \]

For constructive interference between these waves, the path difference must be an integral number of wavelengths,

\[ n \times \text{wavelength (} \lambda \text{)} = 2x \]

This leads to the Bragg equation,

\[ n \times \text{wavelength (} \lambda \text{)} = 2d \sin \theta \]

Let’s reexamine the simple description of Bragg’s law shown in Fig.3.3. In the example shown below, diffraction is only being measured from the horizontal planes of a crystal as function of 2θ. For a complete analysis of a material, the diffraction from all the possible lattice planes should be examined (Moore et al., 1997).
3.2.2. Instrumentation

The X-ray diffraction experiment requires an X-ray source, the sample under investigation and a detector to pick up the diffracted X-rays. Fig. 3.4 is a schematic diagram of a powder X-ray diffractometer.

The X-ray radiation most commonly used is that emitted by copper, whose characteristic wavelength for the K radiation is $\lambda = 1.5418\text{Å}$. When the incident beam strikes a powder sample, diffraction occurs in every possible orientation of $2\theta$. The diffracted beam may be detected by using a moveable detector such as a Geiger counter, which is connected to a chart recorder. In normal use, the counter is set to scan over a range of $2\theta$ values at a constant angular velocity. Routinely, a $2\theta$ range of 5 to 70° is sufficient to cover the most useful part of the powder pattern. The scanning speed of the counter is usually $2\theta$ of $2°\text{min}^{-1}$ and about 30 minutes are needed to obtain a trace. Fig. 3.5 is a photograph of a powder X-ray diffractometer (Bish et al., 1989).
Applications

X-ray powder diffraction is most widely used for the identification of unknown crystalline materials (E.g., minerals, inorganic compounds). Other applications includes characterization of crystalline materials, identification of fine-grained minerals such as clays and mixed layer clays that are difficult to determine optically, determination of unit cell dimensions, measurement of sample purity. Determine crystal structures and modal amounts of minerals (quantitative analysis).

3.3. SINGLE CRYSTAL X-RAY DIFFRACTION METHOD

Single-crystal X-ray Diffraction is a non-destructive analytical technique which provides detailed information about the internal lattice of crystalline substances, including unit cell dimensions, bond-lengths, bond-angles, and details of site-ordering. Directly related is single-crystal refinement, where the data generated from the X-ray analysis is interpreted and refined to obtain the crystal structure.

X-ray diffractometers consist of three basic elements, an X-ray tube, a sample holder, and an X-ray detector. X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons toward a target by applying a voltage and impact of the electrons with the target material. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced. The specific wavelengths are characteristic of the target
material. Filtering, by foils or crystal monochrometers, is required to produce monochromatic X-rays needed for diffraction. Molybdenum is the most common target material for single-crystal diffraction, with MoK$_\alpha$ radiation = 0.7107Å. These X-rays are collimated and directed onto the sample. When the geometry of the incident X-rays impinging the sample satisfies the Bragg Equation, constructive interference occurs. A detector records and processes this X-ray signal and converts the signal to a count rate which is then output to a device computer monitor. X-rays may also be produced using a synchotron, which emits a much stronger beam. Single crystal X-ray diffraction photograph is shown in Fig. 3.6.

![Single crystal X-ray diffraction photograph.](image)

**Fig. 3.6. Single crystal X-ray diffraction photograph.**

Single-crystal diffractometers use either 3- or 4-circle goniometers. These circles refer to the four angles ($\theta$, $\chi$, $\phi$, and $\Omega$) that define the relationship between the crystal lattice, the incident ray and detector. Samples are mounted on thin glass fibers which are attached to brass pins and mounted onto goniometer heads. Adjustment of the X, Y and Z orthogonal directions allows centering of the crystal within the X-ray beam.

X-rays leave the collimator and are directed at the crystal. Rays are either transmitted through the crystal, reflected off the surface, or diffracted by the crystal lattice. A beam stop is located directly opposite the collimator to block transmitted rays and prevent burn-out of the detector. Reflected rays are not picked up by the detector due to the angles involved. Diffracted rays at the correct orientation for the configuration are then collected by the detector. Modern single-crystal diffractometers use CCD (charge-coupled device) technology to transform the X-ray photons into an electrical signal which are then sent to a computer for processing (Putnis 1992).
Applications

Single-crystal X-ray diffraction is most commonly used for precise determination of a unit cell, including cell dimensions and positions of atoms within the lattice. Bond-lengths and angles are directly related to the atomic positions. The crystal structure of a mineral is a characteristic property that is the basis for understanding many of the properties of each mineral. Specific applications of single-crystal diffraction include:

- New mineral identification, crystal solution and refinement.
- Determination of unit cell, bond-lengths, bond-angles and site-ordering.
- Characterization of cation-anion coordination.
- Variations in crystal lattice with chemistry.
- With specialized chambers, structures of high pressure or temperature phases can be determined.
- Determination of crystal-chemical Vs environmental control on mineral chemistry.
- Powder patterns can also be derived from single-crystals by use of specialized cameras.

3.4. FT-IR SPECTROMETER

3.4.1. Introduction

Infrared spectroscopic technique is the most popular vibrational spectroscopic technique used to identify the functional groups in organic and inorganic compounds. IR spectroscopic technique utilizes lower energy IR radiation (4000-400 cm\(^{-1}\)) to induce vibrational and rotational excitation of atoms and groups of atoms within a molecule. Because of the variety of symmetry of atomic groups and their differences in atomic masses and electronic structures, the absorption patterns for a specific species will be unique, which allows for their identification. When photons interact with a molecule, the molecule may respond by absorbing the photons and subsequently the energy of the absorbed photons cause the molecule to vibrate in a
higher energy level. In order to be infrared active, the dipole moment must change during a vibration. Absorption occurs when the incoming IR radiation that is interacting with a molecule has sufficient energy to raise the vibrational energy level of the molecular system to the next allowed level. The allowed level is determined from selection rules, which are based upon the symmetry (orbital overlap probability) and electronic structure of the molecule (the differences in the number of valence electrons influences the spin state). The frequencies of absorption are determined by the masses of atoms, the force constant of bonds and the geometrical shapes of the molecule.

Fig. 3.7. Block diagram of an FTIR

The components of an FTIR include a source, collimator, beam splitter (mirror), fixed mirror, moving mirror, sample compartment, laser for aligning the mirrors as well as for internal calibration and detector. Fig.3.7 and 3.8 shows block diagram and photograph of FTIR instrument. Both the dispersive IR spectrometer and the FTIR use similar radiation sources (Nakamoto 1978).

Fig. 3.8. Photograph of an FTIR

The FTIR varies from the traditional dispersive spectrometer mainly due to the use of the interferometer instead of a monochromator. The interferometer (e.g.
Michelson interferometer) is an optical device used to make the scanning and the spectral collection process faster and more precise. The optics of the FTIR makes this technique precise by controlling the longitudinal shift in the wavelets to a fraction of a percent of the wavelength. The higher throughput of IR frequency that is achieved by avoiding the use of dispersive gratings provides FTIR with an additional advantage. Another advantage that FTIR has over dispersive IR is the simple mechanical design with only the moving mirror as the only moving part. The interferometer splits the FTIR radiation source into two beams using a beam splitter that causes the beams to travel different optical paths. Their path difference, which is achieved by splitting up and then recombining the beams, produces the interference signals measured at the detector. The detector measures all incoming signals simultaneously, which allows for acquisition of a complete spectrum with a single scan of the moving mirror. The simultaneous signal acquisition is the reason that the FTIR interferometer requires a faster scan rate (detection of the source IR signal) (Schoonover et al., 2003).

Applications

Infrared spectroscopy is extensively applied to various samples such as liquid, gas and solid-sate matter to identify the unknown materials. It is a sensitive technique, which can routinely detect microgram-order sample.

3.5. UV-VIS SPECTROPHOTOMETER

3.5.1. Introduction

A Photograph and block diagram of the UV-Visible spectrometer is shown in Fig. 3.9 and 3.10. The functioning of this instrument is relatively straightforward. A beam of light from a visible source is separated into its component wavelengths by a prism or diffraction grating. Each monochromatic beam in turn is split into two equal intensity beams by a half-mirrored device. One beam, the sample beam, passes through a small transparent container containing a solution of the compound being studied in a transparent solvent (Prabhakar Misra et al., 2002). The other beam, the reference, passes through an identical cuvette containing only the solvent. The intensities of these light beams are then measured by electronic detectors and compared. The intensity of the reference beam, which should have suffered little or no light absorption, is defined as $I_0$. The intensity of the sample beam is defined as $I$. 

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Over a short period of time, the spectrometer automatically scans all the component wavelengths in the manner described. The ultraviolet (UV) region scanned is normally from 200 to 400 nm, and the visible portion is from 400 to 800 nm. If the sample compound does not absorb light of a given wavelength, \( I = I_0 \). However, if the sample compound absorbs light then \( I \) is less than \( I_0 \). Absorption may be presented as transmittance \( (T = I/I_0) \) or absorbance \( (A = \log I_0/I) \). If no absorption has occurred, \( T = 1.0 \) and \( A = 0 \). Most spectrometers display absorbance on the vertical axis and the commonly observed range is from 0 (100% transmittance) to 2 (1% transmittance).

Fig. 3.9. Photograph of an UV-Visible spectrophotometer

Fig. 3.10. UV-Visible Spectrophotometer

The wavelength of maximum absorbance is a characteristic value, designated as \( \lambda_{\text{max}} \). Different compounds may have very different absorption maxima and absorbances. Intensely absorbing compounds must be examined in dilute solution, so that significant light energy is received by the detector and this requires the use of completely transparent (non-absorbing) solvents. The most commonly used solvents are water, ethanol, hexane and cyclohexane. Solvents having double or triple bonds,
or heavy atoms (e.g. S, Br & I) are generally avoided. Because the absorbance of a sample will be proportional to its molar concentration in the sample cuvette, a corrected absorption value known as the molar absorptivity is used when comparing the spectra of different compounds (Sooväli et al., 2006).

Applications

UV-Visible spectroscopy is routinely used in the quantitative determination of solutions of transition metal ions and highly conjugated organic compounds. It is useful in characterizing the absorption, transmission and reflectivity of variety of technologically important materials such as pigments, coatings, windows and filters. This more qualitative application usually required recording at least a portion of the UV-Vis spectrum for characterization of the optical or electronic properties of materials.

3.6. SPECTROFLUOROMETER

3.6.1. Introduction

Often, fluorescence spectrometers use double-beam optics to compensate for power fluctuations in the source. The fluorescent emission is measured at right angles to the incident beam. Emitted radiation passes through a second filter or monochromator to isolate the fluorescent peak for measurement. The reference beam passes through an attenuator to reduce its power to that of the fluorescent radiation. Fluorometers use filters to restrict excitation and emission beam wavelengths. Spectrofluorometers have two monochromators; one allowing choice of excitation wavelength and the other allowing fluorescence emission spectra to be scanned.

![Block diagram of Spectrofluorometer](image)

**Fig. 3.11. Block diagram of Spectrofluorometer**
3.6.2. Sources

Generally, the source must be more intense than that required for UV-Visible absorption spectroscopy and magnitude of the emitted radiation is directly proportional to the power of the source. Filter fluorometers often employ a low-pressure mercury vapour lamp. This source produces intense lines at certain wavelengths. One of these lines will usually be suitable for excitation of a fluorescent sample. Spectrofluorometers need a continuous radiation source and are often equipped with a 75-450 W high-pressure Xenon arc lamp. Lasers are sometimes used as excitation sources. A tunable dye laser, using a pulsed nitrogen laser as the primary source can produce monochromatic radiation between 360 and 650 nm. Since the radiation produced is monochromatic, there is no need for an excitation monochromator. Block diagram and photograph of spectrofluorometer are shown in Fig. 3.11 and 3.12.

3.6.3. Filters and monochromators

Fluorometers use either interference or absorption filters. Spectrofluorometers are usually fitted with grating monochromators (Yasuhiro Senga et al., 1991).

3.6.4. Detectors

Fluorescence signals are usually of low intensity. Photomultiplier tubes are in common use as detectors. Diode-array detectors are sometimes used.

Fig. 3.12. Photograph of Spectrofluorometer

Applications

Fluorescence spectroscopy is used in biochemical, medical and chemical research fields for analyzing organic compounds. There has also been a report of its
use in differentiating malignant skin tumors from benign. Fluorescence can also be used to redirect photons.

3.7. THERMAL ANALYSIS

A number of analytical methods have been developed, in which some property of the system is measured as a function of the temperature. In fact, the data’s are obtained as continuously recorded curves, which may be termed as thermal spectra. These spectra characterize a system; single multi component, in terms of the temperature dependence of its thermo-dynamic properties and physico-chemical reaction kinetics.

3.7.1. Thermogravimetric analysis

The essential parts of the modern thermogravimetric instrument remain basically the same as those employed by the earlier researcher. These essential components include, a container in the form of a crucible to hold the sample, a furnace that can heat the sample to a high temperature, and an appropriate balance that can continuously monitor the sample. However, that is where the comparison ends – modern equipment has now become far more sophisticated providing much greater sensitivity, accuracy, precision and speed. It is interesting to note that the main advantage of modern analytical instrumentation is not so much the improved sensitivity, precision, but the advantage of much greater speed. Faster throughput of sample generates much more data with quicker interpretation and consequently, betters quality control and faster scientific progress. A block diagram of thermogravimetric instrument is shown in Fig.3.13.

![Fig. 3.13. A Block Diagram of Thermogravimetric instrument](image-url)
The sample container consists of a small platinum crucible suspended from the arm of a microbalance and situated in a small oven, the temperature of which is carefully monitored by a highly accurate thermocouple or some other appropriate temperature measuring sensor. The oven can be evacuated so the sample can heated and weighed in a vacuum and all volatile substances that are evolved are rapidly removed. Alternatively the atmosphere can be made inert by the introduction of a rare gas such as helium or argon, can be made oxidizing by the introduction of oxygen. In the more sophisticated and expensive instruments, the products evolved from the crucible can also be led into a capillary gas chromatograph. The sample can also be examined at elevated pressures if required.

Applications

Thermo gravimetric analysis has widely been used in testing of sample purity, study of organic compounds, oxide mixtures and glass technology. The most important applications of thermo gravimetric are found in weight loss of material. Thermograms give information about decomposition mechanisms for material.

3.8. Differential thermal analysis

3.8.1. Introduction

Differential thermal analysis is the measurement of the difference in temperature between sample and a reference, as heat is applied to the system. It is a fingerprinting technique which provides information on the chemical reaction, phase transformations and structural changes that occurs in a sample during a heat-up or a cool-down cycle. The DTA measures the differences in the energies released or absorbed and the changes in heat capacity of materials as a function of temperature.

3.8.2. Instrumentation

A technique in which the difference in temperature between the sample and a reference material is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is programmed.
The sample and the reference are placed symmetrically in the furnace. The furnace is controlled under a temperature program and the temperature of the sample and the reference are changed. During this process, a differential thermocouple is set up to detect the temperature difference between the sample and the reference. Also, the sample temperature is detected from the thermocouple on the sample side. ΔT signal is referred to as the DTA signal. Matters that do not change in the measurement temperature range are used as reference. When the furnace heating begins, the reference and the sample begin heating with a slight delay depending on their respective heat capacity, and eventually heat up in according to the furnace temperature. ΔT changes until a static state is reached after the heating begins and after achieving stability, reaches a set amount compliant with the difference in heat capacity between the sample and the reference. The signal at the static state is known as the baseline. A block diagram of Differential thermal analysis is shown in Fig. 3.14.

Applications

Differential thermal analysis is of great importance in the field of ceramics, mineralogy and metallurgy. DTA finds wide spread use in determining the thermal behaviour and composition of naturally occurring and manufacturing products. DTA measurements have been used for studies of thermal behaviour of pure inorganic compounds as well as inorganic substance such as silicates, ferrites, clays, oxides, ceramics and glasses. An important use is for generation of phase diagrams and the study of phase transitions. The differential thermal method provides a simple and
accurate way of determining the melting, boiling and decomposition points of organic compound (Ramos-Sánchez et al., 1988).

### 3.9. Differential Scanning calorimetry (DSC)

DSC is a commercially available instrument which has two types: Heat Flux Type and Power Compensation Type. Heat Flux DSC comprises the sample and reference holder, the heat resistor, the heat sink and the heater. Heat of heater is supplied into the sample and the reference through heat sink and heat resistor. Heat flow is proportional to the heat difference of heat sink and holders. In case the sample occurs endothermic or exothermic phenomena such as transition and reaction, this endothermic or exothermic phenomena is compensated by heat sink. Thus the temperature difference between the sample and the reference is kept constant. The difference the amount of heat supplied to the sample and the reference is proportional to the temperature difference of both holders. By calibrating the standard material, the unknown sample quantitative measurement is achievable. Recently, with the development of new material, these thermal properties analysis needs are increasing dramatically. DTA and DSC detect the temperature differences between the sample and the reference; however, DSC can perform the quantitative measurement of the amount of heat on top. Fig. 3.15 Block diagram of differential scanning calorimeter. The thermal analysis (TG/DTA and DSC) Photograph of instrument is shown in Fig.3.16.

![Fig. 3.15. Block diagram of differential scanning calorimeter](image_url)
3.10. MICROHARDNESS STUDY

Hardness is a physicochemical property that characterizes the state of the material under test and gives information on some specific features of the material such as the character of the chemical bonding. It is the resistance which the material offers to indentation by a much harder body and may be termed as a measure of the resistance against lattice destruction or permanent deformation or damage. As the hardness properties are basically related to the crystal structure of the material and the bond strength, microhardness studies have been applied to understand the plasticity of the crystals. Hardness tests are commonly carried out to determine the mechanical strength of materials and it correlates with other mechanical properties like elastic constants and yield (Pavlina et al., 2008).

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 variables are 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 a hard 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 (Taber 1951).

### 3.10.1. Vickers test

Vickers hardness method is the reliable and most common among the various methods of hardness measurement discussed above.

The Vickers hardness number is thus calculated using the relation

\[
H_v = \frac{1.8544 P}{d^2} \quad \text{kg/mm}^2 \text{ (or) pascal}
\]

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.

\[
P = Kd^n
\]

Where \( K \) and \( n \) are constants for a given material. Kick’s analysis for hardness postulated a constant value of \( n = 2 \) for all indenters and for all geometrically similar impression. This relation has a drawback that \( n \) has a value always less than 2, particularly in the low load region and hence, the relation has not received complete acceptance.

If \( n \) is less than 2, the hardness number increases with decreasing load and if \( n \) is greater than 2, it decreases with decreasing load. The constant \( n \) is usually called as work-hardening coefficient. The value of \( n \) can be determined from the slope of \( \log P \) versus \( \log d \) plot.

### 3.11. DIELECTRIC STUDIES

Dielectric measurement is one of the useful characterizations of electrical response of solids. A 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 \( P \) 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 dielectric constant of a material gives an insight into the nature of bonding in the material.

![Fig. 3.17. Photograph of LCR meter](image)

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. A lot of work had been carried out on dielectric measurement for a variety of materials including ceramics and single crystals by many authors yielding valuable information. The dielectric properties of samples were measured by using LCR meter shown in Fig. 3.17.

### 3.11.1. Dielectric constant

The dielectric displacement or charge density \( D \) produced in a dielectric medium is directly proportional to the applied electric field \( E \).

\[
D = \varepsilon E
\]
where, $\varepsilon$ is the permittivity or dielectric constant of the material placed between the electrodes. Applying the same field in vacuum, the relation will be

$$D = \varepsilon_0 E$$

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

$$\varepsilon_r = \frac{\varepsilon}{\varepsilon_0}$$

It is known that

$$\varepsilon = \frac{Cd}{A}$$

Hence

$$C = \varepsilon_r \varepsilon_0 A$$

where, $A$ is the area of the sample and $d$ is the thickness of the sample. The relative permittivity ($\varepsilon_r$) is usually known as permittivity. It is always greater than unity (Bottcher 1973). The capacitance $C_0$ of a parallel plate condenser having a capacitance $C$ in air can be given by

$$C = \varepsilon_r C_0$$

when the space between the plates is filled by a medium of permittivity $\varepsilon_r$.

Thus

$$\varepsilon_r = \frac{C}{C_0}$$

$\varepsilon_r$ can be found by the measurement of capacitance. The dielectric constant of a substance is a property of the constituent ions.

### 3.11.2. 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 (Bottcher et al., 1978).
Assuming $R$ to be very large

$$\tan \delta = \frac{1}{\omega RC}$$

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

Suitably cut and polished samples (with known dimensions) are subjected to dielectric studies using 3532-50 HIOKI LCR meter. 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. The measurements are made at frequencies ranging from 100 Hz to 5 MHz at room temperature (Xiaobo Dong et al., 2009).

3.12 PHOTOCONDUCTIVITY STUDIES

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 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, effects of electrodes and several mechanisms of recombination are involved in photoconduction. Photoconductivity provides valuable information about physical properties of materials and offers applications in photo detection and radiation measurements.

Smith recorded first the photoconductivity effect in 1873 when he observed the decrease in the resistivity of selenium by the radiation shining on it. This is the first experimental detection of photoconductivity. Einstein’s theory of the photoelectric effect initiated the interpretation of the interaction of radiation with matter, particularly optical absorption, photoconductivity, the photovoltaic effect and other related phenomena.

The basic principle involved in photoconductivity can be stated as follows: 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.

3.12.1. 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 in the valence band. Photo absorption and hence photo conduction takes place by one of the following mechanisms:

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

3.12.2. 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 be always mentioned. Dark current is not a constant background current but also has fluctuations or noise. The average $d.c.$ value of the current is generally mentioned as dark current.

The experimental set-up used in the present study is as shown in Fig.3.18. The crystal sample is well-polished and surfaces are cleaned with acetone. This is attached with a microscopic slide and two electrodes of thin copper wire (0.14 cm diameter) are fixed on to the specimen at some distance apart using silver paint. A $d.c.$ power supply, a Keithley 485 picoammeter and the prepared sample are connected in series. The applied field is increased from 0 to 2000 Vcm$^{-1}$. 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.
3.13. NONLINEAR OPTICS

3.13.1. NLO Test

Nonlinear optics is the area of optics that studies the interaction of light with matter in the regime where the response of the material system with the applied electromagnetic field is nonlinear in the amplitude of this field. In a nonlinear process, the oscillation of electrons will eventually become a harmonic, when a material is subjected to an optical field (i.e. light) of a given frequency and re-emitted light may differ in frequency and amplitude from the incident light.

Laser sources can provide sufficiently high light intensities to modify the optical properties of materials. Light waves can then interact with each other, exchanging momentum and energy and the superposition principle is no longer valid. This interaction of light waves can result in the generation of optical fields at new frequencies, including optical harmonics of incident radiation or sum or difference frequency signals. In short, light of one or more frequencies impinges on a sample and light at a different or several different frequencies emerges. A simple example is Second Harmonic Generations, where the wavelength of the light that emerges is exactly half of the incident beam.

In 1961, the second harmonic generation was first demonstrated by P.A. Franken, A.E. Hill, C.W. Peters and G. Weinreich at the University of Michigan, Ann Arbor. This demonstration was made possible by the invention of the laser, which created the required high intensity monochromatic light. The second harmonic generation (also called frequency doubling) is a nonlinear optical processes, in which photons interacting with a nonlinear material are effectively combined to form new photons with twice the energy, and therefore twice the frequency and half the...
wavelength of the initial photons. Powder Kurtz and Perry technique are often employed to detect the nonlinear optical property of the material (Kurtz et al., 1968).

3.13.2. Instrumentation

The experimental and block diagram setup is shown in Fig. 3.19 and Fig. 3.20. The starting point is the Q-switched Nd: YAG laser with a fundamental laser beam of 1064 nm wavelength which serves as source. The power of the incident beam was measured using a power meter. The laser beam then passes through the energy and polarization control which controls the energy flow. The beam is then focused onto the sample through the focusing lens. The crystal was ground as powder and was packed densely between two transparent glass slides usually made of quartz and exposed to laser radiations. The following parts of NLO setup and their value as

![Fig. 3.19. Experimental setup of NLO test](image1)

![Fig. 3.20. Block diagram of NLO setup](image2)
Scattering Geometry = 90°
Fundamental Wavelength = 1064 nm
Pulse Width = 8 ns
Beam Diameter = 8 mm
Monochromator, Front slit width = 1 mm
Back slit width = 0.25 mm
Repitation rate = 10 Hz
PMT power supply = 1.0 KV/Amp
Focal length of lens = 20 cm

Oscilloscope: TDS 3052 B Tektronix.

A sample of potassium dihydrogen phosphate (KDP), also powered to the same particle size as the experimental sample, was used as reference material. The transmitted fundamental wave was passed over a monochromator which separates 532 nm (second harmonic signal) from 1064 nm. This is then collimated onto the spectral filters. The SHG detector usually employed is a photomultiplier tube. The green light was detected by a photo multiplier tube and displayed on a storage oscilloscope. The emission of green radiation confirms the NLO property of the material under study.

Applications

Nonlinear optical phenomena are becoming increasingly important as a diagnostic tool for wide range of physical properties. NLO finds wide applications in the area of laser technology, laser communication, data storage technology, image processing, optical modulation, optical switching and telecommunications. In recent years, SHG has been extended for biological applications etc.