CHAPTER 2

CHARACTERIZATION TECHNIQUES

2.1 INTRODUCTION

Characterization is a tool for the measurement of physical and chemical properties of materials. Characterization provides a basis for understanding and improving the characteristics of material for specific applications. Characterization of a material essentially depends on the characterization and experimental techniques involved with tools of sophisticated technology. Today scientists and researchers have powerful and elegant tools for obtaining qualitative and quantitative information about the composition and structure of matter. The development of these tools began over two centuries ago and the search still continues. 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.

A complete description of the physical and chemical properties of a material of interest is termed as characterization of that material. Characterization of a crystal essentially consists of determination of chemical composition, structure, defects, study of their optical properties etc (Becker, P., 1998). Crystal studies such as structural analysis, investigation of growth defects, and measurement of linear and nonlinear optical properties are essential in understanding the nature and properties of the grown crystals.

The single crystals chosen for the present investigation were subjected to the following studies:

- UV-Visible analysis for the detection of the transparency region and cutoff wavelength.
- FTIR spectral analysis to confirm the various functional groups present in the compound.
- Single crystal X-ray diffraction analysis and Powder X-ray diffraction to identify the structure and space group.
- EDAX analysis to find the percentage of carbon, nitrogen and sulphur in the sample.
- SEM analysis to identify the structural morphology of the crystals.
- P-E hysteresis loop measurements to identify the ferro electric nature of the grown samples.
- Dielectric measurements to investigate the dielectric response of the crystal with respect to varying frequency and temperature.
- Hardness studies to estimate the hardness.
- Photoconductivity studies to find out the nature of dark current and photocurrent.

2.2 UV - VISIBLE SPECTROSCOPY

Ultraviolet-visible spectroscopy (UV/ VIS) is also known as electronic spectroscopy. Ultraviolet (200 - 400 nm) and visible (400 - 800 nm) absorption spectroscopy is the measurement of the attenuation of a beam of light after it passes through a sample or after reflection from a sample surface. The schematic representation of a UV-Vis spectrophotometer is shown in Figure 2.1. It uses light in the visible and adjacent near ultraviolet (UV) and near infrared (NIR) ranges. In this region of energy space molecules undergo electronic transitions.

Ultraviolet and visible light are energetic enough to promote outer (valence) electrons to higher energy levels. Valence electrons are found in three types of electron orbitals namely σ bonding orbitals, π bonding orbitals and non-bonding orbitals (n-lone pair electrons). Sigma (σ) bonding orbitals tend to be lower in energy than π bonding orbitals, which in turn are lower in energy than non-bonding orbitals. The unoccupied or anti bonding orbitals (π* and σ*) are the orbitals of highest energy. An energy level diagram showing electronic transitions is depicted in Figure 2.2. Of the six transitions outlined, only the two lowest energy ones (left-most, coloured blue) are achieved by the energies available in the 200 to 800 nm spectrum. As a rule, energetically favored electron promotion will be from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) and the resulting species is called an excited state.
In particular, absorption bands result from transitions ($\pi\rightarrow\pi^*$) and ($n\rightarrow\pi^*$) involving $\pi$-orbitals and lone pairs ($n =$ non-bonding) are important and so UV-Vis spectroscopy is of most use for identifying conjugated systems which tend to have stronger absorptions. Absorption bands can also arise from certain molecules where the energy required for removing an electron from one atom and placing it on another falls within the UV/Vis region. This process is known as a charge transfer excitation. Molecules with the ability to exhibit the above types of electronic transitions are said to possess chromophores. 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. The most common are (C=\text{C}) and (C=\text{O}) which exhibits $\pi\to\pi^*$ and $n\to\pi^*$ transitions respectively.

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.

Samples are typically placed in a transparent cell, known as a cuvette. The sample holders (cuvettes) are the rectangular shaped quartz or glass cells of about 10 mm path length. The transmitted light radiation is received at the photomultiplier tube alternately from the reference and the sample beams. A photoelectric signal timing system is synchronized with the alternate pulses which permits the comparison of signals from the two beams. The difference between the two signals is recorded with the help of a motor driven pen or is interfaced with a PC-XT and stored there for easy reference. Samples in solid form, powder, pellets are dissolved in suitable solvents to form the contents of the sample cell and the solvents are taken in the reference cell. In the present work, the UV-Visible spectra were recorded using Perkin Elmer Lamda Instrument.

2.3 FOURIER TRANSFORM INFRARED (FTIR) SPECTRAL ANALYSIS

Fourier Transform Spectroscopy is a simple mathematical technique to resolve a complex wave into its frequency components. The conventional IR spectrometers are not of much use for the far IR region, as the sources are weak and the detectors are insensitive. FTIR has made this energy-limited region more accessible. It has also made the mid infrared more useful. Conventional spectroscopy, called the frequency domain spectroscopy, records the radiant power as a function of frequency. In the time domain spectroscopy, the change in radiant power is recorded as a function of time. In the Fourier Transform Spectrometer, a time domain plot is converted into a frequency domain spectrum. The actual calculation of the Fourier transform of such systems is done by means of high speed computers.
The FTIR 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. Interferometric multiplex instruments employing the Fourier transform are now finding more general applications in both qualitative and quantitative infrared measurements. The interference pattern is obtained from a two beam interferometer, as the path difference between the two beams is altered, then Fourier transformed output gives rise to the spectrum. The transformation of the interferogram into spectrum is carried out mathematically with a dedicated online computer. The spectrometer consists of globar and mercury vapour lamp as sources. An interferometer chamber comprising of KBr and mylar beam splitters is followed by a sample chamber and detector. The schematic diagram of a FTIR spectrometer is shown in Figure 2.3. The spectrometer works under vacuum condition. Solid samples are dispersed in KBr or polyethylene pellets depending on the region of interest. This instrument has resolution of 0.1 cm$^{-1}$. Signal averaging, signal enhancement, baseline correction and other spectra manipulations are possible with multitasking OPUS software on the dedicated PC/AT 486. Spectra are plotted on a HP plotter and data can be printed.

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 employed commonly in recording such spectra. For solid compounds, that are insoluble in the usual solvents, a convenient sampling method is the Pressed Pellet Technique. A few milligrams of the sample are ground together in an agate or mullite mortar with about 100 times the quantity of a material (the matrix) transparent to the infrared. The usual material is KBr, although other compounds such as CsI, TlBr and Polyethylene are used in special circumstances. The ground powder is finally introduced into a mini pressing arrangement made from two half-inch diameter stainless steel bolts and a stainless steel nut. The ends of the bolts must be polished, flat and parallel. One bolt is inserted about half way into the nut and the KBr plus sample mixture. The second bolt is then screwed into the nut and pressure is applied by tightening the bolts together. When the bolts are carefully withdrawn, a pellet suitable for infrared transmission work remains. The pellet is not removed from the nut, which acts as a holder in the spectrometer (Albert Cotton, F. and Wilkinson, G., 1970).
Figure 2.3 Schematic diagram of a FTIR spectrometer
Molecular vibrations that oscillate with the same frequency absorb IR light. The frequency of the vibration and the probability of absorption are influenced by intra and intermolecular effects. Thus, information about structure and environment can be deduced from the spectral parameters, bandwidth and absorption coefficient. There are no rigid rules for interpreting the vibration spectrum. Certain requirements, however, must be met before an attempt is made to interpret a spectrum:

i) The spectrum must be adequately resolved and of adequate intensity.

ii) The spectrum should be that of a reasonably pure compound.

iii) The spectrometer should be calibrated.

iv) The method of sample handling must be specified. If a solvent is employed, the solvent, concentration and the cell thickness should be indicated.

A precise treatment of the vibrations of a complex molecule is not feasible; thus, the spectrum must be interpreted from empirical comparison of spectra and extrapolation of studies of similar molecules. Many of the group frequencies of organic compounds vary over a wide range. Because the bands arise from complex interacting vibrations within the molecule, absorption bands may, however represent predominantly a single vibration mode. Important details of structure may be revealed by the exact position of an absorption band within a narrow region. Shifts in absorption position and changes in band contours, accompanying changes in molecular environment, may also suggest important structural details.

Some of the general uses of FTIR spectra are:

i) Identification of all types of organic and many types of inorganic compounds

ii) Determination of functional groups in organic materials

iii) Determination of the molecular composition of surfaces

iv) Identification of chromatographic effluents

v) Quantitative determination of compounds in mixtures

vi) Determination of molecular conformation (structural isomers) and stereochemistry (geometrical isomers)

vii) Determination of molecular orientation (polymers and solutions)
In the present work the Perkin Elmer FT-IR instrument is used to record the Fourier transform infrared spectra. The instrument consists of Nernst glower as source, an interferometer chamber comprising of KBr beam splitters followed by a sample chamber and detector. Entire region of 4000 - 400 cm⁻¹ is covered by this instrument. The spectrometer works under purged conditions. Solids samples are dispersed in KBr or polyethylene pellets depending on the region of interest. This instrument has a typical resolution of 4.0 cm⁻¹. Signal Averaging, Signal Enhancement, Base Line Correction and other Spectral Manipulations are possible. The photograph of Perkin-Elmer FT-IR instrument is shown in Figure 2.4.
Figure 2.4 Photograph of Perkin-Elmer FT-IR instrument
2.4 X-RAY DIFFRACTION ANALYSIS

X-ray crystallography is a tool used for determining the atomic and molecular structure of a crystal, in which the crystalline atoms cause a beam of incident X-rays to diffract into many specific directions. By measuring the angles and intensities of these diffracted beams, a crystallographer can produce a three-dimensional picture of the density of electrons within the crystal. From this electron density, the mean positions of the atoms in the crystal can be determined, as well as their chemical bonds, their disorder and various other information.

Since many materials can form crystals—such as salts, metals, minerals, semiconductors, as well as various inorganic, organic and biological molecules—X-ray crystallography has been fundamental in the development of many scientific fields. In its first decades of use, this method determined the size of atoms, types of chemical bonds, and the atomic-scale differences among various materials, especially minerals and alloys. X-ray crystallography is still the chief method for characterizing the atomic structure of new materials and in discerning materials that appear similar by other experiments. X-ray crystal structures can also account for unusual electronic or elastic properties of a material, shed light on chemical interactions and processes, or serve as the basis for designing pharmaceuticals against diseases.

X-ray crystallography is related to several other methods for determining atomic structures. Similar diffraction patterns can be produced by scattering electrons or neutrons, which are likewise interpreted as a Fourier transform. If single crystals of sufficient size cannot be obtained, various other X-ray methods can be applied to obtain less detailed information; such methods include fiber diffraction, powder diffraction and small-angle X-ray scattering (SAXS).

2.4.1 POWDER X-RAY DIFFRACTION ANALYSIS

X-ray powder diffraction is a nondestructive technique widely used for the characterization of micro-crystalline materials. This method has been traditionally applied for phase identification, quantitative analysis and the determination of structure imperfections. In recent years, applications have been extended to new areas, such as the determination of moderately complex crystal structures and the three
dimensional micro structural properties. Probably the most common application is to determine the positions of atoms in crystals (Louer, D., 2000).

The powder method of diffraction 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,\textsubscript{α} characteristic component of the filtered radiation from an X-ray tube operated above the K,\textsubscript{α} excitation potential of the target material.

Selection of K,\textsubscript{α} 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 schematic diagram of a powder X-ray diffractometer is shown in figure 2.5.

![Figure 2.5 Schematic diagram of a PXRD diffractometer](image-url)
The diffractometer is connected to a computer for data collection. 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. In the present work high resolution PANalytical powder XRD instrument has been used. In the powder X-ray diffraction method the sample is grounded to a fine powder which contains thousands of grains with random orientations. By scanning through 10° to 80°, we can find where the diffraction has occurred and each of them will be associated with different atomic spacing. In this powder X-ray diffractometer, it is capable of producing a beam of monochromatic X-rays from a CuKα radiation source of wavelength 1.54060 Å.

To detect the diffracted x-rays from the sample an electronic detector is placed on the other side of the sample and it is allowed to rotate it from 10° to 80°. It keeps track of the angle and sends the information to a computer. The X-ray intensity vs 2θ graph is plotted. Angle 2θ for each diffraction peak can be converted to ‘d’ spacing using Bragg’s law, which is used to find out the crystal structure. Photograph of PANalytical X, pert Pro powder XRD instrument is shown in figure 2.6.

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. For the purpose of comparison, many standards are available, some of which are, Willars Hand book, Joint Committee on Powder Diffraction Standards (JCPDS) and National Bureau of Standards.
Figure 2.6 Photograph of PANalytical powder XRD instrument.
2.4.2 SINGLE CRYSTAL X-RAY DIFFRACTION ANALYSIS

Single crystal X-ray diffraction (X-ray crystallography) is an analytical technique in which X-rays are employed to determine the actual arrangement of atoms within a crystalline specimen. Single crystal X-ray diffraction is a non-destructive tool to analyze crystal structure of compounds, which can be grown as single crystals. The molecular structure, atomic coordinates, bond lengths, bond angles, molecular orientation and packing of molecules in single crystals can be determined by X-ray crystallography. Single crystal X-ray diffractometer collects intensity data required for structure determination.

Accurate measurements of intensities of reflections of all Miller indices within a specified reciprocal radius (usually 25° for MoK\(_\alpha\) and 68° for CuK\(_\alpha\)) is needed to find the structure, while unit cell parameters depend only on direction of reflections. As the name implies, a crystalline sample is required. For single-crystal work, the specimen should be smaller than cross section diameter of the beam. Larger crystals can be cut down to proper size and smaller crystals may be suitable if they contain strongly diffracting elements.

The monochromatic X-rays incident on a plane of single crystal at an angle theta are diffracted according to Bragg's relation, 

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

where 'd' is the interplanar spacing of the incident plane, 'λ' is the wavelength of X-rays and 'n' is a positive integer. The intensity of the diffracted rays depends on the arrangement and nature of atoms in the crystal. Collection of intensities of a full set of planes in the crystal contains the complete structural information about the molecule. Fourier transformation techniques are used to determine the exact coordinates of atoms in the unit cell from this data.

With the set of X-ray diffraction data collected, unit cell parameters, space groups, molecular structure of the crystalline solids and Miller indexing the different faces of the crystal are possible. Unit cell parameter is simply the dimension of the basic molecular brick with which the crystal is built. Space group tells us the symmetry with which the molecules are arranged within the unit cell. All the geometrical features of molecules (bond distance, bond angles, torsion angles between bonds, dihedral angles between planes etc.) may be obtained from coordinates.
In the present study, the single crystal X-ray diffraction analysis was performed using an ENRAF NONIUS CAD4-F single crystal X-ray diffractometer. The shield was equipped with graphite monochromated MoKα radiation. Since the crystal was transparent, the single crystallinity was studied with Leica polarizing microscope. Single crystal of suitable size was cut and mounted on the X-ray goniometer. The sample is mounted on a thin glass fiber that is attached to a brass pin and mounted on a goniometer head. Adjustment of the goniometer head in the X, Y and Z orthogonal directions allows centering of the crystal in the X-ray beam. The unit cell dimensions \((a, b, c, \alpha, \beta, \gamma)\) can be determined from the accurately measured 2θ values (the angular deviation from the direct undeviated beam of about 25 reflections. The reflections were indexed using method of short vectors followed by least square refinements. The unit cell parameters thus obtained were transformed to correct Bravais cell.

### 2.5 P-E HYSTERESIS LOOP MEASUREMENT

Ferro electricity is the switching between different metastable states by the application and removal of an electric field. The mechanism of switching is understood to take place on scales longer than the unit-cell scale, and generally to require the growth and shrinking of domains through the motion of domain walls.

In its canonical form, the ferroelectric P–E hysteresis loop is symmetric and the remnant polarization and coercive fields are easily defined and extracted. There are, however, a number of potential pitfalls in the accurate performance of this measurement. The starting point for any measurement of this kind is to realize that the electrical properties of a ferroelectric film can only be measured when it is fabricated as a device (most typically a capacitor). Thus, any measurement actually involves a whole system, with electrodes, wires and interfaces, and sometimes it is these other components of the system that dominate the electrical response, rather than the intrinsic properties of the material of interest. In this section we briefly cover the key ways in which ferroelectric hysteresis measurements are made, with special attention to the potential errors that can be made and the methods that can be used to avoid them.
The Sawyer–Tower circuit (Sawyer, C.B. and Tower, C.H., 1930), the original method for measuring ferroelectric hysteresis, is simple in concept. It is essentially just a capacitance bridge, relying on the fact that two capacitors in series should have the same charge. One of these capacitors is comprised of the ferroelectric, and the other is a standard capacitor with a well-defined capacitance. The potential across the standard capacitor is plotted on the y-axis, and the ac voltage applied to the ferroelectric sample is plotted on the x-axis in the X–Y mode of an oscilloscope. The standard capacitor should be chosen to have a large capacitance so that the potential across it is small enough not to affect the potential across the ferroelectric sample. In the ideal case where the current flowing during this measurement is purely displacive, this measurement will give accurate values of the ferroelectric polarization. Schematic circuit of Sawyer-Tower Bridge for the observation of P-E characteristics of ferroelectrics is shown in figure 2.7.

![Figure 2.7 Schematic circuit of Sawyer-Tower Bridge for the observation of P-E Characteristics of ferroelectrics](image_url)
2.6 PIEZOELECTRIC MEASUREMENT

A piezoelectric substance is one that produces an electric charge when a mechanical stress is applied (the substance is squeezed or stretched). Conversely, a mechanical deformation (the substance shrinks or expands) is produced when an electric field is applied. This effect is formed in crystals that have no center of symmetry. To explain this, we have to look at the individual molecules that make up the crystal. Each molecule has a polarization, one end is more negatively charged and the other end is positively charged, and is called a dipole. This is a result of the atoms that make up the molecule and the way the molecules are shaped. The polar axis is an imaginary line that runs through the center of both charges on the molecule. In a mono crystal the polar axes of all of the dipoles lie in one direction. The crystal is said to be symmetrical because if you were to cut the crystal at any point, the resultant polar axes of the two pieces would lie in the same direction as the original. In a polycrystal, there are different regions within the material that have a different polar axis. It is asymmetrical because there is no point at which the crystal could be cut that would leave the two remaining pieces with the same resultant polar axis. The piezoelectric effect can now be observed in the crystal. Figure 2.8 illustrates the piezoelectric effect. Figure 2.8 (a) shows the piezoelectric material without a stress or charge. If the material is compressed, then a voltage of the same polarity as the poling voltage will appear between the electrodes (b). If stretched, a voltage of opposite polarity will appear (c). Conversely, if a voltage is applied the material will deform. A voltage with the opposite polarity as the poling voltage will cause the material to expand, (d), and a voltage with the same polarity will cause the material to compress (e). If an AC signal is applied then the material will vibrate at the same frequency as the signal (f).
The piezoelectric crystal bends in different ways at different frequencies. This bending is called the vibration mode. The crystal can be made into various shapes to achieve different vibration modes. To realize small, cost effective, and high performance products, several modes have been developed to operate over several frequency ranges. These modes allow us to make products working in the low kHz range up to the MHz range.

2.7 ENERGY DISPERSIVE SPECTRUM ANALYSIS

EDX Analysis stands for Energy Dispersive X-ray analysis. It is sometimes referred to also as EDS or EDAX analysis. It is a technique used for identifying the elemental composition of the specimen, or an area of interest thereof. The EDX analysis system works as an integrated feature of a scanning electron microscope (SEM), and cannot operate on its own without the latter (Nakatani, H. et. al., 1988).

X-rays are produced when materials are irradiated with an electron beam. The high-energy electrons excite the electrons in the electron shells around the atoms in the material, causing them to jump to higher energy shells. When the electrons fall back to the lower energy shells, they emit electromagnetic radiation in the form of X-rays. The wavelengths, and hence energies, of the X-rays are characteristic of the electron shell energies, and the spectrum of X-rays can be used to identify different elements.
It is possible to measure the amount of different elements from the spectrum, and the X-ray spectrum produced by materials in a scanning electron microscope can be used to determine the composition of many materials. High-resolution measurements can determine the differences in composition at different positions on a sample, and very small samples can be observed. The analysis of the energy dispersive X-ray spectrum is a very powerful technique in materials science.

The output of an EDX analysis is an EDX spectrum. The EDX spectrum is just a plot of how frequently an X-ray is received for each energy level. An EDX spectrum normally displays peaks corresponding to the energy levels for which the most X-rays had been received. Each of these peaks is unique to an atom, and therefore corresponds to a single element. The higher a peak in a spectrum, the more concentrated the element is in the specimen.

An EDX spectrum plot not only identifies the element corresponding to each of its peaks, but the type of X-ray to which it corresponds as well. For example, a peak corresponding to the amount of energy possessed by X-rays emitted by an electron in the L-shell going down to the K-shell is identified as a K-Alpha peak. The peak corresponding to X-rays emitted by M-shell electrons going to the K-shell is identified as a K-Beta peak and is illustrated in Figure 2.9.

![Diagram](image.png)

**Figure 2.9** Elements in an EDX spectrum are identified based on the energy content of the X-rays emitted by their electrons as these electrons transfer from a higher-energy shell to a lower-energy one.
2.8 SCANNING ELECTRON MICROSCOPY

Electron microscopy takes advantage of the wave nature of rapidly moving electrons. Where visible light has wavelengths from 4,000 to 7,000 Angstroms, electrons accelerated to 10,000 KeV have a wavelength of 0.12 Angstroms. At the moment, the scanning electron microscope (SEM) is utilized not only in the field of medical science and biology, but also in varied disciplines such as materials development, metallic materials, ceramics, and semiconductors. Optical microscopes have their resolution limited by the diffraction of light to about 1000 diameters magnification. Electron microscopes, so far, are limited to magnifications of around 1,000,000 diameters, primarily because of spherical and chromatic aberrations. Scanning electron microscope resolutions are currently limited to around 25 Angstroms, though, for a variety of reasons.

The scanning electron microscope generates a beam of electrons in a vacuum. That beam is collimated by electromagnetic condenser lenses, focused by an objective lens, and scanned across the surface of the sample by electromagnetic deflection coils. The primary imaging method is by collecting secondary electrons that are released by the sample. The secondary electrons are detected by a scintillation material that produces flashes of light from the electrons. The light flashes are then detected and amplified by a photomultiplier tube. By correlating the sample scan position with the resulting signal, an image can be formed that is strikingly similar to what would be seen through an optical microscope.

The SEM uses electrons instead of light to form an image. A beam of electrons is produced at the top of the microscope by heating of a metallic filament. The electron beam follows a vertical path through the column of the microscope. It makes its way through electromagnetic lenses which focus and direct the beam down towards the sample. Once it hits the sample, other electrons (backscattered or secondary) are ejected from the sample. Detectors collect the secondary or backscattered electrons, and convert them to a signal that is sent to a viewing screen similar to the one in an ordinary television, producing an image Figure2.10 illustrates the working of the SEM.
There are other imaging modes available in the SEM. Specimen current imaging using the intensity of the electrical current induced in the specimen by the illuminating electron beam to produce an image. It can often be used to show subsurface defects. Backscatter imaging uses high energy electrons that emerge nearly 180 degrees from the illuminating beam direction. The backscatter electron yield is a function of the average atomic number of each point on the sample, and thus can give compositional information.

![Figure 2.10 Working principle of SEM.](image)

Scanning electron microscopes are often coupled with x-ray analyzers. The energetic electron beam - sample interactions generate x-rays that are characteristic of the elements present in the sample. Many other imaging modes are available that provide specialized information.

Fig 2.11 shows the schematics of the ray traces for two probe forming lens focusing conditions: small working distance (left) and large working distance (right). Both conditions have the same condenser lens strength and aperture size. However, as the sample is moved further from the lens, the following occurs: the working distance S is increased, the demagnification decreases, the spot size increases, the divergence angle alpha is decreased.

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The decrease in demagnification is obtained when the lens current is decreased, which in turn increases the focal length \( f \) of the lens. The resolution of the specimen is decreased with an increased working distance, because the spot size is increased. Conversely, the depth of field is increased with an increased working distance, because the divergence angle is smaller. SEM inspection is often used in the analysis of die/package cracks and fracture surfaces, bond failures, and physical defects on the die or package surface.

### 2.9 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 materials 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. 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 (Matthias, B.T. and Remeika, J.P., 1951; Triebwasser, S., 1959;

The relative dielectric constant ($\varepsilon_r$) is defined as, $\varepsilon_r = \frac{\varepsilon}{\varepsilon_0}$. It is known that $\varepsilon = \frac{Cd}{A}$

Hence,

$$C = \frac{\varepsilon_0\varepsilon_r A}{d}$$  \hspace{1cm} (2.1)

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. The
 capacitance ‘$C_0$’ of a parallel plate condenser having a capacitance ‘$C$’ in air can be
given by, $C = \varepsilon_r C_0$. 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.

Major contributions to the dielectric constant are from,

i) The extrinsic nature of the material,
ii) The electronic polarizability,
iii) The ionic polarizability and
iv) The deformation of the ions
2.9.1 DIELECTRIC LOSS

Dielectric loss can be defined as the amount of power applied to a dielectric in the form of heat energy under the action of voltage. If the electric polarization in a dielectric is unable to follow the varying electric field, dielectric losses occur. When an alternating electric field \( E \) is applied to dielectric, displacement vector \( D \) varies periodically with time. However, \( D \) lags behind in phase relative to the field. The applied sinusoidal field is, \( E = E_0 \cos \omega t \).

We have the scalar equation \( D = D_0 \cos (\omega t - \delta) = D_1 \cos \omega t + D_2 \sin \omega t \) where \( \delta \) is the phase angle, \( D_1 = D_0 \cos \delta \) and \( D_2 = D_0 \sin \delta \).

For most dielectric, \( D_0 \) is proportional to \( E_0 \), but the ratio \( D_0 / E_0 \) is generally frequency dependent. To describe this situation, two frequency dependent dielectric constants \( \varepsilon' (\omega) \) and \( \varepsilon'' (\omega) \) are introduced which are given by

\[
\varepsilon'(\omega) = \frac{D_1}{E_0} = \left( \frac{D_0}{E_0} \right) \cos \delta \quad (2.2) \text{ and }
\]

\[
\varepsilon''(\omega) = \frac{D_2}{E_0} = \left( \frac{D_0}{E_0} \right) \sin \delta \quad (2.3)
\]

It is convenient to combine these two constants into a complex dielectric constant as \( \varepsilon^* = \varepsilon' - j\varepsilon'' \). D and E can be expressed as complex quantities. The relation between D and E is \( D = \varepsilon_0^*E_0 e^{j\omega t} \). From equations (2.2) and (2.3)

\[
\tan \delta = \frac{\varepsilon''(\omega)}{\varepsilon'(\omega)} \quad (2.4)
\]

Since \( \varepsilon' \) and \( \varepsilon'' \) are frequency dependent, the phase angle \( \delta \) is also frequency dependent. \( \tan \delta \) is called the loss factor.

The A.C. Conductivity is given by:

\[
\sigma_{ac} = 2\pi f \tan\delta \varepsilon_0 \varepsilon_r \quad (2.5)
\]

where \( f \) is the frequency.

In the present work, Digital LCR meter used for the dielectric study is shown in Figure 2.12.
2.10 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, micro hardness 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 stress (Taber, D., 1951). Hardness measurements can be defined as macro, micro and nano according to the forces applied and displacement obtained (Pethica, J.B. and Taber, D., 1979).
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 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 hardness 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, O.H. and Dew Hughes, D., 1974).

2.10.1 VICKERS HARDNESS AND ANISOTROPY STUDIES

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. Smith et al., (1923) 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 the most widely accepted pyramid indenter. A pyramid indenter is suited for hardness tests due to the following reasons (Batta Calleja, F.J. 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 \((1/7)\)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

\[
H_v = \frac{2p\sin(\alpha/2)}{d^2}
\]

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

\[
H_v = \frac{1.8544P}{d^2} \text{ Kg/mm}^2
\]  

(2.6)

where ‘\(P\)’ is the applied load and ‘\(d\)’ is the mean diagonal length of the indenter impression. The applied load is usually specified when \(H_v\) is cited. 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 materials response to the indentation pressure during loading, in the final measurement of the residual impression.

The importance of micro hardness 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.

The hardness measurements may depend upon the orientation of the indented crystals. To study the hardness anisotropy present in crystals, the crystals are initially mounted on the stage of microscope properly and indented. The initial position is 0 degree. The stage of the microscope was then rotated keeping the indenter fixed and ‘\(H_v\)’ was measured at every 30 degrees interval till the original position. No distortion in shape of indenter will be observed with crystal orientation. When the variation of
'Hv' with angular displacement is periodic, then it brings the anisotropic nature of crystals.

The data obtained for P and d can be analyzed by Meyer's equation (Meyer, E., 1908).

\[ P = kd^n \]  \hspace{1cm} (2.7)

where k and n are constants for the material. The constant k is usually referred to as the standard hardness. Meyer index (n) which represents work hardening capacity of the material can be determined by plotting log P vs log d.

The dependence of Vickers hardness number on applied load shows different behaviour on different materials (Meyer, E., 1908; Sherwood, J.N., 1998; Kityk, I.V. et.al., 2001). In certain cases, micro hardness increases with applied load and reaches a constant value at higher loads (Onitsch, E.M., 1947; Hanneman, M., 1941; Hays, C. and Kendall, E.G., 1973). Micro hardness is found to decrease with increasing load and attains a constant value after a particular load for certain crystals. For certain materials, Hv is found to have complex load dependence. Combining Equations (2.6) and (2.7), we have

\[ Hv = 1.8544kd^{n-2} \]  \hspace{1cm} (2.8)

The above expression shows that Hv should increase with increase in P if \( n > 2 \) and decrease with the same if \( n < 2 \). According to Onitsch (1947) and Hanneman (1941), n should lie between 1 and 1.6 for hard materials and above 1.6 for softer ones.

Elastic stiffness constant \((C_{11})\) of a material can be calculated from the Wooster's empirical relation (Wooster, W.A., 1953) as

\[ C_{11} = H_v^{7/4} \]  \hspace{1cm} (2.9)

If the stiffness constant C11 is high, it reveals that the binding forces are quite strong. The experimental setup to measure Vicker’s micro hardness is shown in figure 2.13.
PHOTOCONDUCTIVITY STUDIES

Photoconductivity is an optical and electrical phenomenon in which a material becomes more electrically conductive due to the absorption of electromagnetic radiation such as visible light, ultraviolet light, infrared light, or gamma radiation. In the recent past advancement in the study of quantum well and super lattice structures have dramatically changed the concept of photo sensors. Photo detection technology has become very 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 photo conductivity processes. Photoconductivity is an important property of solids by means of which the bulk conductivity of the sample changes due to incident radiation. Photo conduction includes the generation and recombination of charge carriers and their transport to the electrodes. Smith recorded the first photoconductivity effect in 1873 when he observed the decrease in the resistivity of selenium by the radiation falling on it (Joshi, V.N., 1990).

When a bias voltage and a load resistor are used in series with the semiconductor, a voltage drop across the load resistors can be measured when the
change in electrical conductivity of the material varies the current flowing through the circuit. The experimental set up to measure photo current and dark current is shown in Figure 2.14

Figure 2.14 Photoconductivity experimental setup

Photocurrent is the current that flows through a photosensitive device, such as a photodiode, as the result of exposure to radiant power. The photocurrent may occur as a result of the photoelectric, photo emissive or photovoltaic effect. The photocurrent may be enhanced by internal gain caused by interaction among ions and photons under the influence of applied fields, such as occurs in an avalanche photodiode (APD). When a suitable radiation is used, the photoelectric current is directly proportional to the intensity of the radiation.

Dark current is the relatively small electric current that flows through a photosensitive device when no photons are entering the device. It changes with operating temperature and applied voltage.
2.12 CONCLUSION

Single crystals grown by the slow evaporation method need to be characterized to assess the suitability of the crystal for various applications. In order to understand the behaviour of any solid material, the structural characterization was carried out. The optical characterization was carried out to check the transparency window and cut-off frequency of the grown crystals. Since the entire thrust is with respect to ferroelectric application, the P-E hysteresis loop was traced. In addition, the piezoelectric, mechanical, dielectric and photo conducting nature of the grown crystals were also investigated.