CHAPTER II
2. CHARACTERIZATION TECHNIQUES

We describe here the various characterization techniques followed in the present study.

2.1 INTRODUCTION

A complete description of the physical and chemical properties of a material of interest is termed as characterization of that material. These assessment techniques used for the study of the physical and chemical properties of the grown single crystals assist us to trigger rapid progress in the growth process and to improve the quality of the crystal. The information on the process that occurred during growth of a single crystal is provided by the post growth analysis. Being handicapped of using a number of sophisticated instruments to carry out a variety of tests on the grown crystal, it becomes impossible to characterize a single crystal thoroughly and extensively. Characterization of a crystal essentially consists of determination of chemical composition, structure, defects and study of their optical properties [38].

The study of growth defects includes the defects such as inclusions, mechanical stress, etc that result due to poor control of crystal growth parameters. Standard techniques such as etching, chemical analysis, X-ray topography, scanning electron microscopy, etc can be used for defect characterization. The measurement of optical properties includes the study of optical transmission and absorption of the crystal, SHG conversion efficiency, NLO coefficients, electro-optical coefficients and structural dependence of these properties.
2.2 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 (XRD) 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 MoKα and 68° for CuKα) 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, \( \lambda \) 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 distances, 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 (A photograph is shown in Figure 2.1). 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 crystal was optically centered at the sphere of confusion using the built in tele-microscope. 25 reflections were collected from different zones of the reciprocal lattice using random search procedure. 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.

Figure 2.1: A photograph of the single crystal X-ray diffractometer
2.3 FOURIER TRANSFORM INFRARED (FT-IR) ANALYSIS

Fourier Transform Infrared (FTIR) 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. FT-IR has made this energy-limited region more accessible. It has also made the mid-infrared (4000-400 cm⁻¹) 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 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. 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 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 [39].

In the present study, the FT-IR spectrum was recorded in the range of 4000-400 cm⁻¹ using the instrument Thermo-Nicolet Avatar 370(a photograph is shown in Figure 2.2).
2.4 SEM STUDIES

2.4.1 Introduction

In a scanning electron microscope, the surface of a solid sample is scanned in a raster pattern with a beam of energetic electrons. Several types of signals are produced from a surface in this process. All of these signals have been used for surface studies, but the two most common signals used for surface studies are: (1) backscattered and secondary electrons, which serve as the basis of scanning electron microscopy, and (2) X-ray emission, which is used in electron microprobe analysis.

2.4.2 Instrumentation

Figure 2.3 is a schematic of a scanning electron microscope. Scanning with a SEM is accomplished by the two pairs of electromagnetic coils located within the objective lens (Figure 2.3); one pair deflects the beam in the x-direction across the sample, and the other pair deflects it in the y-direction. Scanning is controlled by
applying an electrical signal to one pair of scan coils, such that the electron beam strikes
the sample to one side of the center axis of the lens system. By varying the electrical
signal to this pair of coils (that is, the x-coils) as a function of time, the electron beam is
moved in a straight line across the sample and then returned to its original position. After
completion of the line scan, the other set of coils (y-coils in this case) is used to deflect
the beam slightly, and the deflection of the beam using the x-coils is repeated. Thus, by
rapidly moving the beam, the entire sample surface can be irradiated with the electron
beam. The signals to the scan coils can be either analog or digital. Digital scanning has
the advantage that it offers very reproducible movement and location of the electron
beam. The signal from the sample can be encoded and stored in digital form along with
digital representations of the x and y-positions of the beam.

The signals that are used to drive the electron beam in the x and
y-directions are also used to drive the horizontal and vertical scans of a cathode-ray tube
(CRT). The image of the sample is produced by using the output of a detector to control
the intensity of the spot on the CRT. Thus, this method of scanning produces a map of the
sample in which there is a one-to-one correlation between the signal produced at a
particular location on the sample surface and a corresponding point on the CRT display.

The specimen stage is provided with a mechanism whereby the sample can be
moved in two mutually perpendicular directions and rotated as well, thus permitting
scanning of the surface.

2.4.3 Applications

The electron microprobe provides a wealth of information about the physical and
chemical nature of surfaces. It has had important applications to phase studies in
metallurgy and ceramics, the investigation of grain boundaries in alloys, the measurement of diffusion rates of impurities in semiconductors, the determination of occluded species in crystals, and the study of the active sites of heterogeneous catalysts. In all of these applications, both qualitative and quantitative information about surfaces is obtained.

![Figure 2.3: Schematic representation of a scanning electron microscope (SEM)](image)

**2.5 ENERGY DISPERSIVE X-RAY SPECTROSCOPY (EDX)**

Energy dispersive X-ray spectroscopy (EDAS, EDX or EDXRF) is an analytical technique used for the elemental analysis or chemical characterization of a sample. As a type of spectroscopy, it relies on the investigation of a sample through interactions between electromagnetic radiation and matter, analyzing X-rays emitted by the matter in response to being hit with charged particles [40]. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing X-rays that are characteristic of an element's atomic structure to be identified uniquely from each other. To stimulate the emission of characteristic X-rays from a
specimen, a high energy beam of charged particles such as electrons or protons or a beam of X-rays, is focused into the sample being studied. At rest, an atom within the sample contains ground state (or unexcited) electrons in discrete energy levels or electron shells bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell while creating an electron hole where the electron was. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower energy shell may be released in the form of an X-ray.

The number and energy of the X-rays emitted from a specimen can be measured by an energy dispersive spectrometer. As the energy of the X-rays is characteristic of the difference in energy between the two shells, and of the atomic structure of the element from which they were emitted, this allows the elemental composition of the specimen to be measured. The amount of energy released by the transferring electron depends on which shell it is transferring from, as well as which shell it is transferring to. Furthermore, the atom of every element releases X-rays with unique amounts of energy during the transferring process. Thus, by measuring the amounts of energy present in the X-rays being released by a specimen during electron beam bombardment, the identity of the atom from which the X-ray was emitted can be established.

There are four primary components of the EDX setup: the beam source; the X-ray detector; the pulse processor; and the analyzer. A number of free-standing EDX systems exist. However, EDX systems are most commonly found on scanning electron microscopes (SEM-EDX) and electron microprobes. Scanning electron microscopes are equipped with a cathode and magnetic lenses to create and focus a beam of electrons. A
detector is used to convert X-ray energy into voltage signals; this information is sent to a pulse processor, which measures the signals and passes them onto an analyzer for data display and analysis.

An electron beam strikes the surface of a conducting sample. The energy of the beam is typically in the range 10-20 keV. This causes X-rays to be emitted from the point of the material. The energy of the X-rays emitted depends on the material under examination. The X-rays are generated in a region about 2 microns in depth, and thus EDX is not a surface science technique [41]. Due to the low X-ray intensity, images usually take a number of hours to acquire. Elements of low atomic number are difficult to be detected by EDX. 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. This is illustrated in Figure 2.4.
Figure 2.4: 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.

The most significant issue to note from this is that the X-rays generated from any particular element are characteristic of that element, and as such, can be used to identify which elements are actually present under the electron probe. This is achieved by constructing an index of X-rays collected from a particular spot on the specimen surface, which is known as a spectrum.

2.6 UV-Vis-NIR Spectroscopy

UV-visible absorption spectroscopy involves the spectroscopy of photons in the UV-visible region. This means it uses light in the visible, near ultraviolet (UV) and near infrared (NIR) ranges. The absorption in the visible ranges directly affects the colour of the chemicals involved. In this region of the electromagnetic spectrum, molecules undergo electronic transitions [42]. This technique is complementary to fluorescence spectroscopy, in that fluorescence deals with transitions from the excited state to the
ground state, while absorption measures transitions from the ground state to the excited state.

Absorption of light by solution is one of the oldest and still one of the more useful instrumental methods. The wavelength of light that a compound will absorb is characteristic of its chemical structure. Specific regions of the electromagnetic spectrum are absorbed by exciting specific types of molecular and atomic motion to higher energy levels. Absorption of microwave radiation is generally due to excitation of molecular rotational motion. Infrared absorption is associated with vibrational motions of molecules. Absorption of visible and ultraviolet (UV) radiation is associated with excitation of electrons, in both atoms and molecules, to higher energy states. All molecules will undergo electronic excitation following absorption of light, but for most molecules very high energy radiation (in the vacuum ultraviolet, <200 nm) is required. For molecules containing conjugated electron systems however, light in the UV-visible region is adequate. As the degree of conjugation increases, the spectrum shifts to lower energy.

**Beer-Lambert Law:** The Beer-Lambert law states that the absorbance of a solution is directly proportional to the concentration of the absorbing species in the solution and the path length.

Thus, for a fixed path length, UV/VIS spectroscopy can be used to determine the concentration of the absorber in a solution [43]. It is necessary to know how quickly the absorbance changes with concentration.

The amount of light, I, transmitted through a solution of an absorbing chemical in a transparent solvent can be related to its concentration by Beer’s Law:
\[ -\log \frac{l}{l_0} = A = \varepsilon_\lambda b c, \]

where \( l_0 \) is the incident light intensity, \( A \) is the absorbance, \( b \) is the cell path length in cm, \( c \) is the solution concentration in moles/liter, and \( \varepsilon_\lambda \) is the molar absorptivity (also referred to as the molar extinction coefficient) which has units of liter/mole/cm. Notice that \( \varepsilon_\lambda \) is a function of wavelength, and it is the quantity which represents the spectrum of the solution. A diagram of the components of a typical spectrometer is shown in Figure 2.5.

\begin{figure}[h!]
\centering
\includegraphics[width=\textwidth]{spectrometer_diagram.png}
\caption{Schematic representation of UV-VIS-NIR spectrometer}
\end{figure}

A beam of light from a visible and/or UV light source (coloured red) 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 (coloured magenta), passes through a small transparent container (cuvette) containing a solution of the compound being studied in a transparent solvent. The other beam, the reference (coloured blue), 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 $I$. 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 190 to 400 nm, and the visible portion is from 400 to 700 nm. In the present study UV-Visible spectra were recorded in the wavelength range 190-900 nm using a Shimadzu UV-2400PC spectrometer.

2.7 NLO TEST: KURTZ-PERRY POWDER METHOD

Recent interest is focused on to find the materials which have suitable nonlinear optical properties for use as the active media in efficient second harmonic generators, tunable parametric oscillators and broadband electro-optic modulators.

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 [44] proposed a powder SHG method for comprehensive analysis of the second order nonlinearity. Employing this technique, Kurtz surveyed a very large number of compounds.

A Q–switched Nd:YAG laser emitting 1.06 μm can be operated in two modes. In the single shot mode the laser emits a single 8 ns pulse. In the multi shot 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 1 mm was used. This experimental setup used a mirror and a 50/50 beam splitter (BS) to generate a beam with
pulse energies. The input laser beam was passed through an IR reflector and then directed on the micro crystalline powdered sample packed in a capillary tube. The light emitted by the sample was measured by the photodiode detector and oscilloscope assembly.

2.8 THERMAL STUDIES

Recent trends indicate that thermal analysis has become an established method in the study of the thermal behaviour of materials and finds widespread applications in diverse industrial and research fields. Thermal analysis is a general term, which covers a group of related techniques in which the temperature dependence of the parameters of any physical property of a substance is measured. In addition to providing valuable information on the thermal stability of the compounds and the decomposition products, these studies often provide an insight into their mode of decomposition. The importance of thermal analysis in quality control, failure analysis and materials research and development is well established.

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 thermogravimetric 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 material, 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 equilibria 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. Figure 2.6 shows the photograph of a TG/DTA analyzer.

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.

Modern commercial TG instrument consists of:

A sensitive analytical balance;

A temperature programmable furnace;

A purge gas system for providing suitable gas atmosphere;

A microprocessor for instrument control, data acquisition and display; etc.
Eventhough different types of balance mechanism are available today, those employing null-point weighing mechanism is favoured as the sample remains in the same zone of furnace irrespective of changes in mass. The furnace is normally an electrical resistive heater and the temperature range for most of the furnace is from ambient to 1000–2000°C. Thermogravimetry is widely used to determine the thermal stability, decomposition temperature, temperature of desorption and drying, oxidative stability, etc.

![Photograph of a TG / DTA analyzer](image)

Figure 2.6: Photograph of a TG / DTA analyzer

Heating rate of the various factors that affect the results of thermal analysis, heating rate is very important. The rate of heat exchange between the furnace and the sample depends upon the heating rate which influences the TGA curve in a number of ways. A slower rate gives a better resolution of the closely lying steps, while the faster heating rate merges such steps.
The type and material of the sample holder affect the TGA curve to a considerable extent. The shape and size of the sample holder determine the thermal gradients within the sample and the area of the sample-environmental gas interface.

One of the objectives 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. Often, the values reported from TGA or DTA measurements differ considerably from the true value. Some of the reasons for this are the effects of self generated atmosphere and heating rate as well as the lag between the sample and furnace temperatures.

In the present study, the thermal analyses were done using an Universal V4.1 DTA Instruments in the temperature range 50-700°C in nitrogen atmosphere at a scanning rate of 10K/min.

2.9 DC CONDUCTIVITY MEASUREMENTS

Conductivity of solid substance is a characteristic property. The conductivity of a solid is due to the mobility of electrons or ions and imperfections which are charged. Although ionic solids are insulators, yet they conduct electricity to a very small extent. This arises due to the migration of ions under an electric field to the vacancies or interstices in the ionic solids.

Ionic conduction occurs either through the migration of positive and negative ions in an external electric field (the ions originate either in the material in question or in interstice impurities) or through the motion of ions in vacancies which reflects the migration of vacancies. If the sample is placed in a stationary electric field, the carriers
may be considered to be contained in an enclosure bounded by the capacitor plates. As the carriers may not leave the enclosure they accumulate in the regions close to the plates which cause a concentration gradient to be formed and this gradient feeds diffusion current. At equilibrium the diffusion current density equals that of the drift current. Charge accumulation is related to inhomogeneities of the material, the agglomeration of impurity ions by diffusion in the vicinity of electrodes or chemical changes in layers close to electrodes.

Crystals with high transparency and large surface defect-free (i.e. without any pit or crack or scratch on the surface, tested with a traveling microscope) size (> 3 mm) were selected and used for the DC electrical conductivity measurements. The extended portions of the crystals were removed completely and the opposite faces were polished and coated with good quality graphite to obtain a good conductive surface layer. The dimensions of the crystals were measured using a traveling microscope (L.C. = 0.001 cm).

The conductivity measurements were carried out to an accuracy of ±2% using the conventional two-probe technique[45] at various temperatures ranging from 40 - 150°C. The resistance of the crystals were measured using a million – megohmmeter. The observations were made while cooling the sample. Temperature was controlled to an accuracy of ±1 °C. The DC conductivity (σ_{dc}) of the crystal was calculated using the relation

\[ \sigma_{dc} = \frac{d}{RA}, \]

where R is the measured resistance, d is the thickness of the sample and A is the area of the face in contact with the electrode.
2.10 DIELECTRIC MEASUREMENTS

Various polarization mechanisms in solids such as atomic polarization of the lattice, orientational polarization of dipoles and space charge polarization can be understood very easily by studying the dielectric properties as a function of frequency and temperature for crystalline solids. The frequency dependence of these properties gives a great insight into the material’s applications. The dielectric constant determines the share of the electric stress which is absorbed by the material without any dielectric breakdown. The dielectric loss is a measure of the energy absorbed by a dielectric.

The capacitance \( C_{\text{cryst}} \) and dielectric loss factor \( \tan \delta \) measurements were carried out to an accuracy of $\pm 2\%$ using an LCR meter (Agilent 4284 A) [A photograph is shown in Figure 2.7] with five different frequencies, viz. 100 Hz, 1 kHz, 10 kHz, 100 kHz and 1 MHz at various temperatures ranging from 40 - 150°C [45-61]. Temperature was controlled to an accuracy of $\pm 1^\circ$C. The samples were prepared and annealed in a way similar to that followed for the resistance measurement. Air capacitance \( C_{\text{air}} \) was also measured.

The dielectric constant of the crystal \( \varepsilon_r \) was calculated by using Mahadevan’s relation (as the crystal area was smaller than the plate area of the cell) [46,49,53,55,62]

\[
\varepsilon_r = \left( \frac{A_{\text{air}}}{A_{\text{cryst}}} \right) \left( \frac{C_{\text{cryst}} - C_{\text{air}} \left( 1 - \frac{A_{\text{cryst}}}{A_{\text{air}}} \right)}{C_{\text{air}}} \right),
\]

where \( A_{\text{cryst}} \) is the area of the crystal touching the electrode and \( A_{\text{air}} \) is the area of the electrode.

The AC conductivity \( \sigma_{ac} \) was calculated using the relation

\[
\sigma_{ac} = \varepsilon_r \varepsilon \omega \tan \delta,
\]
where \( \varepsilon_0 \) is the permittivity of free space \( (8.85 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}) \) and \( \omega \) is the angular frequency.

Figure 2.7: Experimental set-up for AC electrical measurements