2.1 Introduction

Nowadays, scientists and engineers have an impressive array of powerful and elegant tools for acquiring quantitative and qualitative information about the composition and structure of matter. There are variety of crystals grown having numerous applications in science and technology. It is always important to characterize these crystals from various angles of interests by different instruments [1]. The present chapter gives a brief review of experimental techniques, which are used by the present author to characterize the crystal grown.

2.2 Crystal Growth

The crystals for the present investigations have been grown by the single diffusion sodium metasilicate gel column. These particular techniques are briefly reviewed in chapter – I and will be discussed in the following chapters.

2.3 Fourier Transform Infrared Spectroscopy

Multiplex type of instruments employs the mathematical tool of Fourier Transform [2]. The apparatus of Fourier Transform Infrared (FTIR) spectrometer is derived from Michelson interferometer, which is shown in figure (2.1). The main components of the FT-IR spectrometers are: (1) drive mechanism, (2) beam splitters, and (3) sources and transducers. In figure (2.1), a parallel beam of radiation is directed from the source to the interferometer, consisting of a beam splitter and two mirrors mirror 1 and mirror 2. It is well known that for monochromatic radiation the interference patterns are obtained.

Figure (2.1): Schematic diagram of Michelson interferometer
The constructive or destructive interference is produced depending on the relative path lengths B to M₁ and B to M₂. When mirror M₂ moves smoothly towards or away from B, a detector sees radiation of changing intensity. If white radiation is used, the interference patterns are obtained which can be transferred back to the original frequency distribution. This can be achieved by a mathematical process known as Fourier transform, nowadays, this process is carried out by a computer or microprocessor of the spectrometer. Under these conditions, the detector response fluctuates at a rate, which depends upon the rate of movement of mirror and the wavelength of radiation.

In general, any combination of frequencies with corresponding amplitudes will produce an interferogram containing all the spectral information of the original radiation. The interferogram is the Fourier transform of the spectrum and the task of the computer is to apply the inverse Fourier transform.

Interferometric or Fourier transform spectroscopy makes use of all the frequencies from the source simultaneously, rather than sequentially as in scanning instrument. This was first proposed by Fellgett and hence also called as Fellgett.
advantage FTS. The Fellgett advantage is an improvement in signal to noise ratio of $(M)^{1/2}$, where $M$ is the number of resolution elements desired in the particular spectrum. It is worth noting that the resolving power of Fourier transform instrument is constant over the entire spectrum, whereas it varies with frequency in the conventional technique [3]. Fourier transform spectroscopy is providing simultaneous and almost instantaneous recording of whole spectrum in the magnetic resonance, microwave and infrared regions. Fourier Transform (FT) Spectroscopy is equally applicable to both emission and absorption spectroscopy.

The FT-IR set up has, as noted earlier, design based on Michelson interferometer, which is having mainly three important components:

1. A drive mechanism is important for satisfactory interferograms, which needs that the speed of the moving mirror be constant and its position be known exactly at any instant. The planarity of the mirror must remain constant during the entire sweep of 10 cm or more.

2. Beam splitters are constructed of transparent materials with refractive indices such that approximately 50% of the radiation is transmitted and 50% is reflected. A thin film of germanium or silicon coated on cesium iodide or bromide, sodium chloride, or potassium bromide is employed for mid infrared region.

3. The sources of FTIR are usually the same as IR ones. Inasmuch as the slow response times the thermal transducers are not generally preferred in FT-IR, the Triglycine sulphate transducers are widely preferred in the mid frequency range.

The FTIR instrument has many advantages. It has better signal to noise ratio than good quality dispersive type instrument. Another important advantage is that its optics provides a much larger energy throughput (one or two orders of magnitude) than the dispersive type, where it is limited by the necessity of having the narrow slit widths. The prime advantage of FT-IR is that the interferometer is free from the problem of stray radiation because each infrared frequency is chopped at a different frequency.

There are many applications of FT-IR spectroscopy, which are spectroscopic investigations of gaseous mixtures having complex spectra resulting from superposition of vibrational and rotational bands as found in atmosphere; study of samples with high absorbencies; study of the substances with weak absorption bands; collecting data from very small samples; investigations requiring fast scanning such
as kinetic studies or detection of chromatographic effluents and infrared emission studies.

There are different versions, modifications and attachments are available with FT-IR. **Diffuse reflectance infrared Fourier transform spectroscopy** (DRIFTS) uses an effective way of obtaining infrared spectra directly on powdered samples with a minimum sample preparation [4,5]. The advantage is that it permits conventional infrared spectral data to be obtained on the samples that are not altered much from their original state. Apart from this, the **photo-acoustic infrared spectroscopy** is another popular technique. This technique was introduced in 1970s, which provides a mean for obtaining ultraviolet, visible and infrared absorption spectra of solids, semisolids, or turbid liquids. This is based on the effect first investigated by Alexander Graham Bell in 1880. When a gas in a closed cell is irradiated with a chopped beam of radiation of a wavelength that is absorbed by a gas, the absorbed radiation causes periodic heating of the gas which, consequently, gives in regular pressure fluctuations in the chamber. This method has been used for detecting the components of mixtures separated by **thin-layer** and **high-performance liquid chromatography**. Most manufacturers offer photo-acoustic cell along with FT-IR as the accessories.

The FT-IR spectra for the present study were taken at SICART, Vallabh Vidyanagar, using the powdered samples in KBr medium in the range from 400 cm\(^{-1}\) to 4000 cm\(^{-1}\) on Perkin Elmer Spectrum GX FT-IR Spectrometer shown in the figure (2.3).
2.4 Energy Dispersive Analysis of X-ray (EDAX)

![Diagram of electron beam interaction with a specimen](image)

**Figure (2.4): Interaction of an electron beam with a specimen**

An energy-dispersive x-ray analyzer (EDX) is a common accessory which gives the scanning electron microscope (SEM) a very valuable capability for elemental 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.

Figure (2.4) illustrates the interaction of an electron beam (in red) with a specimen (shaded blue). The electron beam in an SEM has energy typically between 5,000 and 20,000 electron volts (eV). The binding energy of electrons in atoms ranges from a few eV up to many KeV. Many of these atomic electrons are dislodged as the incident electrons pass through the specimen, thus ionizing atoms of the specimen. This process is illustrated schematically in the inset box of the figure.

A position vacated by an ejected inner shell electron is eventually occupied by a higher-energy electron from an outer shell. To be able to do so, however, the transferring outer electron must give up some of its energy by emitting an X-ray.

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.
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 [6].

An EDX spectrum 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. See figure 2.5

![Figure (2.5): Shell structure](image)

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 EDAX for the present study was taken at SICART, Vallabh Vidyanagar, on FEG Nano Nova SEM 450 instrument.

**2.5 X-ray Diffraction by Powder Method**

The powder X-ray diffraction (XRD) was devised independently in 1916 by Peter Joseph William Debye, a Nobel Laureate, and P. Scherrer in Germany and in 1917 by A. W. Hull in United States [7]. The powder XRD is widely used for the characterization of a variety of crystalline materials. This method has been conventionally used for phase identification, quantitative analysis and the
determination of structure imperfections. However, in recent years the applications have been extended to new areas, such as the determination of crystal structures and the extraction of three-dimensional micro-structural properties.

Generally, the method is applied to data collected under ambient conditions, but \textit{in situ} diffraction as a function of an external constraint, such as temperature, pressure, stress, electric field, atmosphere, etc, is important for the interpretation of solid state transformations and materials behaviors. Various types of micro and nano crystalline materials can be characterized by powder- XRD, including organic and inorganic materials, drugs, minerals, zeolites, catalysts, metals and ceramics. In the pharmaceutical industries the powder-XRD is popular for identification of drug molecule and its polymorphs. The physical states of the materials can be loose powders, thin films, poly-crystalline and bulk materials. By properly using this technique one can yield a great deal of structural information about the material under investigation. For most applications, the amount of information which is possible to extract depends on the nature of the sample microstructure (crystallinity, structure imperfections, crystallite size and texture) the complexity of the crystal structure (number of atoms in the asymmetric unit cell and unit cell volume), the quality of the experimental data (instrument performances and counting statistics) [8].

![The Principle of Powder X-ray Diffraction](image)

**Figure (2.6 a): The Principle of Powder X-ray Diffraction**

Basically, this method involves the diffraction of monochromatic X-ray by a powdered specimen. Usually ‘monochromatic’ means the strong characteristic K component of the filtered radiation from an X-ray tube operated above the K
excitation potential of the target material. The “Powder” can mean either an actual, physical powder held together with suitable binder or any specimen in polycrystalline form. Since single crystals are not always available, this method is more suitable for structural determination of various substances. The powder method is also known as the Debye-Scherrer method.

The fundamental law, which governs the x-ray diffraction phenomenon, is the Bragg’s Law and the equation is as follows:

$$\Delta S = n\lambda = 2d \sin \theta \quad \text{or} \quad d = \frac{n\lambda}{2\sin \theta}$$

Figure (2.6 b): Powder Sample Diffract X-ray Beam in Cones

When X-ray is incident on the crystalline powdered sample it gets diffracted according to the above mentioned equation in form of cones, which is exhibited in figure (2.6 b).

There are many applications of the powder method, which are summarized in table (2.1). Fundamentally this method provides a way of investigating, within limits, the crystallography of the crystal in the powder form. The powder method can be used as a tool to identify crystals, since the powder XRD patterns produced by a crystalline substance is a characteristic of that particular substance. One of the most important uses of the powder method is in the identification of an unknown material. If a set of standard diagrams of known substances, or tabular representations of them, available, then it is possible to identify a pure substance with the aid of a set of rules for finding an unknown diagram. The ASTM data cards as well as JCPDS data files are available for large number of substances for identifications and comparison. Statistical study of the relative orientations of the individual crystals of an aggregate is one of the important secondary uses of the powder method [9]. Identification of phases can be done by powder technique without solving crystal structure or assigning indices to the
reflections. Apart from these, cold work, recovery and re-crystallization are readily recognized by their effect on the powder patterns.

Table (2.1): Applications of Powder XRD

<table>
<thead>
<tr>
<th>Diffraction Line Parameter</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Peak Position</strong></td>
<td>Unit-cell parameter refinement</td>
</tr>
<tr>
<td></td>
<td>Pattern indexing</td>
</tr>
<tr>
<td></td>
<td>Space group determination ((2\theta / \text{absent reflections}))</td>
</tr>
<tr>
<td></td>
<td>Anisotropic thermal expansion</td>
</tr>
<tr>
<td></td>
<td>Macro stress: (\sin 2\psi) method</td>
</tr>
<tr>
<td></td>
<td>Phase identification ((d / I))</td>
</tr>
<tr>
<td><strong>Intensity</strong></td>
<td>Phase abundance</td>
</tr>
<tr>
<td></td>
<td>Reaction kinetics</td>
</tr>
<tr>
<td></td>
<td>Crystal structure analysis (whole pattern)</td>
</tr>
<tr>
<td></td>
<td>Rietveld refinement (whole pattern)</td>
</tr>
<tr>
<td></td>
<td>Search/match, phase identification</td>
</tr>
<tr>
<td></td>
<td>Preferred orientation, texture analysis</td>
</tr>
<tr>
<td><strong>Width / Breadth and Shape</strong></td>
<td>Instrumental resolution function</td>
</tr>
<tr>
<td></td>
<td>Microstructure: line profile analysis</td>
</tr>
<tr>
<td></td>
<td>Microstructure (crystallite size, size distribution, lattice distortion,</td>
</tr>
<tr>
<td></td>
<td>structure mistakes, dislocations, composition gradient)</td>
</tr>
<tr>
<td></td>
<td>Crystallite growth kinetics</td>
</tr>
<tr>
<td></td>
<td>Three-dimensional microstructure (whole pattern)</td>
</tr>
<tr>
<td><strong>Non-ambient and dynamic diffraction</strong></td>
<td><em>In situ</em> diffraction under external constraints reaction kinetics.</td>
</tr>
</tbody>
</table>

There are three types of powder methods, differentiated by the relative position of the specimen and the film.

1. **Debye-Scherrer Method:**

   The film is placed on the surface of a cylinder and specimen on the axis of the cylinder.

2. **Focusing Method:**

   The film, specimen, and X-ray source are all placed on the surface of a cylinder.

3. **Pinhole Method:**

   The film is flat, perpendicular to the incident X-ray beam, and located at any convenient distance from the specimen.
For the purpose of simultaneous and quick measurement of the positions and intensities of diffraction lines the diffracto-meters using quantum counters are advantageous; on the other hand, the diffraction cameras are preferred when a very small amount of specimen is available, if an entire diffraction ring is required to be recorded in order to do the rapid estimation of grain size and preferred orientation and in case of large immovable specimen.

The powder photographic methods are well described by Klug and Alexander [10] as well as Azaroff and Buerger [9].

In the present work crystals were analyzed by Philips Xpert MPD diffractometer with Cu-K$_\alpha$ radiation by using JCPDF database for powder diffractometry software. The crystal structures were determined by a computer software Powder-X.

The crystal XRD was carried out on PHILIPS X’PERT MPD system, shown in the figure (2.7) at Sophisticated Instrumentation Center for Applied Research and Testing (SICART), Vallabh Vidyanagar, Gujarat.

**Figure (2.7): PHILIPS X’PERT MPD system**
2.6 Thermal Studies

According to widely accepted definition of thermal analysis (Thermo analytical), it is a group of techniques in which physical properties of a substance and/or its reaction products are measured as a function of temperature whilst the substance is subjected to a controlled temperature program [1]. According to International Confederation for Thermal Analysis and Calorimetry (ICTAC), thermal analysis is defined as a group of techniques in which a property of the sample is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is programmed [11]. Nearly over a dozen thermal methods can be identified, which differ in the properties measured and temperature programs [12-14]. These methods find widespread use for both quality control and research applications of various substances, such as, polymers, pharmaceuticals, crystals, clays, minerals, metals and alloys.

2.6.1 Classification of Thermal Analysis Techniques

Thermal analysis techniques involve the measurement of various properties of materials subjected to dynamically changing environments under predetermined condition of heating rate, temperature range and gaseous atmosphere or vacuum. Classification of thermal analysis techniques is as shown in Table 2.2. Among all the thermal methods, the most widely used techniques are TGA, DTA and DSC, which are employed in inorganic and organic chemistry, metallurgy, mineralogy and other areas.

In certain cases, the use of a single thermo analytical 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 thermo gravimetric analysis (TGA) are widely used in studies involving physicochemical changes accompanied by variation in the heat content and the weight of the material.
### Table (2.2): Classification of Thermal Analysis Techniques

<table>
<thead>
<tr>
<th>Techniques Based On Variation of Physical Property</th>
<th>Thermal Analysis (Thermo Analytical) Techniques</th>
<th>Abbreviated Name</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>MASS</strong></td>
<td>Thermo-Gravimetry / Thermo Gravimetric Analysis</td>
<td>TG / TGA</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Derivative Thermo-Gravimetry</td>
<td>DTG</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Isobaric Mass-Change Determination</td>
<td>EGD</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Evolved Gas Detection</td>
<td>EGA</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Thermo Gravimetric Analysis Coupled to a Fourier Transform Infrared Spectrophotometer</td>
<td>• TG – FT-IR</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Thermo Gravimetric Analysis Coupled to a Mass Spectrometer</td>
<td>• TG – MS</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Emanation Thermal Analysis</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Thermo-Particulate Analysis</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>TEMPERATURE</strong></td>
<td>Differential Thermal Analysis</td>
<td>DTA</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Derivative Differential Thermal Analysis</td>
<td>DDTA</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Heating Curve Determination</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Heating Rate Curve</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Inverse Heating Rate Curve</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>ENTHALPY</strong></td>
<td>Differential Scanning Calorimetry</td>
<td>DSC</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Differential Scanning Micro / Nano Calorimetry</td>
<td>DSM/NC</td>
<td></td>
</tr>
<tr>
<td><strong>DIMENSIONS</strong></td>
<td>Thermo- Dilatometry</td>
<td>TD</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Differential Dilatometry</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Derivative Dilatometry</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### 2.6.2 Thermo Gravimetric Analysis (TGA)

Thermo gravimetric analysis 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 thermo gravimetric analysis is called thermo-gram (TG) and its first derivative is called a derivative thermo-gram (DTG).

Modern commercial TG instrument consists of following main parts:

1. A sensitive analytical balance
2. A temperature programmable furnace
3. A purge gas system for providing suitable gas atmosphere
4. A microprocessor for instrument control, data acquisition and display
The null-point weighing mechanism is employed since 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. The rate of heat exchange between the furnace and the sample depends on the heating rate which influences the TG 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.

One of the objectives of TG and DTA is to delineate as accurately as possible the various temperatures associated with the thermal behavior of a given substance, i.e., temperature of decomposition, stability range of an intermediate compound and the temperature at which the reaction get completed. As noted earlier that the TGA involves change in weight with respect to temperature, the acquired data obtained as a plot of mass or loss of mass in percentage as a function of temperature is considered as a thermal spectrum, or a thermo-gram, or a thermal decomposition curve. These thermo-grams characterize a system in terms of temperature dependence of its thermodynamic properties and physical-chemical kinetics. Since the TGA involves measurement of a change in weight of a system as the temperature is increased at pre-determined rate, changes in weight are a result of the rupture and/or formation of various physical and chemical bonds at elevated temperatures that lead to the release of volatile products or the formation of heavier reaction products. From such curves, parameters concerning the thermodynamics and kinetics of the various chemical reactions can be evaluated; moreover, the reaction mechanism, the intermediate and final reaction products can be identified. Usually, the temperature range is from ambient to 1200 °C with inert or reactive atmospheres. The derivative in TG is often used to pinpoint completion of weight-loss steps or to increase resolution of overlapping weight-loss occurrences. The shape of thermo-gravimetric curve of a particular compound is influenced by the heating rate of the sample and the atmosphere surrounding it [1,15,16].

The TGA finds applications in the study of thermal degradation, decomposition, dehydration of different samples. The chemical reaction resulting in changes of mass such as absorption, adsorption and desorption can also be studied.
2.6.3 Differential Thermal Analysis (DTA)

DTA is a technique in which the temperature difference between a substance and a reference material is measured as a function of temperature whilst the substance and reference material are subjected to a controlled temperature program [1,11]. DTA provides information on the chemical reactions, phase transformations, and structural changes that occur in a sample during a heat-up or a cool-down cycle. The DTA measures the differences in energies released or absorbed, and the changes in heat capacity of materials as a function of temperature. The graph of DTA signal, i.e. differential thermocouple output in micro volts on the Y-axis plotted versus the sample temperature in °C on the X-axis gives the results of DTA.

Modern thermo-balances are often equipped so as to record the DTA signal and the actual thermo-gravimetric measurement, simultaneously. In addition to showing the energetic nature of weight loss events, the DTA signal can also show thermal effects that are not accompanied by a change in mass, e.g. melting, crystallization or a glass transition. Transition temperatures are measured precisely using the DTA. The DTA identifies the temperature regions and the magnitude of critical events during a drying or firing process such as binder burnout, carbon oxidation, sulfur oxidation, structural clay collapse, Alpha to Beta quartz transition, carbonate decompositions, recrystallizations, melting and cristobalite (high temperature polymorph of silica) transitions, melting, solidification or solidus temperature, glass transition temperature (TG), Curie point, energy of reaction, heat capacity, and others. The transition enthalpy is estimated from the DTA curve using the heat capacity of the heat sensitive plate as a function of temperature.

2.6.4 Differential Scanning Calorimetry (DSC)

DSC is a technique in which the difference in energy inputs into a substance and a reference material is measured as a function of temperature whilst the substance and reference material are subjected to a controlled temperature program [1,11]. A DSC analyzer measures the energy changes that occur as a sample is heated, cooled or held isothermally, together with the temperature at which these changes occur. The graph of heat flow in mJ/s on the Y-axis plotted versus temperature at a fixed rate of change of temperature in °C on the X-axis shows the output of the DSC. Usually, for the power compensation DSC curve, heat flow rate should be plotted on the ordinate with endothermic reactions upwards, and for the heat-flux DSC curve with
endothermic reactions downwards. The energy changes enable the user to find and measure the transitions that occur in the sample quantitatively, and to note the temperature where they occur, and so to characterize a material for melting processes, measurement of glass transitions and a range of more complex events.

There are two methods of carrying out DSC, namely, (i) Power compensated DSC, and (ii) Heat-flux DSC. Power-compensated DSC is the method usually discussed in textbooks, though most practical instruments are based on heat-flux DSC. However, in practice these usually give equivalent results. In the present study the heat flux type of DSC was used.

**Power-Compensated DSC**

In this method, the sample and reference are in separate furnaces, each with a heater coil and a thermocouple. The aim is to maintain both at the same temperature, even during a thermal event in the sample. The difference in power supplied to the two furnaces to maintain zero temperature differential between the sample and the reference is measured.

**Heat-Flux DSC**

The sample and reference are both within the same furnace and are connected by a low-resistance heat-flow path. If any difference in temperature develops, heat flows in proportion to that temperature difference.

DTA and DSC are sister techniques which provide fast, convenient analysis of the glass characteristic temperatures such as \( T_g \) and temperatures of phase changes, for instance, devitrification and melting. DSC is rather more versatile than DTA. DSC allows quantitative determination of heat capacity, the enthalpy of a phase transformation, the heat of fusion of a crystal phase.

**Experimental Procedure**

In the present study, the thermal analysis TG, DTA and DSC of the grown crystals were carried out to determine simultaneous changes of mass and caloric reactions using PC controlled Linseis Simultaneous Thermal Analyzer (STA) PT-1600, in the atmosphere of air from 35 °C to 700 °C at a heating rate of 10 °C/min. TA-WIN and WIN-STA software used for testing and analysis. The set up for thermal analysis is shown in figure 2.8, which is available at Physics Department of Saurashtra University.
Figure (2.8): Linseis Simultaneous Thermal Analyzer PT-1600

Figure (2.9): Measuring head and crucible

After switching on computer and thermo balance, one has to open furnace using LIFT switch. As shown in the figure 2.9, the measuring head, carries two equal crucibles, one for the reference material and one for the sample substance, each one is sitting on a thermocouple. Carefully remove used crucible and clean it thoroughly. Insert a fine powder of the grown crystals under investigation in the sample crucible in the right side. The sample is evenly distributed in the bottom of the sample crucible. Take Al$_2$O$_3$, with equal amount in reference crucible in the left. The two thermocouples are wired such as to measure the temperature difference between the sample and the reference material. The absolute temperature is measured with the reference thermocouple. Good thermal contact between the sample and heat flux sensor is an indispensable requirement for optimum results. Since the test parameters have a significant influence in thermo analytical investigations, the parameters such as calibration, sample preparation, sample weight, reference material, sample chamber temperature, temperature program and atmosphere should be well considered.
Calibration of the instrument is a prerequisite for quantitative analysis of STA measurements.

2.7 Impedance spectroscopy

Impedance spectroscopy deals with complex quantities, its history really begins with introduction of impedance into electrical engineering by Oliver Heaviside in 1880. His work was soon extended by A. E. Kennelly and C. P. Steinmeto to include vector diagrams and complex representations. Later on, workers in the field started using Argand diagram of mathematics by plotting immittance (a concept combining the impedance and admittance of a system or circuit given by Bode) response in the complex plane. In 1941, the Cole-Cole plot of $\varepsilon''$ versus $\varepsilon'$ was introduced.

The basic concept of electrical resistance is exhibiting the ability of a circuit element to resist the flow of electrical current. Ohm's law defines resistance (R) in terms of the ratio between voltage E and current I, i.e. $R = E / I$. This relationship is used to only one circuit element, the ideal resistor. The real world contains circuit elements that exhibit much more complex behavior. These elements force us to abandon the simple concept of resistance. In its place one uses impedance, a more general circuit parameter. Like resistance, impedance is a measure of the ability of a circuit to resist the flow of electrical current. When ac signal is applied to a system, the impedance of the system obeys Ohm’s law, as ratio of voltage to current in the time domain [17].

The excitation signal, expressed as a function of time, has the form

$$E(t) = E_0 \sin(\omega t)$$

(2.2)

where, $E(t)$ is the potential at time t, $E_0$ is the amplitude of the signal, and $\omega = 2\pi f$ is the radial frequency.

In a linear system, the response signal is given by

$$I(t) = I_0 \sin(\omega t - \phi)$$

(2.3)

The response signal is shifted in phase ($\phi$) and has different amplitude $I_0$.

An expression analogous to Ohm’s Law allows calculating the impedance of the system as

$$Z = \frac{E(t)}{I(t)} = \frac{E_0 \sin(\omega t)}{I_0 \sin(\omega t - \phi)} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t - \phi)}$$

(2.4)
The impedance is therefore expressed in terms of a magnitude (modulus) $|Z|$ and a phase shift $\phi$.

Impedance $Z(\omega) = Z' + jZ''$ is such a vector quantity, which can be plotted in the plane with either rectangular or polar coordinates as shown in figure 2.10.

**Figure (2.10): Impedance plot**

Here, the two rectangular coordinate values are:

- $\text{Re}(Z) = Z' = |Z| \cos \phi$
- $\text{Im}(Z) = Z'' = |Z| \sin \phi$  
  \hspace{1cm} (2.5)

Phase angle $\phi = \tan^{-1}\left(\frac{Z''}{Z'}\right)$  
\hspace{1cm} (2.6)

Modulus $|Z| = \left((Z')^2 + (Z'')^2\right)^{1/2}$  
\hspace{1cm} (2.7)

This defines the Argand diagram or complex plane. In polar form $Z$ can be written as $Z(\omega) = |Z| \exp(j\phi)$  
\hspace{1cm} (2.8)

This can be converted to rectangular form by Euler relation: $\exp(j\phi) = \cos(\phi) + jsin(\phi)$.

Therefore, $Z(\omega) = |Z| [\cos(\phi) + jsin(\phi)]$.

In impedance technique, the real and imaginary parts of impedance of the sample were measured simultaneously as a function of frequency. The measured impedance data can be represented in the other three forms using the inter relations as follows.

Complex impedance $Z^* = Z' + jZ''$  
\hspace{1cm} (2.9)

where, $Z'$ and $Z''$ are the real and imaginary parts of complex impedance.

Complex admittance $Y^* = Y' + jY'' = \frac{1}{Z^*}$  
\hspace{1cm} (2.10)

where, $Y'$ and $Y''$ are the real and imaginary parts of complex admittance.
Complex permittivity \( \varepsilon^* = \varepsilon' - j\varepsilon'' = \frac{1}{j\omega C_0 Z^*} \)  

(2.11)

where, \( \varepsilon' \) and \( \varepsilon'' \) are the real and imaginary parts of complex permittivity.

Complex modulus \( M^* = M' + jM'' = j\omega C_0 Z^* \)  

(2.12)

where, \( M' \) and \( M'' \) are the real and imaginary parts of complex modulus.

Here, \( j = \sqrt{-1} \) and \( C_0 \) is the vacuum capacitance. The admittance and permittivity are parallel functions that can be measured at low frequencies whereas the impedance and modulus are series functions at high frequencies [18]. The four quantities \( M, Z, Y \) and \( \varepsilon \) are known as immittance functions.

2.7.1 Complex Plane Analysis

The complex plane analysis is a mathematical technique involving real and imaginary parts of the complex electrical quantities of complex impedance, complex admittance, complex permittivity and complex modulus. One of the most widely used distribution is given by Cole and Cole [19] to describe the occurrence of depressed semicircle arc in \( \varepsilon'' - \varepsilon' \) plots for variety of polar liquids and solids. The expression for \( Z(\omega) \) is composed of a real and an imaginary part. If the real part is plotted on the X axis and the imaginary part on the Y axis of a chart, a "Nyquist plot" is obtained, which is shown Figure 2.11. Nyquist plot is one popular format for evaluating electrochemical impedance data. Notice that in this plot the y-axis is negative and that each point on the Nyquist plot is the impedance at one frequency.

![Figure (2.11): Nyquist plot](image)

![Figure (2.12)](image)

Figure 2.11 has been annotated to show that the low frequency data are on the right side of the plot and the higher frequencies are on the left. This is true for EIS
(Electrochemical Impedance Spectroscopy) data where impedance usually falls as frequency rises; however, this is not true of all circuits.

On the Nyquist plot the impedance can be represented as a vector of length \(|Z|\). The angle between this vector and the x-axis is \(\phi\).

Nyquist plots have one major shortcoming, when one looks at any data point on the plot, one cannot tell what frequency was used to record that point.

The typical Nyquist plot of Figure 2.11 results from the electrical circuit of Figure 2.12. The semicircle is characteristic of a single "time constant". Many times the impedance plots contain several time constants and as a result only a portion of one or more of their semicircles is seen.

The resultant impedance is given by

\[
Z(\omega) = Z' - jZ'' = \frac{1}{1 + j\omega C} = \frac{1}{R} \left( \frac{1}{1 + j\omega C} \right) \quad R \neq 0
\]

\[
= \frac{R - j\omega R^2 C}{1 + \omega^2 R^2 C^2} = \frac{R}{1 + \omega^2 R^2 C^2} - j\frac{\omega R^2 C}{1 + \omega^2 R^2 C^2}
\]

(2.13)

**Advantages of Nyquist plot**

The Nyquist plot has several advantages. The primary one is that the plot format makes it easy to see the effects of the ohmic resistance. If the data are taken at sufficiently high frequencies, it is easy to extrapolate the semicircle toward the left, down to the X axis to read the ohmic resistance. The shape of the curve (often a semicircle) does not change when the ohmic resistance changes. Consequently, it is possible to compare the results of two separate experiments that differ only in the position of the reference electrode. Another advantage of this plot format is that it emphasizes circuit components that are in series such as resistance developed due to the electrodes and the cables.

**Disadvantages of Nyquist plot**

The Nyquist plot format also has some disadvantages. For example, frequency does not appear explicitly. Secondly, although the series resistance and bulk/grain resistance can be easily read directly from the Nyquist plot, the electrode capacitance
can be calculated only after the frequency corresponding to the top of the semicircle, i.e. $\omega_{(\theta_{\text{max}})}$ is known.

**Advantages and limitations of Impedance Spectroscopy**

Impedance spectroscopy is popular analytical tool in materials research and development as its results may be corrected to mass transport, rates of chemical reaction, corrosion, dielectric properties, defects, microstructures and conductance in solids. Impedance spectroscopy can be used for investigating performance of chemical sensors and fuel cells, electrochemical processes and study of membrane behavior of living cells.

Experimentally obtained impedance data for a given electrode-materials system can be analyzed by using an exact mathematical model based on plausible physical theory that predicts theoretical impedance $Z_C(\omega)$ or by a relatively empirical equivalent circuit whose impedance predictions can be given by $Z_{CC}(\omega)$. In either the case of relatively empirical equivalent circuit or of the exact mathematical model, the parameters can be estimated and experimental $Z_C(\omega)$ data compared to either the predicted equivalent circuit impedance $Z_{CC}(\omega)$ or to the theoretical impedance $Z_C(\omega)$.

The disadvantages of impedance spectroscopy are primarily associated with possible ambiguities in interpretation. An important complication of analysis based on an equivalent circuit is that ordinary ideal circuit element represents ideal lumped constant property. The ideal circuit elements are not adequate to represent microscopic response in the sample.

An equivalent circuit involving three or more circuit components can be arranged in various ways and still give exactly the same $Z_C(\omega)$. For the different interconnections the values of the elements will have to be different to yield the same $Z_C(\omega)$ for all, but an essential ambiguity is present.

There are several important distinctions between solid and liquid electrolytes. Many solid electrolytes and liquid electrolytes have negligible electronic conductivity, however, quite a number of solid electrolyte exhibit substantial electronic conductivity, particularly, for deviation of strict stoichiometric composition. Solid electrolyte may be amorphous, polycrystalline or single crystals and the charges of one sign are immobile. While, all dissociated charges in a liquid electrolyte or fused salts are mobile. In solid electrolytes, mobile ions are considered to be able to move
close to an electrode as permitted by ion size strict considerations. But in liquid electrolytes, there is a compact inner or stern layer composed of solvent molecules, for example, H$_2$O, immediately next to the electrode.

This detailed discussion is given by MacDonald and Johnson [20]. There are several books available on impedance spectroscopy [21, 22].

2.8 Dielectric Studies

Every material has a unique set of electrical characteristics depending upon the type of the materials belongs to, such as the dielectric properties, permittivity, permeability, resistivity, conductivity, etc. A material is classified as “dielectric” if it has the ability to store energy when an external electric field is applied. In other words, materials, which are electric insulators or in which an electric field can be sustained with a minimum dissipation of power, are known as dielectric materials. Simply, dielectrics are insulating materials. In dielectrics all the electrons are bound to their parent molecules and there are no free charges. Even with normal voltage or thermal energy the electrons are not released. Dielectrics are nonmetallic materials of high specific resistance and have negative temperature coefficient of resistance. The dielectric characteristics of the material are important to study the lattice dynamics in the crystal. It is important to note that permittivity and permeability are not constant. They can change with frequency, temperature, orientation, mixture, pressure, and molecular structure of the material. Many authors discussed various dielectric properties, dielectric applications and dielectric theories in details [23-30]. Classical theory of dielectric constant was given by Kachhava and Saxena [31]. Also the predecessors of the present author have described the dielectric properties in detail [32-38], therefore, it is avoided in the present thesis.

**Dielectric constant (k) or Relative Permittivity (εᵣ)**

Dielectric constant is defined as the ratio of the capacitance (C) of a capacitor filled with the given material to the capacitance (C₀) of an identical capacitor in a vacuum without the dielectric material and it is unitless. The dielectric constant can also be defined as the ratio of the permittivity of the dielectric material (ε) to the permittivity of vacuum (ε₀). The dielectric constant is, therefore, also known as the relative permittivity (εᵣ) of the material. Sometimes it is also referred as the absolute permittivity.
Dielectric constant, \( k = \varepsilon_r = \frac{C}{C_0} = \frac{\varepsilon}{\varepsilon_0} \)  

(2.14)

Since the dielectric constant is just a ratio of two similar quantities, it is dimensionless and is always greater than 1. It is a measure of polarization in the dielectric material. It denotes a large-scale property of dielectrics without specifying the electrical behavior on the atomic scale. In the present study dielectric constant was calculated using the following formula:

\[
\text{Dielectric constant} \ k = \varepsilon_r = \frac{t}{\omega A \varepsilon_0} \left[ \frac{Z''}{Z'^2 + Z''^2} \right]
\]

(2.15)

where \( t \) is the thickness of the pellet, \( \varepsilon_0 \) is the vacuum dielectric constant (permittivity of free space, \( \varepsilon_0 = 8.854 \times 10^{-12} \text{ F/m} \)) and \( A \) is the area of the pellet. \( Z' \) and \( Z'' \) are the measured real and imaginary part of the impedance.

**Complex Relative Permittivity (\( \varepsilon^* \))**

Permittivity is determined by the ability of a material to polarize in response to the field and, thereby, reduce the total electric field inside the material. Thus, permittivity relates to the ability of material to transmit (or permit) an electric field. The response of normal materials to external fields generally depends on the frequency of the field. This frequency dependence reflects the fact that the polarization of material does not respond instantaneously to an applied field. The response must always be causal which can be represented by a phase difference. For this reason permittivity is often treated as a complex function. The response of materials to alternating fields is characterized by a complex permittivity,

\[
\varepsilon^* = \varepsilon' - j\varepsilon'' = |\varepsilon|e^{-j\delta}
\]

(2.16)

Where \( \varepsilon' \) is the real part of the relative permittivity (i.e. the dielectric constant), which is related to the stored energy within the medium; and \( \varepsilon'' \) is the imaginary part of the relative permittivity, which is related to the dissipation (or loss) of energy within the medium. Equation (2.16) expresses the complex permittivity in two ways, as real and imaginary or as magnitude and phase.

**Dielectric Loss**

The dielectric loss is a loss of energy which eventually produces a rise in temperature of a dielectric placed in an alternating electrical field. In other words it is a measure of the energy absorbed by dielectric. It is the electrical energy lost as heat...
in the polarization process in applied AC electric field. In the present study dielectric loss was calculated using following formula

\[
\text{Dielectric loss } \varepsilon'' = \frac{t}{\omega A \varepsilon_0} \left[ \frac{Z'}{Z'^2 + Z''^2} \right]
\]  
(2.17)

**ac Conductivity and ac Resistivity**

The ac conductivity is one of the studies done on solids in order to characterize the bulk resistance of the crystalline sample. The values of ac conductivity and ac resistivity were calculated for the different frequencies of the applied electric field using the following formulae,

\[
\text{ac conductivity, } \sigma_{ac} = \frac{2\pi f C \varepsilon'' t}{A}
\]  
(2.18)

where, \( f \) is the frequency, \( C \) is the capacitance, \( \varepsilon'' \) is the dielectric loss, \( t \) is the thickness of the pellet and \( A \) is the area of the pellet.

\[
\text{ac resistivity, } \rho_{ac} = \frac{1}{\sigma_{ac}}
\]  
(2.19)

Figure (2.13): SOLARTRON SI 1260 Impedance/Gain-Phase Analyzer
In the present investigation the dielectric study was carried out by measuring the real and imaginary part of the impedance of the pressed pellets of samples of known dimension at room temperature on SOLARTRON SI 1260 Impedance/Gain-Phase Analyzer using specially designed sample older, within the frequency range from 100 Hz to 6.38 MHz at Solid State Ionics and Glass Research Lab, Department of Physics, Faculty of Science, M S University of Baroda, Vadodara.

Figure 2.13 shows the photograph of the set up. The powdered samples were pelletized by using a die of 1 cm diameter and applying 2 tone pressure. The pellets were placed in a suitably design spring loaded holder.

2.9 Vibrating Sample Magnetometer (VSM)

Vibrating sample magnetometer was developed by S. Foner [39] which is based on the flux change in a coil when the sample is vibrating near it. The sample, usually a sphere or small disc, is centered to the end of a rod and the other end of which is fixed to a loud speaker cone, or to some other kind of mechanical vibrator. The current through the loud speaker vibrates the rod and hence the sample at about 80 cycles/sec and with amplitude of about 0.1 mm in a direction at right angles to the magnetic field. Because of the oscillating magnetic field of the sample, an alternating e.m.f. is induced in the detection coils. In vibrating rod there is also a reference specimen, in the form of a small permanent magnet near its upper end, and the oscillating field of this induces another e.m.f. in two reference coils. The voltages from the two sets of coils are compared and the difference will be proportional to magnetic moment of the sample. The schematic diagram of VSM is shows in figure (2.14).

![Vibrating Sample Magnetometer (VSM)](image_url)
The apparatus should be calibrated with the specimen of known magnetic susceptibility.

This method is very versatile and sensitive. It may be used for both weak and strong magnetic substances and it can detect a change in magnetic moment of $5 \times 10^{-5}$ erg/cc, which corresponds to a change in mass susceptibility of $5 \times 10^{-9}$ emu/gOe for a one gram sample in a field of 10000 Oe. This method has further been modified by several workers [40,41].

In the present work, the magnetic susceptibility of the crystals was measured using EG and PARC-155 Vibrating Sample Magnetometer at room temperature with different applied magnetic fields. In this instrument, when a sample is placed in a homogeneous magnetic field, a moment is induced in the sample. If this sample is made to undergo sinusoidal motion as well, an electrical signal is induced in suitably placed stationary pick up coils. Magnetic field range is 0-1.6 Tesla. A complete $360^\circ$ rotation in the horizontal plane with accuracy of $\pm 0.5^\circ$ is possible for angular variation of magnetic field on a crystal. Noise is less than $5 \times 10^{-4}$ emu with an absolute accuracy better than 2% and reproducibility better than 1%. Pure nickel metal is used to calibrate the instrument. The analysis was carried out at Regional Sophisticated Instrumentation Center (R.S.I.C.), I. I. T., Madras, Chennai.

References


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