3.1 INTRODUCTION

The physical constants which have been measured as a function of various parameters are (i) electrical conductivity (\(\sigma\)) (ii) the dielectric constant (\(K\)) and dielectric loss (\(K''\)) (iii) the magnetic susceptibility (\(\chi\)). The essential details of these measurements have been described in this chapter.

3.2 ELECTRICAL CONDUCTIVITY MEASUREMENT

When the material is subjected to an electric field in a circuit, an electric current flows across it. The current density (\(J\)) which particularly mentioned the net rate of passage of electrical charges across unit cross section is related to the applied electric field (\(E\)) by the following relation

\[
J = \sigma E \quad (3.1)
\]

Where \(\sigma\) is the electrical conductivity tensor and it has nine components for a completely anisotropic medium. However, for a homogeneous and isotropic medium, different components of \(\sigma\) becomes equal and is a scalar quantity, known as electrical conductivity. This quantity depends upon the nature and thermal state of the material but is independent of its shape and size. For a sample of cross sectional area \(A\) and thickness \(t\) maintained at a constant temperature, \(\sigma\) is given by the relation

\[
\sigma = G \left( \frac{t}{A} \right) = \frac{1}{R} \left( \frac{t}{A} \right) \quad (3.2)
\]
Where $G$ is conductance and $R$ is resistance of the sample. The study of electrical conductivity as a function of various parameters gives a lot of information regarding the nature and electrical conduction mechanism of the material. To study the nature and mechanism of electrical conduction, we have measured dc current and voltage and ac resistances of the pellets of tungstate compounds. Using dimensions of the pellet, ac and dc conductivity have been evaluated as a function of temperature, time and also ac conductivity as a function of frequency of applied signal. The steps followed in these measurements are systematically described in this section.

(a) Preparation of pellets

The electrical conductivity of tungstate compounds have been measured in the form of pellets. The method of preparation of pellets from finely ground powders is described in the next chapter. The pellets were made at pelletizing pressure ranging from $3.04 \times 10^{-8}$ to $8.23 \times 10^{-8}$ Nm$^{-2}$. The typical dimensions of the pellets made for conductivity measurements were thickness $\sim 0.3 \times 10^{-2}$m and face area $\sim 0.9 \times 10^{-4}$ m$^2$. The dust on the faces and sides of the pellets was removed using ‘Water paper’. The pellets were cleaned in benzene and dried for few hours. Before measurements on pellets the thickness, area and mass were measured. The density of the pellets, was calculated by knowing all these parameters. Before taking actual measurements pellets were sintered as described in chapter IV.

(b) Electrodes

Throughout the present investigation two electrode method has been used. For electrode material, silver paint or thin plane foils (Silver,
amalgamated silver or platinum) were used. For making electrodes the silver paint is uniformly coated on one face of the pellet, dried properly and then on the other face. It dries within fifteen minute, when kept in oven at about 320K. When properly coated smooth, hard and shining silver electrodes are obtained on the faces of the pellet. The sides of the pellet were cleaned with a sharp blade to remove any shortening between its faces. For silver foil electrodes two pieces which have area equal to the face area of the pellet were taken and put across it gently and fixed mechanically. A better contact between pellet and silver foil electrode interfaces was obtained by annealing this system at a very high temperature (~1140K) for few hours.

(c) Sample Holder

A schematic diagram of a sample holder made from a long transluscent fused silica tubes (inner diameter 3.5cm) carrying two parallel narrow tube (each 20 cm long) of the same material is shown in Fig. 3.1. A silver electrode passes through each narrow tube. The holder is loaded with properly cleaned pellet having silver paint faces. A pressure contact between the pellet and electrodes is achieved by holding them between a quartz clip.

(d) Furnace and Temperature Measuring Device

The furnace used in the measurement of conductivity consists of a transluscent silica tube with uniform windings of canthal wire on its central part. A thick layer of asbestos is coated on the windings and is covered with firebricks to avoid loss of heat by radiation fully. The current in windings is supplied by mains using an auto-transformer. The
furnace so designed is able to provide temperature from 300K to 1200K in its middle portion.

The sample holder loaded with the pellet is kept in the furnace such that it lies very close to the middle of the windings. A thermocouple with digital temperature indicator model T-701, shivaki lying very close to the specimen has been used to measure the temperature of the specimen.

**FIG-3.1** SAMPLE HOLDER FOR ELECTRICAL CONDUCTIVITY MEASUREMENT, C-CLIP, E₁&E₂- ELECTRODES, S- SAMPLE, R₁ & R₂- SILICA RODS, T –SILICA TUBE, T₁&T₂-TERMINALS.
3.2.1 Measurement of dc Electrical Conductivity

(a) Apparatus

dc electrical conductivity at different temperatures has been evaluated by measuring current (I) through and voltage (V) across the specimen using a constant dc voltage source and sensitive current and voltage measuring devices. For this purpose two electrode method has been employed. The schematic diagram of whole setup is shown in Fig. 3.2a. The dc voltage was taken from dc power supply and both current and voltage were measured using keithley digital multimeter, type 171. This is capable of measuring current from $10^{-10}$A to 1A and voltage from $10^{-7}$V to $10^3$V and has internal impedance of the order of $10^{10}$Ω. For raising temperature of the specimen, furnace as described in section 3.2d has been used.

(b) Measuring Procedure

The stringent criteria for dc electrical conductivity measurement is that the contact between electrode and pellet interfaces should be ohmic. The current through the specimen was measured at different applied voltages and using dimensions of the pellet, a graph was plotted between current density (J) and applied electric field (E) across the specimen. This plots for all studied compounds was linear for certain value of electric field. While performing dc electrical conductivity experiment the electric field applied across the specimen is kept in this range for which there is ohmic contact (linear J vs E curve) between pellet and electrode interfaces. To determine $\sigma_{dc}$ at different temperatures, the loaded sample holder is kept in the middle of the furnace and connected with thick
wires are done as shown in Fig. 3.2a. A definite current is then allowed to flow across the winding of the furnace. It normally takes fifteen to twenty minutes to get stability in the temperature. When it is stabilized the current through and voltage across the specimen are measured and conductivity is calculated using following relation.

\[
\sigma = \frac{I}{V} \left( \frac{t}{A} \right)
\]  

(3.3)

Similar process is repeated at different applied voltage and constant temperature.

3.2.2 Measurement of ac Electrical Conductivity, Dielectric Constant and Dielectric Loss

Using bridge technique ac electrical conductivity of the specimen has been measured. The schematic diagram of complete setup is shown in Fig. 3.2b. Most of the apparatus employ the circuit of wheat stone bridge. The specimen in this arrangement is connected across unknown arm (Fig. 3.3). One of the diagonals of the bridge is powered with an ac voltage. The other diagonal has a sensitive detector. When both points B and C are at same potential, then bridge is balanced. The equation which satisfies the condition is

\[
\frac{Z_1}{Z_2} = \frac{Z_3}{Z_x}
\]

(3.4)

\[
\frac{(R_1 + JX_1)}{(R_2 + JX_2)} = \frac{(R_3 + JX_3)}{(R_x + JX_x)}
\]

or,

(3.5)

Where symbols have their usual meaning. This gives resistances \(R_x\) and reactance \(X_x\) of the specimen as
There are two balancing conditions one for the resistance and other for reactance. For measuring $\sigma_{ac}$, capacitance and Q values of the specimen, we have employed Autocompute LCR-Q meter, model, 928 Systronics, India. Details of apparatus are given below.

**a) Autocompute LCR-Q Meter**

The autocompute LCR-Q meter (model 928 Systronics, India), measures inductance, capacitance, resistance and quality factor to a basic accuracy of $\pm0.25\%$ of reading $\pm1$ digit. It measures resistance (from $0.000\Omega$ to $100M\Omega$ ohms), Inductance (from $0.01\mu\text{H}$ to $9999\text{H}$), capacitance (from $0.0\text{pF}$ to $9999\mu\text{F}$) and quality factor (from $0.00$ to

\[
R_X = \frac{R_3R_2}{R_1} \\
X_X = \frac{X_3X_2}{X_1}
\]

(3.6)

(3.7)
99). Measurement can be made at frequencies 100Hz or 1KHz, as required and either the series or parallel equivalent component values can be displayed. Range selection is fully automatic and LCR-Q meter automatically discriminates between inductors and capacitors.

(a) Autocompute LCR-Q Meter

The autocompute LCR-Q meter (model 928 Systronics, India), measures inductance, capacitance, resistance and quality factor to a basic accuracy of ±0.25% of reading ±1 digit. It measures resistance (from 0.000Ω to 100MΩ ohms), Inductance (from 0.01µH to 9999H), capacitance (from 0.0pF to 9999 µF) and quality factor (from 0.00 to 99). Measurement can be made at frequencies 100Hz or 1KHz, as required and either the series or parallel equivalent component values can be displayed. Range selection is fully automatic and LCR-Q meter automatically discriminates between inductors and capacitors.

(b) Measuring Procedure

The arrangement for the measurement of ac electrical conductivity ($\sigma_{ac}$), dielectric constant (K’) and dielectric loss (K’’) at various temperatures and frequencies is shown in Fig. 3.2b. A definite current is allowed to flow across the windings of the furnace to get stable temperature. It normally takes fifteen to twenty minutes to get stability in temperature. The resistance, capacitance and Q value of the specimen are measured at frequencies (100Hz and 1kHz). The current in the windings of the furnace is increased in steps to get higher temperature. The above
FIG. 3.2 BLOCK DIAGRAM FOR (a) dc AND (b) ac ELECTRICAL CONDUCTIVITY MEASUREMENTS [D- DIGITAL MULTI METER, A- CURRENT METER, P.S- POWER SUPPLY, A.T- AUTO TRANSFORMER, T.I- TEMPERATURE INDICATOR, T.C- THERMOCOUPLE, S- SAMPLE HOLDER, F- FURNACE, B- AUTO COMPUTE LCR-Q METER]
parameters are measured at different temperature using parallel equivalent mode connections. From these data the values of $\sigma_{ac}$, $K'$ and $K''$ are evaluated using following relations.

$$\sigma_{ac} = \frac{t}{RA} \quad (3.8)$$

$$K' = \frac{ct}{\varepsilon_0 A} \quad (3.9)$$

$$K'' = \frac{ct}{\varepsilon_0 AQ} \quad (3.10)$$

Where $t$ is the thickness and $A$ the face area of the pellet.

The accuracy of the measurement of these parameters depends upon the temperature range and range chosen in LCR-Q meter. Thus accuracy in $\sigma_{ac}$ measurement varies from 2 to 5 percent, in $K'$ from 2 to 5 percent and in $K''$ from 5 to 10 percent depending upon temperature. $\sigma_{ac}$ measurement at higher temperature are more accurate, whereas better accuracy can be claimed in $K'$ measurement at lower side of temperature. The accuracy in $K''$ is linearly temperature independent.

3.3 MAGNETIC SUSCEPTIBILITY MEASUREMENT

The magnetic susceptibility of the powdered samples of tungstate compounds in very small quantities (50-100 mg) has been measured at different temperatures employing Faraday-method. The electromagnet and magnetic balance had been procured from standard firms. The necessary sample holder, furnace and other accessories were built in the laboratory. The calibration of the apparatus were done using standard samples e.g. ferrous ammonium sulphate and gadolinium tungstate.
3.3.1 Theory of Faraday-Method

When the magnetic material is placed in the magnetic field, it gets magnetized. The ratio of intensity of magnetization (M) to the magnetic field (H) is defined as the magnetic susceptibility ($\chi$). The magnetic susceptibility has been measured by Faraday’s method (Bates 1951). The principle of this method is that a paramagnetic substance, when freely suspended between the pole pieces of a magnet, tends to set itself along the direction of applied magnetic field and has tendency to move towards the region where field is maximum. Thus Faraday method is based upon the measurement of the force on a given specimen placed in a suitable inhomogeneous magnetic field. Such field with an axis of symmetry is obtained by tapering the pole pieces of an electromagnet.

Let $y$-axis be the direction of the lines of force and $z$-axis be the direction along which the specimen is free to move (Fig. 3.4), $V$ is the volume of the material supposed to be very small.

![Diagram of magnetic field](image)
If $\mu_1$ and $\mu_2$ be the relative permeabilities of the specimen and that of the medium (with $\mu_1 > \mu_2$) in which the former is introduced and $\mu_0$ be the permeability of the free space or vacuum, then a change in the potential energy due to the introduction of the specimen in the magnetic field of strength $H$ is given by $-(\mu_1 - \mu_2) \mu_0^2 H^2 V$ and the force acting on the specimen along $z$-direction is given by the expression (Bates 1951).

$$F_z = -\frac{d}{dz} \{-(\mu_1 - \mu_2)\mu_0^2 H^2 V\}$$

(3.11)

But $\mu_1 = (1+\chi_1)$ and $\mu_2 = (1+\chi_2)$ where $\chi_1$ and $\chi_2$ are the magnetic susceptibilities of the specimen and the medium. Using these relations, Eq. 3.11 becomes.

$$F_z = (\chi_1 - \chi_2)\mu_0^2 V \frac{dH^2}{dz}$$

(3.12)

Further, assuming that the field gradient is only in the $z$-direction then above equation becomes

$$F_z = 2(\chi_1 - \chi_2)\mu_0^2 VH \frac{dH_y}{dz}$$

(3.13)

Where $H_y$ is the component of magnetic field strength in the $y$-direction and the field gradient in $z$-direction. Usually, the medium surrounding the specimen is air with a magnetic susceptibility very small compared to that of a paramagnetic substance. Suppose $\chi_2 \approx 0$ for air, $H_y = H$ and $\chi_1 = \chi_v$ then Eq.3.13 becomes

$$F_z = 2\chi_v\mu_0^2 VH \frac{dH}{dz}$$

(3.14)
\( \chi_v \) is the volume susceptibility of the specimen. In solid specimen it is more convenient to measure the mass of the sample rather than its volume. Hence it is more convenient to measure mass magnetic susceptibility where \( \rho \) is the density of the specimen. In terms of the mass magnetic susceptibility above equation reduces to

\[
F_z = 2\chi_m \mu_0^2 H \frac{dH}{dz}
\]  \hspace{1cm} (3.15)

The force acting on the specimen is determined by a change in its weight when the magnetic field is applied. If this change in weight is \( \Delta mg \), then

\[
F_z = \Delta mg
\]  \hspace{1cm} (3.16)

Comparing Eqs. 3.15 and 3.16, we get the expression for \( \chi_m \) as

\[
\chi_m = \left( \frac{\Delta m}{m} \right) \left\{ g \frac{\mu_0^2 H (dH/dz)}{2 \mu_0^2 H (dH/dz)'} \right\}
\]  \hspace{1cm} (3.17)

For a fixed pole gap and definite current in electromagnet, besides being constant, is uniform over a small region. Such situation are often met during measurement. Thus in this condition \( g \frac{\mu_0^2 H (dH/dz)'}{2 \mu_0^2 H (dH/dz)'} \) is constant and is denoted by letter K. In terms of K, the expression for \( \chi_m \) becomes

\[
\chi_m = \left( \frac{\Delta m}{m} \right) K
\]  \hspace{1cm} (3.18)

The value of K is determined by taking a standard salt of known magnetic susceptibility. If \( M \) is the molecular weight of the specimen under consideration, then molecular magnetic susceptibility is given by the relation

\[
\chi_M = \chi_m M
\]  \hspace{1cm} (3.19)
Using Eq. 3.18, above relation becomes

\[ \chi_M = \left( \frac{\Delta m}{m} \right) KM \]  

(3.20)

### 3.3.2 Experimental Setup

The schematic diagram of the set up used for magnetic susceptibility measurement is shown in Fig. 3.5. The main parts of this setup are described as:

**(a) Magnetic Balance**

It is a singal pan analytical balance (Model K-15 DX) with lamp and scale arrangement, obtained from K-ray, Varanasi, India. The stated accuracy of this balance is $10^{-5}$ gm. A hook is attached in place of pan through which a sample holding device may be suspended.

**(b) Sample Holder**

A narrow silica glass tube with length 1.8cm and internal diameter 0.6cm has been used as the sample holder. It may be freely suspended inside the furnace through a thin silica glass rod with the help of a silver wire loop attached to the hook of the balance as shown in Fig.3.5.

**(c) Electromagnet**

An electromagnet with power supply (type EMP : 100, Polytronic, India) has been employed to obtain a magnetic field of few tesla, depending upon the electromagnet current and the gap between adjustable pole pieces. All the measurements have been carried out at a pole gap of 5.2cm. The pole pieces of the electromagnet are flat at the centre but tapered at the edges at an angle of 30 degrees. They are accordingly capable of producing an inhomogeneous magnetic field to meet the requirement of Faraday-method.
FIG 3.5 MAGNETIC SUCEPTIBILITY MEASUREMENT
(d) Furnace and Temperature Measuring Device

To get higher temperature a small furnace has been fabricated. It is made from a silica tube (inner diameter 3.3 cm) closed at one end to prevent the air current by convection at higher temperatures. The tube carries non-inductive windings of nichrome wire and is covered with sheet of asbestos to prevent loss of heat by radiation. The furnace can be inserted vertically between the pole pieces of the electromagnet. The zone where the specimen has been suspended lies well inside the furnace.

The temperature measuring device is a chromel-alumel thermocouple and is recorded with the help of digital temperature indicator (model M 3900, India). It has been observed that insertion of thermocouple inside the tube creates problem in the free suspension of the sample holder and is therefore undesirable. To avoid this difficulty the furnace has already been calibrated with respect to the furnace current. A calibration graph between furnace temperature $T'(k)$ at different values of furnace current $I$ (A) is as shown in Fig. 3.6. Each point has been obtained with an stay of fifteen minutes for a specific zone inside the tube where the specimen hangs. This discipline has been strictly followed for all the measurements. As this thermocouple reads a temperature with respect to the room temperature ($T_R$), actual temperature of the specimen is obtained by adding room temperature to $T'$. Therefore the temperature $T$, of the object is given by the relation

$$T = T' + T_R$$  \hspace{1cm} (3.21)
FIG. 3.6 CALIBRATION CURVE FOR FURNACE USED IN MAGNETIC SUSCEPTIBILITY MEASUREMENTS (T IS THE TEMPERATURE READ BY THERMOCOUPLE AND I IS THE FURNACE CURRENT)
3.3.3 Measuring Procedure

Various measurements which are to be done step wise in the determination of magnetic susceptibility are described below.

(a) Demarcation of Constant Region

The magnetic pull on the specimen at certain temperature remains constant in the region of constant $K$. This region is determined by nothing the change in weight ($\Delta m$) of a standard salt. We have used gadolinium tungstate for this purpose. The change in weight ($\Delta m$) is noted in the magnetic field at different heights ($h$) measured from the base of an electromagnet. The change in weights are plotted against heights. This plot is shown in Fig. 3.7. The flattened portion of the curve gives the constant region. In our setup this region was found to be nearly 1.0cm wide (21.2 to 22.2cm from the base). It is observed that this region is independent of (a) the change in current in the coil of electromagnet (b) the introduction of furnace between the pole pieces of electromagnet and (c) the change in current in the coil of furnace. These conditions were verified using the same standard salt. During the measurement of magnetic susceptibility, the specimen is kept confined to this region.

(b) Evaluation of Constant K

The value of $K$ depends upon the magnetic field which is a function of separation between the pole pieces and the current in the electromagnet. Pole gap is made fixed for any particular measurement. The choice of the gap width depends upon the nature of the specimen whose susceptibility is being measured as well as on the magnetic field in which we want to perform the measurement. The pole gap at which
we have performed measurement is 5.2cm. For any value of electromagnet current, $\Delta m$ for the standard salt has been obtained by hanging it in the region of constant. Using Eq. 3.18 experimental value of K has been calculated.

$$Z_{POLE GAP} = 5.2\text{ Cm}$$

$$I = 2.6\text{ A}$$

**FIG. 3.7 PLOT OF CHANGE IN THE MASS ($\Delta m$) OF STANDARD SUBSTANCE PLACED AT DIFFERENT HEIGHTS (h) MEASURED FROM THE BASE OF THE ELECTROMAGNET AT FIXED POLE GAP AND FIXED ELECTROMAGNET CURRENT (CONSTANT $H(dh/dz)$ REGION CORRESPONDS TO THE FLAT PART OF THE CURVE BECAUSE $dH/dz$)**
An apparent reduction in the mass of container ($\delta m$) at various values of the electromagnet current has been observed because the glass offers a diamagnetic contribution of considerable magnitude for different values of magnetic field (Fig. 3.8a). Accordingly, the variation of $K$ after applying a glass correction for various values of electromagnet current has been given in Fig. 3.8b. From these figures it is evident that above 2.6A, $\delta m$ rises steeply while below it $K$ rises steeply. A slight change in electromagnet current may cause a significant change in either of the two factors. Therefore 2.6A has been considered most favourable value for experimental purpose.

(c) Evaluation of Magnetic Susceptibility

The powdered specimen whose magnetic susceptibility is to be determined, is put in the silica tube and hung in constant region through the hook of suspension rod of the balance. A definite current is allowed to flow in windings of the furnace. After about fifteen minutes a suitable current is put in the electromagnet and the change in weight ($\Delta m$) of the specimen is measured with the help of magnetic balance (described earlier). Such process is repeated by increasing current in windings of furnace in steps. Knowing change in weight ($\Delta m$) and calibration constant ($K$), the magnetic susceptibility of the specimen is calculated using Eq. 3.20 at different temperatures. The maximum probable error in this measurement is about 2% at lower temperature. But at higher temperature, despite closing one end of the furnace, the movement of hot air disturbs the sample holder. This makes the balance somewhat unsteady. At higher temperature (above 600K) the probable error becomes as high as 5%.
3.4 THERMAL ANALYSIS

The use of heat as a reagent, to determine the various physical and chemical changes occurring in the materials, started initially with minerals and other materials which were observed to undergo phase
transitions. Such a method has been named ‘thermal analysis’. Thermal analysis techniques are widely applied in research, development and product evaluation activities. The studies of the physico-chemical changes occurring in the substances during heating or cooling are generally utilized to elucidate the thermal stability of materials in terms of its physical or chemical nature. The physical or chemical changes, whether it be a change in sample weight, energy, dimensions, conductivity, specific heat etc. (Veale 1972) is monitored by a transducer which converts the measured change into an electrical signal. This signal is subsequently amplified and fed into some type of output device, generally an x-y recorder, where it is plotted on the y-axis, as the difference in temperature $\Delta T$, between the test sample and the reference material verses temperature (or time in the case of isothermal operation) on the x-axis. The thermal analysis techniques include:

(a) Differential thermal analysis (DTA)

(b) Differential scanning calorimetry (DSC)

(c) Thermogravimetry (TGA)

(d) Derivative thermogravimetry (DTG)

(e) Thermomechanical analysis (TMA) and

(f) Dynamic mechanical analysis (DMA)

In the present investigation DTA, TGA and DTG of the samples have been carried out by an instrument (Perkin Elmer) at a wide temperature range (50ºC to 850ºC) on about 5mg of the sample and heating rate of the furnace was 10ºC/min in a static nitrogen atmosphere.

A brief account of some of these technique (i.e. DTA, TGA and DTG) used in the present study has been given below.
3.4.1 Differential Thermal Analysis

Differential Thermal Analysis (DTA) is a major techniques for the identification and investigation of rapid changes of state under dynamic thermal conditions. DTA is used to study high temperature phase changes or reactions. Even thermal reactions of very low intensity can be utilized in the method if they begin abruptly and are completed in a short temperature interval. This technique is based on measurement of the difference in the temperature of material sample (usually alumina) as a function of temperature or time. The sample and the inert reference material are contained with the same heating block to maintain the same heat input for both. The mass of the material taken is kept in close proximity to that of the thermal mass of the reference material. Since the sample and the reference undergo controlled heating or cooling varying linearly with time during thermal event, the temperature of the sample will differ from that of the reference. Usually linear heating rate is maintained during experiment. The difference of temperature $\Delta T$ when plotted as a function of time or temperature, this results the DTA curve. Any phase transformation of the sample upon thermal cycling is accompanied either by absorption (endothermic) or release of heat (exothermic). The results are generally recorded in the form of a continuous curve on which endothermic reactions are deflected downwards and exothermic reactions upward from the base line as shown in Fig. 3.9. The enthalpy changes either exothermic or endothermic are caused by various phase transition, dehydration, decomposition and crystallization (Braido 1969, Verdonk and Broersma 1979, Beasley et al. 1972).
(i) If $\Delta T = 0$, it indicates that no physical or chemical change takes place.

(ii) If $\Delta T = -\text{ve}$, then it shows that absorption of heat takes place due to thermal energy promoting being used up in the phase transformation. This transformation is accompanied by the relative cooling of the sample with respect to the difference and is indicated by the appearance of an endothermic peak in the DTA pattern. The endotherm may be sharp or broad depending upon the nature of the physical changes.

(iii) If $\Delta T = +\text{ve}$, it shows that heat is released in phase transformation such as crystallization of a solid from glassy state and is indicated by the appearance of an exothermic peak.

### 3.4.2 Thermogravimetric Analysis

Thermogravimetry is a technique in which the mass of the material under investigation is continuously followed as a function
of temperature or time as it is heated or cooled at the predetermined rate. It is useful strictly for transformations involving the absorption or evolution of gases from a specimen consisting of a condensed phase. When the sample is heated dynamically in a programmed manner as change in mass (weight loss) as a function of temperature or time results in a definite pattern known as TGA curve. The TGA curve provides the following information regarding the sample.

(i) TG curve is basically quantitative in nature and given as estimate of the material stoichiometry at any given temperature.

(ii) The horizontal portion (slope) on the thermogram indicates weight loss, which provides an understanding of chemical nature of the material coupled with the analysis of volatiles and residues.

(iii) It enables us to obtain a differential TG curve (DTG) when the rate of change of weight loss (dw/dt) with time is plotted with temperature. The peak indicates the temperature at which mass loss is maximum corresponding to $dw/dt = 0$. On the other hand, minimum is the plot characterised by the inflexion (i.e. change in slope in TGA curve) corresponding to $dw/dt \neq 0$ represents the situation of weight loss followed by transformation of an intermediate product.

Thermogravimetric curve are known to be influenced by a number of experimental factors, such as heating rate, type of sample containers, amount of sample, particle size of the sample etc. (Kutty and Balachandran 1984, Kakegawa et al. 1988). The effect of these factors can be minimised by taking proper care and experimental planning.

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