Chapter 4: Thermal Characterization

4.1 INTRODUCTION

Thermal gravimetric analysis was to determine the quality of the sample with temperature, the sample on the sample pool temperature program, sample rod and balance beam one end of the connection, before heating, using weight and TG control circuit regulating the balance in balance, and then heat up at certain speed \[1,3\]. If the quality of the sample without changing the balance scale and record document in a straight line (baseline). If a certain temperature, the quality of the sample began to change, such as the thermal decomposition of the sample weight loss, the loss of the balance beam at the other end slopes downward, the gate through the light irradiation of light energy to Guangdian Ikegami change photocurrent change, Thinkpad x200 tablet battery enter the coil current changes to move down the magnet core, so the balance has to restore balance. Therefore, the determination process, the scales will always maintain a balanced position; the control coil current intensity changes, which is equivalent to the percentage of sample weight loss or weight loss. Also used to connect thermocouple in the sample pool at the bottom of a continuous determination of the temperature of the sample, and recorded records with the other branch can be studied using thermal gravimetric analysis of material thermal stability, thermal decomposition temperature, decomposition reaction speed. If both the decomposition of the volatile component input gas chromatography to determine the composition of decomposition products, you can study the thermal degradation mechanism of material. Weight loss of points from the slope of the curve can be calculated in the temperature of the weight loss rate, which can calculate the decomposition rate constant K and activation energy.
Furthermore, mini 1000 battery thermogravimetric analysis could also examine a variety of additives on thermal stability.

Differential thermal analysis (DTA) is the earliest and the most commonly used thermal analysis techniques[3]. Measuring instrument generally consists of three parts:

1. furnace and temperature process control;
2. sample container and the temperature detection portion;
3. recorder.

Sample and reference material (the so-called reference material is in the determination of the temperature range of any thermal effect is not material) were placed in the sample pool and the reference pool, to a certain speed isokinetic temperature. When the sample without thermal changes, the time recorded document in a straight line (called the baseline). If the sample began in a hot temperature changes, such as sample melting occurs, in the melting process, the external supply of heat is absorbed as latent heat of melting, temperature of the sample itself is unchanged, but the reference material temperature continues to rise, so the two produce temperature difference, that is lower than the melting temperature of the sample during the reference material temperature. Therefore, the endothermic peak draw down records, after the melting process, the sample temperature gradually and reference the same object again becomes zero, recording document return to baseline. The peak position can be judged according to the financial melt temperature[4-7]. As the melting peak is proportional to the area and the melting heat, it can calculate the melting heat. Likewise, exothermic reaction occurs when the sample, that sample temperature Gao in the reference material temperature, will draw up the exothermic peak. From the DTA curve shape and peak position, can determine the
type of thermal changes and transition temperature. Thermogravimetric analysis (TGA or TG) is considered to be one of the five basic thermal analysis techniques. It involves the measurement of change of sample mass with change of temperature. In TGA, mass loss is observed if a thermal event involves loss of a volatile component. Chemical reactions, such as combustion, involve mass losses, whereas physical changes, such as melting, do not. The latter may be studied by differential thermal analysis (DTA) or differential scanning calorimetry (DSC), both of which measure the variation of heat flux in a sample with variation of temperature[8-10]. Both physical and chemical changes in a sample can be measured simultaneously by using simultaneous thermal analysis (STA or TGA-DTA), which is a combination of TGA and DTA or, less commonly, DSC (TGA-DSC). Simultaneous thermal analysis involves measurement of both mass loss and heat flux of a sample simultaneously with variation of temperature. However, thermal analysis techniques cannot be used in general for the identification or characterization of a sample. A more detailed analysis of the thermal behavior of a sample is possible if the volatile components released from a thermal decomposition can be identified. While TGA provides mass loss data related to such volatiles, DTA gives the temperature range over which such volatiles are released; but neither data set unambiguously identifies such volatiles. This can be achieved by evolved gas analysis (EGA), which is a combination of TGA-DTA system and a gas analysis system such as an infrared spectrophotometer (TGA-DTA-FTIR), a gas chromatograph, or a mass spectrometer (TGA-DTA-MS). Recently, TGA has become refined and considerably augmented as the principal component of sample controlled thermal analysis (SCTA). In SCTA, the heating rate is varied so as to produce a constant rate of mass loss[11-14]. Thus, the rate of mass loss, rather than its magnitude, controls the overall analysis.
process. It essentially overcomes the problems associated with linear heating rates in conventional thermal analysis techniques such as TGA, which can cause significant temperature and pressure gradients in the sample. Judicious use of heating regimes, which are modified in some way by the reaction rate, can greatly reduce these problems, giving enhanced resolution in analytical and characterization investigations. Crystal typically display broad melting endotherms and glass transitions as major analytic features associated with their properties. Both the glass and melting transitions are strongly dependent on processing conditions and dispersion in structural and chemical properties of crystal. Characterization of crystals requires a detailed analysis of these characteristic thermal transitions using either differential scanning calorimeter (DSC) or differential thermal analysis (DTA). Additionally, crystals are viscoelastic materials with strong time and temperature dependencies to their mechanical properties. Temperature scans across the dynamic spectrum of mechanical absorptions are commonly required for characterization of crystals, especially for elastomers. These thermal/mechanical properties are characterized in dynamic mechanical/thermal analysis (DMTA). Additionally, weight loss with heating is a common phenomena for crystals due to degradation and loss of residual solvents and monomers[15,16]. Weight loss on heating is studied using thermal gravimetric analysis (TGA).

4.2 SOME COMMON THERMAL ANALYSIS TECHNIQUES[17]

Differential Thermal Analysis (DTA)

The temperature difference between a sample and an inert reference material, $\Delta T = T_S - T_R$, is measured as both are subjected to identical heat treatments
Differential Scanning Calorimetry (DSC)

The sample and reference are maintained at the same temperature, even during a thermal event (in the sample). The energy required to maintain zero temperature differential between the sample and the reference, $d\Delta q/dt$, is measured.

Isothermal titration calorimetry (ITC)

The temperature of a “reaction” is kept constant whilst the energy change is measured.

Thermogravimetric Analysis (TGA)

The change in mass of a sample on heating is measured:

- Melting temperature
- Heat of melting
- Percent crystallinity
- Tg or softening
- Crystallization
- Presence of recyclates/regrinds
- Plasticizers
- Polymer blends (presence, composition and compatibility)

A complete thermal analysis of a yields inferential information concerning the chemical composition and structure of the material. Examples:
1. The Hoffman-Lauritzen description of the crystalline melting point associates shifts in the melting transition temperature with the thickness of lamellar crystallites in crystals. Such structural based shifts would
suggest further study using the Scherrer approach for diffraction peak broadening and small-angle x-ray and TEM analysis.

2. Dramatic weight loss in a TGA analysis of this types of crystals at temperatures above 100°C indicate some association of water with the crystal chemical structure. Such an observation would suggest further study using spectroscopic techniques.

3. In a complex alloy, the observation of two glass transition temperatures indicates a biphasic system, a single glass transition, a miscible system following the Flory-Fox equation. Further support for miscibility would come from microscopy and scattering (neutron, x-ray and light can all be used to characterize miscibility).

Generally, thermal analysis is the easiest and most available of techniques to apply to a sample and for this reason thermal analysis is often the first technique used to analytically describe a crystal material. Error analysis in thermal techniques usually is conducted by repetition of the measurement for at least 3 to 10 identical samples in order to determine the standard deviation in the measurement. In all thermal analysis techniques the instruments must be calibrated with standard samples displaying sharp and constant transition temperatures and enthalpies of transition.

4.3 CALORIMETRY (DIFFERENTIAL SCANNING CALORIMETRY, DSC; DIFFERENTIAL THERMAL ANALYSIS, DTA):

Calorimetry involves the measurement of relative changes in temperature and heat or energy either under isothermal or adiabatic conditions. Chemical calorimetry where the heats of reaction are measured, usually involve isothermal conditions. Bomb or flame calorimeters involve adiabatic systems where the change in
temperature can be translated, using the heat capacity of the system, into the enthalpy or energy content of a material such as in determination of the calorie content of food. In materials characterization calorimetry usually involves an adiabatic measurement. A calorimetric measurement in materials science is carried out on a closed system where determination of the heat, $Q$, associated with a change in temperature, $\Delta T$, yields the heat capacity of the material,

$$C = \frac{Q}{\Delta T}$$

4.1

At constant pressure:

$$\frac{dQ}{dT} = \left( \frac{\partial H}{\partial T} \right)_{P,N} = C_p$$

4.2

The enthalpy can be calculated from $C_p$ through,

$$H(T) = H(T_0) + \int_{T_0}^{T} C_p dT$$

4.3

4.3.1 Instrumentation for Thermal Analysis, DTA and DSC:

Figure 12.1 of Campbell and White shows a schematic of a differential thermal analysis (DTA) instrument. The instrument is composed of two identical cells in which the sample and a reference (often an empty pan) are placed. Both cells are heated with a constant heat flux, $Q$, using a single heater, and the temperatures of the two cells are measured as a function of time. If the sample undergoes a thermal transition such as melting or glass transition a difference in temperature is observed, $\Delta T = T_{\text{sample}} - T_{\text{reference}}$. Negative $\Delta T$ indicates an endotherm for a heating cycle. Quantitative analysis of DTA data is complicated and the instrument is usually viewed as a fairly crude sibling of a...
differential scanning calorimeter (DSC) discussed below. Recent instrumental advancements have improved the quantitative use of DTA instruments. A DTA instrument is generally less expensive than a DSC. Determination of transition temperatures are accurate in a DTA. Estimates of enthalpies of transition are generally not accurate. In the DTA heat is provided at a constant rate and temperature is a dependent parameter. In the equation above for $C_p$, the normal order of dependent and independent parameters in the differential is reversed, so $dT/dQ$ is actually measured rather than $dQ/dT$. This distinction is critically important in transitions where kinetics become important such as in polymer melting and glass transition. Figure 12.2 of Campbell and White shows a schematic of a differential scanning calorimeter (DSC). The arrangement is similar to the DTA except that the sample and reference are provided with separate heaters. The independent parameter is the temperature which is ramped at a controlled rate. Feedback loops control the feed of heat to the sample and reference so the temperature program is closely followed. The raw data from a DSC is heat flux per time or power as a function of temperature at a fixed rate of change of temperature (typically $10^\circ\text{C}/\text{min}$). Since the heat flux will increase with temperature ramp rate, higher heating rates lead to more sensitive thermal spectra. On the other hand, high heating rates lead to lower resolution of the temperature of transition and can have consequences for transitions which display kinetic features. Campbell and White go through a useful comparison of the DSC and DTA techniques which should be reviewed.

4.3.2 Data Interpretation:

The output of a DSC is a plot of heat flux (rate) versus temperature at a specified temperature ramp rate. The heat flux can be
converted to $C_p$ by dividing by the constant rate of temperature change. The output from a DTA is temperature difference ($\Delta T$) between the reference and sample cells versus sample temperature at a specified heat flux. Qualitatively the two plots appear similar. Both DSC’s and DTA’s must be calibrated, essentially, for each use since small changes in the sample cells (oil from fingers etc.) can significantly shift the instrumental calibration. For crystal samples these instruments are typically calibrated with low melting metal crystals that display a sharp melting transition such as indium ($T_m = 155.8^\circ$C) and low molecular weight organic crystals such as naphthalene. The volatility of low molecular weight organic crystals requires the use of special sealed sample holders. An instrumental time lag is always associated with scanning thermal analysis. The observed transitions may be "smeared" by this instrumental time lag (typically close to $1^\circ$C at $10^\circ$/min heating rate). Some account can be made for this time lag by comparison of results from different heating rates. Often this time lag is accounted for by taking the onset of melting as the melting point rather than the peak value for sharp melting standard samples used in calibration. For crystal samples, significant broadening of the melting peak (up to 25 to 50°C) is the norm and this is associated with the structural and kinetic features of polymer melting. Typically the peak value is reported for crystal melting points. The instrumental error in temperature for a DSC is typically ±0.5 to 1.0°C.
Figure 4.1: Typical DSC trace for a Semi-Crystalline material

The Figure above is a typical schematic for a heating run on a quenched sample of semi-crystalline material such as metal complex, polyethylene, polyester (such as PETE) or isotactic polystyrene (typical atactic polystyrene does not display a crystalline endotherm). The left axis is \((dH/dT)\), \(C_p\), or heat flux depending on the normalization of the heat flux. Also, the left axis is often plotted with the endotherm pointing down rather than up, flipping the curve. The curve can change dramatically with heating rate especially with respect to the hysteresis of the glass transition (residual enthalpy) and cold crystallization phenomena. The mechanical properties of the sample change from a brittle solid such as polystyrene at room temperature at the left, to a typical semi-crystalline material such as polyethylene in a milk jug in the middle to a viscous liquid like molasses to the right.
4.3.3 Determination of $T_g$:

To determine $T_g$ two lines are drawn parallel to the baseline above and below the inflection at $T_g$. The midpoint of the departure from the left and the intersection with the baseline nearest $T_g$ on the right is determined by the instrument. This midpoint is taken as the glass transition temperature. The residual enthalpy associated with $T_g$ is sometimes also recorded from the high temperature baseline. This residual enthalpy will decrease with heating rate and has a strong dependence on the processing conditions of the sample and the length of time the sample is allowed to anneal near $T_g$. $T_g$ is a second order transition since it displays a discontinuity in the derivative of the enthalpy (heat capacity). It is often termed a pseudo-second order transition because it displays a finite range of temperatures over which it occurs at finite heating rates and often displays a residual enthalpy.

4.3.4 Determination of $T_m$:

The melting point, $T_m$ is determined, for broad melting polymers, by the temperature at the maximum in the $(dH/dT)$ plot near this transition. The enthalpy of melting is determined by constructing a baseline above the melting and extending it to below any cold crystallization phenomena (exothermic peak below $T_m$ and above $T_g$). Generally, the enthalpy of crystallization is taken as the area above this baseline. Sometimes the enthalpy of crystallization, which has occurred in the DSC measurement, is subtracted from this value to adjust the enthalpy as an estimate of the enthalpy associated with the original sample. The onset of melting is taken as the initial rise of the curve above baseline. The maximum melting temperature at this heating rate is taken as the final point which deviates from the baseline.
4.3.5 Melting Endotherm: Gibbs-Thompson Relationship for Polymers (Hoffman-Lauritzen Theory):

In addition to the broad melting endotherms and the presence of cold crystallization as a dominant feature in semi-crystalline polymers a number of unique complications exist in the interpretation of calometric data. A variant of the Gibbs-Thompson equation, known as the Hoffman-Lauritzen equation governs the relationship between structure and melting point for lamellar crystallites which are present in essentially all semi-crystalline materials. The Hoffman equation notes that there is a direct, inverse relationship between the undercooling at which the polymer crystallites melt and the thickness of the lamellar crystallites through:

\[ L = \frac{2\sigma_e T_m}{\Delta H_c \Delta T} + \partial L \]

where \( \Delta T \) is the difference between the melting point of an infinite thickness and perfect crystallite and the observed melting point, \( \sigma_e \) is the free energy associated with the lamellar fold surfaces and \( \partial L \) is a term which accounts for the necessary deviation from equilibrium in the crystallization process. The latter term is usually neglected, i.e. \( \partial L >> 0 \).

The Hoffman approach gives rise to a possible description of the broad endotherm associated with melting of material crystallites, that is polydispersity in lamellar thickness. In many material, particularly in branched polyethylene, multiple melting endotherms are observed and the Hoffman relationship has been used to support the presence of discrete populations of crystallites associated, perhaps, with initial
crystallization and formation of spherulitic structures, followed by decoration of spherulites by lower melting (i.e. thinner) lamellae.

A problem with the above analysis based on the Hoffman equation is that the degree of crystallinity (DOC) measured calorimetrically rarely agrees with that measured by XRD. XRD’s DOC is usually taken as the best value since the myriad of complications which can be associated with a thermal measurement are mostly avoided. The value of the DOC obtained from thermal analysis, if all endotherms are included is usually higher than that of XRD which indicates that at least some of the endotherm measured calorimetrically is associated with enthalpies of association present in the amorphous phase, such as tethered chains at the lamellar interface or interlamellar amorphous polymer. In some highly branched polyethylenes, it has been proposed that the bulk of the melting endotherm can be associated with such associated amorphous materials.

### 4.3.6 Melting Point Depression for Polymers:

The presence of miscible, non-crystallizing components are known to depress the melting point of all crystalline materials, i.e. adding salt to ice:

\[
\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{R}{\Delta H_m} \ln(\alpha)
\]

where \( \alpha \) is the activity of the crystallizable component. Often the mole fraction of crystallizable component is substituted for the activity as an ideal approximation. In polymers, the noncrystallizable component can
be a low-molecular weight impurity, but is often a non-crystallizable comonomer, an atactic segment, end-groups or a branch site. Substitution of the crystallizable fraction for "a" in the above equation yields the Sanchez-Eby Equation for copolymers. For low fractions non-crystallizable component, such as when considering end-group effects the log term can be approximated using,

\[ \ln(\alpha) \approx \ln(X_{\text{cry}}) = \ln(1-X_{\text{noncry}}) = X_{\text{noncry}}. \]

For end-groups \( X_{\text{noncry}} = 2M_0/M_n \),

where \( M_0 \) is the molecular weight of the end-group and \( M_n \) is the number average chain molecular weight. Thus, \( T^0 \) for a polymer reflects the melting point of an infinite molecular weight sample. For a thermodynamically miscible polymer or solvent at low concentrations the melting point depression can be expressed through a viral expansion where \(-\ln(\alpha)\) is replaced by a second order viral expansion involving the interaction parameter, \( X \)

\[ \frac{1}{T_m} - \frac{1}{T_m^0} = \frac{R}{\Delta H_m} \frac{V_{\text{mer}}}{V_{\text{solvent}}} \left( \phi_{\text{solvent}} - X\phi_{\text{solvent}}^2 \right) \]

where \( V \) represents molar volumes and \( \phi \) is the volume fraction of solvent at low volume fractions. This equation is appropriate for melting point depression in the presence of a plasticizer for instance. The melting point of a semi-crystalline plastic sample is strongly effected by distributions in morphology (lamellar thickness), impurity concentration and distribution in the sample, and processing history (thermal history) as well as the residual strain and orientation in the samples. All of these effects lead to a characteristically broad melting endotherm for plastics.
4.3.7 Glass Transition:

The melting point is a first order transition, in the Ehrenfest sense, since it involves a discontinuity in the first derivative of the Gibbs free energy with respect to temperature (-entropy) or pressure (volume). That is, there is a discontinuity in volume, for instance, at the melting point. The glass transition, in the most ideal case, is a second order transition since the first derivatives of the Gibbs free energy are not discontinuous but the second derivatives with respect to temperature (-heat capacity/T), pressure (-volume X compressibility) and temperature/pressure (volume X thermal expansion) show a discontinuity. Polymers are unique in the dominance of the glass transition as the decisive factor in their mechanical properties. Polymers are the only material for which the equilibrium ground state is often glassy rather than crystalline. This is because topological and stereochemical constraints prevent the formation of crystals in many cases. The glass transition is often called a pseudo-second order transition because of the dominance of kinetics. Slower cooling rates in the DSC, for instance, lead to lower measured values of the glass transition. This time-temperature superposition is described by the Williams Landel Ferry (WLF) equation for example. This rate dependence hints at the basis of the glass transition in molecular motion. The glass transition is effected by orientation, rate, molecular weight, crosslink density and impurity content.

4.4 THERMAL GRAVIMETRIC ANALYSIS (TGA):

Many DTA instruments include the ability to measure mass as a function of temperature as well as the DTA output. In some cases such
a thermal gravimetric analysis instrument is coupled with a mass spectrometer or an infrared absorption instrument for analysis of decomposition gasses. Typically, a superimposed plot of DTsam-ref and weight can yield critical information concerning the changes which occur on processing a polymer. For instance, the thermal cycling of a processing operation can sometimes be mimicked in a DTA/TGA instrument to understand degradation and thermal transitions which effect the viscosity and other properties of a plastic. Often, a DTA/TGA analysis is used to define the processing limits for a polymer, at the lower temperature associated with the glass transition or melting point and at the upper temperature associated with degradation of the polymer. Polymers which absorb water, such as nylon, have been studied in depth using TGA instruments and an example of such a study is shown in figure 12.9 of Campbell and White. Since the TGA instrument is fairly simple and self-explanatory it will not be extensively discussed.

Thermogravimetric analysis or thermal gravimetric analysis (TGA) is a type of testing that is performed on samples to determine changes in weight in relation to change in temperature. Such analysis relies on a high degree of precision in three measurements: weight, temperature, and temperature change. As many weight loss curves look similar, the weight loss curve may require transformation before results may be interpreted. A derivative weight loss curve can be used to tell the point at which weight loss is most apparent. Again, interpretation is limited without further modifications and deconvolution of the overlapping peaks may be required. TGA is commonly employed in research and testing to determine characteristics of materials such as polymers, to determine degradation temperatures, absorbed moisture content of materials, the level of inorganic and organic components in materials, decomposition points of explosives, and solvent residues. It is also often
used to estimate the corrosion kinetics in high temperature oxidation. Simultaneous TGA-DTA/DSC measures both heat flow and weight changes (TGA) in a material as a function of temperature or time in a controlled atmosphere. Simultaneous measurement of these two material properties not only improves productivity but also simplifies interpretation of the results. The complementary information obtained allows differentiation between endothermic and exothermic events which have no associated weight loss (e.g., melting and crystallization) and those which involve a weight loss (e.g., degradation). Analysis is carried out by raising the temperature of the sample gradually and plotting weight (percentage) against temperature. The temperature in many testing methods routinely reaches 1000°C or greater, but the oven is so greatly insulated that an operator would not be aware of any change in temperature even if standing directly in front of the device. After the data are obtained, curve smoothing and other operations may be done such as to find the exact points of inflection. A method known as hi-resolution TGA is often employed to obtain greater accuracy in areas where the derivative curve peaks. In this method, temperature increase slows as weight loss increases. This is done so that the exact temperature at which a peak occurs can be more accurately identified. Several modern TGA devices can vent burnoff to an infrared spectrophotometer to analyze composition. Thermogravimetric analysis (TGA) is one of the members of the family of thermal analysis techniques used to characterise a wide variety of materials. TGA provides complimentary and supplementary characterisation information to the most commonly used thermal technique, DSC. TGA measures the amount and rate (velocity) of change in the mass of a sample as a function of temperature or time in a controlled atmosphere. The measurements are used primarily to determine the thermal and/or oxidative stabilities of materials as well as their compositional

130
Chapter 4 Thermal Characterization
properties. The technique can analyze materials that exhibit either mass loss or gain due to decomposition, oxidation or loss of volatiles (such as moisture). It is especially useful for the study of polymeric materials, including thermoplastics, thermosets, elastomers, composites, films, fibres, coatings and paints. TGA measurements provide valuable information that can be used to select materials for certain end-use applications, predict product performance and improve product quality. The schematic of TGA apparatus is shown in figure 4.2. The technique is particularly useful for the following types of measurements:

- Compositional analysis of multi-component materials or blends
- Thermal stabilities
- Oxidative stabilities
- Estimation of product lifetimes
- Decomposition kinetics
- Effects of reactive atmospheres on materials
- Filler content of materials
- Moisture and volatiles content
DSC and TGA are often used for characterisation of pharma materials. DSC is able to differentiate between different polymorphic structures and, by using different heating rates, can investigate the transformations which occur during the polymorphic transformation. By using appropriate heating rates, polymorphic purity can be determined, and can involve heating rates up to 750°C/min. TGA is often used to measure residual solvents and moisture, but can also be used to
determine solubility of pharma materials in solvents. Analysis of pharma materials is probably the largest area of application for thermal analysis. Polymers represent another large area in which thermal analysis finds strong applications. Thermoplastic polymers are commonly found in everyday packaging and household items, but for the analysis of the raw materials, effects of the many additive used (including stabilisers and colours) and fine-tuning of the moulding or extrusion processing used can be achieved by using DSC. An example is oxidation induction time (OIT) by DSC which can determine the amount of oxidation stabiliser present in a thermoplastic (usually a polyolefin) polymer material. Compositional analysis is often made using TGA, which can separate fillers, polymer resin and other additives. TGA can also give an indication of thermal stability and the effects of additives such as flame retardants. Thermal analysis of composite materials, such as carbon fibre composites or glass epoxy composites are often carried out using DMA or DMTA, which can measure the stiffness of materials by determining the modulus and damping (energy absorbing) properties of the material. Aerospace companies often employ these analysers in routine quality control to ensure that products being manufactured meet the required strength specifications. Formula 1 racing car manufacturers also have similar requirements! DSC is used to determine the curing properties of the resins used in composite materials, and can also confirm whether a resin can be cured and how much heat is evolved during that process. Application of predictive kinetics analysis can help to fine-tune manufacturing processes. Another example is that TGA can be used to measure the fibre content of composites by heating a sample to remove the resin by application of heat and then determining the mass remaining. Production of many metals (cast iron, grey iron, ductile iron, compacted graphite iron, 3000 series aluminium alloys, copper alloys, silver, and complex steels) are aided by a production
technique also referred to as thermal analysis. A sample of liquid metal is removed from the furnace or ladle and poured into a sample cup with a thermocouple embedded in it. The temperature is then monitored, and the phase diagram arrests (liquidus, eutectic, and solidus) are noted. From this information chemical composition based on the phase diagram can be calculated, or the crystalline structure of the cast sample can be estimated. Strictly speaking these measurements are *cooling curves* and a form of sample controlled thermal analysis whereby the cooling rate of the sample is dependent on the cup material (usually bonded sand) and sample volume which is normally a constant due to the use of standard sized sample cups. Advanced techniques use differential curves to locate endothermic inflection points such as gas holes, and shrinkage, or exothermic phases such as carbides, beta crystals, intercrystalline copper, magnesium silicide, iron phosphide's and other phases as they solidify. Detection limits seem to be around 0.01% to 0.03% of volume. In addition, integration of the area between the zero curve and the first derivative is a measure of the specific heat of that part of the solidification which can lead to rough estimates of the percent volume of a phase. (Something has to be either known or assumed about the specific heat of the phase versus the overall specific heat.) In spite of this limitation, this method is better than estimates from two dimensional micro analysis, and a lot faster than chemical dissolution.
4.5 EXPERIMENTAL (TGA)

Figure 4.3: Thermal Analysis System (DSC, TGA, DTA) at SICART, V.V.Nagar

Make Model
Perkin Elmer Pyris-1 DSC, Pyris-1 TGA, DTA-7

Small Description:
**Thermal Analyzer (DSC, TGA, DTA),** PerkinElmer Pyris1 DSC, Pyris1 TGA, DTA 7, Temp.
Range: TGA: Room Temperature to 1000°C; DSC: -100°C to 600°C and DTA: Room Temperature to 1200°C. All types of thermal analysis studies /testing.
Specifications:

(TGA)
- Temperature Range: Ambient to 1000° C
- Sensitivity: 0.1 gm (0.0001mg)
- Atmosphere: N₂, or Air

(DSC)
- Temperature range: -100 °C to 600 °C
- Temperature Accuracy: ± 0.2 °C
- Heating Rate: 0.1 to 100 °C / min

(DTA)
- Temperature range: -Ambient to 1200 °C
- Heating Rate: 0.1 to 100 °C / min
- Atmosphere: Air or Nitrogen

Applications:

Thermal Analysis (DSC,TGA,DTA)
Thermal Gravimetric Analyzer measures the change in mass of a sample as a function of time or temperature in inert or oxidative atmosphere.

- Chemical changes occurring in an oxidative atmosphere provide useful information regarding characterization of the sample.
- TGA-1 is based on a rugged microbalance which is sensitive to measure even a few micrograms of weight loss.
- It employs computer controlled gas switching to regulate furnace atmosphere.
- There are preset programs to allow complete separations, Decomposition studies, proximate analysis of coal, auto stepwise analysis of filled polymers, curing characteristics High temperature studies, Thermal stability and compositional analysis are possible with this instrument.
• Used for Melting, Crystallization, Glass Transitions Temperature, Polymorphism, Kinetic Studies, Curing Reaction.
• Endothermic and Exothermic effects
• Isothermal Cure kinetics studies.
• Characterization of polymorphism of pharmaceuticals.
• Characterization of pharmaceuticals formulations.
• Characterization of multicomponent materials by TGA.
• Thermal decomposition study

Widely used in polymer, pharmaceuticals, cosmetics industry
4.6 RESULT AND DISCUSSION(TGA)

Thermo gravimetric analysis or thermal gravimetric analysis (TGA) is a type of testing that is performed on samples to determine changes in weight in relation to change in temperature. Such analysis relies on a high degree of precision in three measurements: weight, temperature and temperature change. As many weight loss curves look similar, the weight loss curve may require transformation before results may be interpreted. A derivative weight loss curve can be used to tell the point at which weight loss is most apparent. Again, interpretation is limited without further modifications and deconvolution of the overlapping peaks may be required. TGA is commonly employed in research and testing to determine characteristics of materials such as polymers, to determine degradation temperatures, absorbed moisture content of materials, the level of inorganic and organic components in materials, decomposition points of explosives and solvent residues. It is also often used to estimate the corrosion kinetics in high temperature oxidation. Simultaneous TGA-DTA/DSC measures both heat flow and weight changes (TGA) in a material as a function of temperature or time in a controlled atmosphere. Simultaneous measurement of these two material properties not only improves productivity but also simplifies interpretation of the results. The complementary information obtained allows differentiation between endothermic and exothermic events which have no associated weight loss (e.g., melting and crystallization) and those which involve a weight loss (e.g., degradation).

The factors that influence the thermogram of a sample fall into two categories:
Chapter 4  Thermal Characterization

(A) Instrumental factors

1. Furnace heating rate
2. Recording or chart speed
3. Furnace atmosphere
4. Geometry of sample holder and furnace
5. Sensitivity of recording mechanism
6. Composition of sample container

(B) Sample characteristics

1. Amount of sample
2. Solubility of evolved gases in sample
3. Particle size
4. Heat of reaction
5. Sample packing
6. Nature of the sample
7. Thermal conductivity

In present investigation, thermogravimetric analysis of the crystals was carried out in air by heating at a constant rate of 10° C per minute using a Perkin-Elmer TGA-7DSC-PYRIS-1-DTA-7 thermal analysis system. The thermograms of metal complexes are presented in Figure: 4.4 to 4.6. Under the conditions employed in this analysis, the crystals lost weight gradually during every phase of the experiment, then the samples underwent an accelerated weight loss and finally, in the
temperature range of about 500-600°C the rate of weight loss become much more moderate.

Thermo gravimetric analysis data of the crystals are presented in Table: 4.1 The cumulative weight loses of metal complexes at 50°C, 100°C, 150°C, 200°C and 250°C are presented in Table: 4.2.

The following important observations have been made:

(i) The Schiff base used in this study starts decomposing from 170°C and its complete decomposition takes place 300°C

(ii) Decomposition of all crystals starts above 350°C.

(iii) The rate of decomposition of crystals is lower than that of the ligand suggested that there may be weak intermolecular hydrogen bonding.

(iv) In Cr(VI) complexes shows cumulative weight loss above 150°C and between 200 to 250°C is 14 to 18%. It indicates two water molecules as coordinated

(v) Co(II) thermograms also shows the presence of six water molecules & loss in weight equivalent to 15-20% at 100 to 150°C.

(vi) The final product is found to be metal oxide in all the complexes.

Thermo gravimetric analysis shows that all synthesized complexes are hydrated and have water molecules associated to them. Co(II) has six while Cr(VI) and Cu(II) has two water molecules as part of their structure. Loss of this water of hydration is not instant but a continuous process with sustainability.
<table>
<thead>
<tr>
<th>Crystal</th>
<th>50</th>
<th>100</th>
<th>150</th>
<th>200</th>
<th>250</th>
<th>300</th>
<th>350</th>
<th>400</th>
<th>450</th>
<th>500</th>
<th>550</th>
<th>600</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metformin</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>1.2</td>
<td>12.1</td>
<td>42.0</td>
<td>71.2</td>
<td>80.0</td>
<td>82.0</td>
<td>86.5</td>
<td>88.0</td>
<td>90.0</td>
</tr>
<tr>
<td>Schiff Base</td>
<td>0.1</td>
<td>0.1</td>
<td>1.5</td>
<td>1.8</td>
<td>8.0</td>
<td>31.5</td>
<td>56.5</td>
<td>70.0</td>
<td>74.2</td>
<td>77.5</td>
<td>79.9</td>
<td>80.0</td>
</tr>
<tr>
<td>[CrO$_3$·L$_2$·2H$_2$O]</td>
<td>0.1</td>
<td>8</td>
<td>12</td>
<td>14</td>
<td>18</td>
<td>25</td>
<td>35</td>
<td>45</td>
<td>53</td>
<td>55</td>
<td>55</td>
<td>54</td>
</tr>
<tr>
<td>[Co·L$_2$]·6H$_2$O·Cl$_2$</td>
<td>1</td>
<td>15</td>
<td>20</td>
<td>24</td>
<td>27</td>
<td>30</td>
<td>35</td>
<td>40</td>
<td>43</td>
<td>46</td>
<td>52</td>
<td>58</td>
</tr>
</tbody>
</table>

Table – 4.1
Cumulative % Weight Loss Data of Crystal
### Table – 4.2

**Cumulative Weight Loss Data of Crystal at 50°C to 250°C**

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Found</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>50°C</td>
<td>100°C</td>
<td>150°C</td>
<td>200°C</td>
<td>250°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>G</td>
<td>%</td>
<td>G</td>
<td>%</td>
<td>G</td>
<td>%</td>
<td>g</td>
<td>%</td>
<td>g</td>
</tr>
<tr>
<td>[CrO$_3$·L$_2$·2H$_2$O]</td>
<td>0.61</td>
<td>0.1</td>
<td>49.11</td>
<td>8</td>
<td>73.67</td>
<td>12</td>
<td>85.95</td>
<td>14</td>
<td>110.05</td>
<td>18</td>
</tr>
<tr>
<td>[Co·L$_2$]6H$_2$O·Cl$_2$</td>
<td>7.14</td>
<td>1</td>
<td>107.23</td>
<td>15</td>
<td>142.98</td>
<td>20</td>
<td>150</td>
<td>24</td>
<td>193.00</td>
<td>27</td>
</tr>
</tbody>
</table>
Figure 4.4: TGA spectra of Schiff Base
Figure 4.5: TGA spectra of [CrO$_3$·L$_2$·2H$_2$O] Crystal
Figure 4.6: TGA spectra of [Co·L₂]6H₂O·Cl₂ Crystal
4.7 THERMAL CONDUCTIVITY

In physics, thermal conductivity, k, is the property of a material reflecting its ability to conduct heat. It appears primarily in Fourier's Law for heat conduction. Thermal conductivity is measured in watts per kelvin-metre (W·K\(^{-1}\)·m\(^{-1}\), i.e. W/(K·m). Multiplied by a temperature difference (in kelvins, K) and an area (in square metres, m\(^2\)), and divided by a thickness (in metres, m), the thermal conductivity predicts the rate of energy loss (in watts, W) through a piece of material. The reciprocal of thermal conductivity is thermal resistivity\[18\]. There are a number of ways to measure thermal conductivity. Each of these is suitable for a limited range of materials, depending on the thermal properties and the medium temperature\[19,20\]. There is a distinction between steady-state and transient techniques. In general, steady-state techniques are useful when the temperature of the material does not change with time. This makes the signal analysis straightforward (steady state implies constant signals). The disadvantage is that a well-engineered experimental setup is usually needed. The Divided Bar (various types) is the most common device used for consolidated rock samples. The transient techniques perform a measurement during the process of heating up. Their advantage is quicker measurements. Transient methods are usually carried out by needle probes. The reciprocal of thermal conductivity is thermal resistivity, usually measured in kelvin-metres per watt (K·m·W\(^{-1}\)). When dealing with a known amount of material, its thermal conductance and the reciprocal property, thermal resistance, can be described. Unfortunately, there are differing definitions for these terms. For general scientific use, thermal conductance is the quantity of heat that passes in unit time through a plate of particular area and thickness when its opposite faces differ in temperature by one
kelvin. For a plate of thermal conductivity k, area A and thickness L this is $kA/L$, measured in $W\cdot K^{-1}$ (equivalent to: $W/°C$). Thermal conductivity and conductance are analogous to electrical conductivity ($A\cdot m^{-1}\cdot V^{-1}$) and electrical conductance ($A\cdot V^{-1}$). There is also a measure known as heat transfer coefficient: the quantity of heat that passes in unit time through unit area of a plate of particular thickness when its opposite faces differ in temperature by one kelvin. The reciprocal is thermal insulance. In summary:

Thermal conductance = $kA/L$, measured in $W\cdot K^{-1}$

Thermal resistance = $L/(kA)$, measured in $K\cdot W^{-1}$ (equivalent to: $°C/W$)

Heat transfer coefficient = $k/L$, measured in $W\cdot K^{-1}\cdot m^{-2}$

Thermal insulance = $L/k$, measured in $K\cdot m^2\cdot W^{-1}$.

The heat transfer coefficient is also known as thermal admittance. When thermal resistances occur in series, they are additive. So when heat flows through two components each with a resistance of 1 $°C/W$, the total resistance is 2 $°C/W$. A common engineering design problem involves the selection of an appropriate sized heat sink for a given heat source. Working in units of thermal resistance greatly simplifies the design calculation. For example, if a component produces 100 W of heat, and has a thermal resistance of 0.5 $°C/W$, what is the maximum thermal resistance of the heat sink? Suppose the maximum temperature is 125 $°C$, and the ambient temperature is 25 $°C$; then the $ΔT$ is 100 $°C$. The heat sink's thermal resistance to ambient must then be 0.5 $°C/W$ or less.
A third term, thermal transmittance, incorporates the thermal conductance of a structure along with heat transfer due to convection and radiation. It is measured in the same units as thermal conductance and is sometimes known as the composite thermal conductance. The term U-value is another synonym. In summary, for a plate of thermal conductivity \( k \) (the \( k \) value [21]), area \( A \) and thickness \( t \):

\[
\text{Thermal conductance} = \frac{k}{t}, \text{measured in } W \cdot K^{-1} \cdot m^{-2};
\]
\[
\text{Thermal resistance (R-value)} = \frac{t}{k}, \text{measured in } K \cdot m^2 \cdot W^{-1};
\]
\[
\text{Thermal transmittance (U-value)} = \frac{1}{\Sigma(t/k)} + \text{convection} + \text{radiation}, \text{measured in } W \cdot K^{-1} \cdot m^{-2}.
\]

\( K \)-value refers to the total insulation value of a building. \( K \)-value is obtained by multiplying the form factor of the building (= the total inward surface of the outward walls of the building divided by the total volume of the building) with the average \( U \)-value of the outward walls of the building. \( K \) value is therefore expressed as \((m^2 \cdot m^{-3}) \cdot (W \cdot K^{-1} \cdot m^{-2}) = W \cdot K^{-1} \cdot m^{-3}\). A house with a volume of 400 m³ and a \( K \)-value of 0.45 (the new European norm. It is commonly referred to as K45) will therefore theoretically require 180 W to maintain its interior temperature 1 K above exterior temperature. So, to maintain the house at 20 °C when it is freezing outside (0 °C), 3600 W of continuous heating is required.

In metals, thermal conductivity approximately tracks electrical conductivity according to the Wiedemann-Franz law, as freely moving valence electrons transfer not only electric current but also heat energy. However, the general correlation between electrical and thermal
conductance does not hold for other materials, due to the increased importance of phonon carriers for heat in non-metals. Highly electrically conductive silver is less thermally conductive than diamond, which is an electrical insulator. Thermal conductivity depends on many properties of a material, notably its structure and temperature. For instance, pure crystalline substances exhibit very different thermal conductivities along different crystal axes, due to differences in phonon coupling along a given crystal axis. Sapphire is a notable example of variable thermal conductivity based on orientation and temperature, with 35 W/(m·K) along the c-axis and 32 W/(m·K) along the a-axis.[22] Air and other gases are generally good insulators, in the absence of convection. Therefore, many insulating materials function simply by having a large number of gas-filled pockets which prevent large-scale convection. Examples of these include expanded and extruded polystyrene (popularly referred to as "styrofoam") and silica aerogel. Natural, biological insulators such as fur and feathers achieve similar effects by dramatically inhibiting convection of air or water near an animal's skin. Light gases, such as hydrogen and helium typically have high thermal conductivity. Dense gases such as xenon and dichlorodifluoromethane have low thermal conductivity. An exception, sulfur hexafluoride, a dense gas, has a relatively high thermal conductivity due to its high heat capacity. Argon, a gas denser than air, is often used in insulated glazing (double paned windows) to improve their insulation characteristics[23]. Thermal conductivity is important in building insulation and related fields. However, materials used in such trades are rarely subjected to chemical purity standards. Several construction materials' k values are listed below. These should be considered approximate due to the uncertainties related to material definitions. Heat flux is exceedingly difficult to control and isolate in a laboratory setting. Thus at the atomic
level, there are no simple, correct expressions for thermal conductivity. Atomically, the thermal conductivity of a system is determined by how atoms composing the system interact. There are two different approaches for calculating the thermal conductivity of a system. The first approach employs the Green-Kubo relations. Although this employs analytic expressions which in principle can be solved, in order to calculate the thermal conductivity of a dense fluid or solid using this relation requires the use of molecular dynamics computer simulation. The second approach is based upon the relaxation time approach. Due to the anharmonicity within the crystal potential, the phonons in the system are known to scatter. There are three main mechanisms for scattering:

1. Boundary scattering, a phonon hitting the boundary of a system;
2. Mass defect scattering, a phonon hitting an impurity within the system and scattering;
3. Phonon-phonon scattering, a phonon breaking into two lower energy phonons or a phonon colliding with another phonon and merging into one higher energy phonon.

A kinetic theory of solids follows naturally from the standpoint of the normal modes of vibration in an elastic crystalline solid (see Einstein solid and Debye model) – from the longest wavelength (or fundamental frequency of the body) to the highest Debye frequency (that of a single particle). There are simple equations derived to describe the relationship of these normal modes to the mechanisms of thermal phonon wave propagation as represented by the superposition of elastic waves—both longitudinal (acoustic) and transverse (optical) waves of atomic displacement[24-27]. Longitudinal compression (or acoustic or pressure) wave oscillating within the dimensions of a 2-dimensional lattice.
Transverse (shear) wave in a 2-dimensional lattice, oscillating in the 3rd spatial dimension. The velocities of longitudinal acoustic phonons in condensed matter are directly responsible for the thermal conductivity which levels out temperature differentials between compressed and expanded volume elements. For example, the thermal properties of glass are interpreted in terms of an approximately constant mean free path for lattice phonons. Furthermore, the value of the mean free path is of the order of magnitude of the scale of structural (dis)order at the atomic or molecular level[28-30]. Thus, heat transport in both glassy and crystalline dielectric solids occurs through elastic vibrations of the lattice. This transport is limited by elastic scattering of acoustic phonons by lattice defects. These predictions were confirmed by the experiments of Chang and Jones on commercial glasses and glass ceramics, where mean free paths were limited by "internal boundary scattering" to length scales of $10^{-2}$ cm to $10^{-3}$ cm. [31,32]. The phonon mean free path has been associated directly with the effective relaxation length for processes without directional correlation. The relaxation length or mean free path of longitudinal phonons will be much greater. Thus, thermal conductivity will be largely determined by the speed of longitudinal phonons. [31,33]. Regarding the dependence of wave velocity on wavelength or frequency (aka “dispersion”), low-frequency phonons of long wavelength will be limited in relaxation length by elastic Rayleigh scattering. This type of light scattering form small particles is proportional to the fourth power of the frequency. For higher frequencies, the power of the frequency will decrease until at highest frequencies scattering is almost frequency independent. Similar arguments were subsequently generalized to many glass forming substances using Brillouin scattering. [34-37]. Often in heat transfer the concept of controlling resistance is used to determine how to either
increase or decrease heat transfer. Heat transfer coefficients represent how much heat is able to transfer through a defined region of a heat transfer area. The inverse of these coefficients are the resistances of those areas. If a wall can be considered, it would have a heat transfer coefficient representing convection on each side of the wall, and one representing conduction through the wall. To obtain an overall heat transfer coefficient, the resistances need to be summed up. Due to the nature of the above reciprocal relation, the smallest heat transfer coefficient \( h \) or the largest resistance is generally the controlling resistance as it dominates the other terms to the point that varying the other resistances will have little impact on the overall resistance:

4.8 EXPERIMENTAL (THERMAL CONDUCTIVITY)

Thermal Conductivity of All the materials were measured at Laljibhai Chaturbhai Institute of Technology, Gujarat. Thermal conductivity measured in powder form with hot-wire method with precision measurement. The measurement was done at equal interval of 5°C.
Figure 4.7: Quick Thermal Conductivity Meter

Model No. : QTM-500

Brand Name: KEM

Country: Japan

**Specification:**

Thermal conductivity of all types of sample materials can be measured quickly and easily. Just place the probe on sample surface of temperature equilibrium and wait for 60 seconds. You will obtain the results. For thin sample materials like film (30 - 100µm), sheet or board (0.1 - 8mm), use the optional software for measurement of thin films

<table>
<thead>
<tr>
<th>Measurement method</th>
<th>Hot Wire Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Range</td>
<td>0.023 - 12W/m • K (standard probe)</td>
</tr>
<tr>
<td>Precision</td>
<td>±5%/reading value per reference plate</td>
</tr>
<tr>
<td>Reproducibility</td>
<td>±3%/reading value per reference plate</td>
</tr>
</tbody>
</table>
4.9 RESULT AND DISCUSSION (THERMAL CONDUCTIVITY)

The thermal conductivity of all crystals was measured using Hot Wire Method and measured on Quick Thermal Conductivity Meter. Thermal conductivity of all crystals measured between 283°C to 373°C with equal interval of 5°C. Thermal conductivity increased as temperature increased in all the crystals which indicate that all the crystals are good conductor of heat but thermal conductivity almost remain constant in Schiffbase. In Cr(VI) Crystal a thermal conductivity increased continuously up to 363°C and then become constant. The rate of increased in thermal conductivity of Cr(VI) Crystal is higher and it is near about metal. This is observed because crystal synthesized by metal of Cr(VI). The maximum value of thermal conductivity observed in this work was 0.828 W/cmK. The tabulation and graphical result shown in Table – 4.3 and Figure 4.9 respectively. In Co(II) Crystal a thermal conductivity increased continuously but the rate of change observed very lower than the Cr(VI) crystal. The maximum value of thermal conductivity of Co(II) Crystal was observed in this work is 0.8161 W/cmK. The tabulation and graphical result shown in Table – 4.3 and Figure 4.10 respectively. In Schiffbase a thermal conductivity almost remain constant and observed very lower than the crystals. The maximum value of thermal conductivity of Schiffbase was observed in this work is 3.0314W/cmK. The tabulation and graphical result shown in Table – 4.3 and Figure 4.8 respectively. The rate of change in thermal conductivity is higher in Cr(VI) crystal and lower in Cu(II) crystal and Schiffbase of in Cr(VI) crystal a composition of metal is higher than the Co(II) crystal.
### Table - 4.3: Thermal conductivity of Crystal

<table>
<thead>
<tr>
<th>Temperature in C</th>
<th>Temperature in K</th>
<th>Thermal Conductivity in W/cmK</th>
<th>Schiffbase</th>
<th>Cr(VI) Crystal</th>
<th>Co(II) Crystal</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>283</td>
<td>0.072</td>
<td>0.8005</td>
<td>0.6005</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>288</td>
<td>0.0723</td>
<td>0.8015</td>
<td>0.6015</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>293</td>
<td>0.0725</td>
<td>0.8025</td>
<td>0.6025</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>298</td>
<td>0.0727</td>
<td>0.8035</td>
<td>0.6035</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>303</td>
<td>0.0729</td>
<td>0.8045</td>
<td>0.6045</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>308</td>
<td>0.0729</td>
<td>0.8055</td>
<td>0.6055</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>313</td>
<td>0.0729</td>
<td>0.8065</td>
<td>0.6065</td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>318</td>
<td>0.0729</td>
<td>0.8075</td>
<td>0.6075</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>323</td>
<td>0.0729</td>
<td>0.8085</td>
<td>0.6085</td>
<td></td>
</tr>
<tr>
<td>55</td>
<td>328</td>
<td>0.0729</td>
<td>0.8095</td>
<td>0.6095</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>333</td>
<td>0.0729</td>
<td>0.8105</td>
<td>0.6105</td>
<td></td>
</tr>
<tr>
<td>65</td>
<td>338</td>
<td>0.0729</td>
<td>0.8115</td>
<td>0.6115</td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>343</td>
<td>0.0729</td>
<td>0.8125</td>
<td>0.6125</td>
<td></td>
</tr>
<tr>
<td>75</td>
<td>348</td>
<td>0.0729</td>
<td>0.8135</td>
<td>0.6135</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>353</td>
<td>0.0729</td>
<td>0.8145</td>
<td>0.6145</td>
<td></td>
</tr>
<tr>
<td>85</td>
<td>358</td>
<td>0.0729</td>
<td>0.8155</td>
<td>0.6155</td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>363</td>
<td>0.0729</td>
<td>0.816</td>
<td>0.616</td>
<td></td>
</tr>
<tr>
<td>95</td>
<td>368</td>
<td>0.0729</td>
<td>0.8163</td>
<td>0.6163</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>373</td>
<td>0.0729</td>
<td>0.8161</td>
<td>0.6161</td>
<td></td>
</tr>
</tbody>
</table>
Figure 4.8: Thermal conductivity of schiffbase
Figure 4.9: Thermal conductivity of $[\text{CrO}_3\cdot\text{L}_2\cdot2\text{H}_2\text{O}]$ crystal
Figure 4.10: Thermal conductivity of \([\text{Co} \cdot \text{L}_2] \cdot 6\text{H}_2\text{O} \cdot \text{Cl}_2\) crystal
REFERENCES

1. Charsley, E.L. and Warrington, S.B.
Thermal Analysis: Techniques and Application,

2. Daniels, T.C.
Thermal Analysis

3. Ferry, J.D.
Viscoelastic Properties of Polymers

4. Garn, P.D.
Thermoanalytical Methods of Investigation

5. Haines, P.J. et al.
Thermal Methods of Analysis: Principles, Applications and
Problems, Blackie Academic and Professional, England,

6. Hatakeyama, T. and Quinn, F.X.
Thermal Analysis: Fundamentals and Applications to Polymer

Differential Thermal Analysis
   Calorimetry and Thermal Analysis of Polymers

   Experimental Thermodynamics, 1 (Calorimetry of Non-Reacting Systems), UIPAC

10. Milhail, R.S. and Robens, E.
    Microstructure and Thermal Analysis of Solid Surfaces

11. Nielsen, L.E.
    Mechanical Properties of Polymers

12. Nielsen, L.E.
    Mechanical Properties of Polyers and Composites

    Hyphenated Techniques in Polymer Characterization:
    Thermal-Spectroscopic and Other Methods

    Experimental Thermochemistry I
   Special Issue Journal of Thermal Analysis: ‘Thermodynamic Applications in Materials


17. Skinner, ed.
   Experimental Thermochemistry II


21. Definition of k value from Plastics New Zealand


23. Walter, M.
   Extrusion Dies for Plastics and Rubber, 2nd Ed.
24. Einstein, A.
   Plancksche Theorie der Strahlung und die Theorie der Spezifischen Wärme
   Ann. Der Physik, 22, 180 (1907).
   Berichtigung zu meiner Arbeit
   Die Plancksche Theorie der Strahlung etc., 22, 800 (1907)

25. Debye, P.
   Zur Theorie der spezifischen Wärme
   Ann. Der Physik, 39, 789 (1912).

   Phys. Zeitschr., 13, 297 (1912); 14, 15 (1913)

27. Blackman, M.
   Contributions to the Theory of the Specific Heat of Crystals. I.
   Lattice Theory and Continuum Theory
   On the Vibrational Spectrum of Cubical Lattices and Its Application to the Specific Heat of Crystals
   On the Existence of Pseudo-T3 Regions in the Specific Heat Curve of a Crystal
   Contributions to the Theory of Specific Heat. On the Calculation of the Specific Heat of Crystals from Elastic Data
   On the Vibrational Spectrum of a Three Dimensional Lattice
Some Properties of the Vibrational Spectrum of a Lattice, Math

28. Rosenberg, H.M.
Low Temperature Solid State Physics

29. Kittel, C.J.
Ultrasonic Propagation in Liquids. II. Theoretical Study of the Free Volume Model of the Liquid State

30. Kittel, C.J.
Interpretation of the Thermal Conductivity of Glasses

31. Klemens, P.G.

32. Chan, G.K. and Jones, R.E.

33. Pomeranchuk, I.
Thermal conductivity of the paramagnetic dielectrics at low temperatures
J. Phys.(USSR) 4, 357 (1941).
34. Zeller, R.C. and Pohl, R.O.
Thermal Conductivity and Specific Heat of Non-crystalline Solids

35. Love, W.F.
Low-Temperature Thermal Brillouin Scattering in Fused Silica and Borosilicate Glass

36. Zaitlin, M.P. and Anderson, M.C.
Phonon thermal transport in noncrystalline materials

Boundary scattering of phonons in noncrystalline materials