3
Experimental Details

This chapter provides a review about the different experimental techniques used to measure structural, micro-structural and thermophysical properties of phase change materials. Furthermore, it also includes enthalpy versus temperature measurements of PCMs utilizing thermal response measurements of PCM and reference sample.

The details of structural, microstructural and vibrational (Raman and Fourier Transform Infrared spectroscopy) characterization techniques are explained in section 3.1. Further, the details about characterization techniques for thermophysical properties such as melting point, latent heat of fusion, degree of supercooling, enthalpy as a function of temperature, and thermal conductivity are described in section 3.2.

3.1 STRUCTURAL AND MICRO STRUCTURAL CHARACTERIZATION TECHNIQUES

Investigation of structural, microstructural and vibrational properties of materials is necessary to develop new PCMs with desired structural and microstructural properties required for different applications. Various characterization techniques include Powder X-ray diffraction (pXRD), scanning electron microscopy (SEM), Raman and Fourier transform infrared (FTIR) vibrational spectrophotometer, are used to characterize above mentioned properties of PCMs. The fundamental principle of these characterization techniques and brief details about the respective instrument used to characterize PCMs are deliberated in the subsequent sections.

3.1.1 X-ray Diffraction (XRD)

X-ray diffraction technique is a powerful technique to recognize the crystallinity and associated crystal phases of the materials. The X-rays are produced through collision of highly accelerated electrons on metal target. The velocity of electrons gets reduced in the metal target and the continuous X-rays are generated. Some high energy electrons collide to the innermost electrons of metal and remove subsequently from metal atom, producing characteristic X-rays. The generated characteristic X-rays are used for XRD experiments to analyze the crystal structure and related information. For example, the inter planer spacing can be extracted using Bragg's diffraction law (2d $\sin\theta$= n λ).

We used Bruker D8 Advance Powder X-ray diffractometer for structural analysis of materials. The actual photograph of instrument is shown in Figure 3.1. The structural properties of graphite materials, sodium acetate trihydrate (SAT) and SAT-EG (ethylene glycol) composite samples are carried out using X-ray diffractometer equipped with copper Kα radiation ((λ= 1.5406Å). The XRD measurements are recorded in the range of 10 to 40° with step size 0.02^o s^{-1}.
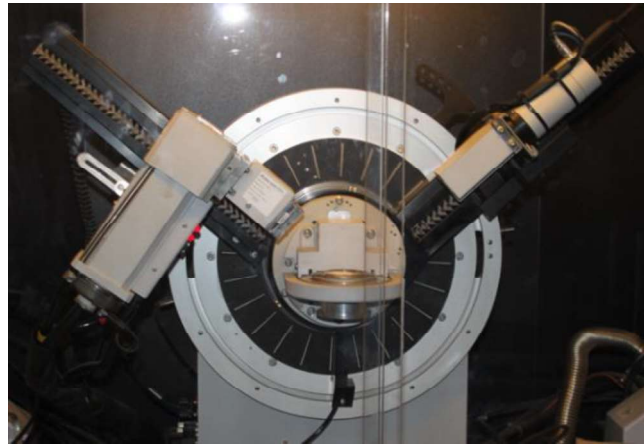
Figure 3.1 : D8 advance powder X-ray diffractometer installed at IIT Jodhpur

Further details about parameters used for collection of X-ray diffraction data on materials under investigation are described in results and discussion segments of different chapters.

3.1.2 Scanning Electron Microscope (SEM)

Scanning electron microscope (SEM) is used to analyze the micro structure, more specifically the structure of crystallites, crystallite surfaces, through scanning the material surfaces. The schematic structure of SEM is shown in Figure 3.2(a). SEM consists of electron gun, electromagnetic lenses and apertures for manipulating the electron beam before falling on the sample. The electromagnetic lenses are used to form collimated electron beam. The electron beam is focused as a nanometer diameter probe using objective lenses. Further, electromagnetic coils are used to control the electron beam deflection for scanning system. Apertures are mostly used to limit the divergence of electron beam.

It is important to control the operating parameters to acquire the preferred depth of field (DoF) and resolution for capturing better SEM images. The aperture size and working distance strongly affects the DoF. The image resolution is manipulated using two operating variables: (i) the electron gun's acceleration voltage and (ii) probe current. These parameters are important to achieve the higher resolution and required to be adjusted properly to obtain better SEM images.

We used Carl Zeiss SEM EVO 18 special edition to investigate the crystallite structure, surface morphologies of natural graphite flakes (NGF), graphite intercalation compounds (GIC)/expandable graphite, exfoliated graphite (ExG), PCM-ExG composites, SAT and SAT-EG composites. Figure 3.2(b) displays the scanning electron microscope (Carl Zeiss) system installed at IIT Jodhpur.
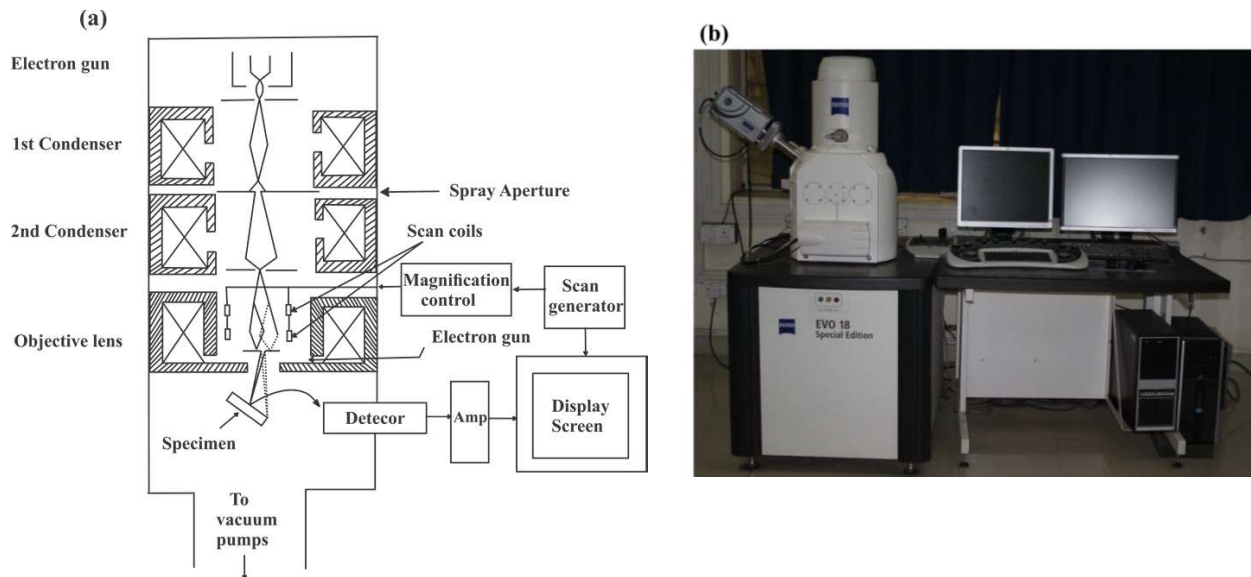
Figure 3.2 : (a) Schematic of a SEM (Source: Leng, 2013). (b) actual photograph of scanning electron microscope system (Carl Zeiss) combined with EDS at IITJ.

3.1.3 Raman Vibrational Spectroscopy (RVS)

RVS is based on inelastic interaction between incident monochromatic electromagnetic radiation and atomic vibrations in molecules and crystals. This is used to analyze the vibrational spectroscopic features associated with molecules and crystals. The spectral range of vibrational energy levels lies in infrared (~ 10^{-7} m) region. Vibrational spectroscopy identifies the molecular vibrational energy levels either by absorption and/or by inelastic scattering of the incident light through a molecule.

A monochromatic radiation, falling on the material, will be scattered both elastically and inelastically after interaction. Elastically scattered radiation consists of the identical frequency as that of the incident one, whereas, the inelastically scattered radiation consists of frequencies different than that of the incident one. There are two types of inelastic scattering: (i) the energy of scattered light is more than that of incident light and the process is called anti-Stokes process, and (ii) the energy of scattered light is less than that of incident light and the process is called Stokes process. The probability of anti-Stokes process is much lower than Stokes process, and that's why Raman vibrational spectrums are recorded in Stokes mode. Moreover, the recorded intensity as a function of change in frequency or wavenumber, is called Raman spectrum.

Molecules/crystals are made of atoms, which vibrate around their equilibrium positions. The vibrational frequencies depend on molecules/crystals atomic bonding, surrounding environment and relative crystallographic positions. The vibrational modes are usually defined in terms of normal modes of the system, depending on the total degrees of freedom, available for the system. Among these vibrational modes, only modes showing change in polarizability are Raman active and are observed in Raman vibrational spectroscopic measurements. Figure 3.3 (a) illustrates the optical arrangement of a Raman vibrational spectrophotometer. A monochromatic light (mostly laser light) is focused on a sample surface using the optical microscope. The Raman scattered signals are the inelastically scattered radiations after incident light – matter interaction.
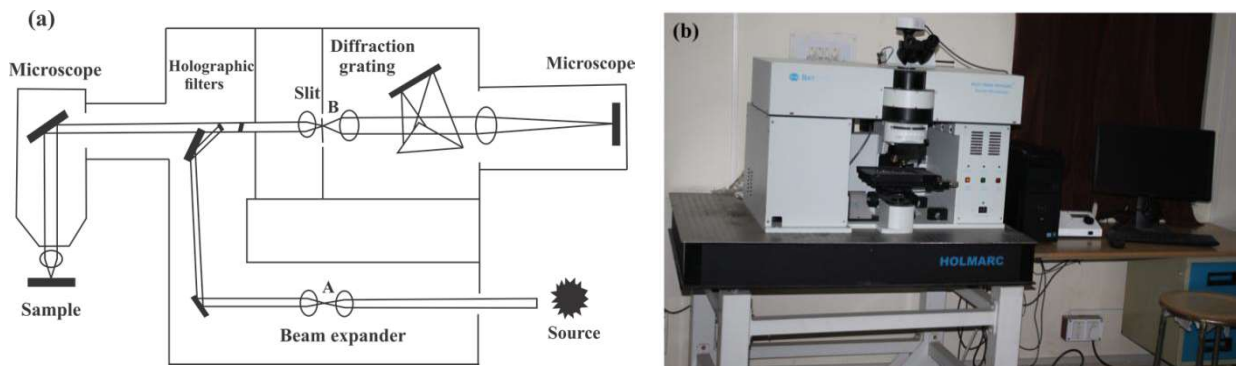
Figure 3.3 : (a) Schematic of optical diagram of Raman microscope (Source: Leng, 2013), (b) Nomadic Raman microscope in our lab used to measure the vibrational properties of selective absorber materials in this study

The Raman vibrational signatures are too weak against the Rayleigh scattered signals. A holographic filter is used to block the Rayleigh scattered light and allow the only Raman scattered signals. The wavelength dispersion of Raman scattering light is selected by a diffraction grating system before recorded at the detector, Figure 3.3(a).

Nomadic™ Raman Microscope (Bay Spec, USA make) is used to analyze the vibrational properties of graphite samples, used for thermal conductivity enhancement of PCMs for the thesis work. Figure 3.3(b) shows the Nomadic Raman microscope at IIT Jodhpur, used to measure the vibrational properties for the presented work. It is equipped with multiple excitation sources (355 nm, 532 nm, and 785 nm), for Raman vibrational spectroscopy experiments, depending on the system of interest. In the present study, 532 nm green monochromatic incident light source is used. The system also consists of dedicated spectrographs and optimized detectors for individual wavelength source to ensure optical spectral coverage, resolution, and sensitivity. It is also featured with integrated laser control and motorized ND filters for attenuating laser power. A fully functional Olympus microscope is integrated with motorized stage providing a 3"x 2" platform for transmittance and reflectance mode operation. Moreover, a charged coupled device (CCD) camera is equipped on the top of the microscope for capturing bright field image.

3.1.4 Fourier Transform Infrared Spectrophotometer

The Fourier Transform infrared (FTIR) spectrophotometer works in the infrared electromagnetic wavelength region from 2.5 to 25 μm. This wavelength range is essential to understand the optical and thermal properties of materials optical/thermal properties and may be used as feedback to develop new materials as per preferred physical properties.

The FTIR has widely been used for vibrational spectroscopic measurements. The vibrational modes of materials under investigations are identified using Bruker vertex 70v Fourier Transform Infrared (FT-IR) Spectroscopy system in the wave number range of 4000-400 cm^{-1}. The actual photograph of FTIR is shown in Figure 3.4. This spectrometer comprises a room temperature Deuterated L-alanine doped Triglycine sulphate (DLaTGS) detector. The resolution of FTIR spectrophotometer is ~ 0.4 cm^{-1}. This consists of an entirely evacuable optical bench to eradicate the remaining environmental background residuals such as moistures, and gases etc. in the course of the experiments.

Figure 3.4 : Bruker FTIR spectrometer vertex 70v in our lab used to collect the reflectance spectra of spectrally selective absorbers

3.2 CALORIMETRIC AND THERMAL CONDUCTIVITY CHARACTERIZATION TECHNIQUES

In conjunction with structural properties, thermophysical properties such as melting point, latent heat of fusion, degree of supercooling, and thermal conductivity of PCMs are essential for possible applications. We used differential scanning calorimeter (DSC), in-house developed temperature-history (T-history) measurement systems and thermal constant analyzer to probe these properties and are discussed in the following sub-sections.

3.2.1 Differential Scanning Calorimeter (DSC)

DSC is widely used to measure thermophysical properties of PCMs such as latent heat of fusion, melting temperature, solidification temperature, glass transition temperature and thermal stability over large number of heating and cooling cycles etc.. It measures the change in heat released/absorbed for the materials because of changes in physical and chemical properties as a function of time or temperature. The enthalpy is estimated by evaluating the area under the curve of peak in DSC thermograph. Here, the sample under investigation and reference sample are symmetrically arranged, as shown schematically in Figure 3.5. There are two types of differential scanning calorimeters, (i) power compensation DSC and (ii) heat flux DSC (Heat flow DSC).

In power compensation DSC, both sample pan and reference material pan are heated with two different heaters situated underneath, Figure 3.5(a). The temperature difference between sample and reference is maintained zero. The complete assembly is positioned inside a furnace to maintain the heat losses very low from both sides [Demirel, Y., and Paksoy, 1993; Klancnik *et al.* 2010].
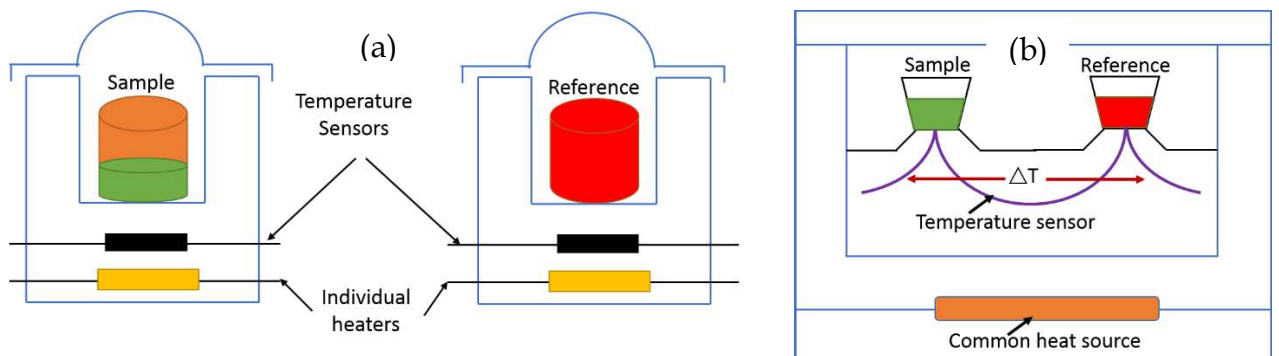

Figure 3.5 : Schematic structure of (a) power compensation DSC, (b) heat flux DSC (Source: *Hone et al.,* 2003)

In a heat flux DSC, both sample under investigation and reference holders are symmetrically arranged and connected by a heat conducting path in the furnace. Two individual thermocouples are situated underneath the sample and reference holders to measure temperature difference among the reference and sample [Demirel, Y., and Paksoy, 1993; Klancnik et al., 2010]. The schematic structure of heat flux DSC is shown in Figure 3.5(b).
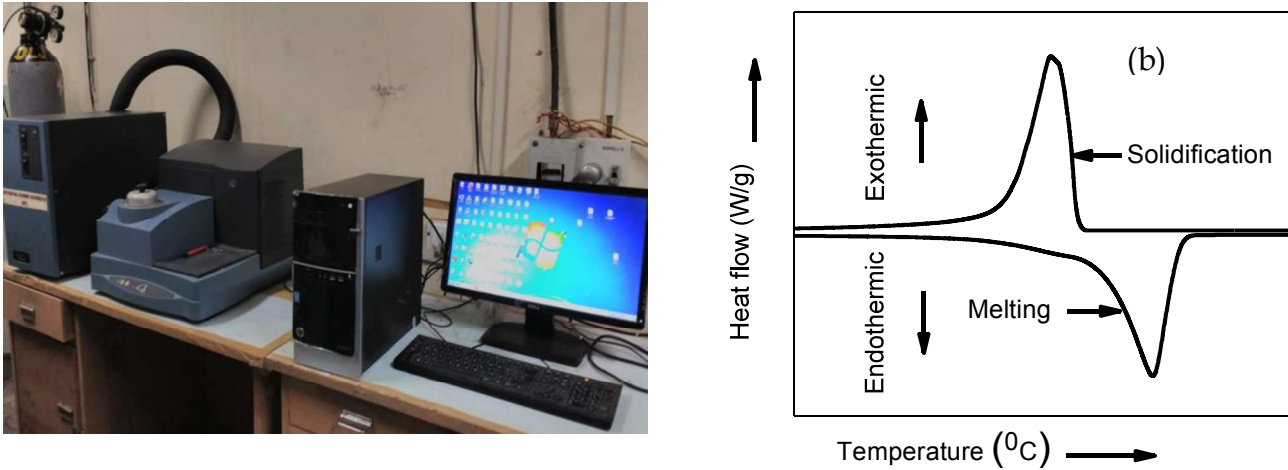

Figure 3.6 : (a) Actual photograph of DSC Q10 (TA Instruments), and (b) DSC thermograph explaining melting and solidification process

When sample under investigation undergoes any physical or chemical changes such as melting, vaporization, solidification, endothermic or exothermic reactions etc., it absorbs or releases the corresponding heat. The sample under investigation and reference samples are kept at same temperature before starting the measurements. The heating and cooling rates can be selected from 0.1 to 100 K min^{-1}. The materials to be investigated are weighed (few mg) and hermetically sealed in Al pan. An identical empty crimped Al pan is used as a reference sample to nullify the effect of Al pan in the measurements. The measurements are carried out under continuous purging of inert gas (such as N_2). The DSC is calibrated using indium as a calibrating sample for enthalpy and temperatures before carrying out measurements on the samples used in the present work. We used DSC, model Q10 (TA Instruments, USA make, Figure 3.6(a)) to measure thermophysical properties of PCMs. The schematic of DSC thermograph showing both melting and solidification phase changes is shown in Figure 3.6(b)

3.2.2 Temperature History (T-history) Measuring Setup

T-history method works on the principle of comparing change in temperature of a reference and a test sample substance under identical environmental conditions. The reference and sample substances are exposed to high temperature to ensure the complete melting of samples under identical ambient conditions, and the temperature versus time data are recorded for both reference and test samples. The schematic of a T-history measurement setup and the respective temperature profiles for the reference, test sample and ambient with time are shown in Figure 3.7. The recorded heating and cooling profile of reference and test sample are used to derive the thermophysical properties of PCM such as enthalpy as a function of temperature, specific heat in solid and liquid phases, supercooling, melting and solidification temperature, available enthalpy at different supercooling temperatures, enthalpy loss during supercooling etc. This method works on two key

assumptions: (i) the temperature distribution in the samples is considered uniform throughout; (ii) the heat transfer coefficient for a specified temperature change among each sample and its surroundings is assumed as identical. The lump capacitance method ($Bi = h \cdot L_c/k < 0.1$) is used under such assumptions, where Bi is Biot number, h is heat transfer coefficient, L_c is characteristic length of test tube and k is thermal conductivity of the material [Goose, 1986].
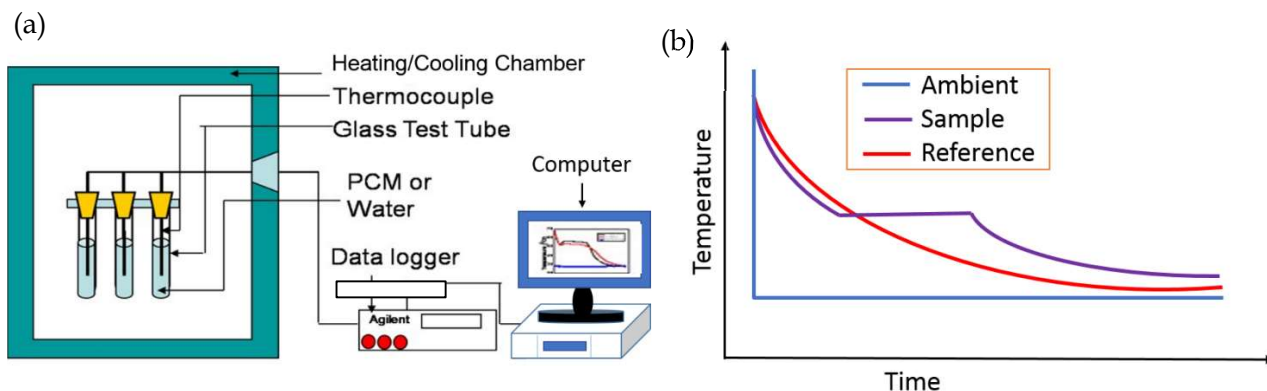

Figure 3.7 : (a) Schematic representation of T-history set up and (b) temperature profile for sample (violet), reference (red) and environment (blue) for a T-history measurements (Source: Kumar et al., 2016)

The T-history method was initially proposed by Yinping [Yinping, 1999] using a simple heating and cooling experimental setup. He used water as a reference sample for T- history measurements. PCMs in liquid state in conjunction with water in glass test tubes are subjected to free cooling in a relatively colder environment (below PCMs solidification temperature) to record the change in temperature as a function of time. Yinping assumed the constant heat transfer coefficient for the investigated temperature and time range and the respective thermophysical properties of PCMs are derived.

Yinping method is suitable for materials exhibiting well defined phase transformation zones such as, pure and eutectics. However, Yinping's model is not sufficient to derive the enthalpy versus temperature information. In addition, the importance of enthalpy associated with phase change is not defined clearly for well-behaved solid and liquid phase boundaries. Therefore, Yinping's T-history model was further improved by considering change in temperature over small time intervals to derive enthalpy as a function of temperature [Marin *et al.*, 2003]. Marin method provides precise results as compared to Yinping's approach with the same temperature versus time measurements.

This method is useful in characterizing massive samples against DSC, where only few milligram material is used for measurements. A detailed comparison for DSC and T-history measurements are summarized in Table 3.1, showing the respective advantages and disadvantages. Considering the usefulness of T-history method for the present work, we designed and developed an in-house T-history measurement setup and details are discussed in Chapter 4.

Table 3.1: Advantage and disadvantages of DSC and T-history methods for PCMs (Yinping, 1999; Marin et al., 2003; Hong et al., 2003 & 2004; Lazaro et al., 2006; Sandnes and, Rekstad, 2006; Gunther et al., 2009; Cabeza et al., 2014)

Method	Advantages	Disadvantages
DSC	❖ High accuracy ❖ Highly controlled and accurate ambient conditions ❖ Standard instruments available in market ❖ Less temperature gradients inside sample	❖ Very small sample used (few mg) ❖ Specific heat c_P can't be measured in phase change region ❖ Onset melting and solidification temperature depends on heating and cooling rates ❖ Less suitable to investigate volume dependent properties such as supercooling and phase separation ❖ Numerous samples can't characterized simultaneously ❖ Can't measure enthalpy lost in initial supercooling ❖ User requires to understand complex measuring procedures ❖ Costly ❖ High maintenance cost
T-history	❖ Large sample size (10-50 g) ❖ Numerous samples can be characterized simultaneously ❖ More practical values for volume dependent properties such as supercooling and phase separations ❖ Measurement of rise in temperature while solidification ❖ Enthalpy at different supercooling temperarue ❖ Measurement of enthalpy lost in initial supercooling ❖ Provides information about useful temperature range for practical applications ❖ Very simple economic and reliable ❖ Easy to maintain	❖ Poor reproducible results ❖ less controlled ambient condition ❖ comparatively large temperature gradient inside sample ❖ No standard instrument available commercially ❖ Less accurate for pristine materials compared to DSC

3.2.3 Thermal Constant Analyzer

The knowledge of PCMs thermal conductivity is required to design an efficient latent heat thermal energy storage systems (LHTESS) for desired applications. We used TPS 2500S thermal constant analyzer make Hot Disk AB, Sweden system to investigate thermal conductivity of pristine and composite material systems used in the present work. The schematic structure and actual photograph of system are shown in Figure 3.8.
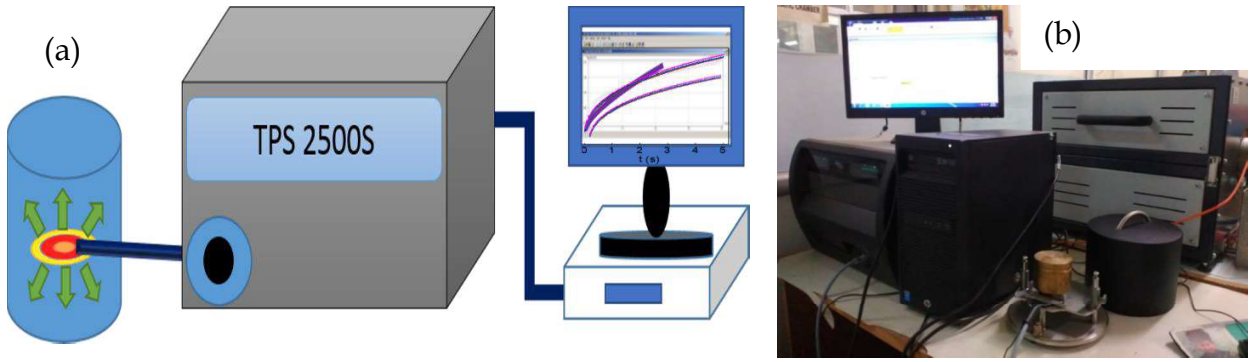
Figure 3.8 : (a) Schematic structure and (b) actual photograph of TPS 2500S thermal constant analyzer

The instrument is based on transient plane source (TPS) technique, where average change in temperature at plane sensor surface is measured as a function of time [Gustafsson, 1991; Gustavsson *et al.*, 1994; He, 2005; Gustafsson, 2014]. The sensor consists of a very thin Ni metal double spiral structures, embedded between thin Kapton polyimide insulating layers to provide the mechanical strength and electrical insulation for conducting samples. An electrical current is passed through the sensor, causing the resistive heating to the sample. The same sensor is used for resistive heating the sample and measuring temperature simultaneously. The rate of heat propagation in the sample relies on its thermal conductivity, suggesting the selection of input power and total measuring time interval are important input parameters for such measurements. Considering such constraints, the input power and the total time interval are selected carefully for both liquid and solid phase change materials. The change in temperature as a function of time is recorded with small time intervals and used to determine thermal conductivity of materials.

The time intervals used for temperature difference measurements are used to calculate the dimensionless characteristic time function $f(\tau)$ [Gustafsson, 1991 and 2014], which is defined as

$$f(\tau) = \frac{1}{(n(n+1))^2} \cdot \int_0^\tau \frac{d\sigma}{\sigma^2} \left[\sum_{l=1}^n l \left\{ \sum_{p=1}^n p.exp\left(\frac{-(l^2+p^2)}{2\sigma^2 n^2}\right).I_0\left(\frac{l\,p}{2\sigma^2 n^2}\right)\right\}\right] \qquad (3.1)$$

Where, n is the number of spirals in sensor, I_0 is modified Bessel function, $\tau = \sqrt{\alpha.t}/r_s = \sqrt{t/\Theta}$ is and characteristic time ratio, $\Theta = r_s^2/\alpha$ is characteristic time of measurement and α is thermal diffusivity of the sample and t is total measurement of time for experiment. The increase in average temperature of sensor, while passing a constant current through the sensor is given by

$$\overline{\Delta T\ (t)} = \frac{P_0}{\pi^{\frac{3}{2}} r_s k} f(\tau) \qquad (3.2)$$

Where, P_0 is the power output at the sensor, r_s is the radius of the sensor, and k is thermal conductivity of sample. This relation suggests that the slope of $\overline{\Delta T\ (t)}$ versus $f(\tau)$ curve can be used to estimate the thermal conductivity of the sample [Gustafsson, 1991, He, 2005; and Gustafsson, 2014].

…