1
Introduction

1.1 MOTIVATION

The extensive depletion of fossil fuels is responsible for global warming, exhaustion of ozone layer, escalating environmental pollution, rapid depletion and increasing cost of fossil fuels [Dhaidan and Khodadadi, 2015, Sharma and Kar, 2015; Alva *et al*. 2017]. The contribution of energy consumption is shown in Figure 1 from different resources. The contribution of fossil fuels (coal, oil & gas) is still dominating and is more than 80% of the total global energy production and supply. About ~ 30 Gt CO_2 is added directly to the environment due to combustion of fossil fuels [IEA2012]. If appropriate measures are not considered, an increase of about 2.6 ºC in global temperature is envisaged at the end of 21st century [IEA, 2012]. This trend will lead to rise in average Earth's temperature ~3.6 ºC after 22nd century [IEA, 2015]. These climatic changes are responsible for natural calamities such as drought, flood, epitomic, air pollution etc. and also affecting the temperature of surrounding atmosphere [Lior, 2008]. The World Health Organization (WHO), data is showing death of ~ 1,60,000 people per year and tends are horrific showing further increase in this number about twice by 2020 [Mekhilef *et al.*, 2011]. Hence, there is urgency without any compromise to make concentrated efforts towards development of new technologies to utilize available conventional and renewable energy resources more intelligently, efficiently and effectively [Totala *et al.*, 2013]. Additionally, the escalating energy demand because of industrial growth and increasing world population, the effective management of energy consumption and minimization of energy wastage are imperative.

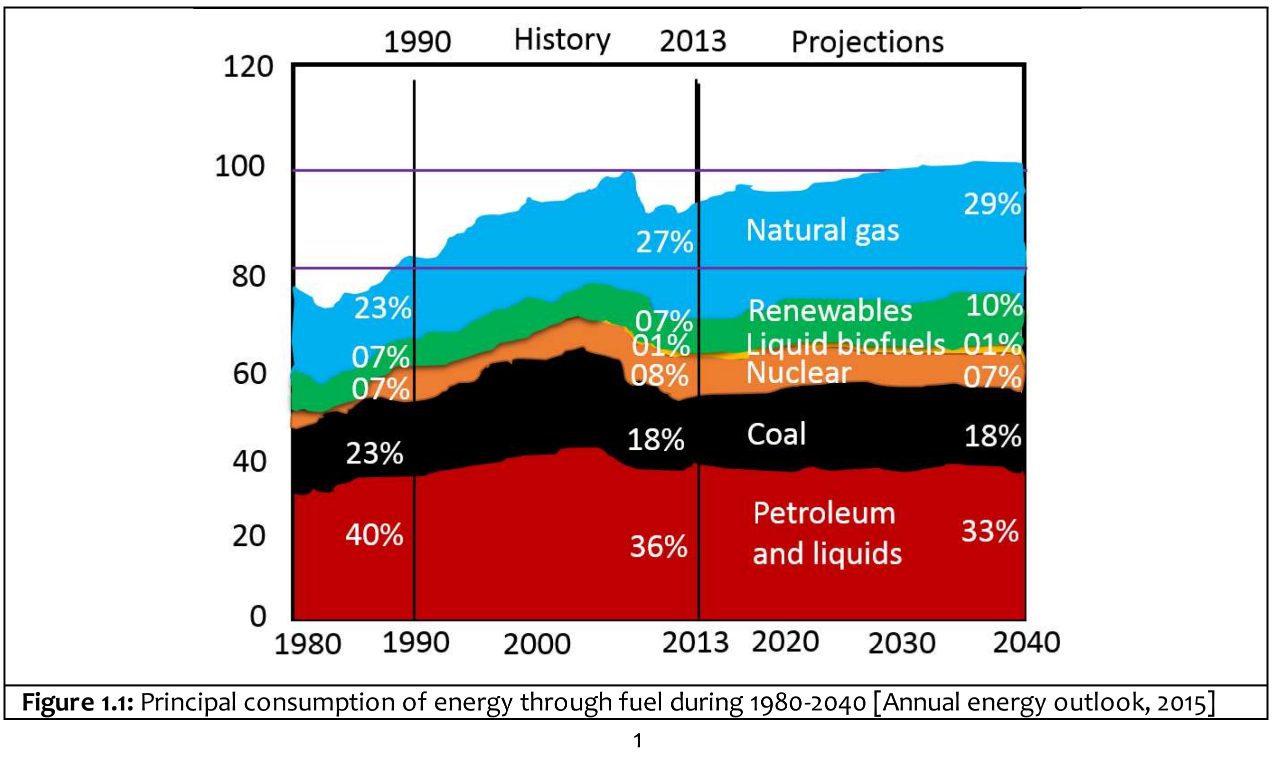

Figure 1.1: Principal consumption of energy through fuel during 1980-2040 [Annual energy outlook, 2015]

The energy from renewable sources such as Sun, wind, biomass, ocean/marine and geothermal is considered as clean energy [Zalba *et al.*, 2003]. These renewable energy resources are of great potential to meet the energy requirement. Solar energy is considered as one of the most abundant renewable energy source and thus, has a potential in providing clean and pollution free energy to the world's energy requirements [Liu *et al.,* 2013]. The Sun is emitting energy at the rate of ~ 3.8×10^{23} kW, and only ~1.8×10^{14} kW solar energy is captured by the earth and the rest is reflected back to the atmosphere [Thirugnanasambandam *et al.*, 2010]. The captured solar energy is about thousands times more than that is required for our current energy requirements. Nevertheless, ~ 0.008 TW of solar energy is being used in different means [Aman *et al.*, 2015]. This demand can be partially compensated by using solar energy either converting directly into electricity or converting into thermal energy to meet direct thermal requirements such as space heating and cooling, water heating, thermal energy based industrial processes, water desalination including electricity generation [Mekhilef *et al.,* 2011].

Further, the amount of thermal energy wasted by industries, residents and commercial sectors is also substantial as compared to the energy produced. For example, more than one-half of the industrial involved energy is wasted in the form of flue gases or other low grade energy [Ettouney *et al.,* 2005]. Hence, recovering this waste energy will be very economical and environment-friendly for probable reuses [Stritih, 2004].The statistics based on the comparison of thermal energies utilized by different sectors revealed that the major portion of total energy produced is consumed in space/building heating and cooling applications. This can toll up to 40% [Tian *et al.*, 2013, and Zhou *et al.*, 2015]. Considering such constraints on energy consumption, renewable sources seem essential for direct thermal energy generation for either their direct usages or integrating with the existing ones, mitigating the dependencies. Such developments are unavoidable as emphasized in Paris protocol 2015, where development of new energy technologies was considered as one of the main agenda to augment the utilization of unconventional energy in saving environment for the next generations [Paris Protocol, 2015].

However, in spite of such tremendous potential for renewable energy, there are some barriers such as irregular availability, large inconsistency/variability in energy intensities because of seasonal variants, disparity between energy demand and supply, nonuniform distribution of energy due to the geographical localities and low conversion factors as compared to the conventional fossil fuels based systems. These challenges associated with renewable energy resources impede the effective and efficient utilization of these renewable energies [Annual energy outlook 2015].

Fortunately, these issues of renewable energy sources can be mitigated by introducing energy storage. The stored energy can be used later or simultaneously to provide regulated uninterrupted energy needs. Further, efficiency of building heating-cooling systems, solar water heaters, solar cookers, concentrated solar power plants etc. can be improved by integrating thermal energy storage systems (TESSs). The thermal energy storage systems can also be used in recovering waste heat, which can be recycled wherever necessary. [Kakac and Yener, 1995; Mehling and Cabeza, 2008; Dincer and Rosen, 2010; Nicole et al., 2015; Alva et al., 2017; Salunkhe and Krishna, 2017]. TESSs may play very important role for concentrated solar power plants to improve their operating hours and overall efficiencies minimizing short term solar insolation fluctuations. Generally, power units are operating at higher capacity and lower efficiency at peak load time to fulfill the instant power requirements. Hence, operating conditions and efficiency of the power producing units can be enhanced by operating for optimal conditions, where load peak can be shifted/managed using TESSs. A TESS stores thermal energy in a medium by absorbing thermal energy from heat transfer fluid passing through TESS. The stored heat is extracted by reversing the process of heat storage.

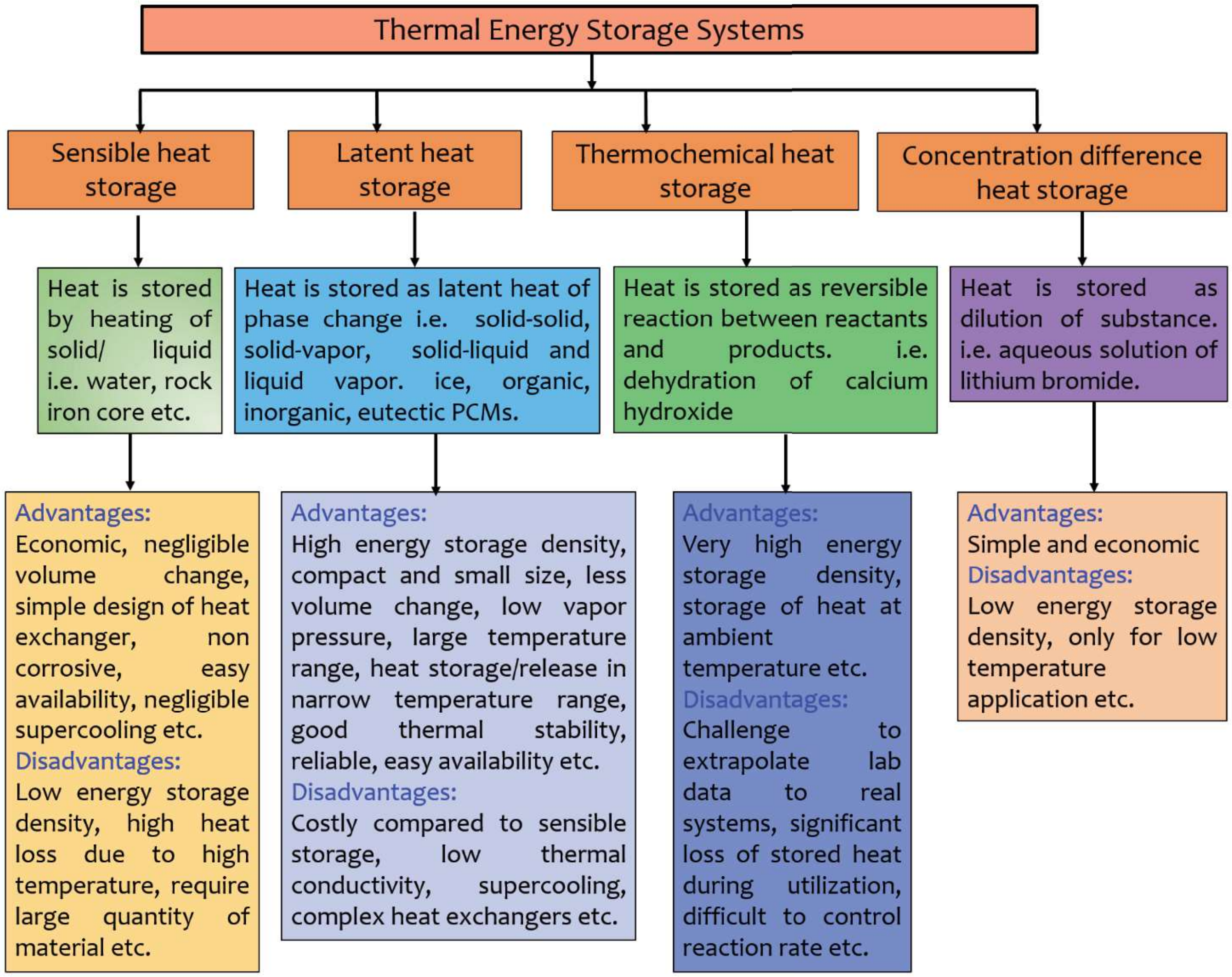

Figure 1.2: Types of thermal energy storage systems

These thermal energy storage systems are categorized into four categories and shown in Figure 1.2. Further details about thermal energy storage systems are as follows:

1.1.1 Sensible Heat Thermal Energy Storage System (SHTESS)

In such storage systems, thermal energy is stored in the form of sensible heat by changing its temperature and do not involve any phase transformation (solid-solid, solid-liquid, and/or liquid-gas). The basic principle of sensible heat storage is explained in Figure1.1

If temperature of material is changed from initial temperature T_1 to final temperature T_2, the total heat stored/released in SHTESS is given as Eq. (1.1)

$$Q = \int_{T_1}^{T_2} m\, C_p dT = m.C_p(T_2 - T_1) \tag{1.1}$$

Here, Q is total heat stored in storage material, m is mas and C_p is heat capacity of sensible heat storage material.

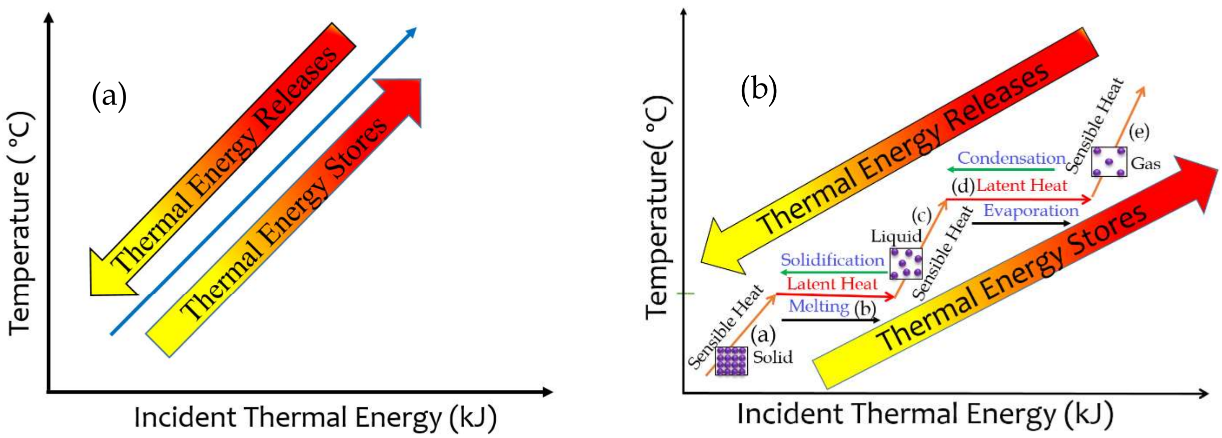

Figure 1.3: Schematic for basic principle of (a) sensible heat storage and (b) latent heat storage

Total energy stored in SHTESS depends on total mass, temperature increase and specific heat capacity of storage material. Materials such as water, rock salts, stones, oils, molten salts etc. are used as storage material for SHTESS. Sensible storage materials are advantageous in the sense that these are economical, non-corrosive, easily available, and negligible volume change while storing heat. However, these systems are less preferred because of their less heat storage density, and large volume requirements for storage systems. SHTESSs are being used for various applications such as solar power systems, switching regenerators, steam accumulators and solar ponds etc. (Wood, 1981, Kauravi et al., 2013)

1.1.2 Latent Heat Thermal Energy Storage System (LHTESS)

LHTESS consists of materials, which exhibit phase transformation (solid-solid, solid-liquid, liquid-gas and vice-versa) and stores heat in the form of latent heat. These materials are known as latent heat storage materials or phase change materials (PCMs). The basic working principle of thermal energy storage in PCMs is explained in Figure 1.3(b). Initially, a system/material acts as sensible heat storage, where temperature is continuously rising, shown as part a of Figure 1.3(b). This is followed by a solid to liquid constant temperature phase transition, storing equivalent latent heat, shown as part b of Figure 1.3(b). Further heating will again exhibit sensible heat storage and temperature of liquid phase will keep on rising (part c of Figure 1.3(b)) till the next liquid to vapor phase transition point). At this point, again the system will absorb equivalent amount of latent heat of fusion, showing a phase transition without rising temperature, shown as part d of Figure 1.3(b). Beyond this phase transition, the temperature of the system will increase further as sensible heat storage, shown as part e of Figure 1.3(b). The complete process is explained in Figure 1.3 (b). LHTESSs are compact in size as compared to that of SHTESSs because of PCMs' high energy storage density as compared to that of sensible storage materials (Sharma et al., 2009; Kauravi et al., 2013). LHTESSs also release/store heat at nearly constant temperature (phase change temperature of PCM). Thermal energy stored in PCMs is given as Eq. (1.2)

$$Q = m\,[c_{p,s}\,(T_m - T_s) + \Delta h + m\,c_{p,l}(T_l - T_m) \quad (1.2)$$

Where, m is mass of thermal energy storing material, Δh is the phase transformation enthalpy, $C_{p,s}$ and $C_{p,l}$ are average specific heats for solid and liquid phases, T_m is the melting point of PCM. T_s and T_l are temperature of solid and liquid phase respectively.

1.1.3 Thermochemical Thermal Energy Storage System: (TCTESS)

This storage system involves the chemical reactions during heat storage or liberation. Thermal energy can be stored by changing reactants into a new chemically stable products and stored heat can be released by reversing the chemical reaction. These thermal storage systems offer benefits against SHTESS and LHTESS in terms of high energy density and lower operating temperatures without any significant losses. One of the chemical systems which has received attention is Eva-Adam concept [Fedders and Hohlein, 1980; Cabeza, 2014] i.e. the conversion of carbon-monoxide and hydrogen into methane and steam, and vice-versa. Numerous chemical reactions are considered for such applications [Bauerle, 1976; Simons, 1976; Mettle *et al.,* 2012]. There are some issues with TCTESS such as difficulty in controlling rate of reaction for solids and gases, thermal energy wastage during storage/transportation [Dickinson and Chermisinoff, 1980, Jonksmanns et al. 2012]. For example, dehydration of calcium-hydroxide comprises about 1590 kJ/kg of thermal energy but effective thermal energy recovery is only ~996 kJ/kg and thus, about 594 kJ/kg thermal energy is lost during condensation of water and as the sensible heat for water and calcium-oxide [Linder *et al.*, 2014].

1.1.4 Concentration Difference Energy Storage System: (CDESS)

In such systems, thermal energy is stored by diluting a substance, for example saturated aqueous solution of salts have been found suitable for room heating/cooling and water heating applications [Kauffman and Lorsch; 1976, Cabeza, 2014]. The foremost disadvantage of these storage systems is that these systems can be used only for low temperature applications because of exclusive usage of aqueous solutions.

Among these, solid to liquid phase transition based phase change materials are considered for design and development of thermal energy storage systems because of their relatively higher energy density, smaller volume and thermal stability. Considering the same, the present work aimed to explore solid to liquid phase transition related phase change materials for solar thermal applications.

1.2 OBJECTIVES

The thesis work has focused on the design and development of low and high temperature phase change material (PCMs) and PCM based devices for thermal energy storage applications. The salient objectives covered in this thesis are:

- Design and development of new organic eutectic PCMs with suitable melting temperatures and their experimental validation for low temperature solar thermal applications
- Development of sodium acetate-trihydrate and ethylene glycol composite PCMs with enhanced thermophysical properties for thermal comfort and therapeutic applications
- Design, development and thermal performance evaluation of parabolic dish solar energy concentrator for charging of SAT based heat packs in extreme conditions such as high altitude area
- Design and development of temperature–history experimental setup to measure thermophysical properties of PCMs
- Synthesis of high temperature eutectic PCMs at room temperature
- Process optimization for exfoliation of natural graphite flakes and development of ExG-PCM composites for thermal conductivity enhancement of low and high temperature PCMs

1.3 THESIS OUTLINE

The thesis layout is summarized in Figure 1.4, explaining the main features for individual chapters.

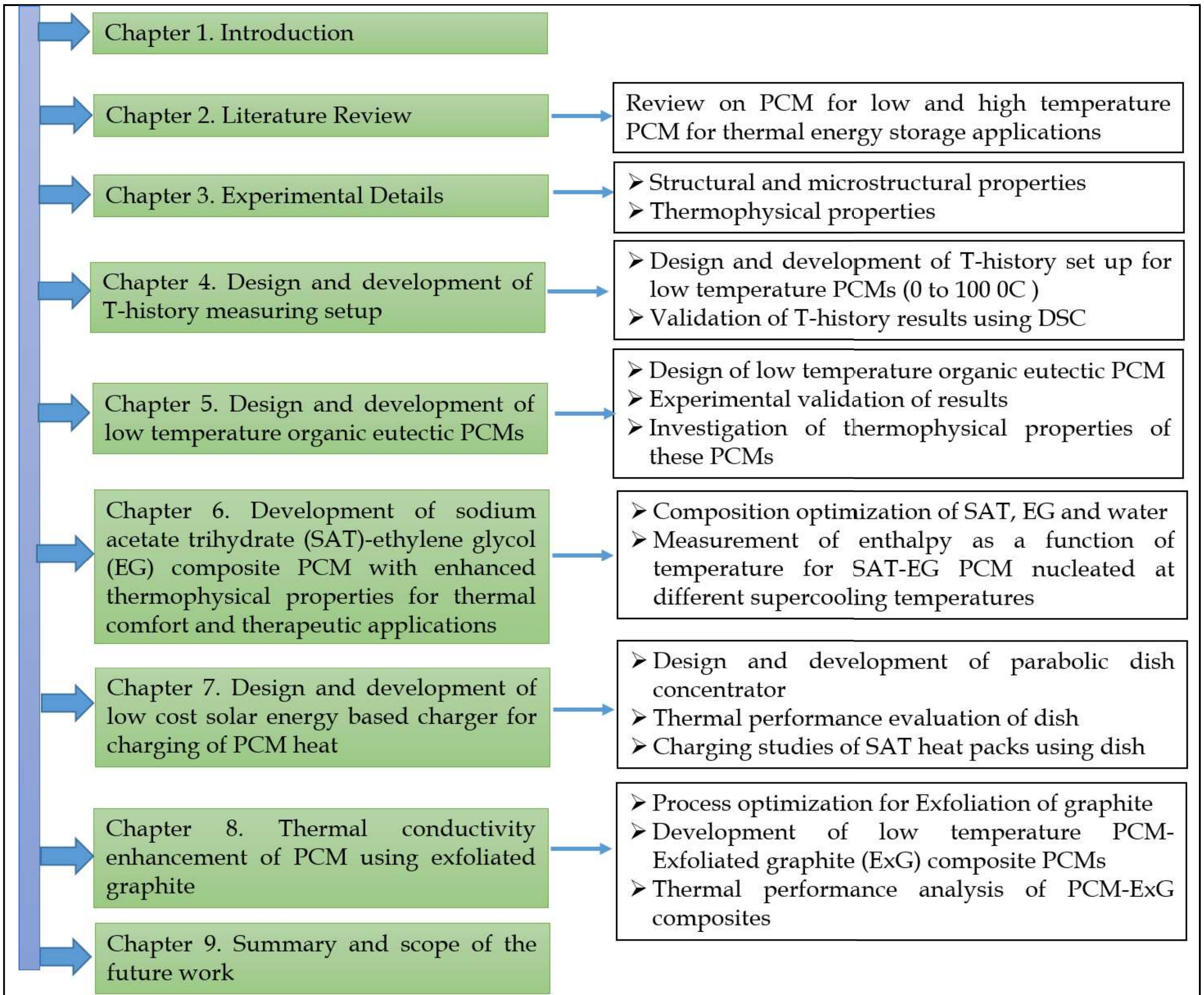

Figure 1.4: Flow chart demonstrating the thesis structure

The **first chapter** presents the wider aspect of present research through describing the importance of thermal energy storage in energy saving and sustainability context. It defines about the alternative ways for thermal energy storage and advantages and disadvantages of these technologies. After that, the objectives of the current research are described.

The **second chapter** provides the general background of PCMs, PCM based latent heat thermal energy storage and a brief review about the previous work done so far on low and high temperature PCMs. It highlights the existing challenges and difficulties associated to phase change materials and their characterizations. The subject matter of the present study is to overcome some of the challenges in the development of phase change materials and their characterization.

In **third chapter,** the experimental techniques used in current research discussed briefly including sample preparations. A detailed description about temperature – history (T-history) method is also provided in this chapter, covering its advantages and disadvantages with conventional t differential scanning calorimetric (DSC) measurement technique.

The **fourth chapter** emphasizes on the designing low temperature organic eutectics phase change materials theoretically and their experimental validation. These organic eutectic PCMs may be used for low temperature solar thermal applications such as building cooling and body cooling applications in extreme hot environments.

In **fifth chapter** the details about development of sodium acetate trihydrate-ethylene glycol composite phase change materials with enhanced thermophysical properties for therapeutic and body warming applications is provided.

The **chapter six** focuses on design and development of T-history measuring test setup for low temperature PCMs. A detailed discussion on T-history measurements of PCMs and determination of thermophysical properties of PCMs using simple T-history data of PCM is provided in this chapter.

In **seventh** chapter, the design and fabrication details are presented for a parabolic dish concentrator for charging/discharging of SAT heat packs under extreme environmental conditions such as high altitude geographical regions. A universal performance curve is presented for a parabolic dish concentrator, which can be used to predict thermal performance of parabolic dish concentrator under different ambient temperature and solar insolations.

The **eighth chapter** summarizes the process of exfoliation of natural graphite flakes and preparation of PCM-ExG composite PCMs realizing enhanced thermal conductivity of PCMs. The comparative studies are presented to analyze the effect of ExG on thermal transport properties for low and high temperature PCMs. It also provides information of preparation of high temperature PCM and PCM-ExG composites at room temperature.

Finally, **chapter nine** summarizes the work carried out and presents the scope for future work in the field of thermal energy storage systems for solar and non-solar applications.

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