

Literature Review

Thermal energy storage (TES) is the most suitable approach to mitigate the energy demand and supply gap including power generation and other related applications. This makes TES the utmost striking component with a great potential for several thermal applications. Furthermore, phase change material (PCM) based latent heat thermal energy storage has become one of the well-known efficient method for thermal energy storage applications. This section will focus on primary advantages and necessities of latent heat thermal energy storage system (LHTESS), types of phase changes in PCMs, essential requirements for selection of PCM, discussion on various low and high temperature PCMs with respective melting and latent heat of fusion reported in literature, associated limitations and issues for deploying PCMs in LHTESS. In conjunction, we will also cover the some of the phase change materials suitable for low and high temperature thermal energy storage applications.

2.1 LATENT HEAT THERMAL ENERGY STORAGE (LHTESS)

The latent heat thermal energy storage system (LHTESS) stores and releases heat in the form of latent heat of the storage material, while changing its phase. The primary advantages of LHTESS are summarized as follows:

- (i) It helps to attain a better and effective usage of stored energy;
- (ii) It improves the performance and reliability of the system via integration of additional renewable energies;
- (iii) It functions almost isothermally at PCM phase change temperature;
- (iv) It helps to reduce capital and operational cost and
- (v) It helps to reduce the environmental pollution causing lesser greenhouse emission.

2.2 NECESSITIES of LATENT HEAT THERMAL ENERGY STORAGE SYSTEM (LHTESS)

LHTESSs are getting attention to address not only the intermittency in power generation but also for distributed solar thermal applications. This will assist in reducing the thermal variability and also provide thermal energy during off Sun hours. This can be achieved by suitable PCM for LHTESS. In order to design an efficient LHTESS several requirements such as thermodynamic, kinetic, chemical and economic requirements of PCM as discussed under section 2.3.2, efficient heat transfer between PCM and heat transfer fluid (HTF), maximum load, operational strategy and integration with other systems should be addressed [Hale *et al.*, 1971; Budhi *et al.*, 1994; Sharma *et al.*, 2009; Dincer and Ronsen, 2010].

2.3 PHASE CHANGE MATERIALS (PCMs)

PCMs can store and release thermal energy in the form of latent heat at nearly constant temperature. When the temperature of heat source increases above the material's phase change temperature, it starts storing thermal energy by changing its phase. The temperature of PCM remains

constant during the phase change process. The stored thermal energy while phase change is called the latent heat for that material. After completing the phase change process, the temperature of material starts increasing, storing energy as sensible heat. The thermal energy storage densities of PCMs are normally 5 - 10 times higher and required storage volume is nearly two times lesser with respect to water [Garg *et al.*, 1985; Hasnain, 1998]. The different classes of PCMs based on their operating temperature and melting enthalpies are summarized in Figure 2.1. This includes water, aqueous salts, gas hydrates, paraffins, fatty acids, salt hydrates and their eutectic mixtures, sugar alcohols, nitrates, hydroxides, chlorides carbonates and fluorides based PCMs, suitable for different applications.

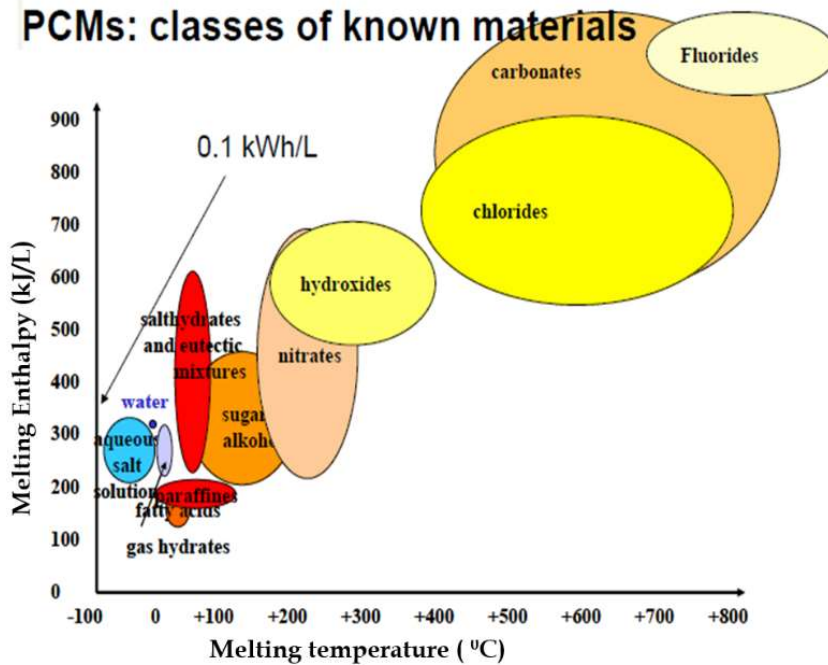


Figure 2.1: Phase change materials explored for thermal energy storage applications (Source: Mehling and Cabeza, 2008)

2.3.1. Types of Phase Transformations in PCMs

There are four types of phase transformations in PCM, (i) solid to solid, (ii) solid to vapor, (iii) liquid to vapor, and (iv) solid to liquid and each of these can be used as PCM for energy storage applications. However, solid to liquid based phase change materials are commonly used for thermal energy storage applications due to their inherent advantages over other phase change based energy storage systems. The brief advantages and disadvantages for each type of phase change systems are summarized in Figure 2.2.

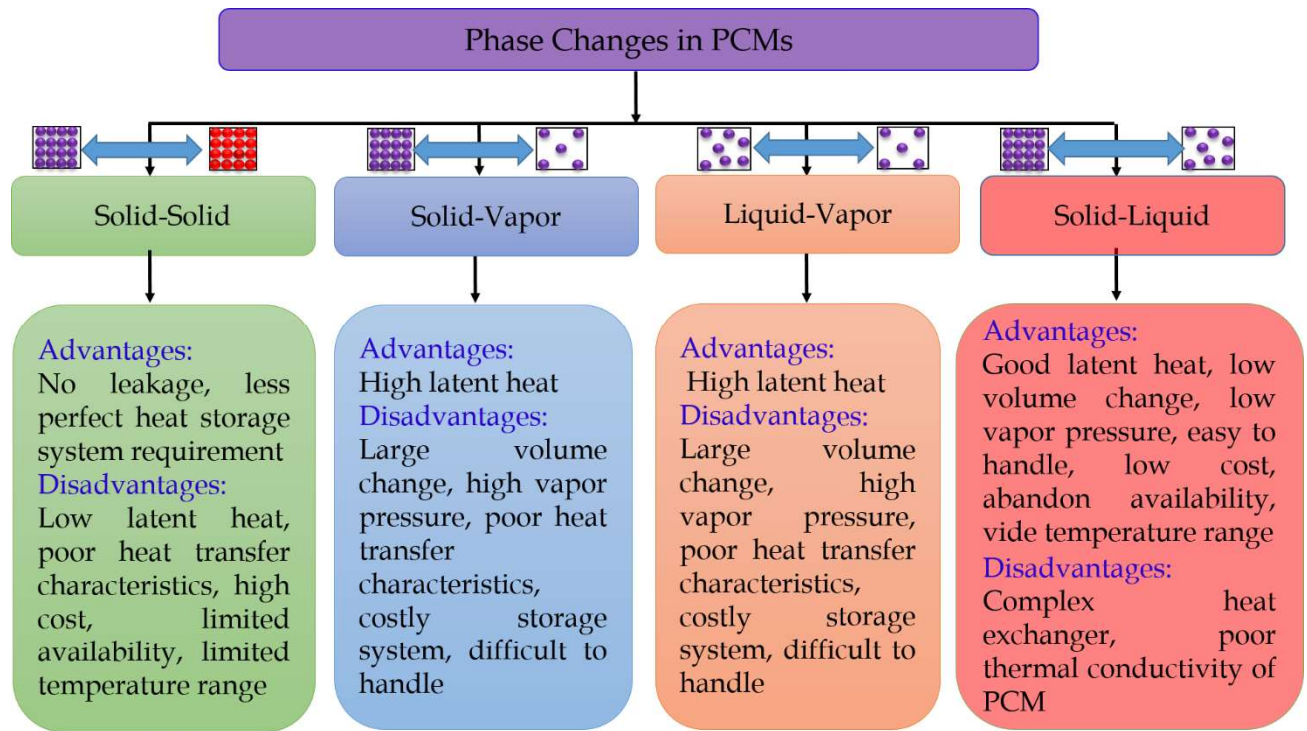


Figure 2.2: Schematic for types of phase changes in PCMs (Mehling and Cabeza, 2008; Sharma et. al, 2009)

Following sections are explaining these about phase changes in PCMs in detail.

2.3.1.1 Solid-Solid Phase Change (SSPC)

The PCM exhibiting SSPC stores heat by changing the molecular structures such as polymers stores heat by changing phase from crystalline solid to amorphous solid. These PCMs have some advantages such as no leakage during changing phase and additional storage vessel is not required for encapsulation. However, low latent heat and high cost of these PCMs are major limitations for using these PCMs for LHTES applications.

2.3.1.2 Solid-Vapor Phase Change (SVPC)

Solid-Liquid phase change systems involve sublimation of material. Thermal energy associated with this transition is very high, yet associated change in volume and poor heat transfer properties and high cost of storage system make this transition, a less common choice for practical applications

2.3.1.3 Liquid-Vapor Phase Change (LVPC)

This phase transformation also has high latent heat of vaporization, but suffers from some drawback such as large change in volume, voluminous storage system, high pressure, poor heat transfer characteristics, and high cost of storage system. The use of such phase changes material is also very limited.

2.3.1.4 Solid-Liquid Phase Change (SLPC)

Latent heat involved in Solid-Liquid phase change process is smaller as compared to that of solid-vapor and liquid-vapor phase transformations, but change in volume is very small (<10) (Sharma *et al.*, 2009; Cabeza, 2014) and rate of heat transfer is better in such systems as compared to that of solid-vapor and liquid-vapor transformations based systems. Hence, the handling of such

phase change materials is relatively easier in conjunction with compact heat exchanger integrations. LHTESSs based on PCMs showing this transformation are economic also. LHTESS based on these PCMs requires an efficient heat exchanger to transfer heat from heat source to PCM and PCM to load and effective utilization of PCM.

2.3.2 Essential Requirements for Selection of PCM

The PCM selection criteria for a LHTESS are summarized in the accompanying flow chart shown in Figure 2.3.

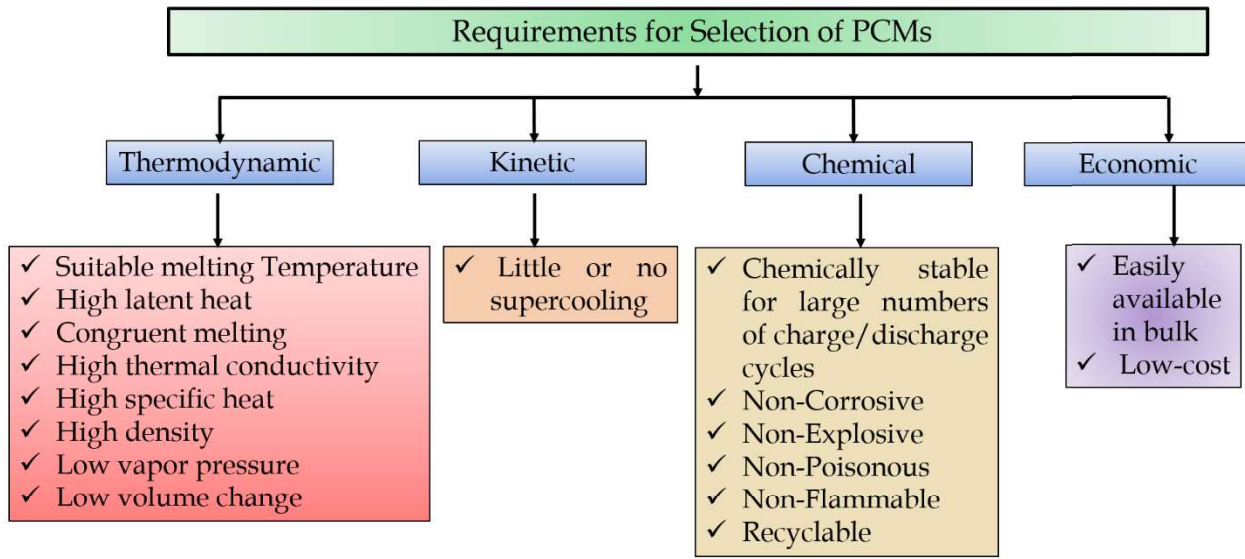


Figure 2.3: Requirements for selection of PCM (Budhi et al., 1994; Dincer and Ronsen, 2010; Hale et al., 1971; Sharma et al., 2009)

The existing PCM materials meet one or the other such requirements and thus there is a need to design and develop PCMs with suitable chemical, kinetic and thermodynamic properties. Following sections are explaining these requirements in detail.

2.3.2.1 Thermodynamic Requirements

2.3.2.1.1 Suitable Melting Temperature

The melting temperature of a material should be in the appropriate working temperature range for storage and release of thermal energy for desired applications.

2.3.2.1.2 High Latent Heat

High latent heat of material is required for high energy storage density. This will minimize the amount of PCM required and may lead to compact LHTESS.

2.3.2.1.3 High Specific Heat

It is advantageous to store additional thermal energy storage with latent heat, e.g. in the form of sensible heat above/below phase transition temperature.

2.3.2.1.4 Congruent Melting

It is essential to maintain same chemical composition of material in solid and liquid phases to avoid segregation due to density differences in solid and liquid phase. Incongruent melting will lead to change in materials' composition and difference in stored/released heat during melting/solidification of PCM as observed in the case of hydrated salts.

2.3.2.1.5 High Density

This will help in storing more thermal energy per unit volume and thus, compact requirements of thermal energy storage system

2.3.2.1.6 High Thermal Conductivity

High thermal conductivity of PCM is required to store and extract heat from PCM efficiently with high heat flux.

2.3.2.1.7 Low Volume and Pressure Change

It is required to diminish mechanical instability of container storing the PCM and heat exchanger.

2.3.2.2 Kinetic Requirements

2.3.2.2.1 Little or No Supercooling

The solidification of a material below its melting temperature is called supercooling or undercooling as shown in Figure 2.4. Here ΔT represents the degree of supercooling of PCM and PCM remains in metastable supercooled liquid state below its solidification temperature. For most of the applications, supercooling in PCM is a major problem, especially in hydrated salts, leading segregation of material and reduced thermal energy of PCM and hampering the storage system performance. Even 1-2 °C supercooling may have major effect on the performance of PCM for building applications [Mehling and Cabeza, 2008; Dincer and Ronsen, 2010]. However, for some thermal applications, e.g. heat packs, seasonal energy storage etc. supercooling is beneficial as well [Sandnes and, Rekstad, 2006].

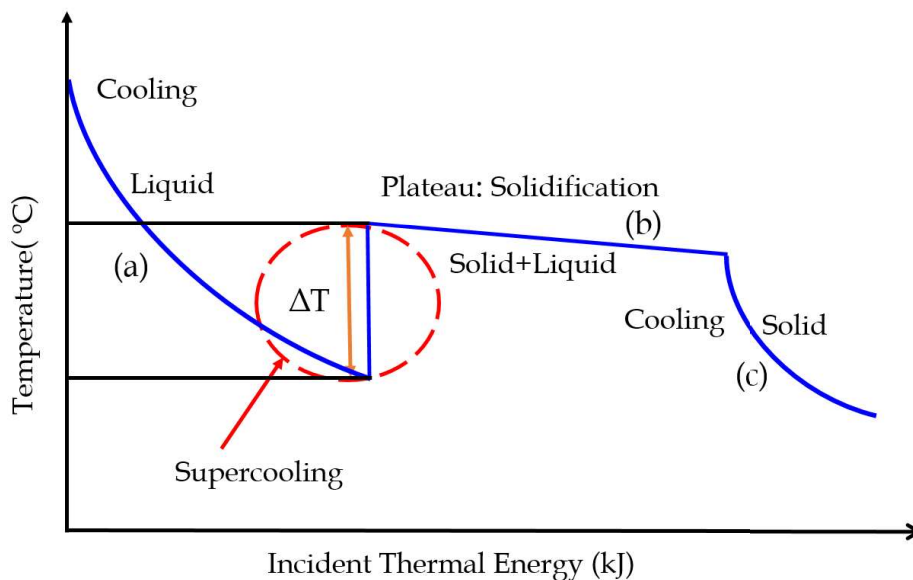


Figure 2.4: Cooling of PCM with Supercooling before starting solidification

2.3.2.3 Chemical Requirements

PCM should be chemically and physically stable under large number of heating and cooling cycles to ensure the extended PCM lifecycles. PCM should also be non-toxic, non-flammable, and non-explosive for environmental and safety considerations. It should be compatible to storage vessel and heat exchanger materials, i.e. non corrosive, for their long lifespan.

2.3.2.4 Economic Requirements

The PCM should be cost effective, easily recyclable with enhanced environmental compatibility for better lifetime cycling assessment. This should be easily available in bulk quantities to compete with other thermal energy storage systems.

2.3.3 Classifications of PCMs

The PCMs are classified into three major categories: (i) organic PCMs, (ii) inorganic PCMs and (iii) eutectic PCMs, as explained in Figure 2.5.

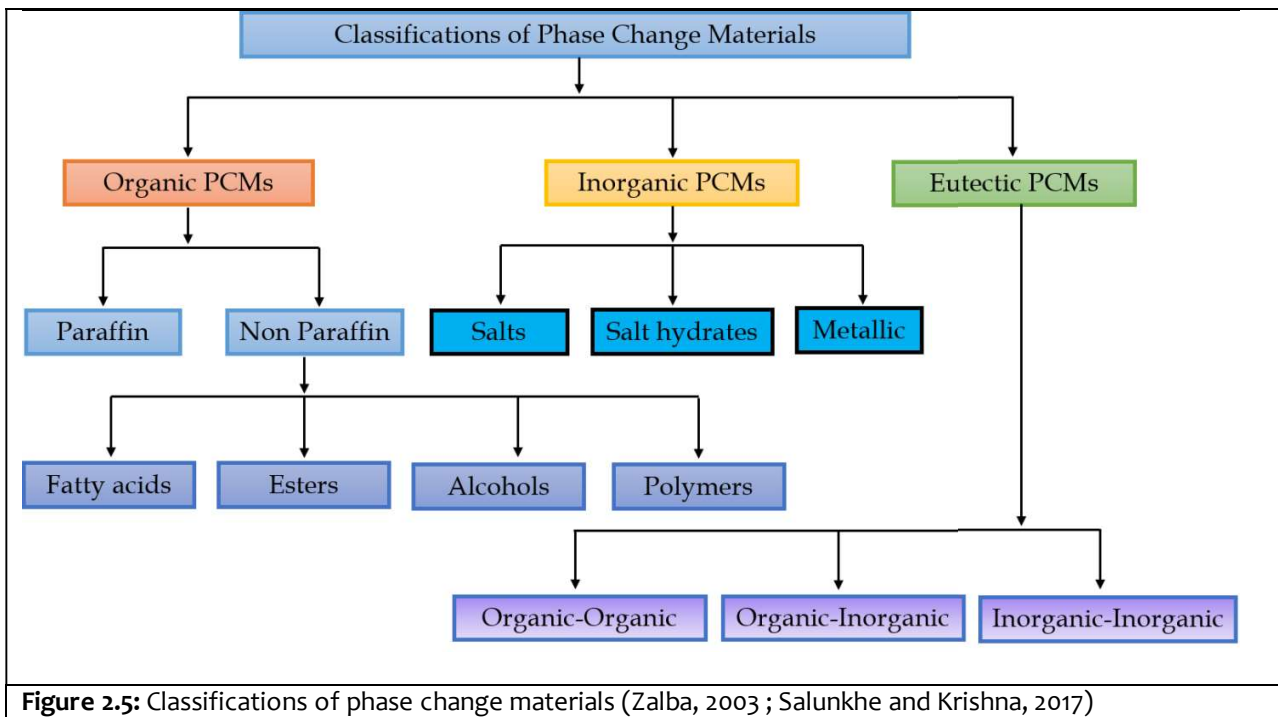


Figure 2.5: Classifications of phase change materials (Zalba, 2003 ; Salunkhe and Krishna, 2017)

These different phase change materials are suitable for different applications based on respective thermophysical properties. The associated advantages and disadvantages for such PCMs are listed in Table 2.1.

Table 2.1: Advantage and disadvantages of organic, inorganic and eutectic PCMs (Farid et al., 2004; White, 2005; Sari & Karaipekli, 2007; Mehling & Cabeza, 2008; Pasupathy et al., 2008; Sharma et al., 2009; Kuznik et al., 2011; Cabeza et al., 2011; Oro et al., 2012)

PCMs	Advantages	Disadvantages
Organic PCMs	<ul style="list-style-type: none"> ❖ Available in wide temperature range ❖ Reasonable latent heat of fusion ❖ Congruent melting ❖ Low supercooling ❖ Thermal stability over large heating and cooling cycles ❖ No segregation ❖ Non hygroscopic ❖ Chemically stable ❖ Non corrosive ❖ Low volumetric change while phase change ❖ Non toxic 	<ul style="list-style-type: none"> ❖ Low thermal conductivity ❖ Low density compared to organic PCMs ❖ Low thermal energy storage density compared to organic PCMs ❖ Flammable ❖ Higher cost compared to organic PCMs
Inorganic PCMs	<ul style="list-style-type: none"> ❖ Available in wide temperature range ❖ High latent heat of fusion ❖ sharp temperature range ❖ High thermal conductivity compared to organic PCMs ❖ High density ❖ High volumetric thermal energy storage capacity ❖ Economic and easily available in bulk quantities ❖ Non flammable ❖ Non toxic 	<ul style="list-style-type: none"> ❖ Incongruent melting in hydrated salts ❖ Segregation ❖ Reduction in latent heat of fusion during melting and solidification cycles ❖ High degree of supercooling ❖ High volumetric change during phase change ❖ Corrosive for metallic containers ❖ Hygroscopic
Eutectic PCMs	<ul style="list-style-type: none"> ❖ Sharp melting temperature ❖ Congruent melting ❖ No segregation ❖ Tuning of melting temperature as per requirements ❖ Reasonable latent heat ❖ Thermal stability over large heating and cooling cycles 	<ul style="list-style-type: none"> ❖ Limited availability of data on thermophysical properties

2.3.4. Low Temperature Phase Change Materials (LTPCMs)

The phase change materials, with melting temperature up to 120 °C are known as LTPCMs. Organic and inorganic salts are mostly considered as LTPCMs. This may include aqueous salts, water, paraffin, fatty acids, fatty esters, hydrated salts, glycols, sugar alcohols etc. The melting temperature and latent heat of fusion of numerous low temperature PCMs are listed in Table 2.2.

Table 2.2: Low temperature phase change materials with corresponding melting point and latent heat of fusion

Type	PCM	Melting Point (°C)	Heat of Fusion (kJ/kg)	References
Organic PCM				
Paraffin	n-dodecane	-10	216	Shabgard et al., 2010
	n-tridecane	-5	160	Shabgard et al., 2010
	n-tetradecane	6	229	Pielichowska, 2014
	n-pentadecane	10	206	Pielichowska, 2014
	n-hexadecane	20	236	Pielichowska, 2014
	n-eicosane	36.6	247	Pielichowska, 2014
Fatty acids	Caprylic acid (CyA)	16	148	Hasnain, 1998; Farid et al., 2004
	Capric acid (CA)	32	152.7	Hasnain, 1998; Farid et al., 2004
	Lauric acid (LA)	42	171	Hasnain, 1998; Pielichowska, 2014
	Myristic acid (MA)	54	190	Pielichowska, 2014
	Palmitic acid (PA)	64	185.4	Hasnain, 1998; Farid et al., 2004
	Stearic acid (SA)	69	209	Hasnain, 1998; Pielichowska, 2014
Esters	Isopropyl palmitate	11	100	Pielichowska, 2014
	Isopropyl stearate	14	142	Pielichowska, 2014
	Propyl palmitate	20	190	Pielichowska, 2014
	Butyl stearate	23	200	Pielichowska, 2014
	Methyl palmitate	27	163	Pielichowska, 2014
	Methyl stearate	39	160.7	Pielichowska, 2014
Glycols	Poly ethylene glycol (PEG)-400	4.2	117.6	Hasnain, 1998
	PEG-600	12.5	129.1	Pielichowska, 2014
	PEG-1000	40	168.6	Pielichowska, 2014
	PEG-10000	65.9	171.6	Pielichowska, 2014
	PEG-20000	67.7	160.2	Pielichowska, 2014
	PEG-100000	67	175.8	Pielichowska, 2014
Alcohols	Xylton	93	280	Pielichowska, 2014
	Sorbitol	97	110	Pielichowska, 2014
	Erythritol	117	344	Pielichowska, 2014
Inorganic PCM				
Salt Hydrates	LiClO ₃ ·3H ₂ O	8	253	Naumann and Emons, 1989
	Mn(NO ₃) ₂ ·6H ₂ O	18.5-19	231	Paris et al., 1993
	CaCl ₂ ·6H ₂ O	29	190.8	Farid et al., 2004
	Na ₂ SO ₄ ·10H ₂ O	32	251	Hasnain, 1998
	Na ₂ CO ₃ ·10H ₂ O	36	247	Hasnain, 1998
	Na ₂ HPO ₄ ·12H ₂ O	36	280	Hasnain, 1998; Pielichowska and Pielichowski, 2014
	Ba(OH) ₂ ·8H ₂ O	78	265.7	Farid et al., 2004
	Mg(NO ₃) ₂ ·6H ₂ O	89	162.8	Farid et al., 2004
	MgCl ₂ ·6H ₂ O	117	168.6	Farid et al., 2004
Eutectic PCM				
	LA-CA (80:20 wt%)	21.4	177	Yan, 2011
	CA-PA (75.2:24.8 wt%)	22.1	153	Kauranen et. al., 1991
	LA-MA (66:34 wt%)	34	167	Sari, 2005
	LA-PA (69:31 wt%)	35.2	166.3	Tuncbilek et al., 2005

Organic	LA-SA (75.5:24.5 wt%)	37	182.7	Kauranen et. al., 1991
	MA-PA (58:42 wt%)	42.6	169.7	Sari, 2003(a)
	MA-SA (64:36)	44	182	Sari, 2003(a)
	PA-SA (64.2:35.8 wt%)	52.3	181.7	Baran and Sari, 2003
	Urea/Acetamide (38:62 wt%)	53	224	Zalba, 2003
	Stearic acid/Acetamide (83:17 wt%)	65	213	Zalba, 2003
Inorganic	Na ₂ SO ₄ /H ₂ O/NaCl/NH ₄ Cl (32.5:41.4:6.66:6.16 wt%)	13	146	Hasnain, 1998
	CaCl ₂ .6H ₂ O/CaBr ₂ .6H ₂ O (45:55 wt%)	14.7	140	Hasnain, 1998
	Na ₂ SO ₄ .10H ₂ O/NaCl	18	-	Pielichowska and Pielichowski, 2014
	CaCl ₂ .6H ₂ O/ MgCl ₂ .6H ₂ O (66.6:33.3wt%)	25	127	Pielichowska and Pielichowski, 2014
	CaCl ₂ /NaCl/KCl/H ₂ O (48:4.3:0.4:47.3)	27	188	Pielichowska and Pielichowski, 2014
	CH ₃ COONa.3H ₂ O/NH ₂ CONH ₂ (40:60 wt%)	30	200.5	Pielichowska and Pielichowski, 2014
	Mg(NO ₃) ₂ .6H ₂ O/NH ₄ NO ₃ (61.2:38.8 wt%)	44.8	-	Gao and Deng, 2013
	LiNO ₃ /NaNO ₃ /KNO ₃ /CsNO ₃ /Ca(NO ₃) ₂ .4H ₂ O (18.6:14.4:54.3:102.7:62.1 wt%)	65	-	Raade and Padowitz, 2011
	LiNO ₃ /Mg(NO ₃) ₂ .6H ₂ O (14:86 wt%)	72	180	Sharma et al., 2009
Ca(NO ₃) ₂ /NaNO ₃ /KNO ₃ (36:16:48 wt%)	100	-	Gomez et al., 2013	

2.3.5. High Temperature Phase Change Materials (HTPCMs)

The materials can be considered as HTPCMs showing melting temperature in the range of 120 °C to 1000 °C [Kenisarin, 2010; Nomura *et al.*, 2010]. Several organic, inorganic, eutectic and metal alloys based HTPCMs are listed in Table 2.3 with respective thermophysical properties.

Table 2.3 : High temperature phase change materials with corresponding melting point and latent heat of fusion

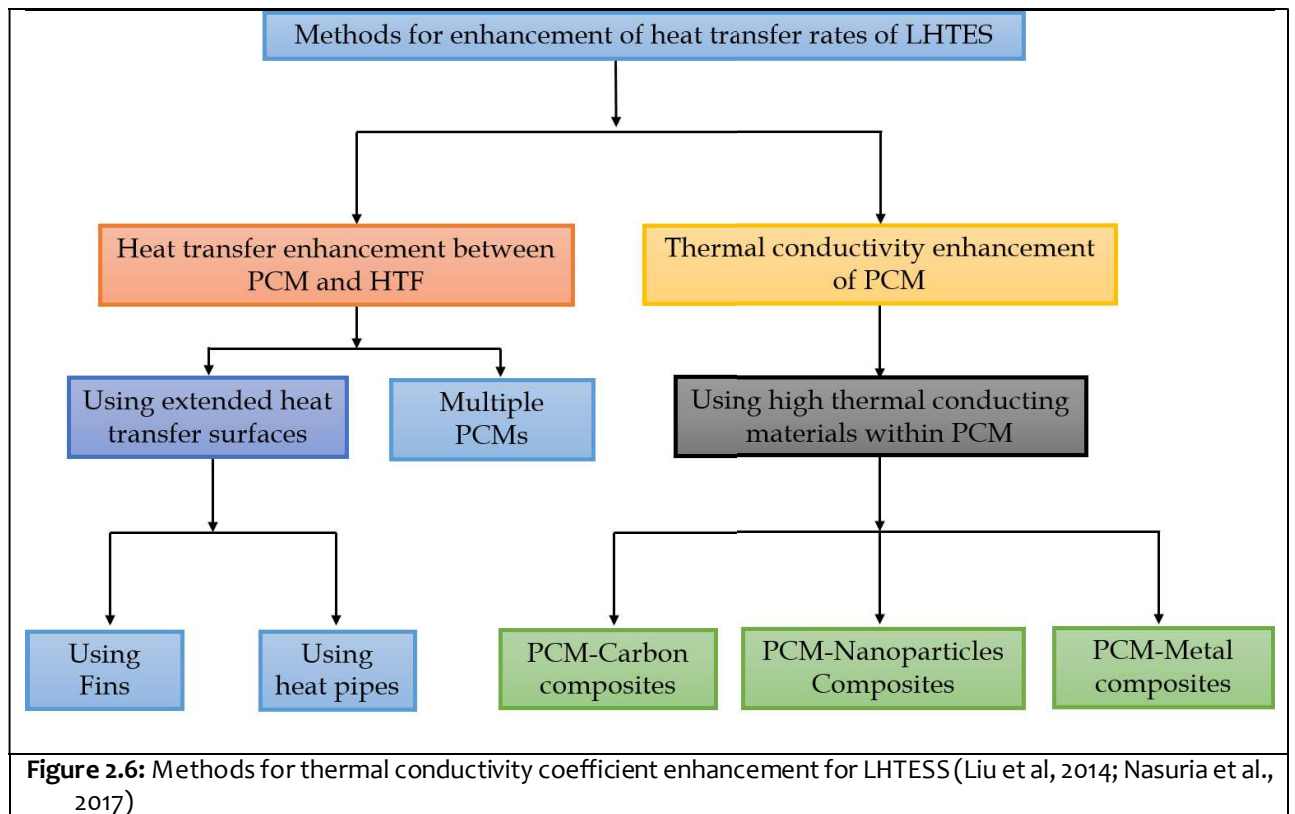
Type	PCM	Melting Point (°C)	Heat of Fusion (kJ/kg)	References
Organic	Urea	134	250	Hailot et al., 2011
	Maleic acid	141	385	Hailot et al., 2011
	Adipic acid	152	275	Hasl and Jiricek, 2014
	d-Mannitol	165	300	Krishna et al., 2009
	Hydeoquinone	172	258	Gil et al., 2014
Inorganic PCMs	AlCl ₃	192	280	Hasanain, 1998
	LiNO ₃	250	370	Hasanain, 1998
	Na ₂ O ₂	360	314	Hasanain, 1998

	KClO ₄	527	1253	Hasanain, 1998
	LiH	699	2678	Hasanain, 1998
	LiF	868	932	Hasanain, 1998
	NAF	993	750	Hasanain, 1998
Eutectic	LiNO ₃ /NaNO ₃ /KNO ₃ (30:18:52 wt%)	123	140	Olivares and Edwards, 2013 and Roget <i>et al.</i> , 2013
	LiNO ₃ /KNO ₃ (34:66 wt%)	133	150	Gamataeva <i>et al.</i> , 2014
	KNO ₃ /NaNO ₂ (56:44 wt%)	141	97	Jang and Tomkns, 1983
	KNO ₃ /NaNO ₃ /NaNO ₂ (53:6:41 wt%)	142	110	Miller, 1941
	KNO ₂ /NaNO ₃ (56:44 wt%)	149	124	Jang and Tomkns, 1983
	LiNO ₃ /NaNO ₂ (62:38 wt%)	156	233	Jankowski <i>et al.</i> , 2014
	LiNO ₃ /NaNO ₃ (58:42 wt%)	160	272	Jankowski <i>et al.</i> , 2014
	LiNO ₃ /NaNO ₃ /KCl (45:50:5 wt%)	160	266	Gasanaliev and Gamataeva, 2007
	LiNO ₃ /NaNO ₃ (49:51 wt%)	194	262	Gasanaliev and Gamataeva, 2007
	LiNO ₃ /NaCl (87:13 wt%)	208	369	Gasanaliev and Gamataeva, 2007
	KNO ₃ /NaNO ₃ (55:45 wt%)	222	110	Janz <i>et al.</i> 1980
	LiBr/LiNO ₃ (27:73 wt%)	228	279	Janz <i>et al.</i> 1980
	NaNO ₂ /NaNO ₃ (55:45 wt%)	233	163	Janz <i>et al.</i> 1983
	NaNO ₂ : NaOH (80:20 wt%)	232	252	kensarin 2010
	LiOH:LiCl (63:37 mol%)	264	437	Philips and Stearns, 1985
	KOH/LiOH (60:40 wt%)	314	341	Liu <i>et al.</i> , 2012,
	KNO ₃ /KCl (96:04 wt%)	320	150	Liu <i>et al.</i> , 2012
	KNO ₃ /KBr/KC (80:10:10 mol%)	342	140	Liu <i>et al.</i> , 2012
	LiCl/NaCl/KCl (43:33:24 wt%)	346	281	Liu <i>et al.</i> , 2012
	LiCl/KCl (58:42 mol%)	348	170	Cardenas and Leon, 2013
MgCl ₂ /NaCl/KCl (50:30:20 mol%)	396	291	Cardenas and Leon, 2013	
NaCl/MgCl ₂ (56:44 mol%)	430	320	Cardenas and Leon, 2013	
NaCl/NiCl ₂ (52:48 mol%)	573	558	Philips and Stearns, 1985	
Metal Alloys	Zn/Al (96:4 wt%)	381	138	Alva <i>et al</i> , 2017
	Al/Mg/Zn (59:33:6 wt%)	443	310	Alva <i>et al</i> , 2017
	Mg/Cu/Zn (60:25:15 wt%)	452	254	Alva <i>et al</i> , 2017
	Al/Mg (65.35:34.65 wt%)	497	285	Alva <i>et al</i> , 2017
	Al/Si/Mg (83.14:11.7:5.16 wt%)	555	485	Alva <i>et al</i> , 2017
	Cu/Al/Si (49.1:46.3:4.6 wt%)	571	406	Alva <i>et al</i> , 2017
	Si/Al (86:14 wt%)	576	560	Alva <i>et al</i> , 2017
	Cu/Si (80:20 wt%)	803	197	Alva <i>et al</i> , 2017

2.3.6 Thermal Conductivity Enhancement Techniques for PCMs

The currently available commercial and pristine PMCs have sufficiently low thermal conductivity and is considered as one of the major drawbacks for PCM to deploy them in LHTESS. In LHTESS, the thermal energy needs to be transferred into the PCM from the external thermal energy source and later to be recovered from PCM for probable applications. This thermal energy storage and recovery needs to be completed within the desired time. In the charging process, the thermal energy is transferred from heat transfer fluid (HTF) to PCM and PCM undergoes solid-liquid

phase change process. The thickness of solid layer of PCM decreases and liquid layer thickness increases during this process. The conduction heat transfer process is more dominant in solid phase, while the convection heat transfer process is more dominant in liquid phase. Thus, the convection is more dominant as compared to the conduction due to the presence of density gradients during charging process [Lopez *et al.*, 2010]. The solid phase is created at the surface of the heat transfer surface and reduces the influence of convection during discharging process. Therefore, PCMs with low thermal conductivity exhibits high thermal resistance and low charge/discharge cycling rates. It significantly reduces thermal performance of LHTESS and restricts potential applications. Therefore, thermal conductivity of PCM should be enhanced to a desired level for efficient thermal energy transfer for such applications. The commonly used techniques used for the enhancement of heat transfer in LHTESS are shown in Figure 2.6.



The details of different methodologies used for enhancing heat transfer in LHTESS are tabulated in Table 2.4. These are based on designing conducting matrix, which can be combined with PCMs to achieve the desired heat transfer rates during charging and discharging of PCMs used in LHTESS.

Table 2.4 : Methods used for thermal conductivity enhancement of PCMs and main outcomes

Method Used	Heat Transfer Enhancing Material	PCM Used	Main Outcomes	References
Fins	Rectangular Al Fins	Paraffin RT 60	The solidification time is reduced and reciprocal to the fin numbers	Velraj <i>et al.</i> , 1993
	Rectangular steel fins	Paraffin	Solidification time reduced about 40%	Strith, 2004
	Spiral Cu fins round heating rod	Stearic acid	PCM thermal conductivity (TC) enhanced about 3 times. Additionally, melting time reduced by reduction in fin pitch	Liu <i>et al.</i> , 2004
	Rectangular Cu fins around the HTF tube	Not mentioned	The melting time reduced about 35% by maximum fin numbers	Al-Abidi <i>et al.</i> , 2013
	Y-shaped Brass fins around the HTF tube	Not mentioned	The system efficiency can increase by 24% for optimized unit	Sciacovelli <i>et al.</i> , 2015
	Rectangular Al fins between two base plates	Not mentioned	The minimum heat transfer rate is about 3 times greater through wide spaced fins	Gharebaghi and Sezai, 2007
Heat pipes	SS-Mercury shell & tubes	Not mentioned	Thermal energy stored by PCM near single heat pipe is around 13% of stored energy next to HTF tube	Shabgard <i>et al.</i> 2010
	SS-Mercury rectangular shell & tube	Not mentioned	The system efficiency is enhanced	Nithyanandam , 2011
	SS-potassium rectangular	Not mentioned	Increased condenser length/diameter of heat pipe increases melting rates	Sharifi <i>et al.</i> , 2012
	Cylindrical Cu-water	Not mentioned	Heat transfer rate while solidification is increased about 2 times	Robak <i>et al.</i> , 2011
Cascade PCM	Three types of PCM in vertical and cylindrical capsules	n-octadecane having different MP	The heat transfer rate can be enhanced by multiple PCMs with different melting points	Farid and Kanzawa, 1989
	Two PCMs in shell & tube	n-octadecane & P116	Heat transfer rate is enhanced about 57%	Adine and El Qarnia, 2009
	Two PCMs in rectangular slabs	CaCl ₂ .6H ₂ O, RT 25	The exergy efficiency reduces by increasing inlet air-temperature while charging	Mosaffa and Garousi, 2014
	03 and 05 PCMs in cylindrical shell &	Not mentioned	The total melting time can reduced about 5.1% and 21.5% with 3 and 5 types PCMs	Hu <i>et al.</i> , 2015

	frustum inner tubes			
	03 PCMs in cylindrical capsules	Commercial wax with different MP	About 15% enhancement in latent heat storage is achieved	Farid and Kansawa, 1990
	05 PCMs in vertical shell & tube heat exchanger	MgCl ₂ /KCl/NaCl, KOH, KNO ₃ , KNO ₃ /KCl, NaNO ₃	The heat is stored in wide temperature range and released at nearly constant temperature. Thermal conductivity of PCM needs to be improved	Michels and Pitz-Paal, 2006
Porous materials	Graphite matrix	Paraffin	TC is enhanced about 20-130 times	Mills et al., 2006
	Metal foam	Paraffin wax RT58	The rate of heat transfer is increased about 5 to 20 times	Tian and Zhao, 2011
	Al foam	Paraffin wax	The discharge time is reduced about 42.42% and charge time decreased about 15.37%	Dukhan and Bodke, 2010
	Exfoliated graphite (ExG)	n-dodocosane	TC of PCM is enhanced by ExG	Sari and Karaipekli, 2007
	Cu foam	Eicosane	PCM TC is enhanced from 0.42 W m ⁻¹ K ⁻¹ to 3.06 W m ⁻¹ K ⁻¹	Siahpush et al., 2008
	Compressed ExG	Paraffin wax	TC of PCM is enhanced 28-180 times	Zhong et al., 2010
	Copper foam, ExG and copper steel alloy	NaNO ₃	The rate of heat transfer enhanced 190%, 210% and 250% using ExG, metal foam and mixture of ExG and metal foam respectively	Wu and Zhao, 2011
	Graphite foam	Cyclohexane	The effective TC enhanced from 30 to 25 W m ⁻¹ K ⁻¹ in temperature range 20 to 900C compared to pristine cyclyhexane thermal conductivity (0.13 W m ⁻¹ K ⁻¹)	Moieni and Khodadadi, 2013
	Cu matrix	NaNO ₃	Solidification and melting times reduced significantly	Li and Wu, 2014
	ExG	LiNO ₃ -KCL, LiNO ₃ -NaCl and LiNO ₃ -NaNO ₃	TC of PCMs enhanced substantially.	Zhong et al., 2014
Porous materials	Cu and Ni foam	Eutectic of NaNO ₃ and KNO ₃	The heat discharge rate is enhanced with metal foams	Zhang et al., 2015
	ExG	LiNO ₃ -KCL, LiNO ₃ -NaCl and LiNO ₃ -NaNO ₃	TC is enhanced from 4.9 to 6.9 times using ExG	Zhong et. al. , 2014
	ExG	Eutectic KNO ₃ and NaNO ₃	TC is enhanced by 3 to 30 times	Bauer et al., 2006

	EXG	n-docosane	TC of n-docosane is enhanced up to $0.84 \text{ W m}^{-1} \text{ K}^{-1}$ with 10 wt% of ExG	Sari, and Karaipekli, 2007
	EXG	Salt nitrates, hydroxides and chlorides	TC is enhanced from 3.9 to $9 \text{ W m}^{-1} \text{ K}^{-1}$ with 20 wt% of ExG	Pincermain et al., 2008
	EXG	$\text{KNO}_3/\text{NaNO}_3$ Eutectic	TC is enhanced about 20 times ($20 \text{ W m}^{-1} \text{ K}^{-1}$)	Acem et al., 2010
	EXG and metal foam	NaNO_3	Charge/discharge time is reduced.	Zhao et al., 2011
	EXG	Paraffin	The heat storing coefficient of cement mortar with PCM/ExG composite is about 1.74 time compared to cement mortar without PCM/ExG composite	Li et al., 2013
	EXG	Neopentyl Glycol	TC of PCM is increased 11-88 times	Wang et al., 2013
	EXG	$\text{NaNO}_3, \text{KNO}_3$	TC is enhanced about 30-40% with 10 wt% of ExG	Xiao et al., 2013
	EXG	n-Octadecane	In indoor temperature variation is reduced and helps in decreasing energy consumption in buildings	Zhang et al., 2013
Nano-particles	Al_2O_3	n-Octadecane	The convection heat transfer coefficient for melting region decreases with increasing nanoparticle mass fraction	Ho and Gao, 2013
	SWCNTs, MWCNTs and CNFs	Paraffin wax	Latent heat of fusion is enhanced. maximum 13% for PCM/SWCNTs is observed	Shaikh et al., 2008
	MWCNTs	Palmitic acid	TC in solid and liquid phases enhanced 36% and 56% using 5 wt% MWCNTs	Wang et al., 2008
	GNPs	Lauric acid	PCM TC is enhanced about 230% with 1 vol% of GNPs	Harish et al., 2015
	GNPs	n-eicosane	TC of PCM is enhanced more than 400 % using 10wt% of GNPs	Fang et al., 2013
	Cu Nano wires (NWs)	Tetradecanol	TC of PCM increases considerably faster by increasing loading of Cu NWs above 1.5 vol%	Zeng et al., 2012
	Ag NWs	Tetradecanol	TC of PCM/Ag NWs containing about 11.8 vol% of Ag NWs is about $1.46 \text{ W m}^{-1} \text{ K}^{-1}$	Zeng et al., 2010
Carbon fiber brush	Carbon fibers	n-coctadecane	TC of PCM/carbon fibers is about 03 times higher with 1.2 vol% of carbon fibers compared to pristine PCM	Fukai et al., 2000
Carbon fibers	Carbon fibers	PCM44	TC of composite is about 4 time higher at 8 vol% of carbon fibers	Frusteri et al., 2006

The present works aim to achieve the efficient heat transfer by manipulating the thermal conductivity of PCMs. This is achieved by developing the exfoliated graphite and its composite with different PCMs. The details are discussed in Chapter 8.

2.3.7 Applications of PCMs

Telkes (1949), advised the use of LHTESSs long back and since then the use of LHTESSs for different applications such as building heating/cooling, water heating, food cooking, storage/transport of heat sensitive materials, concentrated solar power (CSP) plants are attracting researchers attention across the globe. The detailed applications of PCMs are shown in Figure 2.7, including solar and non-solar applications. The solar applications are differentiated with red color boxes.

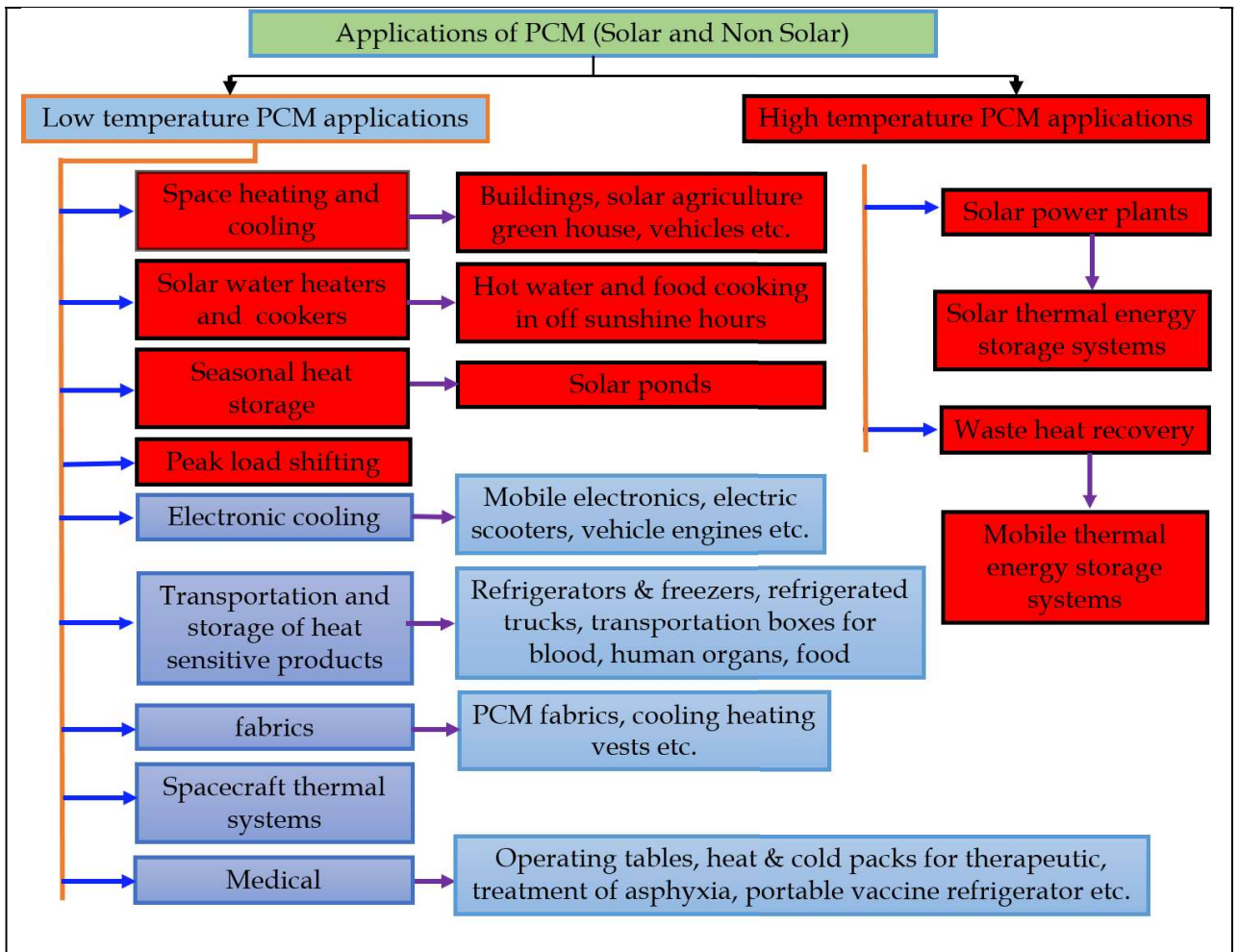


Figure 2.7 : Applications of phase change materials (Hung et al., 1975, 1983; Lane, 1980; Abhat, 1981; Prakash et al., 1985; Ramadan et al., 1987; Chen and Yue, 1991; Bansal and Budhi, 1992; Farid et al., 1994; Santamouris et al., 1994; Domanski et al., 1995; Feldman et al., 1995; Kaygusuz 1995; Yagi and Akiyama, 1995; Budhi, 1997; Espeau et al., 1997; Hasnain, 1998; Mehmet, 2000; Sharma et al., 2000; Turpenney et al., 2000; 2003; Ventola et al., 2002; Buddhi, et al., 2003 ; Budhi and Sahoo, 2003; Mehling et al., 2003; Mondeig et al., 2003; Nagano et al., 2003, 2004; Zalba et al., 2003; Huang et al., 2004; Ying et al., 2004; Takeda et al., 2004; Tan et al., 2004; Cabeza et al., 2006; Cheralathan et al., 2007; Tyagi and Buddhi, 2007; Wang et al., 2007; Ladfi et al., 2008; Laguerre et al., 2008; Sharma et al., 2009; Ahmed, 2010; Azzouz et al., 2010; Dincer and Rosen, 2010; Gin et al., 2010; Subramaniam et al., 2010; Castell et al., 2011; Gracia et al., 2011; Liu et al., 2012, Kuravi et al., 2013; Cabeza, 2014; Shukla et al., 2016)

2.4 IDENTIFIED GAPS

There is huge literature available on PCMs aiming for different applications. However, only a little are satisfying the need for real applications. There are numerous PCMs developed and have shown potential for efficient thermal energy storage systems. Nevertheless, there are still issues and challenges for respective technological applications and needs to be addressed. Some of such challenges are summarized as follows:

1. Design and development of low cost phase change materials with sufficiently high latent heat of fusion and suitable melting temperatures for possible applications
2. Synthesis of homogeneous eutectic mixtures of high temperature phase change materials
3. Measurement of thermophysical properties of PCMs such as exact melting temperature range, heat storage capacity, temperature rise while solidification, supercooling temperature etc. is essential to design efficient thermal energy storage system. Commonly, DSC is being used to determine such thermophysical properties of PCM and has its own limitation, as discussed in Chapter 3. A T-history method is more suitable for characterization of PCMs. However, a standard T-history instrument is not available commercially.
4. Low thermal conductivity of PCMs is one of the major drawbacks in deployment of PCM in thermal energy storage systems.
5. Aqueous sodium acetate PCM based heating pads are being used for thermal comfort and therapeutic applications. However, few drawbacks such as lumped, hard, and sharp crystallites of PCM, unpredicted nucleation at lower ambient temperature, low heat retention time etc. are still associated with such heat packs.

This compels to develop new phase change materials or tailor the existing PCMs with superior thermophysical properties for low and high temperature thermal energy storage applications i.e. building heating and cooling, comfortable clothings, solar water heaters, solar cookers, CSP plants etc. The first step of the present work aimed the selection of materials with suitable melting temperature and significantly high latent heat of fusion and development of eutectic PCMs by mixing these materials in specific ratio. Further, a T-history measurement setup is developed in-house and used in investigating the thermophysical properties of materials. The exfoliated graphite process is developed and optimized for large scale production. The exfoliated graphite based composites are developed with pristine and eutectic PCMs to realize the enhanced thermal conductivity of composite phase change materials.

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