



# Determination of thermo-physical properties and stability testing of high-temperature phase-change materials for CSP applications

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## ABSTRACT

This paper presents the thermo-physical properties and stability testing results of six high-temperature phase-change candidate materials for potential use as a cascaded storage system for concentrating solar power applications. This type of storage is a promising technology because it offers a higher utilization of the possible phase change and a more uniform heat-transfer fluid outlet temperature, compared with the single phase-change material (PCM) storage system. The tested materials were inorganic eutectic PCMs with reported phase-change temperatures between 300 °C and 600 °C. Four PCMs were made from carbonate salts ( $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ , and  $\text{Li}_2\text{CO}_3$ ) and two from chloride salts ( $\text{NaCl}$ ,  $\text{MgCl}_2$ , and  $\text{KCl}$ ). The phase-change temperature, phase-change enthalpy, and specific heat of these PCMs were measured using a differential scanning calorimeter. Large material samples were tested in an oven subjected to multiple melt–freeze cycles. The results showed that the carbonate PCMs have a very high degree of sub-cooling in the initial cycles, which decreased in subsequent cycles. The chloride PCMs have a negligible degree of sub-cooling. There is some disagreement between the measured and reported thermo-physical property values of the tested materials, which demonstrates the uncertainty associated with published property values. One carbonate PCM and one chloride PCM were recommended as promising latent heat storage materials.

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## 1. Introduction

Concentrating solar power (CSP) plants constitute an increasing proportion of future power generation worldwide. CSP systems can incorporate thermal energy storage (TES), which solves the time mismatch between the solar energy supply and electricity demand profiles, and allows for more efficient use of the turbine and other power-block components. The state-of-the-art TES system relies on sensible storage and employs molten salts in cold and hot tanks. Compared to sensible heat storage, latent heat storage using phase-change materials (PCMs) allows large amounts of energy to be stored in relatively small volumes, resulting in a smaller storage system and reduced cost of energy for CSP plants [1,2]. Latent heat storage has been applied in numerous low-temperature applications [3–6] and is quite promising for future high-temperature thermal storage applications [7,8].

The required PCMs must have a phase-change (melting and freezing) temperature within the desired usage temperature range. For the majority of parabolic trough and solar tower power plants, the operating temperature of the solar field is 290–390 °C and 290–565 °C,

respectively. The currently available heat-transfer fluids (HTFs) are synthetic oil, water/steam, and molten nitrate or nitrite salts [9]. Alternative HTFs, such as supercritical carbon dioxide ( $s\text{-CO}_2$ ) and other molten salts, are being investigated by research teams worldwide. Higher operating temperatures of over 650 °C are achievable, and it is known that higher HTF operating temperature generally allows for higher turbine efficiency. Michels and Pitz-Paal [10] designed and tested a cascaded PCM system using a series of three PCMs, spanning the operating temperature range from 290 °C to 350 °C. The experimental results indicated that the cascaded system offers a higher utilization of the possible phase change compared with the single PCM system. Enormous works have been carried out by Abengoa Solar LLC [11] to develop cascaded arrangement storage systems by using a variety of eutectic salts and metal alloys as PCMs. The cascaded storage system offers a more uniform HTF outlet temperature [10,12] and higher exergy efficiency [13,14]. Therefore, it is worthwhile to identify candidate PCMs with melting temperatures in the range of 300–650 °C.

Inorganic salts are promising candidates for high-temperature PCMs because they produce a large enthalpy change without substantial density change during solid–liquid phase transformation. Kenisarin [15] published a comprehensive review on PCMs in the melting temperature range of 120–1000 °C. The PCMs include fluorides, chlorides, bromides, hydroxides, nitrates, carbonates,

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molybdates, and others. Binary and ternary eutectic compositions based on fluorides and chlorides have high latent heat of fusion; also, the cost of the latter is low. Fluoride salts are less attractive because of their relatively high cost and high corrosion to the containment materials [16]. It has been reported that the melting temperature and heat capacity increase is in the following order: nitrates, chlorides, carbonates, and fluorides [1]. The German aerospace center did intensive research to investigate sodium nitrate as a storage medium in direct steam generation technology [17–19]. Gomez et al. [20] identified three PCMs with melting temperatures near 320 °C, 350 °C, and 380 °C. They evaluated the properties of these PCMs and found that the PCMs with chloride anions only were chemically unstable.

The storage capacity of a latent heat storage system is determined by the specific heat of the storage material as well as the enthalpy of the phase change (latent heat of fusion), which can potentially result in a smaller and lower-cost alternative to the currently available sensible storage system. Therefore, it is necessary to investigate the thermo-physical properties of the candidate PCMs because they have a direct impact on the thermal performance and cost analysis of the storage system in the CSP plants. In general, because many of the properties given in the literature are usually calculated rather than experimentally verified values, there is a discrepancy between these two values [20]. As an example, the measured latent heat of fusion determined by Gomez et al. [20] is only half of the theoretical value for some eutectic nitrate and chloride PCMs. The discrepancy occurs because the mixtures and eutectics do not exhibit ideal mixing behavior [8].

The candidate PCMs should melt congruently and have insignificant sub-cooling; otherwise, the storage capacity of the system will be reduced. Also, good chemical and thermal stability are necessary to ensure a reasonable life span of the storage system, which is another important criterion for the PCM selection. The life span of the storage system for CSP plants is considered to be between 20 and 30 years. However, only limited research exists on the thermal stability of high-temperature PCMs. Laing et al. [18] tested a prototype PCM storage unit filled with sodium nitrate. The operation of 172 cycles (more than 4000 h) proved that there was no change in the melting temperature and no decomposition of the PCM. Shin et al. [16] tested a salt eutectic (32 wt%  $\text{Li}_2\text{CO}_3$ –35 wt%  $\text{K}_2\text{CO}_3$ –33 wt%  $\text{Na}_2\text{CO}_3$ ) and found that it exhibits a distinct phase-change temperature (395–397 °C) without phase separation or sub-cooling over 50 thermal cycles, and the corrosion of the salt within the SS316 container was negligible. Petri et al. [21] evaluated four carbonate salts ( $\text{Li}_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3$ , 52.2 wt%  $\text{BaCO}_3$ –47.8 wt%  $\text{Na}_2\text{CO}_3$ , and 81.3 wt%  $\text{Na}_2\text{CO}_3$ –18.7 wt%  $\text{K}_2\text{CO}_3$ ) as PCMs and they cycled those candidates for 13, 21, 36, and 38 cycles, respectively. They found that the eutectic salt with 52.2 wt%  $\text{BaCO}_3$  and 47.8 wt%  $\text{Na}_2\text{CO}_3$  showed stable performance, but the melting point measured was 30 °C higher than the published value (686 °C). The salt mixture with 81.3 wt%  $\text{Na}_2\text{CO}_3$ –18.7 wt%  $\text{K}_2\text{CO}_3$  was not stable and it melted incongruently. When the pure salts ( $\text{Li}_2\text{CO}_3$  and  $\text{Na}_2\text{CO}_3$ ) were tested in sealed containers, they leaked through the weld and fittings.

This paper aims to characterize the thermo-physical properties of the six PCM candidates with melting temperatures between 300 °C and 600 °C. The temperature range was selected to allow a cascaded PCM storage system to be developed for current and future solar tower power plants. The composition of the carbonate and chloride salt eutectic PCMs was taken from the literature. The properties measured include the phase-change temperature, latent heat of fusion, and solid and liquid specific heat capacities. Also, the thermal stability of the salt eutectics has been examined by repeatedly cycling the candidates between 300 °C and 600 °C in a furnace. To our knowledge, this is the first time that the thermo-physical properties of the investigated PCMs have been measured by experiment and their thermal stability is evaluated.

## 2. Materials and methodology

### 2.1. Materials

Table 1 provides the listing of the compositions and thermo-physical properties of the salt mixtures studied. Candidates CA1–CA4 are eutectic mixtures of carbonate salts and CH1 and CH2 are eutectic mixtures of chloride salts. The thermo-physical properties of candidate CA1 were obtained by experiment, whereas the properties of the other candidates are calculated values. The individual carbonate and chloride salts were supplied by the Alfa Aesar and Sigma Aldrich with purity levels greater than 99%. The salts were dried in a muffle furnace at 120 °C for 24 h. The single dried salts were weighed in a balance with a resolution of 0.1 mg and mixed at a specific ratio as shown in Table 1. Because chloride salts are highly hygroscopic, the weighing and mixing procedures were performed inside a dry glove-box under UHP nitrogen atmosphere. Before performing the differential scanning calorimeter (DSC) test, the samples were placed in a furnace at 120 °C for 2 h to remove any moisture absorbed during sample handling and preparation.

### 2.2. Methodology

#### 2.2.1. Differential scanning calorimeter

The specific heat capacity and latent heat of fusion and phase-change temperature were evaluated using a DSC (Netzsch DSC 404), which operates according to the heat-flux principle. A sample and a reference are subjected to a controlled temperature program (heating, cooling, or isothermal segment) and the DSC sensor measures the temperature of the sample and the difference between the sample and reference. Then the heat-flow difference between the sample and the reference can be determined. To measure the solid and liquid specific heat capacities for the PCM samples, the ASTM E1269-05 standard was followed, in which a sapphire disk with known heat capacity is employed as the reference material.

Before performing the test, the chemical stability of the DSC container materials (aluminum, SS316, aluminum oxide, and graphite) with the PCMs was evaluated in a controlled-atmosphere furnace under UHP nitrogen gas. Aluminum oxide and graphite crucibles with lids were used in the phase-change temperature and enthalpy measurement because they showed good corrosion resistance. In the heat-capacity measurement, graphite crucibles were used to obtain fast heat transfer into the sample due to the high thermal conductivity of the graphite. The analyses were conducted under a constant stream of UHP nitrogen at a flow rate of 20 mL/min at a heating/cooling rate of 10 K/min for phase-change temperature and enthalpy measurements, and 20 K/min for specific-heat capacity measurements. A smaller heating/cooling rate of 5 K/min was also employed in the preliminary test, but no obvious discrepancy was found in the results; hence 10 K/min was used for the temperature

**Table 1**

Composition of candidate PCMs and their melting temperatures ( $T_m$ ), latent heats of fusion ( $\Delta H$ ), and solid and liquid specific heats ( $C_{p,s}$  and  $C_{p,l}$ ) [15].

Candidate	Eutectic composition (wt%)	Reported values			
		$T_m$ (°C)	$\Delta H$ (J/g)	$C_{p,s}$ (J/g K)	$C_{p,l}$ (J/g K)
CA1	32 $\text{Li}_2\text{CO}_3$ –35 $\text{K}_2\text{CO}_3$ –33 $\text{Na}_2\text{CO}_3$	397	276	1.67	1.63
CA2	28.5 $\text{Li}_2\text{CO}_3$ –71.5 $\text{K}_2\text{CO}_3$	498	316	–	–
CA3	35 $\text{Li}_2\text{CO}_3$ –65 $\text{K}_2\text{CO}_3$	505	344	1.34	1.76
CA4	22 $\text{Li}_2\text{CO}_3$ –62 $\text{K}_2\text{CO}_3$ –16 $\text{Na}_2\text{CO}_3$	580	288	1.80	2.09
CH1	52 $\text{MgCl}_2$ –48 $\text{NaCl}$	450	430	0.92	1.00
CH2	64 $\text{MgCl}_2$ –36 $\text{KCl}$	470	388	0.84	0.96

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