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Evaluation of thermal physical properties of molten nitrate salts with low melting temperature

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ABSTRACT

$NaNO_3$-KNO_3 (60–40 wt%, Solar salt) has been used as medium for TES and HTF in the CSP system. One of the key challenges using Solar salt is its high melting temperature, which may freeze and block the pipeline. In this work, a novel eutectic nitrate molten salt of the $LiNO_3$-$NaNO_3$-KNO_3-$CsNO_3$ system with low melting temperature of 368 K is designed using Calphad method. Its thermal physical properties, as well as that of Solar salt, $LiNO_3$-$NaNO_3$-KNO_3, $NaNO_3$-KNO_3-$CsNO_3$, $NaNO_3$-KNO_3-$Ca(NO_3)_2$, and $LiNO_3$-$NaNO_3$-KNO_3-$CsNO_3$-$Ca(NO_3)_2$ molten salts are comprehensively determined and evaluated for better understanding their thermal storage and heat transfer performances, such as the melting temperature, thermal stability, specific heat capacity, thermal diffusivity, density and viscosity. The energy storage capacities and figures of merit of the six molten nitrate salts are calculated based on their thermophysical properties to evaluate their TES and HTF performances. This work not only provides the basic engineering data for CSP system, but is useful for choosing media of TES and HTF.

1. Introduction

Solar energy as a clean and sustainable energy has drawn increasing attention worldwide, but its intermittent energy production has been a challenge for a long time. Concentrated solar power (CSP) plant coupled with storage tank enables continuous energy production even at night or during cloudy days, moreover, it is a reliable electrical power option and carbon free energy production [1]. Medium for thermal energy storage (TES) and heat transfer fluid (HTF) is one of the key techniques because it affects not only the energy production efficiency but also the cost of operation and maintenance of CSP plant [2]. A potential method is to look for a medium with lower melting point and appropriate thermophyscial properties, such as viscosity, density, thermal diffusivity and specific heat capacity [1].

The thermal physical properties of $NaNO_3$-KNO_3, $LiNO_3$-$NaNO_3$-KNO_3 ($LiNaKNO_3$), and $NaNO_3$-KNO_3-$Ca(NO_3)_2$ ($NaKCaNO_3$) systems have been reported by several researchers, especially for $NaNO_3$-KNO_3 system, the mixture of 40 wt% KNO_3-60 wt% $NaNO_3$ (Solar salt), was commercialized as the thermal storage and heat transfer medium in 1937 [3]. Its relatively high melting temperature (~ 493 K) represents an important risk of local solidification and thus block the pipeline during absence of sunshine [4]. Moreover, the investment and operation costs produced by auxiliary facilities of thermal insulation due to high melting temperature are so high that searching for new medium with low melting temperature (lower than 373 K) is necessary. Adding $LiNO_3$, $CsNO_3$, and $Ca(NO_3)_2$ to Solar salt is intended to reduce the melting temperature [5]. A molten salt in the $LiNO_3$-$NaNO_3$-KNO_3-$CsNO_3$-$Ca(NO_3)_2$ ($LiNaKCsCaNO_3$) system was reported to melt at 338 K with a thermal stability over 773 K [6]. We studied the $LiNO_3$-$NaNO_3$-KNO_3-$CsNO_3$ ($LiNaKCsNO_3$) system using the Calphad method and found a novel molten nitrate salt with low melting temperature of 368 K.

Well known, melting temperature is not the only criterion to evaluate TES and HTF medium. Thermal physical properties are also important, such as viscosity, density, specific heat capacity, and thermal diffusivity, because they are the basic and essential engineering data. However, the thermal physical properties are not comprehensively studied in a same work, and the results from different work show discrepancy from each other [7]. For example, the melting temperature of Solar salt is reported to be from 493 to 500 K [8]. The thermal physical properties of $LiNaKNO_3$ system were studied by several researchers, including thermal stability, density, viscosity and specific heat capacity [9–15]. For the $NaKCaNO_3$ system, its thermal physical properties were also reported in Refs. [16,17]. The melting point, stability limit, specific heat capacity, viscosity, density, and thermal conductivity of the nitrate molten salts were summarized in Refs. [10,18]. Although the thermophysical properties of Solar salt, $LiNaKNO_3$ and $NaKCaNO_3$ molten nitrate salts were studied by several researchers, the experimental data are scattered. More important, the thermal diffusivity/conductivity in the liquid state is sparsely available in literatures.

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Table 1
Compositions and cost of the six molten salts.

	Composition (wt%)					Cost (yuan/kg)
	$LiNO_3$	$NaNO_3$	KNO_3	$CsNO_3$	$Ca(NO_3)_2$	
Solar salt		60	40			43.6
$LiNaKNO_3$	30	18	52			144.88
$NaKCsNO_3$		20	24	56		10,771.44
$NaKCaNO_3$		48	36		16	42.8
$LiNaKCsNO_3$	18	12	25	45		8724.58
$LiNaKCsCaNO_3$	8	6	23	44	19	8498.56
Price (yuan/kg)	378	42	46	19,200	38	–

In this work, a novel eutectic molten salt of $LiNO_3$-$NaNO_3$-KNO_3-$CsNO_3$ system with the melting temperature of 368 K is found. The thermophysical properties of Solar salt, $LiNaKNO_3$, $NaNO_3$-KNO_3-$CsNO_3$ ($NaKCsNO_3$), $NaKCaNO_3$, $LiNaKCsNO_3$ and $LiNaKCsCaNO_3$ molten salt systems are systematically and comprehensively determined and evaluated, including melting point, thermal stability, density, specific heat capacity, thermal conductivity, and viscosity. Their thermal energy capacity and figures of merits to evaluate heat transfer capacity are subsequently studied. This work is significant for selection and development of TES and HTF media in the CSP plant.

2. Experimental details

2.1. Sample preparation

The compositions of each molten salts are listed in Table 1. Raw materials of $LiNO_3$, $NaNO_3$, KNO_3 and $CsNO_3$ with purity of 99.9% were separately dried at 473 K under argon atmosphere for 24 h. The mixture of Solar salt was kept at573 K, and the mixture of $LiNaKNO_3$, $NaKCsNO_3$, and $LiNaKCsNO_3$ salt was kept at 473 K for 48 h to make it homogeneous, and then cool down. For $NaKCaNO_3$ and $LiNaKCsCaNO_3$ molten salts, $Ca(NO_3)_2{\cdot}4H_2O$ was used, the raw materials were mixed and transferred in a furnace and heated to 473 K for 48 h, and then heated to 573 K for 72 h to dehydrated.

2.2. Thermal analysis and specific heat capacity

Melting temperatures and specific heat capacities are carried out using the differential scanning calorimeter (DSC, NETZSCH DSC 404 F3). The device was calibrated by six certified reference materials, In, Bi, Sn, Zn, Al, and Au, in the temperature range of 373–1473 K before nitrate molten salts measurement. The extrapolated onset temperature is adopted as the melting temperature, and the peak area is regarded as the melting enthalpy. Both calibration and measurement were finished in the Ar atmosphere flowing at 50 ml/min at the heating rate of 5 K/min.

The specific heat capacities of the six molten nitrate salts in the liquid state were determined using the Ratio method [19]. Two empty high purity graphite crucibles coupled with Pt lids were measured to obtain a baseline. The Pt lid was used to reduce the thermal radiation from furnace. Then, the reference material of monocrystalline sapphire and sample mixtures were subsequently measured using the same crucibles under the same conditions. The specific heat capacity was analyzed by use of Eq. (1), performed automatically using the NETZSCH Proteus program. The uncertainty of specific heat capacity is estimated to be 0.08 J/g K [20].

$$c_{p,S} = \frac{c_{p,R}{\cdot}m_R}{m_S} \times \frac{DSC_S - DSC_B}{DSC_R - DSC_B} \tag{1}$$

Where *DSC* (μV) is DSC signal, *m* (g) the mass, c_p (J/g K) the specific heat capacity. *B*, *R* and *S*, are the corresponding parameters of baseline, reference and sample, respectively.

Thermal stability of the molten nitrate salts was determined using the simultaneous thermal analysis (Setaram Labsys Evo TG-DSC) at 10 K/min with the blanket of argon atmosphere, and the flowing rate is also 50 ml/min.

2.3. Determination of density

Density measurements of the Solar salt, $LiNaKNO_3$, $NaKCsNO_3$, $NaKCaNO_3$, $LiNaKCsNO_3$, and $LiNaKCsCaNO_3$ molten salts were realized by a device constructed based on the Archimedes theory. The dimensions of the crucible, platinum cylinder and platinum wire are identified, and the effect of the surface tension on the density has been elaborately discussed in our previous work [20]. The device was calibrated by NaCl and confirmed by LiF-NaF-KF eutectic molten salt [21]. Before measuring the molten nitrate salts density, the volume of a platinum cylinder was calibrated by distilled water at ambient temperature, expressed as Eq. (2)

$$V_0 = \frac{m_0 - m_1}{\rho_w} + \pi D\sigma_w/\rho_w g \tag{2}$$

About 200–300 g molten nitrate salt powder or ingot was melted at target temperature in a furnace with the blanket atmosphere of argon. The platinum cylinder connected to the electronic balance through a platinum wire was completely dipped into the molten salt, and the electronic balance values were recorded at desired temperatures during cooling down at the rate of 1 K/min. The density is calculated by Eq. (3). The uncertainty of density is estimated to be 0.0039 g/cm^3 [21].

$$\rho = \frac{m_1 - m_2 + \pi D\sigma/g}{V_0[1 + \beta(T-298)]^3} \tag{3}$$

Where ρ is the density, m_0 and V_0 (*ca.* 2.6 cm^3 in our experiment) are the weight and volume of the platinum cylinder in air, respectively; m_1 and m_2 are the weight of the platinum cylinder in distilled water and molten salts, respectively; σ_w and σ are the surface tension of pure water and molten salts, respectively; ρ_w is the density of distilled water; *D* is the diameter of platinum wire ($D = 0.2$ mm), *g* is the gravitational constant; *T* (K) is the temperature of molten salts; and β is the linear expansion coefficient of platinum ($\beta = 9 \times 10^{-6}$/K).

The surface tension of nitrate salts is usually in 90–120 mN/m [22]. According to Eq. (3), the error caused by surface tension is just 0.00294 and 0.00293 g/cm^3 respectively, when temperature is 473 and 673 K. The uncertainty caused by surface tension is just 0.000245 g/cm^3. The effects of surface tension on the total error ($<$ 0.2%) and uncertainty are very small and can be negligible for nitrate salts.

2.4. Determination of thermal diffusivity

The thermal diffusivities of the Solar salt, $LiNaKNO_3$, $NaKCsNO_3$, $NaKCaNO_3$, $LiNaKCsNO_3$, and $LiNaKCsCaNO_3$ molten salts were measured using the laser flash analysis (Linseis LFA 1000) in helium atmosphere. Sample pretreatment is a key point to determine thermal diffusivity of liquid molten salt using this method. Appropriate amount (about 1.5–2.5 g) of nitrate salt powder was pressed into a disc before it was set in a special designed graphite crucible. The crucible filled with nitrate was heated and kept at a target temperature in a special vacuum furnace for at least half an hour, and then cool down. This heating-cooling under vacuum was repeated 3 times to make the molten salt free from gas bubbles. Finally, the crucible filled with homogeneous molten salt is transferred to the sample cell for thermal diffusivity determination. The molten nitrate salt was kept at each desired temperature for at least 40 min to make temperature homogeneous. The bottom of the crucible was heated by a single laser pulse, and the temperature of front surface was detected by an infrared detector. The temperature rise of front surface with a plot of time was recorded for data analysis, which is finished using the combined model [20,23]. Data analysis was performed automatically using the Evaluation