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Experimental study on the thermal stability of a new molten salt with low melting point for thermal energy storage applications

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ABSTRACT

This paper presents a new kind of KNO_3–$NaNO_3$–$LiNO_3$–$Ca(NO_3)_2{\cdot}4H_2O$ with certain proportion, which is potentially suitable for high-temperature thermal energy storage in concentrating solar power technology. Its primary thermophysical properties were evaluated. Thermal physical tests were conducted for the samples obtained at different stages during the tests of 1,200-h exposure to constant high temperature and thermal shock cycling for 1000 times. Results show that a comprehensive grasp of the time evolution of its thermophysical properties and their respective changes with heating time and thermal cycles were achieved. The thermophysical properties of the molten salt show good repeatability before and after the experiments, and most variations are within ± 10%. In addition, the normal temperature X-ray diffraction diagram of the candidate was measured and analyzed after 1200 h of heating and 1000 times of thermal cycling. Although part of calcium nitrates has been dissolved and formed a new solution, this phenomenon does not affect the performance of the candidates, which showed high-temperature tolerance and good thermal stability. Therefore, this new kind of molten salt thermal storage materials is a promising candidate for both heat transfer and energy storage in large-scale solar thermal power plants.

1. Introduction

As the global sustainable development becomes popular, the concepts of green energy and low carbon life have received attention. Many countries start to conduct studies on renewable energy, such as wind, solar, biomass, geothermal, and ocean energy. Solar energy has become one of the most popular energy because of its properties, such as unlimited reserves, non-pollution, and economic efficiency [1,2]. Concentrated solar thermal power (CSP), which has long been considered as the most promising way of large-scale use of solar energy, has quickly entered a commercial growth stage and become an emerging industry to solve current problems related to energy, resources, and environment [3,4].

Thermal energy storage (TES) technology is a key factor for solar thermal power plants [5] and thus is important to improve thermal efficiency, stability, and reliability. With the rapid development of CSP technology and the continuous improvement of large-scale energy storage equipment, molten salt has become a popular topic of research because its unique characteristics, such as low melting point, good thermal conductivity, wide temperature range, low vapor pressure, high capacity, low viscosity, and good stability [6–11]. Furthermore, searching for new types of mixed molten salt with superior heat transfer and heat storage characteristics has become the main direction of current studies on mixed molten salt.

Solar salt (60 wt% $NaNO_3$, 40 wt% KNO_3) and HITEC salt (53 wt% KNO_3, 40 wt% $NaNO_2$, and 7 wt% $NaNO_3$) have been widely used as heat transfer and heat storage media [12]. In particular, solar salt has been studied extensively and employed successfully as the TES medium in Andasol-1 and Gemosolar programs. Its thermal physical properties, including melting point, density, specific heat, viscosity, thermal conductivity, have been widely studied [13]. However, using these two kinds of molten salts as the heat storage medium still has serious disadvantages, such as high melting point and low operating temperature. In using a medium with high melting point heat transfer, additional heat tracing systems, thermal insulation systems, and emergency response systems must be installed, the risk of frozen pipes blocking caused by temperature fluctuations would be greatly enhanced. Thus, the initial investment and initial running costs of the system would be increased. Iversona et al. [14] studied the thermal and mechanical properties of solar salt, HITEC salt, and low-melting point quaternary

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salt (2.3 wt% KNO_3, 39.4 wt% $Ca[NO_3]_2$, 12.1 wt% $NaNO_3$, and 6.1 wt % $LiNO_3$) for latent heat storage in solid state. Tao Wang et al. studied the thermodynamic properties of $LiNO_3$–$NaNO_3$–KNO_3–$2KNO_3$·$Mg(NO_3)_2$ system [15] and preliminarily explored the basic physical properties of a new type of low-melting point salts containing nitrite [16]. Zhao et al. [17] studied the thermal properties of ternary mixed nitrates consisting of KNO_3, $LiNO_3$, and Ca $(NO_3)_2$. Although their melting point is lower than 100 °C, DSC test results showed that the sample exhibited large endothermic peaks at ~ 150 °C; thus, the sample did not form good eutectic. In addition, the author did not present the data of initial crystallization point. If the initial crystallization point is not considered, then its application in heat transfer in the system will result to increased temperature fluctuations and enhanced risk of pipeline freezing and blocking.

Various kinds of molten salts with low melting point were explored in our previous work. A new kind of KNO_3–$NaNO_3$–$LiNO_3$–$Ca(NO_3)_2$·$4H_2O$ with ratio of 6:1:2:2 has been developed, and its melting point is ~ 90 °C. Other thermophysical properties of the aforementioned system are presented in the paper of Nan Ren [18]. Several thermophysical properties of the quaternary salt mixture are compared with those of conventional solar salt and HITEC salt as shown in Table 1 [19–21]. The melting point of the new binary eutectic salt mixture is lower than those of conventional solar salt at 220 °C and HITEC salt at 142 °C. In actual large scale applications, the thermal stability of the heat transfer and storage materials is important and must be seriously considered to secure long cyclic life. Molten salt heat transfer and storage materials will experience high-temperature static and dynamic working conditions in the loop of absorption of heat transfer and storage. The static condition is the constant high temperature condition in the absence of heat loss of the heat storage system, whereas the dynamic condition is the sudden cold/hot loading condition with large temperature difference (also called thermal shock conditions). Deterioration of the performance of molten salt is not evident under these conditions in short term. However, long-term operation may affect the thermal properties of molten salt, thereby leading to the decrease in thermal storage efficiency. The resistance of molten salt with low melting point (called as the new molten salt) to change under these two conditions is important to ensure its thermal stability. Variations on the thermophysical properties of the candidate in the experiment can reflect its stability under significant changes in temperature, and the quality of its performance would affect the heat transfer efficiency of the molten salt and the safe and economic operation of the system.

In this paper, thermal shock and constant high temperature experiments were conducted in our laboratory to test and verify the stability of the new quaternary mixtures. Thermophysical properties, including melting point, initial crystallization point, latent heat of melting, and thermal decomposition temperature, were measured using differential scanning calorimetry (DSC) and thermogravimetry (TG). The specific heat of each sample was measured with synchronous thermal analyzer (STA). Thermal conductivity was measured with a laser thermal conductivity analyzer (LFA). Viscosity of the samples was measured using oscillation high-temperature viscometer. The composition changes in the samples were determined by X-ray diffraction (XRD). Experimental results show that the thermophysical properties of the candidate show good repeatability as a whole, and part of the calcium nitrate was converted to calcium carbonate after either the long-term exposure to air or the year-long repeated heating cycles. Nevertheless, this result does not affect the performance test of the candidate, which shows certain high-temperature tolerance and good thermal stability.

2. Experiment scheme

To obtain the thermal stability of the new molten salt, we measured the repeatability of thermophysical properties, including melting point, decomposition temperature, crystallization point, specific heat, density, viscosity, and thermal conductivity of the quaternary molten salts, under constant high temperature and thermal shock. The XRD patterns of the quaternary molten salts were also studied.

The experimental scheme is presented as follows:

(1) Preparation of mixed molten salt. All salts obtained from Beijing Chemical Reagent Factory were at least 99% pure, and the calcium nitrates contain crystallized water molecules. The quaternary molten salt mixture was prepared by mixing four salt components (KNO_3–$NaNO_3$–$LiNO_3$–$Ca[NO_3]_2$·$4H_2O$). Afterward, the molten salt mixture was weighted to the mass ratio of 6:1:2:2 and placed in two molten salt containers made of 316 L stainless steel with good corrosion resistance. The salts were rapidly premelted at 300 °C at a rate of 10 K/min in muffle furnace without nitrogen to ensure that the mixture was completely melted and evenly mixed. The products were naturally cooled down until the salt mixture was solidified to a white mass, which was then sealed in containers with lid and kept in a sweatbox for subsequent experiments. For constant high-temperature experiments, one of the salt containers was heated in the muffle furnace at 520 °C at a rate of 10 K/min for 1200 h. This salt mixture was sampled every 24 h. For thermal shock experiments, the other salt container was rapidly heated in the muffle furnace at 520 °C at a rate of 20 K/min, removed, forcibly cooled down to room temperature, quickly reheated, and then forcibly cooled down again. The same procedure was repeated for 1000 times. Afterward, the salt mixture was sampled at heating–cooling cycles of 1, 10, 30, 50, 70, 90, 100, 150, 200, 300, 400, 600, 800, and 1000. The solidified sample was then ultrafine-pulverized into powder, sealed in corundum crucible with lid, and kept in a sweatbox for further tests and analyses.
(2) STA tests of the new molten salt. The mixture was heated from 30 °C to 500 °C at 10 K/min heating rate. Afterward, the mixture was cooled down from 500 °C to 30 °C at 5 K/min cooling rate under N_2 purging of 30 mL/min. This procedure was repeated three times.
(3) Decomposition temperature measurement. To obtain decomposition temperature, we measured the samples with aluminum oxide crucible. After preheating at 300 °C, this sample was heated from 30 °C to 700 °C at 10 K/min heating rate. The TG curve of the molten salt was determined.
(4) Specific heat, thermal diffusivity, and thermal conductivity measurements. The specific heat of the molten salt was obtained by comparing it with standard sapphire with known specific heat using STA. Thermal diffusivity and thermal conductivity of the mixture were measured by LFA.
(5) Viscosity measurement. The viscosity of mixed molten salt at high

Table 1
Comparison of melting points, decomposition temperature, densities, thermal storage cost of conventional solar salt, HITEC salt, and the quaternary molten salts with low melting point.

Eutectic salt mixture	Melting point (°C)	Decomposition temperature (°C)	Density at 500(°C)	Average specific heat (J/(g·K))	Thermal conductivity (W/(m K))	thermal storage cost ($·kW h)
Solar salt	220	565	1.752	1.50	0.52	5.8
HITEC salt	142	535	1.723	1.40	0.35	10.7
the quaternary salts	96.8	612	1.754	1.56	0.528	8.2