Effect of SiO$_2$ nanoparticles on specific heat capacity of low-melting-point eutectic quaternary nitrate salt

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ABSTRACT

In order to evaluate the effect of nanoparticles on the specific heat capacity of a low-melting-point eutectic quaternary nitrate salt, 1.0 wt% SiO$_2$ nanoparticles with an average size of 20 nm was doped into the mixed salt Ca(NO$_3$)$_2$·4H$_2$O-KNO$_3$-NaNO$_3$-LiNO$_3$. A mechanical dispersion mixer was developed to prepare molten salt nanofluids. The effects of the mixing time (15, 45, 90, 120, and 150 min) and stirring rate (600, 750, and 1000 rpm) on the specific heat capacity of the nanofluids were analyzed using a differential scanning calorimeter. The results showed that the specific heat capacity of the nanofluids varied with the mixing time and stirring rate. It increased by ~ 17.0% at a mixing time of 15 min and stirring rate of 750 rpm. Microstructural characterization of the molten salt nanocomposites was performed using scanning electron microscopy, which showed that special nanostructures, which resemble chain-like nanostructures, were formed on the surface of the solid nanofluids. The special nanostructures with a large specific surface area and high surface energy could increase the specific heat capacity of the molten salt nanofluids.

1. Introduction

Concentrating solar power (CSP) system is an emerging power-generation technology. It uses a concentrator to gather the solar radiation, converts the solar radiation energy into high temperature heat, and then transforms the heat into power [1]. Molten salts are often used as the thermal energy storage materials in the CSP system owing to their desirable properties, such as low melting point, wide temperature range (exceeding 500 °C), low vapor pressure, low viscosity, good chemical stability, and low cost; in addition, they are environment-friendly materials [2–4].

The specific heat capacity of the molten salts is an important property, as it determines the amount of heat that can be stored in the TES materials. The specific heat capacity of the molten salts is usually low, which implies that a large TES volume is required to store a certain amount of thermal energy. By introducing a small amount of nanoparticles (~ 1.0 wt%) in the molten salt (as a base fluid), the specific heat capacity can be increased by more than 20% [5–8].

In 2011, Shin et al. [9] mixed carbonate eutectic (Li$_2$CO$_3$-Na$_2$CO$_3$) with 10 nm SiO$_2$ nanoparticles (1.0 wt%) to obtain a nanofluids and observed that the specific heat capacity increased by 20.0%. Tiznobaik et al. [10] obtained nanofluids with different sizes (5–60 nm) of the SiO$_2$ nanoparticles (1.0 wt%) in carbonate eutectic and revealed that

the specific heat capacity increased by 25.0%. Ho et al. [11] reported an improvement of 19.9% in the specific heat capacity of Hitec salt (KNO$_3$-NaNO$_3$-NaNO$_2$) with an optimal concentration of Al$_2$O$_3$ of 0.063 wt%. An increasing number of studies confirmed that the addition of nanoparticles in eutectic nitrate salts and carbonate can significantly increase their specific heat capacity [12–20].

However, all of the preparation methods for molten-salt nanofluids mainly involve mixing of nanoparticles in a water solution with ultrasound, and then adding the salt into the aqueous nanofluids for sonication (two-step method). This two-step preparation method, which involves the use of water is time-consuming and, in addition, can affect the salt's behavior [13]. Only few works reported the preparation of molten-salt nanofluids without the use of water [21].

In 2017, Chieruzzi et al. [21] proposed a novel preparation method for molten-salt nanofluids, based on high temperature mixing. In their study, the solar salt and nanoparticles were directly mixed at a high temperature using a twin screw micro-compounder. The specific heat capacity increased by 52.1% in the solid phase and by 18.6% in the liquid phase, upon the introduction of 1.0 wt% silica/alumina nanoparticles for 30 min at 200 rpm. However, the base fluid was a binary salt (NaNO$_3$-KNO$_3$, 60–40 wt%) with a melting point of ~ 220 °C, which increases the risk of freezing if the process temperature unexpectedly decreases.

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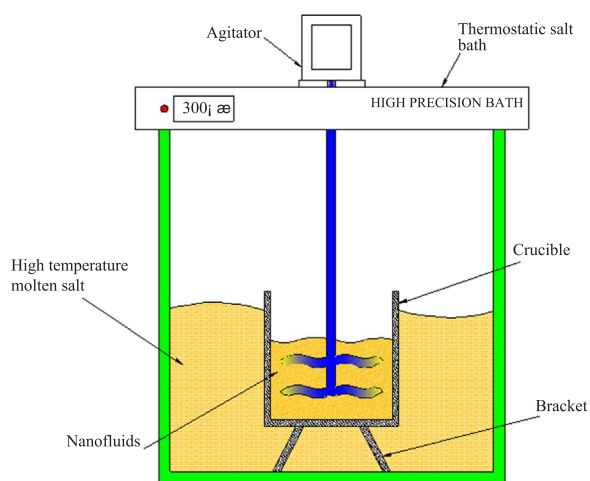 *E-mail address:* luyuanwei@bjut.edu.cn (Y. Lu).

Fig. 1. Schematic diagram of molten-salt nanofluids preparation equipment.

Table 1
Sample of nanofluids prepared by the mechanical dispersion method with different mixing time (15, 45, 90, 120, and 150 min) and stirring rate (600, 750, and 1000 rpm).

Samples	Stirring rate (rpm)	Mixing time (min)
1	600	15
2	600	45
3	600	90
4	600	120
5	600	150
6	750	15
7	750	45
8	750	90
9	750	120
10	750	150
11	1000	15
12	1000	45
13	1000	90
14	1000	120
15	1000	150

Our group developed a new quaternary nitrate ($Ca(NO_3)_2$-$4H_2O$-KNO_3-$NaNO_3$-$LiNO_3$) with a melting point smaller than 90 °C, and a decomposition temperature larger than 610 °C [22]. We prepared a molten-salt nanofluid with the quaternary nitrate as the base salt (BS), and realized that the preparation process was time-consuming [23]. We tried to mix the SiO_2 nanoparticles directly with the BS at a high temperature, using the magnetic stirring method. We revealed that the prepared molten-salt nanofluid had a good stability. However, the magnetization of the magnetic stirrer can be easily lost at higher temperatures [24]. In this study, a novel nanofluid preparation method, which involves mechanical dispersion, was proposed for the synthesis of molten-salt nanofluids. Molten-salt nanofluids were prepared directly by mixing the nanoparticles without water, which can reduce the nanofluid preparation time and improve the preparation efficiency.

2. Experiment

2.1. Experimental setup

Fig. 1 illustrates the proposed molten-salt nanofluid preparation. The setup comprises four main parts: a thermostatic salt bath (FLUKE 6050H), a crucible bracket (SS316), a crucible (SS316), and an electric agitator. The stainless steel crucible containing the high-temperature molten BS is fixed on the trestle, placed in the thermostatic salt bath at a constant temperature of 300 °C (∼ 200 °C larger than the melting point of BS); then, the nanoparticles are dispersed into the molten BS using the agitator. In order to prevent the aggregation of the nanoparticles, the agitator was specially designed with a two-row impeller. The stirring rate and duration can be varied to analyze their effects on the specific heat capacity of the molten-salt nanofluid.

2.2. Nanofluids materials preparation

The molten-salt nanofluids were prepared by the following process.

(1) Base salt preparation. Four types of nitrates $Ca(NO_3)_2 \cdot 4H_2O$, KNO_3, $NaNO_3$, and $LiNO_3$ with a purity of 99.9% were mixed in a fixed weight proportion (2:6:1:2) to prepare the BS.
(2) Nanoparticle addition ratio. The value of 1 wt% of the nanoparticles was chosen as the addition proportion in the study of Zhang et al. [23]. The effects of the nanoparticles on the specific heat capacity of the molten-salt were investigated; the specific heat capacity of the molten salt could be effectively improved. The concentration value of 1 wt% has also been used in other studies for the preparation of molten-salt nanofluids [10,12,14,15,21]. The weights of the BS and SiO_2 nanoparticles were accurately measured using a

high-precision balance (Mettle Toledo, ML204/02). For example, in order to prepare a 30 g molten-salt nanofluid sample, 29.7 g BS and 0.3 g SiO_2 nanoparticles with an average diameter of 20 nm (1.0 wt %) are required, accurately weighted by the balance.
(3) Molten salt melting. A 29.7 g BS was placed in the stainless-steel crucible, and melted in the thermostatic salt bath at 300 °C through stirring for more than 30 min.
(4) Nanofluids preparation. 0.3 g SiO_2 nanoparticles were slowly mixed into the molten BS; they were efficiently mixed with different mixing times and stirring rates. A total of 15 nanofluid samples were prepared with mixing time values of 15, 45, 90, 120, and 150 min and stirring rate values of 600, 750, and 1000 rpm, in an orthogonal experiment. The samples are listed in Table 1.
(5) Nanocomposite salts preparation. Solid-phase nanocomposites with a mass of 30 g were obtained through secondary coagulation of the nanofluids. All of the nanocomposite samples were put in a drying oven at 80 °C to keep them dry before the specific heat capacity measurement.

2.3. Measurement of specific heat capacity

The specific heat capacity was measured using a differential scanning calorimeter (DSC, NETSCH, STA-449F3) with a standard automated procedure (ASTM E1269). The solid nanofluid material was introduced in a sealed aluminum pan with a weight in the range of 10–15 mg, and subjected to the following thermal cycle in a nitrogen atmosphere. At the beginning of each thermal cycle, the sample temperature was maintained at 40 °C for 15 min to stabilize the signal of the calorimeter, and then it was ramped up to 520 °C at a fixed rate of 10 K/min. Then, the sample was maintained at 520 °C for 10 min to ensure a stable temperature base-line.

It is crucial to verify the accuracy of the measurements using an aluminum crucible. Zhang et al. [23] measured the specific heat capacity of lithium nitrate using aluminum crucibles, and revealed that the specific heat capacity was in a better agreement with that reported in the literature. Therefore, the DSC measurements of the heat specific capacity with aluminum crucibles are accurate.

2.4. Scanning electron microscopy

In general, the specific heat capacity of a material is significantly dependent on its phase and structure. In order to understand the origin of the specific heat capacity enhancement in nanofluids, the microstructures of the solid-phase nanofluids and BS were investigated using scanning electron microscopy (SEM, SU8020). Furthermore, energy-dispersive X-ray spectroscopy (EDS) was performed to analyze the