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Preparation and thermal properties of quaternary mixed nitrate with low melting point

Nan Ren, Yu-ting Wu *, Chong-fang Ma, Li-xia Sang

Key Laboratory of Enhanced Heat Transfer and Energy Conservation, Ministry of Education and Key Laboratory of Heat Transfer and Energy Conversion, Beijing municipality, Beijing University of Technology, Beijing 100022, China

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ABSTRACT

Mixed molten salt is considered as a promising medium for both heat transfer and energy storage in solar thermal power because of its many advantages such as large heat capacity, low vapor pressure, low cost, wide range of temperature in application, etc. In order to obtain molten salt with lower melting point and higher decomposition temperature, a new kind of nitrate was prepared based on different mixing ratios of KNO_3–$NaNO_3$–$LiNO_3$–$Ca(NO_3)_2 \cdot 4H_2O$. Experimental results show that the melting point of some molten salts can be down to below 90 °C with their decomposition temperature above 600 °C. The new kind of mixed molten salts has a lower melting point and wider usable temperature range. In addition, other thermal properties such as latent heat of melting, specific heat, density, viscosity, thermal conductivity and thermal stability are measured and analyzed, which are also not worse than that of commonly used mixed molten salt. Therefore, it is a promising medium for both heat transfer and energy storage in solar thermal power plants.

1. Introduction

A concentrating Solar Power (CSP) system is a large-scale, commercially viable way to generate electricity. The use of molten salt heat transfer fluid (HTF) in a CSP system has several obvious advantages. For instance, for a trough plant with salt, it may be possible to raise the solar field output temperature to 450–500 °C, thereby increasing the Rankine cycle efficiency of the power block steam turbine to the 40% range, compared to 393 °C with the current high-temperature oil and a cycle efficiency of 37.6%. The HTF temperature rise in the collector field can increase up to a factor of 2.5, reducing the physical size of the thermal storage system for a given capacity. Moreover, molten salt is cheaper and more environment friendly than the traditional HTF [1]. However, the disadvantage of molten salt as heat transfer fluids is their relatively high melting point, typically 140–240 °C. The operational risk of a freezing-up if the process temperature drops unexpectedly adds cost to systems that use salt as heat transfer fluids. Additional hardware must be installed, such as heat tracing, insulation, or emergency water-dilution systems [2]. The high melting point limits the application of molten salt in CSP system. Therefore, people have been actively developing molten salt with low melting point in recent years.

Sandia National Laboratories has investigated a variety of molten salt mixtures of alkali nitrates and, most recently, quaternary mixtures of sodium, calcium, lithium, and potassium nitrate salts. This effort led to the discovery of mixtures with liquefaction temperatures below 100 °C [3]. These alternative molten salts have demonstrated chemical stability in the presence of air up to approximately 500 °C in laboratory testing, and display chemical equilibrium behavior similar to that of Solar Salt. However, only the viscosity and thermal stability were available, neither specific heat nor thermal conductivity of molten salt was presented in their paper. Through using a Brookfield DV-II+ viscometer, the viscosity of molten salt mixtures was measured. The viscosity near the liquefaction temperature was approximately 200 cP, which is not an unreasonable value for handling in a TES system although the viscosity at temperatures in the middle range of normal operation of a trough system, e.g., 300 °C, is approximately 5–6 cP and is 2–3 cP at 400 °C, as determined by extrapolating the data from the measurable temperature range. However, this method is more suitable for measuring the viscosity of low temperature liquid with high viscosity. There may be relatively large error in using this method to measure the viscosity of high temperature molten salts with low viscosity. Soon afterwards, they explored the lithium, sodium, and potassium compositional space with a 1:1 molar mixture of nitrate/nitrite and identified a five components system with a liquefaction temperature near 70 °C [4]. The melting point of molten salt was further reduced, which opened up a new way for molten salt exploitation. However, the nitrite is not very stable at high

* Corresponding author. Tel.: +86 1067391612x8323.
E-mail address: wuyuting1970@126.com (Y.-t. Wu).

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temperature, and no commercial source of $LiNO_2$ is available. The preparation method is complex, so there is some difficulty for this kind of molten salts to achieve large-scale applications. In addition, they also summarized the most current thermodynamic measurements for some pure salts and mixtures which are of interest as heat transfer fluids and phase change materials (PCM), especially regarding apparent heat of fusion (ΔH_{fus}) and heat capacity (C_p). These are critical for estimating costs when used in thermal storage systems [5]. Iverson et al. researched the thermal properties of three representative salts in the solid-phase: Solar Salt (60 wt% $NaNO_3$, 40 wt% KNO_3), HITEC salt (40 wt% $NaNO_2$, 7 wt% $NaNO_3$, 53 wt% KNO_3) and a low melting point quaternary salt (42.3 wt% KNO_3, 39.4 wt% $Ca(NO_3)_2$, 12.1 wt% $NaNO_3$,6.1 wt% $LiNO_3$) [6]. This work supplements and perfects the low temperature database of molten salts. Accurate information of salt properties in the solid-phase is necessary for understanding recovery from a freezing event as well as for phase change thermal energy storage applications. However, only specific heat value and coefficient of thermal expansion were available, and thermal conductivity was not presented in [6]. Broome et al. tested the temperature-dependent mechanical property of the above three salts compositions, including unconfined compressive strength, Young's modulus, Poisson's ratio, and indirect tensile strength [7]. Concerns regarding the use of molten salt are often related to issues of salt solidification and recovery from freezing events. Their paper provided essential data. Raade et al. exploited a novel composition of nitrates, resulting in a low melting point of 65 °C and a thermal stability limit over 500 °C [8]. However, it contains the common cesium nitrate, which limits the application of molten salt in CSP system. Zhao et al. exploited ternary mixed nitrates composed of 50–80 wt% KNO_3, 0–25 wt% $LiNO_3$ and 10–45 wt% $Ca(NO_3)_2$ (melting point < 100 °C) [9]. In their paper, the melting point, heat capacity, chemical stability and viscosity of molten salt mixtures were measured through experiments, and the thermal conductivity was calculated by the Arrhenius equation. However, the testing temperature of viscosity is only from 130 °C to 190 °C and the freezing point was not presented. In addition, there was an obvious melting peak on the heat capacity curve at about 150 °C. This means that the compositions cannot form an eutectic at about 80 °C, so there may be an operational risk of a freezing-up if the process temperature drops unexpectedly when it is used in the CSP system.

In general, the development tendency of molten salt preparation is to exploit molten salts with low melting point and wide usable temperature. The abovementioned efforts greatly promoted the development of the heat transfer and storage technology of molten salts. However, there are still some problems unsolved, such as lack of high temperature data, difficulty of large-scale application and others.

The authors did a lot of work to exploit molten salts with low melting point. In order to obtain molten salts with lower melting point and higher decomposition temperature, a new kind of molten salts was prepared based on different mixing ratios of KNO_3–$NaNO_3$–$LiNO_3$–$Ca(NO_3)_2 \cdot 4H_2O$. Primary physical and thermodynamic properties of molten salts, including melting point, crystallization point, latent heat, density, viscosity, short-time thermal stability and thermal conductivity, were measured and analyzed comprehensively. Thermodynamic properties such as melting point, latent heat of melting, and thermal decomposition curve of mixed molten salts were measured by Differential Scanning Calorimetry (DSC) and Thermogravimetric (TG) analysis. The density of mixed nitrate was measured by the Archimedean principle. The viscosity of molten salt described in this paper was measured by a high-temperature viscometer. Thermal diffusivity and thermal conductivity were measured by a laser thermal conductivity analyzer (LFA). Experimental results show that the melting point of some molten salts can be down to below 90 °C with their liquefaction temperature above 500 °C.

2. Experimental scheme

In order to obtain molten salt with lower melting point and higher decomposition temperature, a new kind of molten salts was prepared based on different mixing ratios of KNO_3–$NaNO_3$–$LiNO_3$–$Ca(NO_3)_2 \cdot 4H_2O$. Thermodynamic properties were measured, including melting point, crystallization point, latent heat, thermal stability, density, viscosity, specific heat, thermal diffusivity and thermal conductivity of mixed molten salt.

The experimental scheme is presented as follows:

(1) *Preparation of mixed molten salt*. 16 kinds of mixed nitrates were prepared by mixing KNO_3, $NaNO_3$, $LiNO_3$ and $Ca(NO_3)_2 \cdot 4H_2O$ at different mixed ratios. Then, the prepared samples were stored in a drying box kept at 150 °C for 48 h. Thirdly, the dried salts were stored in a muffle furnace at 300 °C for 12 h to melt the mixture completely. This is the method of static melting. Finally, the mixture was taken out, ground, dried and preserved for experiments.
(2) *Optimum selection of mixed salts with lower melting point and crystallization point*. Through analyzing the DSC curves obtained, the mixed molten salts with lower melting point and crystallization point were selected to be utilized for further study.
(3) *Latent heat measurement*. Latent heat is an important parameter to characterize phase change heat storage capacity. Latent heat of the selected salts is measured by analyzing the DSC curves.
(4) *Density measurement*. Density is an important physical and chemical property of molten salts, and has its significance in practical and theoretical research. In this paper, the density of mixed molten salts was measured by the Archimedean principle.
(5) *Viscosity measurement*. The viscosity of molten salt at high temperature is close to or less than that of water, and the molten salt has a strong corrosiveness at high temperature. Therefore, it is very difficult to measure the viscosity of molten salt at high temperature. By means of rotary oscillation, the viscosity of mixed molten salt was measured.
(6) *Thermal stability research of molten salt*. Through analyzing the TG curves, the decomposition temperature of sample was obtained. Then the mass loss of sample after the cyclic experiments of four cycles from 20 °C to 550 °C was measured. After the above analysis, the molten salts were further screened to get an optimum one.
(7) *Specific heat and thermal conductivity measurements of the optimum molten salt*. Specific heat of molten salt was measured by a Simultaneous Thermal Analyzer (STA). Thermal diffusivity and thermal conductivity were measured by the laser thermal conductivity analyzer (LFA).

Table 1
Mass ratio of mixed nitrates (KNO_3:$NaNO_3$:$LiNO_3$:$Ca(NO_3)_2 \cdot 4H_2O$).

No.	Mass ratio (KNO_3:$NaNO_3$: $LiNO_3$:$Ca(NO_3)_2 \cdot 4H_2O$)	No.	Mass ratio (KNO_3:$NaNO_3$: $LiNO_3$:$Ca(NO_3)_2 \cdot 4H_2O$)
1	1:1:7:1	9	1:3:1:5
2	1:1:1:7	10	3:1:1:5
3	1:7:1:1	11	3:2:1:4
4	7:1:1:1	12	5:2:1:2
5	4:1:1:4	13	6:1:1:2
6	1:1:4:4	14	5:1:2:2
7	2:2:2:4	15	6:1:2:2
8	2:1:3:4	16	5:1:1:2