Solar Energy Materials and Solar Cells 169 (2017) 297–303

Contents lists available at ScienceDirect

Solar Energy Materials and Solar Cells

journal homepage: www.elsevier.com/locate/solmat

The enhanced specific heat capacity of ternary carbonates nanofluids with different nanoparticles

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A R T I C L E I N F O

Keywords:
Ternary carbonate
Specific heat capacity
Nanoparticle
Nanofluid

A B S T R A C T

Ternary carbonates with a relative low melting point and a high operating temperature is one of the promising heat transfer fluids for Concentrated Solar Power (CSP). In the present work, ternary carbonates nanofluids of K_2CO_3-Li_2CO_3-Na_2CO_3 (4:4:2, mass ratio) with nanoparticles were prepared by using a two step solution method. The specific heat capacity of ternary carbonates nanofluids with different nanoparticles (SiO_2, CuO, TiO_2, Al_2O_3) or SiO_2 with different size (5, 20, 30, 60 nm) were investigated. The results show that SiO_2 nanoparticles are the most effective additive among of the chosen nanoparticles in enhancing the specific heat capacity of ternary carbonates. The enhancement of specific heat capacity of ternary carbonates is 78.0–116.8% in the range of 500–540 °C when adding SiO_2 in the range of 5–30 nm. The enhancement of specific heat capacity of ternary carbonates nanofluids with CuO, TiO_2 and Al_2O_3 are 50.6–73.9%, 31.1–56.5% and 50.6–66.5% in the range of 500–540 °C, respectively. It is proved that there is no chemical reactions between ternary carbonates and the added nanoparticles. The difference in the enhanced specific heat capacity is mainly depended on the dispersive state of nanoparticles and the resulting amount of needle-like nanostructures in ternary carbonates nanofluids.

1. Introduction

Concentrated Solar Power (CSP) is considered as a reliable large-scale renewable energy to produce electricity. To decline the cost of generation electricity, the heat transfer fluid in CSP system should be operated at the temperatures of 600–800 °C, and its heat capacity need to be more than 2.25 J/g K [1]. The molten salts such as nitrates, chlorides, carbonates can operate at high temperature. However, their specific heat capacity are generally less than 2 J/g K [2]. Therefore, enhancing the specific heat capacity of molten salts is important to improve the overall efficiency of CSP and to reduce the generation cost of electricity.

Nanofluid is a new type of heat transfer fluid containing a small amount of nanoparticles (1–100 nm) [3]. Many researches indicated that the thermal conductivity of fluid can be greatly enhanced by adding nanoparticles. Choi [4] discovered that the enhancement of thermal conductivity for 1.0 vol% carbon nanotubes in oil is 150%. Murshed [5] reported that the enhancement of thermal conductivity for 5.0 vol% TiO_2 in water is 30%. Harikrishnan [6] found that the enhancement of thermal conductivity for 0.3 wt% TiO_2 in stearic acid is 70.53%.

Similarly, specific heat capacity of molten salts can be highly enhanced by doping with a minute concentration of nanoparticles. The specific heat capacity of binary nitrates can be increased by 10.48% by adding 0.1 wt% CuO nanoparticles [7]. The specific heat capacity of Hitec can be increased by 19.9% by adding 0.063 wt% Al_2O_3 nanoparticles [8]. In addition, Tiznobaik [9] dispersed 1.5 wt% SiO_2 (5, 10, 30 and 60 nm) in binary carbonates by a two step solution method and found that the specific heat capacity of binary carbonates is enhanced by 25%, regardless of the size of the embedded nanoparticles. However, Dudda [10] reported that the enhancement of specific heat capacity of binary nitrates nanofluids is related to the size of SiO_2 (5, 10, 30 and 60 nm). That is to say, the effects of the nanoparticles size on the specific heat capacity of molten salts nanofluids is not consistent. In addition, there are few studies to explore the effects of different kinds of nanoparticles on the specific heat capacity of the same molten salts. Moreover, there is yet no a clear picture of mechanism for the enhancement of specific heat capacity. The proposed mechanisms [9,11] of molten salts nanofluids include the size effect of nanoparticles, the high thermal resistance between solid-fluid interfaces, the semi-solid layer around the nanoparticles and the special needle-like nanostructures. Therefore, more studies should be conducted to focus on the enhancement mechanisms for molten salt nanofluids with different kinds of nanoparticles.

In the present work, we try to prepare ternary carbonates K_2CO_3-Li_2CO_3-Na_2CO_3 (4:4:2, mass ratio) with nanoparticles and measure

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http://dx.doi.org/10.1016/j.solmat.2017.05.032
Received 30 September 2016; Received in revised form 30 December 2016; Accepted 15 May 2017

their specific heat capacity. Compared with binary carbonates, ternary carbonates K_2CO_3-Li_2CO_3-Na_2CO_3 (4:4:2, mass ratio) has a relatively low melting point (410.5 °C) and a high operating temperature (over 800 °C), which can significantly improve the Rankine cycle efficiency of CSP [12]. Therefore, in this work, this ternary carbonates are used as base salt to prepare high temperature nanofluids. Different spherical nanoparticles (SiO_2, CuO, TiO_2, Al_2O_3) and SiO_2 nanoparticles in the range of 5–60 nm are chosen as additive. Effects of the type and size of nanoparticles on specific heat capacity of ternary carbonates are investigated. An electric thermostatic drying oven is used to dry the mixture solution, which can help to uniformly heat in all direction. Differential scanning calorimetry (DSC), scanning electron micrography (SEM) and X-ray diffraction (XRD) are employed to characterize the as-prepared ternary carbonates nanofluids.

2. Experimental

2.1. Preparation of ternary carbonates nanofluids

The purity of potassium carbonate, lithium carbonate and sodium carbonate is all 99.7%, without further purification. Ternary carbonates of K_2CO_3-Li_2CO_3-Na_2CO_3 were prepared through the direct mixing method according to mass ratio (4:4:2). A two step solution method to prepare ternary carbonates nanofluids is as follows. Firstly, 2.5 g of ternary carbonates is dissolved in 250 ml deionized water and then 25 mg of spherical nanoparticles is dispersed in the water solution. Secondly, the water solution is sonicated for 120 min to get a uniform solution. At last, the obtained mixed solution is evaporated in an electric thermostatic drying oven at 180 °C. The chosen spherical nanoparticles are SiO_2, CuO, TiO_2, and Al_2O_3 with the average size of 20 nm. The ternary carbonates nanofluids with different sized spherical SiO_2 nanoparticles (5, 20, 30, 60 nm) are prepared at the same procedure. The samples are listed in Table 1.

2.2. Measurement of specific heat capacity and density

A Simultaneous Thermal Analyzer (STA-449F3, NETZSCH) is employed to analyze the specific heat capacity. Aluminum crucibles with lids are used as the container of the sample. The standard procedures of DIN51007 is used to measure the specific heat capacity of as-prepared samples. The specific heat capacity of all samples are measured three times in the range of 40–560 °C. The specific heat capacity of binary carbonates Li_2CO_3-K_2CO_3 (32:68, molar ratio) is measured to verify the accuracy of the instrument. The average specific heat capacity of binary carbonates is 1.56 J/g K in the range of 525–555 °C, which is in agreement with the value reported in previous literature (1.60 J/g K) [13]. The density of ternary carbonates at 540 °C is measured by using the molten material physical capability instrument (RTW-10) based on the principle of Archimedes.

2.3. Characterization

Scanning electron micrography (SEM, S-3400N or S4800) and X-ray diffraction (XRD, D8 Advance Bruker/AXS) are used to determine the change of the microstructure and the composition of ternary carbonates after adding nanoparticles. All samples are needed to be heated to 600 °C and kept constant for 30 min, and then cooled to the room temperature.

3. Results and discussions

3.1. Effects of adding different nanoparticles on specific heat capacity of ternary carbonates

In this section, we investigate the specific heat capacity of ternary carbonates nanofluids containing SiO_2, CuO, TiO_2, Al_2O_3 nanoparticles, respectively. All ternary carbonates nanofluids were prepared at the evaporation temperature of 180 °C in an electric thermostatic drying oven. Fig. 1 shows the specific heat capacity curves of ternary carbonates and ternary carbonates nanofluids with different nanoparticles. The obtained specific heat capacity values are listed in Tables 2, 3.

As we can see in Fig. 1, the specific heat capacity of the pure ternary carbonates is very stable in both solid and liquid. However, for ternary carbonates nanofluids with different nanoparticles, the specific heat capacity increases with the increase of temperature in liquid. The reason may be that Brownian motion of nanoparticles becomes strong at high temperature, and the electrostatic interaction between nanoparticles and molten salts enhances with the increase of temperature. Shown in Table 2, the specific heat capacities of all ternary carbonates containing different nanoparticles in solid are more than that of ternary carbonates. From Table 3, the enhancement of specific heat capacity in liquid changes more obviously. As for TC-CuO-180-20 and TC-Al_2O_3-180-20, adding CuO and Al_2O_3 nanoparticles induces a great enhancement in specific heat capacity of ternary carbonates. The enhancement of specific heat capacity is 50.6–73.9% and 50.6–66.5% in the range of 500–540 °C, respectively. The difference in the enhancement of specific heat capacity for TC-CuO-180-20 and TC-Al_2O_3-180-20 is small. However, it is reported that the enhancement of specific heat capacity of binary nitrate nanofluids is only 10.48% when 0.1 wt% CuO is doped into binary nitrate by mechanical dispersion method [7]. In addition, the enhancement of specific heat capacity of Hitec with 0.063 wt% Al_2O_3 is 19.9% [8]. Maybe, CuO and Al_2O_3 nanoparticles can enhance effectively the specific heat capacity of ternary carbonates. In the case of TC-TiO_2-180-20, it shows relatively low rise in specific heat capacity, but the standard deviation is the smallest. Among of all samples, the specific heat capacity of TC-SiO_2-180-20 is the maximum. That is, SiO_2 nanoparticles are the most effective additive among of the chosen nanoparticles in enhancing the specific heat capacity of ternary carbonates, which can make enhancement of 79.9–113.7% in the range of 500–540 °C.

According to the above results, we can conclude that the chosen nanoparticles can effectively improve the specific heat capacity of ternary carbonates as the base salt. During the preparation, the mixture solution of ternary carbonates and nanoparticles is dried in an electric thermostatic drying oven, which is different from heating at the bottom.

Table 1
Ternary carbonates and ternary carbonates nanofluids with different nanoparticles.

Samples	Constituents	Evaporation temperature
TC (ternary carbonates)	K_2CO_3-Li_2CO_3-Na_2CO_3(4:4:2, mass ratio)	–
TC-SiO_2-180-20	K_2CO_3-Li_2CO_3-Na_2CO_3, 1 wt% SiO_2(20 nm)	180 °C
TC-CuO-180-20	K_2CO_3-Li_2CO_3-Na_2CO_3, 1 wt%CuO(20 nm)	180 °C
TC-TiO_2-180-20	K_2CO_3-Li_2CO_3-Na_2CO_3, 1 wt%TiO_2(20 nm)	180 °C
TC-Al_2O_3-180-20	K_2CO_3-Li_2CO_3-Na_2CO_3, 1 wt%Al_2O_3(20 nm)	180 °C
TC-SiO_2-180-5	K_2CO_3-Li_2CO_3-Na_2CO_3, 1 wt% SiO_2(5 nm)	180 °C
TC-SiO_2-180-30	K_2CO_3-Li_2CO_3-Na_2CO_3, 1 wt% SiO_2(30 nm)	180 °C
TC-SiO_2-180-60	K_2CO_3-Li_2CO_3-Na_2CO_3, 1 wt% SiO_2(60 nm)	180 °C