



# Heat capacity of nanofluids for solar energy storage produced by dispersing oxide nanoparticles in nitrate salt mixture directly at high temperature



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## ABSTRACT

Molten salts as phase change materials (PCMs) can be used as thermal storage media in concentrated solar power (CSP) plants. The addition of nanoparticles into a base fluid (producing the so called nanofluid) can enhance its thermal properties. The most common technique involves the use of water. We present a new procedure based on high temperature mixing. In particular, different nanofluids were developed by mixing NaNO<sub>3</sub>-KNO<sub>3</sub> (60–40 wt %) solar salt with 1.0 wt% of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and a mix of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> nanoparticles at 300 °C using a twin screw micro-compounder. The effect of different screw speeds (100 and 200 rpm) and mixing times (15 and 30 min) were studied. The results showed that the nanoparticles induce an increase of the heat of fusion of 1.5–7.4% while the onset temperatures decrease for all the nanofluids independently from the processing conditions (up to 9.7 °C). Moreover, an increase in the specific heat (*C<sub>p</sub>*) is recorded mainly for the nanofluid with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> with a maximum of 52.1% in solid phase and 18.6% in liquid phase after 30 min of mixing at 200 rpm. The same nanofluid showed the highest stored heat. Particle aggregation into clusters in solid state was detected by scanning electron microscopy (SEM) but smaller aggregates resulted for higher mixing times and screw speed related to the highest *C<sub>p</sub>*. Moreover, smaller grains in the nanofluids were detected with respect to the base salt morphology. Thus, the nanofluid produced with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> nanoparticles at 200 rpm for 30 min gives the best overall performances.

This work showed that nanofluids with enhanced thermal properties can be obtained with an innovative mixing process directly at high temperature, eliminating the water evaporation step.

## 1. Introduction

The increase of carbon dioxide emissions due to the increase of the world energy demand can be faced by increasing the energy efficiency of the industrial processes (heat recovery) and by promoting the use of renewable sources such as solar energy. The main issue is then to make these natural sources more competitive by reducing their cost. This can be done, for example, by using an efficient thermal energy storage system (TES) [1] at medium temperature (ranging from 100 °C to about 300 °C) or high temperature (*T* > 400 °C).

Since the latent heat for a solid-liquid phase change is high compared to sensible heat, Latent Heat Thermal Energy Storage (LHTES) systems utilizing phase change materials (PCMs) can be reduced in size respect to systems based on sensible heat. In particular, PCMs needed for thermal energy storage must be characterized by large latent heat and high thermal conductivity as well as thermal stability at high temperatures. They should possess a melting temperature lying in

the practical range of operation, offer chemical stability and they should be low cost, nontoxic and non-corrosive.

Several studies on PCMs used as thermal energy storage material have been published [2–5]. In particular improving TES performance using these molten salts have been reported by many research groups [6]. Molten salts in fact are the most suitable PCMs for latent heat storage in concentrated solar plants (CSP) due to their wide range of melting points ranging from 200 °C to 500 °C [2,3,7,8] their large latent heat, their stability over a relatively wide range of temperatures, their excellent heat capacity.

One of the most used molten salt as thermal energy storage fluid consists of sodium nitrate and potassium nitrate mixture (60–40 wt%). However, for energy storage applications an improvement of the thermophysical properties (such as thermal conductivity, specific heat, melting point, latent heat, density) of molten salts is often desirable. In order to achieve this enhancement several researchers studied the effect of the addition of a small amount of nanoparticles (mainly oxide

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nanoparticles like silica, alumina, titania) to the molten salt (as base fluid) thus obtaining the so called nanofluid (the concept of nanofluid was introduced by Choi [9] in 1995 as nanometer-sized particles suspended in heat transfer fluids). These nanofluids can be efficiently used as storage media with obvious advantages for the thermal energy storage systems since a high thermal capacity allows the storage of a greater amount of heat in a smaller volume [10].

Among all the thermal properties of nanofluids the specific heat needs further investigation.

It is known that the specific heat of nanofluids depends on both the specific heat of the base fluid and the nanoparticles as well as to the percentage of nanoparticles and the temperature at which the nanofluids work. The preparation method could also influence the final thermal properties.

Up to now a standard preparation method for nanofluids has not been identified depending mainly on the base fluid used [11]. In general, the most common technique consists in mixing the materials with ultrasound at low temperatures (when the melting point of the base fluid is very low) or in water solution (when the melting point of the base fluid is high). In particular, the nanofluids based on molten salts are mainly prepared by mixing the nanoparticles and the salts in water solution in order to dissolve the salts without melting them [12–20]. However, the procedure involving the use of water is a time consuming method and can also affect the salt behavior [21]. Only few works report the preparation of nanofluids based on molten salt and nanoparticles without water, by mixing them in liquid state in a crucible [22] or by mixing them in solid state with a ball mill [23].

In this work a new a mixing method made directly at high temperature was used to prepare the nanofluids and the effect of different process parameters as well as the type of nanoparticles on the thermal properties and the microstructure of the nanofluids was evaluated.

## 2. Materials and methods

### 2.1. Materials

A nitrate salt mixture (60 wt% NaNO<sub>3</sub> and 40 wt% KNO<sub>3</sub>) commonly used in high temperature solar plants as thermal energy storage media has been selected as PCM. The salts were provided from Sigma-Aldrich (St. Louis, MO, USA). The melting point of this mixture is about 220 °C which is a suitable temperature for different medium-low power applications [5].

The nanoparticles added were: SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (82–86/14–18 wt%) called Aerosil300, Aerioxide AluC, Aerosil Cok84 (supplied by Evonik Industries, Hanau-Wolfgang Germany) with an average diameter of 7, 13 and 2–200 nm respectively. These nanoparticles were used in our previous work where they were mixed in water solution [12]. In this work we decided to use the same materials in order to make a comparison.

### 2.2. Nanofluid preparation

The salt mixture was firstly prepared by mixing 60 parts of NaNO<sub>3</sub> with 40 parts of KNO<sub>3</sub> in powder followed by heating at 300 °C in order to mix the two salts by melting. The neat molten salt used was kept at 300 °C for 48 h in order to remove all the entrapped water. The mixture was then cooled down at room temperature and ground and 1.0 wt% of nanoparticles was added to the base salt.

In this work a new procedure was used to prepare the nanofluids. The binary salt and the nanoparticles were directly mixed at high temperature by using a twin screw micro-compounder shown in Fig. 1 (DSM Xplore, Model 2005, Geleen, Netherlands). It is based on a conical twin-screw extruder with an incorporated recirculating channel. During the mixing phase, the recirculating channel is used to recycle the melt for more thorough mixing.

The two screws permit a complete mixing of the nanoparticles with the base salt. The mixing time and rotor speed were the two main processing parameters.

In order to investigate the influence of these parameters on the thermal properties of the nanofluids, the materials were mixed at 100 and 200 rpm, for 15 and 30 min. The chamber was filled with 19.8g of NaNO<sub>3</sub>-KNO<sub>3</sub> and 0.2g of nanoparticles measured on an analytical balance with ± 0.1 mg precision (Mettler Toledo, type AB104-S, Greifensee, Switzerland). At the end of the mixing phase, the nanofluid obtained was allowed to cool down at room temperature. The samples obtained were immediately used for the calorimetric analysis and the morphology investigation.

### 2.3. Differential scanning calorimetric analysis

The nanofluid samples were introduced in sealed aluminum pans and analyzed by differential scanning calorimetry (DSC) tests performed on a Mettler-Toledo DSC 822E/400 and subjected to the following thermal cycle in nitrogen atmosphere: held at 150 °C for 5 min (to remove any absorbed water), heating from 150 °C to 300 °C at 20 °C/min, held at 300 °C for 5 min, cooling from 300 °C to 150 °C at 20 °C/min. This scanning rate was chosen as a compromise between low scanning rates (around 2 °C/min) needed for latent heat measurements and higher scanning rates (around 40 °C/min) that should be used for specific heat evaluation to minimize the precipitation of nanoparticles during DSC measurement [16]. The use of 20 °C/min is also reported in literature [16,19,24,25]. Five consecutive cycles were run on each sample. The base salt was subjected to the same thermal cycle and its thermal properties compared with those obtained with the nanofluids. In particular, the phase change heats, the melting temperatures and the specific heats (*C<sub>p</sub>*) of the samples were evaluated from the calorimetric analysis.

The procedure followed to calculate the specific heat was the three-step procedure [26]. In the first step a measurement was taken with two empty pans and the baseline heat flux (*Q<sub>0</sub>*) recorded. In the second step two pans were introduced into the calorimeter: one with the reference sample with a known specific heat and one empty. The heat flux recorded was *Q<sub>ref</sub>*. In the third step a pan with the sample and an empty pan were introduced into the calorimeter and the heat flux into the sample (*Q<sub>sample</sub>*) recorded. The specific heat of the sample was obtained as follows:

$$C_{p, sample} = \frac{Q_{sample} - Q_0}{Q_{ref} - Q_0} \frac{m_{ref}}{m_{sample}} C_{p, ref} \quad (1)$$

where *m<sub>ref</sub>* and *m<sub>sample</sub>* are the reference and sample masses respectively. The maximum uncertainty related to Eq. (1) was ± 3%. The thermal equilibrium model (also called simple mixing model) was also used to compare the specific heat values obtained with experimental analysis and the theoretical predictions [27]. Based on this model the predicted specific heat of a nanofluid can be expressed by:

$$C_{p, nf} = \frac{\rho_{np} \phi_{np} C_{p, np} + \rho_f \phi_f C_{p, f}}{\rho_{np} \phi_{np} + \rho_f \phi_f} \quad (2)$$

where *C<sub>p</sub>* is specific heat, *φ* is the volume fraction, *ρ* is the density and the subscripts np, nf, and f refers to nanoparticle, nanofluid and base fluid.

### 2.4. Scanning electron microscopy

After DSC measurement the samples were stored in a desiccator in order to avoid moisture absorption. One specimen for each system was metallized with a thin layer of gold (15 nm, 99.99% of gold, 2 × 10<sup>-6</sup> Torr) in a thermal evaporator (Sistec thin film equipment model GP 20 by Kenosistec Angelantoni Group, Massa Martana (PG) - Italy) and then analyzed with a Field Emission Scanning Electron Microscope (FESEM

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