

# Experimental investigation on supercooling, thermal conductivity and stability of nanofluid based composite phase change material

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## ABSTRACT

With increasing concerns over global warming, there is compelling need to apply energy technologies to improve energy efficiencies. One of the new technologies is the use of phase change materials (PCMs) to store energy and release it on demand. However, most of these materials undergo supercooling, aggregation and have low thermal conductivity that inhibits effective heat transfer. In this paper supercooling, stability, energy storage, thermal conductivity and latent heat of fusion of water based nanofluid of barium chloride dehydrate ( $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ) were experimentally studied by adding a mass fraction of 0.2 wt.%–1 wt.% magnesium oxide (MgO) and 0.2 wt.%–1 wt.% multi-walled carbon nanotubes (MWCNTs). Results show that by adding separately mass fraction of 1% of MgO and MWCNTs reduce the supercooling degree of barium chloride dehydrate by 85% and 92% respectively. At the same mass fraction, thermal conductivity also improves by 6% on addition of MWCNTs and 17% on addition of MgO. However, the enthalpies reduce by 7% at 1 wt.% MgO and by 12.3% at 1 wt.% MWCNTs. It was found that MgO exhibited relatively higher thermal conductivity and a lower reduction in latent heats at a mass fraction of 1 wt.%. Surfactant was also found to prevent aggregation at low temperatures.

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## 1. Introduction

Cool thermal energy storage (CTES) technology, which is storing cool thermal energy in order to bridge the time gap between the energy availability and energy use is being considered as one of the best method for thermal energy management [1,2]. The CTES is useful in central air-conditioning systems in large buildings [3,4], supermarkets refrigeration, high powered electronic cooling applications, marine applications, pharmaceutical field and various industrial cooling process applications where the cooling requirement is highly intermittent. The efficient operation of CTES system reduces the additional energy consumption during its cyclic charging and discharging operations. Therefore, PCMs have been applied to increase thermal energy storage capacity of different systems [5]. The use of PCMs provides higher heat storage capacity and a constant temperature behavior during charging and discharging compared to sensible heat storage. High energy storage density is a desirable property of any storage system which guarantees smaller size for the storage system. In the application of PCMs, the most used phase change is solid–liquid

phase change as the volume is easily controlled. The substances used can be organic such as paraffin and fatty acids or inorganic such as aqueous salts solutions. Water based inorganic salts are widely used as a PCMs because of low cost, readily available and environmental friendly [6]. However, the most serious problem encountered when using these PCMs is the supercooling phenomenon during solidification [7,8], aggregation at low temperature [9,10] and a low thermal conductivity [11]. A lower degree of supercooling results in a better coefficient of performance of the refrigeration system [12] and a high thermal conductivity reduces the solidification and melting time of PCMs. In recent years, many researchers have studied ways of reducing supercooling and at the same time increase thermal conductivity [13,14]. One of the ways is to use nanoparticles to make nanofluid which can be used as a PCMs. Researchers have pointed out that nanostructures can reduce the supercooling degree and increase thermal conductivity [13,15,16]. Qinbo et al. [17] carried out thermal conductivity, supercooling degree, latent heat, specific heat, and rheological behaviors of nano PCMs by suspending a small amount of  $\text{TiO}_2$  nanoparticles in saturated barium chloride aqueous solution; his experimental results showed that with volume fraction of 1.130%, the thermal conductivities of nanofluids PCMs were enhanced by 12.76% at  $-5^\circ\text{C}$  and the supercooling degree was reduced by 84.92% but the latent heat and specific heat were slightly decreased. Yudong et al. [15] carried out an experimental study

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on the supercooling degree and nucleation behavior of nanofluids phase change material which were prepared by adding small fraction of graphene oxide nanosheets in deionized water without any dispersants. The results showed that the supercooling degree was reduced by 69.1%, and the nucleation started in advance, reducing the time by 90.7%. Liu et al. [18] carried out a research on nucleation rates and supercooling degree of deionized water and graphene oxide nanofluids using classical nucleation theory. He found that whereas the supercooling degree of deionized water was approximately 31.5 K, the supercooling degrees of four different concentrations of graphene oxide nanofluids were 7.98, 7.93, 3.05, and 3.03 K concluding that the supercooling degrees were reduced by more than 74% with the corresponding increase in volume concentration. Stability of nanofluid has also been carried out by many researchers [19,20] where the focus was on stability with respect to pH, zeta potential, particle size distribution, and its effect on viscosity and thermal conductivity. Most of these previous researchers' mainly focused on the nanofluid PCMs used in the air conditioning cool storage, where the phase change temperatures are above 0 °C. However, some enterprises, such as ice and chemical plant, need the cool storage temperature below 0 °C. At the moment there are few researches and applications for nanofluid PCMs in sub-zero temperature cool storage available [5]. In this paper, considering the application in water ice making plant where the temperature is between -1 °C to 0 °C. While the phase-change temperature of 24 wt.% BaCl<sub>2</sub>·2H<sub>2</sub>O solution is about -7.5 °C and considering heat losses together with overcoming supercooling problem of water in some cases [21–23], the 7.5 °C temperature difference is appropriate. Compared with other phase change materials that have found use in sub-zero temperature application such NaCl–H<sub>2</sub>O and CaCl–H<sub>2</sub>O, barium chloride dehydrate is found to have the highest latent heat of fusion. So it was screened out as a suitable candidate for PCMs. The main focus in this paper was to experimentally study supercooling, stability, latent heat of fusion and thermal conductivity of barium chloride dehydrates under the effect of different cooling temperatures, freeze cycling and nano particles concentration of MgO and MWCNTs. Nanofluids were prepared using a two-step method. *N,N*-dimethyl formamide was used as surfactant to stabilize the dispersion of MWCNTs nanoparticles in aqueous barium chloride dehydrate. SDS surfactant was used for MgO nanofluid to enhance its stability.

## 2. Material and methods

### 2.1. Experimental setup

The experiment was set up as shown in Fig. 1. It consists of agilent data logger (34972A), computer, low-temperature thermostatic bath (DC-6515, supplied by Shanghai HengPing Instrument Factory), thermocouples and polyurethane sealing cover.

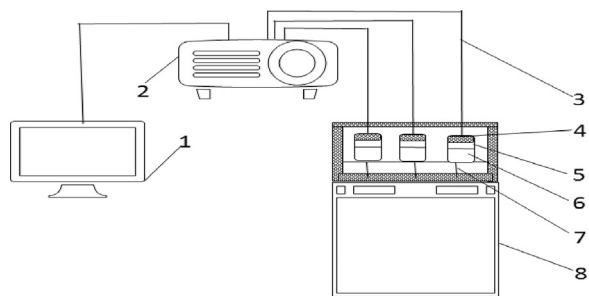


Fig. 1. Experimental setup.  
1-computer; 2-agilent data logger; 3-thermocouple; 4-polyurethane sealing cover; 5-beaker; 6-nanofluid PCM; 7-bracket; 8-low- temperature thermostat bath.

temperature thermostat bath has a temperature range of -65 °C to 100 °C; its precision is ±0.05 °C. For the purpose of this experiment, the low temperature thermostat bath's temperature was set at -20 °C for freezing and 20 °C for melting. The T-type thermocouples which were used to take temperature measurements at various points have a precision of ±0.5 °C and thermal response period of 0.4 s.

### 2.2. Experimental technique

In order to evaluate how different factors influence supercooling degree of water based barium chloride dehydrate, different cooling temperatures and nanoparticle concentrations were used. The supercooling characteristic test was carried out using constant temperature bath (DC 6115, Shanghai Hengping Equipment Company). To avoid the contamination of barium chloride dehydrate solution which may interfere with the supercooling degree and thermal conductivity measurements, different beakers, glass rod and tweezers were placed into the ultrasonic machine to clean them by means of ultrasonic vibrations. Polyurethane sealing covers were used to cover the tops of the beakers to avoid the content from being contaminated by external environment. The thermocouples wires pass through the polyurethane sealing covers and stretch into the solution with thermocouple probes being placed at the mid position of the beaker where temperature is taken. An electronic balance (FA2004) which was used to measure the weights of experimental materials has a precision of ±0.1 mg. Thermal conductivities of nanofluids were measured by the Hot disk (TPS 500, Thermal Constant Analyser, TCA, Sweden) where KS-1 probe sensor was used. Calibration of instrument with DI water was performed before starting off the measurements of thermal conductivities of the nanofluids. Thermal conductivity of DI water at 20 °C was found to be 0.602 W/mK. The latent heat of the base fluids and the nanofluids were measured with a differential scanning calorimeter (DSC 200, NETZSCH, German) with an accuracy of ±1.0%. The DSC instrument was first calibrated using a standard high-purity indium specimen prior to use. For each sample at least five measurements were carried out and average value with a standard deviation of less than 1% was given as a result. To test stability of nanofluid, a volume of nanofluid sample was kept in glass beaker and photographs were taken at regular time interval.

### 2.3. Preparation of nanofluid

A BaCl<sub>2</sub>·2H<sub>2</sub>O (produced by Sinopharm Chemical Reagent Co, Ltd purity ≥99.5%) without additives was prepared by dissolving it in deionized water to make an aqueous solution of 24 wt.% BaCl<sub>2</sub>·2H<sub>2</sub>O. The solution was evenly stirred in order to ensure all the barium chloride dehydrate dissolves. The nanofluid was prepared by a two-step method. The nanoparticle has a bigger specific surface area and surface energy because of its small size. It is apt to reunite in the process of preparation, reprocessing and the application therefore obtaining a well-distributed and stabilized nanofluids is a critical step. Five samples of 0.2, 0.4, 0.6, 0.8 and 1 wt.% MgO and 1 wt.% of SDS as surfactant (Supplied by Aladdin Industrial Corporation, Shanghai, China) were prepared for experiment. First the solution was stirred in a magnetic stirrer for 30 min and a then ultrasonicated for 45 min at temperature of 50 °C, with a working time of 5 s and stop time of 10 s. The same mass fraction was used to prepare MWCNTs (Supplied by Aladdin Industrial Corporation, Shanghai, China) nanofluid. 1 wt.% of *N,N*-dimethyl formamide, having a molecular formula C<sub>3</sub>H<sub>7</sub>NO (Supplied by Aladdin Industrial Corporation, Shanghai, China) was first put into each five samples then stirred in a magnetic stirrer (HJ-6A, West Jintan Zhengrong Experiment Equipment Company,

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