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# PHASE CHANGE MATERIAL FOR THERMAL ENERGY STORAGE IN BUILDINGS BASED ON SODIUM SULFATE DECAHYDRATE AND DISODIUM HYDROGEN PHOSPHATE DODECAHYDRATE

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## ABSTRACT

The worldwide increasing energy demand and 2050 net zero carbon target urge the globe to solve the energy challenge. Thermal Energy Storage (TES) has received significant attention in recent years as TES can be integrated into heating, ventilation, and air-conditioning systems where the energy would be stored during low-demand times and dispatched during high-demand times, resulting in controlling the peak load and improving energy savings. Material development is an integral part of TES. Salt hydrates are appealing due to cost-effectiveness, low- to no toxicity, and their high melting enthalpy, where energy is stored as latent heat. However, most salt hydrates are prone to incongruent melting (i.e., phase separation upon melting), which results in poor stability and large supercooling. In this study, we produced a highly stable novel energy storage material at a composition of 32 wt% sodium sulfate decahydrate, 52 wt% sodium phosphate dibasic dodecahydrate, 12 wt% milled expanded graphite, and 4 wt% borax. The material has a melting temperature of 28°C and an energy storage capacity of 167 kJ/kg with a supercooling of less than 3°C. The system showed no loss in energy storage performance after 150 cycles. The findings suggest that the novel energy storage material developed in this might be utilized in building heating and cooling applications.

*Keywords: thermal energy storage, phase change materials, building energy storage*

## 1. INTRODUCTION

Buildings are one of the most energy-intensive sectors and a critical contributor to carbon dioxide emissions while accounting for one-third of energy consumption worldwide [1]. Among all building energy consumptions (heating and cooling, lighting, ventilation, and major appliances), heating and cooling account for almost half of the energy consumed in residential buildings [2]. To reach the 2050 net zero carbon target, significant energy and carbon emission reductions in buildings are critical. Thermal Energy Storage (TES) has received significant attention due to offering a possible sustainable solution to grid resilience and energy savings. When TES materials are integrated into heat exchangers or heat pump in buildings, they can assist in controlling the energy demand to utilize the stored energy to manage high-demand hours as well as provide energy savings. One of the integral elements for TES deployment in buildings is to develop low-cost, high-performance, and durable materials that operate near room temperature. Among TES materials, salt hydrates as phase change materials (PCMs) are attractive due to their abundance, cost-effectiveness, non-flammability, and non-toxicity. Recent phase change material development efforts aim to mitigate some challenges such as instability, phase separation, and supercooling as the instability and phase separation cause energy storage loss. Also, supercooling reduces the full utilization of the latent heat storage due to reduced freezing temperature resulting in large temperature differences between melting and freezing temperatures. Some methods to overcome these challenges are the addition of materials such as thickeners, and nucleating agents or that alter the system thermodynamics or facilitate the nucleation kinetics, to name a few [3] Among inorganic phase change materials, sodium sulfate decahydrate is frequently investigated as it is inexpensive and has a high thermal storage capacity, (~100 kWh/m$^3$) However, it is prone to incongruent melting (i.e., phase separation upon melting), which results in poor stability and loss in energy storage capacity over even a few melt-freeze cycles. Sodium phosphate dibasic dodecahydrate is a congruently melting material with high melting storage capacity. However, it exhibits large supercooling

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(14°C) [4]. Due to the prominent properties of the aforementioned salt hydrates, the mixture of these hydrates has gained attention in recent years. Xin et al. [3]reported a composite at a composition of 1.8 wt% nano-aluminum nitride, 1.5 wt% borax, 4.8 wt% hydroxyethyl cellulose, 4 wt% sodium alginate and 1.5 wt% sodium polyacrylate in the 80 wt% $Na_2SO_4.10H_2O$ and 20 wt% $Na_2HPO_4.12H_2O$ eutectic system where nano-aluminum nitride and borax were used as composite nucleating agent; and hydroxyethyl cellulose, sodium alginate and sodium polyacrylate were used as composite thickeners. The phase change enthalpy was 180.2 kJ/kg and the supercooling degree of the material was 3.1°C. A 2.72% and 3.61% decrease in phase change enthalpy after 50 and 100 melt-freeze cycles were reported, respectively. Huo et al. [5] prepared a eutectic hydrated salt system consisting of 25 wt% $Na_2SO_4.10H_2O$ and 75 wt% $Na_2HPO_4.12H_2O$ with a phase change temperature of 29.3°C and a phase change enthalpy of 218.58 kJ/kg. This PCM was encapsulated in ethyl cellulose/acrylonitrile butadiene styrene, which showed a relatively high energy storage capacity of 178.36 kJ/kg, although it was noted that the low thermal conductivity and mechanical strength of the polymer shell material might limit the application of the material. Zheng et al. [4] reported that a binary system at 10 wt% $Na_2SO_4.10H_2O$ and 90 wt% $Na_2HPO_4.12H_2O$ had a melting temperature of 28.2°C and supercooling of about 4.8°C. The authors reported that the PCM system showed no phase separation and the material is stable up to 200 melt-freeze cycles. Fang et al. [6] reported a eutectic system at 20 wt% $Na_2SO_4.10H_2O$ and 80 wt% $Na_2HPO_4.12H_2O$. The porous hydrophilic fumed silica was utilized as the support material which showed the best performance at 30 wt%. Sodium metasilicate nonahydrate ($Na_2SiO_3.9H_20$) was also used as a nucleating agent. The composite material has a melting temperature of 25.16°C, a melting enthalpy of 142.9 kJ/kg, and experienced negligible supercooling of 0.24°C. Despite its good properties, a 6.16% loss in melting enthalpy was reported after 200 cycles, although an insignificant change in phase transition temperature was reported.

The listed studies indicate that the mixture of and $Na_2SO_4.10H_2O$ and $Na_2HPO_4.12H_2O$ formed a eutectic mixture around a composition near 20:80 ratio, although the mixtures were prone to lose some energy storage capacity after melt-freeze cycles and there are some inconsistencies that exist regarding the eutectic composition. In this study, our key objective is to develop a low-cost, stable, high-energy density and high-performance material that can be utilized in building applications. Therefore, we prepared novel material that consists of $Na_2SO_4.10H_2O$ and $Na_2HPO_4.12H_2O$ as phase change materials, borax as a nucleating agent and graphite as a thermal conductivity enhancer. The results showed that the stable material was formed at a concentration of 31.7 wt% $Na_2SO_4.10H_2O$, 51.6 wt% $Na_2HPO_4.12H_2O$, 12.5 wt% graphite, and 4.2 wt% borax. This novel material has a melting enthalpy of 167 kJ/kg, a melting temperature of 28.2°C, and exhibited supercooling of 2.5°C. The energy storage capacity remained stable after 150 cycles. The finding of this study suggests that the material has great potential to be utilized for thermal energy storage in heating-cooling systems in buildings.

## 2. MATERIALS AND METHODS

### 2.1 Sample Preparation

Sodium sulfate decahydrate $Na_2SO_4.10H_2O$, purity of 99.0%, CAS No. 7727-73-3, Sigma Aldrich) and sodium phosphate dibasic dodecahydrate $Na_2HPO_4.12H_2O$, purity of ≥ 99.9%, CAS No. 10039-32-4, Sigma Aldrich) were used as inorganic salt hydrates. Sodium tetraborate decahydrate (also known as borax, $Na_2B_4O_7.10H_2O$, purity of ≥ 99.5%, CAS No. 1303-96-4, Sigma Aldrich) was used as a nucleator. Salt hydrates were ordered in small quantities and only handled under humidity- and temperature-controlled glovebox to prevent the impact of ambient humidity on materials. $Na_2SO_4.10H_2O$ and $Na_2HPO_4.12H_2O$ binary mixtures were prepared using the solid mixing method. In a borosilicate glass vial, salt hydrates were mixed in various weight ratios. The solid mixtures in the glass vials were then mixed in a shaker for an hour and then sonicated in a water bath at room temperature for an additional hour. As the mixtures have shown significant supercooling, borax was used as a nucleator. Graphite (TG-679 Expanded Graphite Powder, NeoGraf) was also added to the mixture to improve thermal conductivity.

### 2.2 Differential Scanning Calorimetry (DSC)

The melting enthalpy and melting temperature of the materials were measured using Differential Scanning Calorimeter (DSC) (DSC2500, TA Instruments, Inc). For DSC measurements, 10-15 mg of PCM sample was placed in hermetically sealed aluminum pans (TA Instruments Tzero pan and TA Tzero hermetic lid). The samples underwent 25 melting and freezing cycles under constant nitrogen flow between -50 and 50°C with a heating rate of 5°C/min. The endothermic peak on the heating curve (heat flow versus temperature) corresponding to the PCM material is calculated by integrating the peak under the curve. Both onset and peak temperatures are measured; however, the peak temperature of the PCM peak has been reported as the melting temperature in this study.

### 2.3 Temperature-History (T-history) Method

DSC is a robust, rapid, and reliable characterization method for PCM materials. However, the minute amount of sample in DSC characterization makes the method susceptible to the representation of the thermal behavior of the PCM in large quantities, especially if any phase separation and supercooling exist. Therefore, the T-history method is preferable to represent large-scale characterization. However, the T-history technique requires an extended period and a relatively large amount of sample (~15g). Therefore, in this study, only the best performance sample was investigated using the T-History method. The experimental procedure and data analysis of the T-h method have been discussed in detail elsewhere [7]; therefore, only a brief description is provided here. In the given T-history experiment, 15-20 g of the PCM sample was loaded into a


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borosilicate glass tube and was sealed with a rubber stopper with a center hole for the T-type thermocouple to be inserted into the material, about midway in the tube. A second borosilicate glass tube was prepared with distilled water as a reference medium. The glass tubes were placed in a bench-top environmental temperature chamber (ESPEC SH-242) and thermally cycled between 15 to 45 °C at a ramp rate of 5°C/min. The temperature in the chamber was measured with 1/16" sheathed T-type thermocouple. The temperature of the chamber, reference sample (distilled water) and PCM samples were recorded using a National Instruments cDAQ 9214 data acquisition system at a frequency of 0.2 HZ (5 s/sample). The melting temperature, melting enthalpy, and supercooling were obtained as described elsewhere[7].

## 3. RESULTS AND DISCUSSION

### 3.1 Melting Point Depression

A eutectic mixture is defined as a mixture of at least two solid components having a single phase change temperature, which corresponds to the minimum melting temperature of the different possible compositions for a given mixture. At the eutectic point, the phase transition process is congruent. Although the purpose of this study was not to find the eutectic point, this approach here was utilized to find the mixture at the lowest melting point even if the mixture might not congruently melt or freeze. Therefore, initially, the binary mixture of $Na_2SO_4.10H_2O$ and $Na_2HPO_4.12H_2O$ was prepared by varying the composition of $Na_2SO_4.10H_2O$ from 0 wt% to 100 wt% with an interval of 10 wt%. Then, the composition of $Na_2HPO_4.12H_2O$ was varied from 50 wt% to 70 wt% with an interval of 4 wt% and later from 60 wt% to 70 wt% with an interval of 2 wt%.

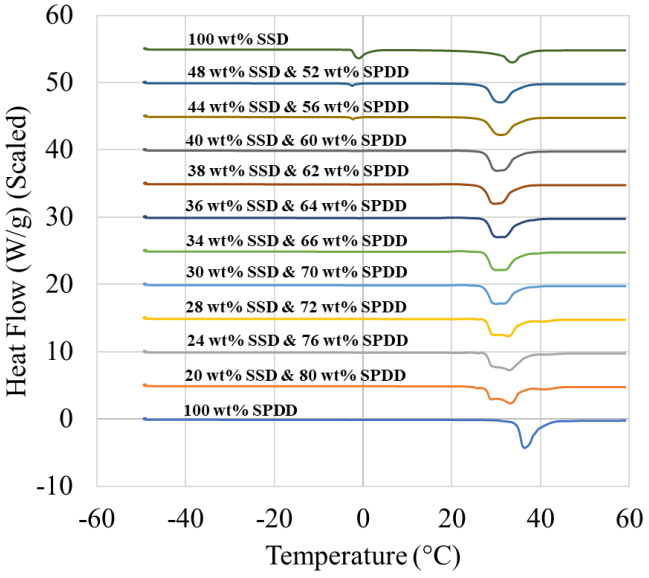


**FIGURE 1:** THE WEIGHT FRACTION TRIAL-ERROR METHOD TO DETERMINE THE SODIUM SULFATE DECAHYDRATE AND SODIUM PHOSPHATE DIBASIC DODECAHYDRATE

Figure 1 illustrates the results of the weight-fraction-based concentration study to determine the minimum melting temperature of the binary mixture of $Na_2SO_4.10H_2O$ and $Na_2HPO_4.12H_2O$. As can be seen in Figure 1, the system reached one uniform peak at the composition of 38 wt% SSD and 62 wt% SPDD with the lowest melting point across the entire concentration range. Although the system has one uniform melting peak, a closer look at DSC (not shown here) showed a small melting peak appears at -2°C. More importantly, multiple peaks in the freezing cycles indicate the given composition not being a eutectic point. On the same line, we found out that the mixture at $Na_2SO_4.10H_2O$: $Na_2HPO_4.12H_2O$ at 24:76 composition in fact has only one melting and one freezing peak in the entire DSC scan in a given melt-freeze cycle, which might be indicative of the eutectic point despite the fact that this composition was not the one with the lowest melting point across entire composition range. As discussed in section 1, the goal of this study is to produce a stable phase change material that would be utilized in heating-cooling units in buildings that require materials with a melting point near ambient temperature. Since 38 wt% SSD and 62 wt% composition gives the lowest melting point across the entire concentration range, we report the best performance composition as 38:62 $Na_2SO_4.10H_2O$: $Na_2HPO_4.12H_2O$, although the eutectic point might be claimed at 28:72, which is close to some literature values.

### 3.2 Stabilization and Supercooling

The binary mixture of $Na_2SO_4.10H_2O$ and $Na_2HPO_4.12H_2O$ at a ratio of 38:62 resulted in reduced melting temperature However, the DSC results showed that the mixture has a high supercooling (~ 20°C). As borax has been shown to be an effective nucleator for $Na_2SO_4.10H_2O$[8,9]; it was utilized as a nucleator for the $Na_2SO_4.10H_2O$ and $Na_2HPO_4.12H_2O$ systems in this study as well. In our previous study[9], we found that 5 wt% borax in $Na_2SO_4.10H_2O$ yielded optimal performance. Thus, 5 wt% of borax was added to the mixture to initiate the nucleation. To investigate the impact of borax on melting point and energy storage capacity, the DSC was utilized. The results showed a small melting point shift of ~1°C upon borax addition (increased from 30.11 to 31.23°C at cycle 10) and the energy storage capacity decreased upon borax addition was only 17 kJ/kg (decreased from 220.51 to 203.79 kJ/kg at cycle 10). Although DSC might be used as an indicator for supercooling and a first indication for stability investigation, the T-history method is more reliable to obtain the supercooling information as well as long-term energy storage capacity, as discussed previously. Before the T-history experiment, 12.5 wt%[9] graphite was also added to the mixture to enhance the thermal conductivity of the material. Expectedly, the energy storage capacity of the PCM sample decreased due to the addition of graphite into the system which displaces PCM. For example, at cycle 10, the storage capacity without graphite was 220 kJ/kg (DSC) whereas the storage capacity with graphite addition was 167 kJ/kg (T-history). Despite the loss of energy density with the addition of borax and graphite, the energy storage capacity was not


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altered after 150 cycles, as can be seen in Figure 2. The T-history results also demonstrated the supercooling of the system. As shown in Figure 2, the supercooling was 2.5°C, and has remained very nearly constant changed even after 150 cycles, indicating that the addition of borax also serves as a good nucleator for the $Na_2SO_4.10H_2O$ and $Na_2HPO_4.12H_2O$ system.

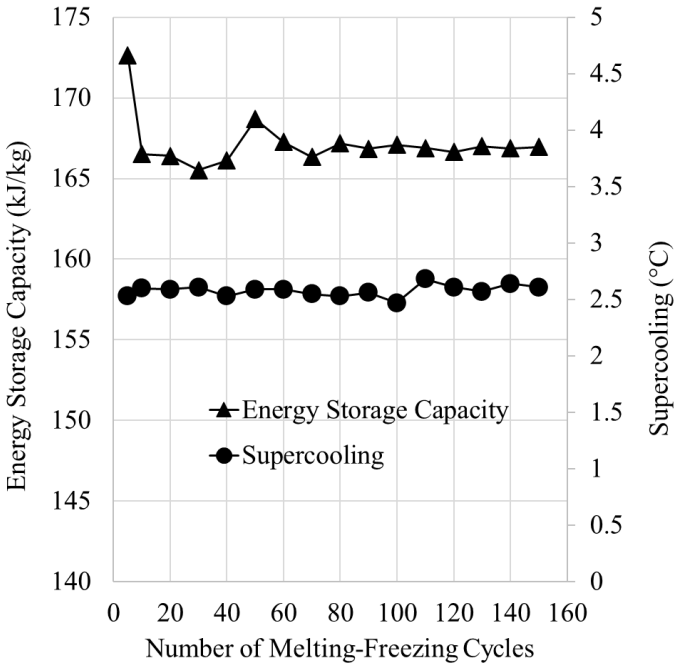


**FIGURE 2:** ENERGY STORAGE CAPACITY AND SUPERCOOLING OF PHASE CHANGE MATERIAL MEASURED BY TEMPERATURE-HISTORY METHOD (31.7 wt% $Na_2SO_4.10H_2O$, 51.6 wt% $Na_2HPO_4.\ 12H_2O$, 12.5 wt% graphite, and 4.2 wt% borax)

## CONCLUSION

Salt hydrates ,phase change materials, are attractive thermal energy storage materials due to their abundance, cost-effectiveness, non-flammability, and non-toxicity. Sodium sulfate decahydrate ($Na_2SO_4.10H_2O$) and sodium phosphate dibasic dodecahydrate ($Na_2HPO_4.\ 12H_2O$) have excellent potential as energy storage materials due to their high energy storage capacity although the materials can suffer some common issues such as large supercooling and poor stability due to incongruent melting which results in a loss in energy density over even a few melt-freeze cycles. In this study, we have shown that $Na_2SO_4.10H_2O$ and $Na_2HPO_4.\ 12H_2O$ formed a low melting point mixture at a composition of 38 wt% $Na_2SO_4.10H_2O$ and 62 wt% $Na_2HPO_4.\ 12H_2O$. The phase change material at a composition of 1.7 wt% $Na_2SO_4.10H_2O$, 51.6 wt% $Na_2HPO_4.\ 12H_2O$, 12.5 wt% graphite, and 4.2 wt% borax had a melting temperature of 28°C and a melting enthalpy of 167 kJ/kg as well as exhibited consistent low supercooling of ~2.5°C. The novel PCM materials showed no loss in energy storage capacity or change in supercooling after 150 cycles. The finding of this study suggests that the material has excellent potential to be utilized as thermal energy storage media for heating-cooling systems in buildings. In the future, we plan to investigate various compositions of borax and graphite addition, evaluate the impact of graphite addition on thermal conductivity, and characterize the material via spectroscopic and microscopic techniques to elucidate the molecular interaction among the salts.

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