



# MgCl<sub>2</sub>·6H<sub>2</sub>O-Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O eutectic/SiO<sub>2</sub> composite phase change material with improved thermal reliability and enhanced thermal conductivity

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## ABSTRACT

MgCl<sub>2</sub>·6H<sub>2</sub>O-Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O eutectic has a proper melting point and high latent heat for solar water heating systems with latent heat storage. In this paper, the exact composition of the eutectic and the corresponding phase change temperature are determined by measuring the phase change characteristics of mixtures of MgCl<sub>2</sub>·6H<sub>2</sub>O and Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O in various ratios. MgCl<sub>2</sub>·6H<sub>2</sub>O-Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O eutectics, the melting temperature of which is around 58 °C, can be obtained with the mass fraction of MgCl<sub>2</sub>·6H<sub>2</sub>O ranging from 35% to 50%. The eutectics are composited with porous fumed silica to improve its thermo-physical properties. The eutectic/SiO<sub>2</sub> composite retains a similar melting point of the pure eutectic, is of no liquid leakage even after melting while the SiO<sub>2</sub> weighs more than 15 wt%, and the specific enthalpy reaches 88.13 kJ kg<sup>-1</sup>. The eutectic/SiO<sub>2</sub> composite has a thermal conductivity 5% higher than pure eutectics and better thermal stability and cycle stability. The thermogravimetric analysis shows its weight loss is 8.03% less than pure eutectic at 300 °C. And the eutectics suffers a decrease in phase change enthalpy after 100 thermal cycles by 9.2%, much lower compared with the 37.23% for pure eutectics due to the phase separation during the thermal cycles. Thermo-physical properties and stability of MgCl<sub>2</sub>·6H<sub>2</sub>O-Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O eutectic have been enhanced by fumed silica.

## 1. Introduction

Latent heat storage with phase change materials (PCMs) is one of the most efficient way of storing the free and clean solar thermal energy for domestic water heating. PCMs provide high energy storage density by allowing large quantities of heat stored in a narrow temperature range during phase change. Studies have shown incorporating PCMs into solar water heating system not only solves the mismatch between energy supply and demand, but also increases energy efficiency of the heating systems [1–3]. Organic PCMs with melting point around 60 °C are mostly used in the latent heat storage unit for solar water heating [4,5]. However, most organic PCMs have low thermal conductivity and are expensive and flammable. By contrast, inorganic PCMs, especially salts and salt hydrates, have advantages of high volumetric phase change enthalpy, relatively high thermal conductivity, non-flammability and more competitive price, making them show greater potentials for use in solar water heating systems.

MgCl<sub>2</sub>·6H<sub>2</sub>O is one kind of hydrated salts that is abundant in Qinghai Lake, China. Recent studies have shown that MgCl<sub>2</sub>·6H<sub>2</sub>O with melting point of 111 °C and phase change enthalpy of 155 kJ kg<sup>-1</sup> have

potentials on medium-temperature solar thermal energy storage [6]. Gasia et al. [7] studied the thermal behavior of bischofite which contains 95% MgCl<sub>2</sub>·6H<sub>2</sub>O in the thermal storage system in pilot plant scale. The results show that the 204 kg low-cost bischofite can store 3.07 kW h as sensible heat but as high as 11.97 kW h as latent heat. However, MgCl<sub>2</sub>·6H<sub>2</sub>O also have problems as other salt hydrate do. First, MgCl<sub>2</sub>·6H<sub>2</sub>O suffers severe sub-cooling, with a degree as high as 37 °C. Second, MgCl<sub>2</sub>·6H<sub>2</sub>O is not thermally stable as dehydration and phase separation between salts and water leads to the problems that the melting point keeps changing and phase change enthalpy decreases in hundreds thermal cycles. In the unsealed system, even with the extra water, the phase change temperature of MgCl<sub>2</sub>·6H<sub>2</sub>O after 500 cycles increased from 111.5 °C to 124.12 °C, and the phase change enthalpy decreased from 155.11 kJ kg<sup>-1</sup> to 85 kJ kg<sup>-1</sup> [8,9]. Adding nucleating agents such as SrCO<sub>3</sub>, Sr(OH)<sub>2</sub> have been found effective to suppress sub-cooling [10,11]. But those materials still suffer from low thermal stability along with the shortcoming that dehydration easily happen above 75 °C while its melting point is 111 °C [12].

Developing MgCl<sub>2</sub>·6H<sub>2</sub>O-based eutectics with phase change temperatures of around 60 °C, not only makes MgCl<sub>2</sub>·6H<sub>2</sub>O usable as

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thermal storage medium for solar water heating, but also helps alleviate the dehydration of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . The eutectic of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  -  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  has been found to have lower a melting point than  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . Nagano et al. [13,14] prepared a salt hydrate mixture with melting point of 60 °C for waste heat storage, in which the mass ratio of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was 20:80. The latent heat storage system with PCMs in a single vertical tube shows high energy storage density. But controversies exist on the mass ratio of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  to form eutectics. Lane [15] shows  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  -  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  forms eutectic with  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  of 41.3 wt% while Yoneda [16] claims  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  mass fraction should be 47 wt%. Preparing  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ - $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  provides a solution to reducing phase change temperature of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , but a more comprehensive study needs to be carried out to find out the exact eutectic temperature and the compositions of the eutectics. Nevertheless, reducing phase change temperature cannot resolve the cycling stability problem, as salts easily separate from the water after melting, causing difficulties in recrystallizing. One can expect that, if the hydrates are confined within a small limited space, even salts are separated from water, they can still easily reach the water and salt hydrates can recrystallize. Porous matrix, such as expanded graphite [17–23], silica [24,25] or other materials [26] etc., having great numbers of micro-size pores, have been used to absorb PCMs into the pores by capillary force to prepare shape-stabilized composite PCMs, which prevents liquid leakage after melting. Compared with hydrophobic surface of expanded graphite, the hydrophilic silica has better compatibility with salt hydrates.

In this paper, we intend to prepare  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ - $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  eutectics with melting point around 60 °C for latent heat storage unit used in solar water heating system. First, the composition of the eutectics is determined by preparing  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  - $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  with different proportions. Second, the eutectic is composited with fumed silica to improve the cycle stability and thermal stability as well. Crystal structures and thermo-physical properties such as phase change temperature, phase change enthalpy, thermal conductivity etc. of both the eutectic and the eutectic/ $\text{SiO}_2$  are compared before and after 100 thermal cycles.

## 2. Experiment

### 2.1. Materials

Magnesium chloride hexahydrate,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  (purity > 99%) and magnesium nitrate hexahydrate,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (purity > 99%), were purchased from Aladdin and Tianjin Fuchen chemical Co. Ltd. Expanded graphite (EG) was prepared from expandable graphite (50 mesh, from Shandong Graphite Co. Ltd., China) in microwave under 750 W for 30 s.

### 2.2. Preparation of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ - $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ eutectic salts (ES)

$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  were accurately weighed in a glove box, mass fraction of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  ranged from 0 wt% to 100 wt% with an increment of 10 wt%. Based on the measured data as described in the following, a further study to determine the exact composition of the ES was then carried out – in which the mass fraction of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  included (1)35 wt%, (2)38.4 wt%, (3)40 wt%, (4)41.3 wt%, (5)43 wt%, (6)45 wt%, (7)47 wt%, (8)49.3 wt%, (9)50 wt%. The two salt hydrates were mixed together in a sealed flask. Then the mixture was put into a furnace and heated to 85 °C. After melting, the hydrated salts were taken out from the furnace every 30 min and stirred with a magnetic stirrer under 500r/min for 5 min, then cooled to room temperature.

### 2.3. Preparation of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ - $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ /fumed silica composites

ES/fumed silica composite was prepared with impregnation method, simply mixing prepared ES with dried fumed silica together,

heating the mixture up to 85 °C for 2 h. Mass fraction of silica in the composite ranged from 5 wt% to 20 wt%. The mixture was taken out every 15 min for a stirring lasting for 5 min. Then composite was dried in vacuum at 45 °C and cooled to room temperature.

## 2.4. Characterization

Morphologies of PCMs were observed by scanning electron microscope (SEM, S-3700N, Hitachi). FTIR spectra were obtained using a Nicole Magna-750 IR spectro photometer on the KBr sampling sheet with a scanning number of 32. X-ray diffraction (XRD, D8 ADVANCE, Bruker, Cu-K  $\alpha$  radiation) was used to collect the diffraction patterns in the  $2\theta$  ranging from 10° to 80°. Phase change temperature and enthalpy were measured by DSC Q20 (TA Instruments). Thermogravimetric analysis was carried out with TG 209F3, NETZSCH, to characterize the thermal stability of PCMs between 30 °C and 300 °C. Thermal conductivity of PCMs were measured by TPS 2500 thermal constant analyzer, Hotdisk.

In order to obtain the data for thermal stability of the ES and ES/fumed silica composite PCMs, all PCMs were characterized before and after 100 thermal cycles. In each cycle test, 20 g PCMs were heated up to 85 °C and cooled down to 20 °C within 2 h repeatedly.

## 3. Results and discussions

### 3.1. Composition and properties of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ - $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ eutectics

Fig. 1 shows DSC curves of the  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  -  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  mixtures with different compositions. Both the phase change

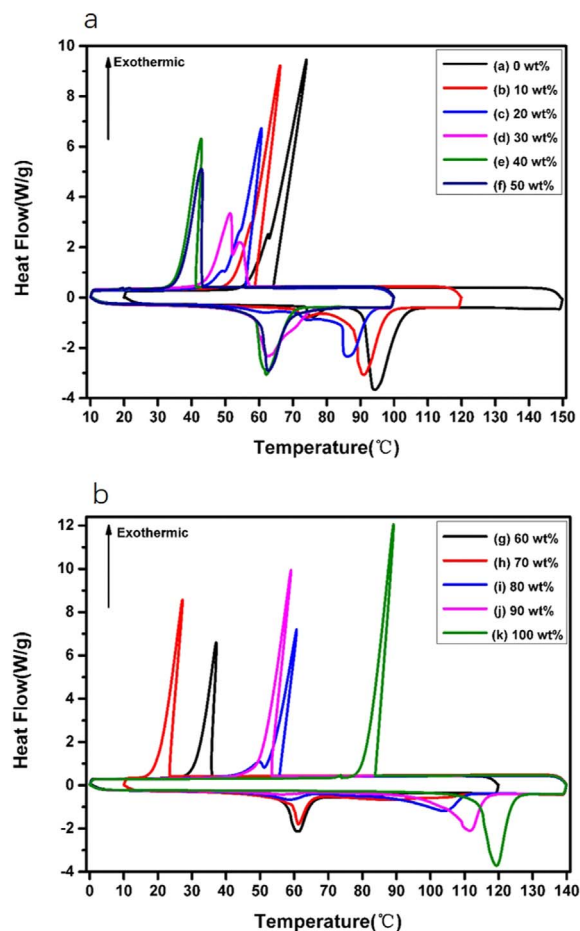


Fig. 1. DSC curves of magnesium chloride  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  -  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  mixtures with  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  mass fraction ranging from 0 to 100 wt%.

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