Preparation and characterization of composite material Na$_2$SO$_4\cdot$10H$_2$O - KAl(SO$_4$)$_2\cdot$12H$_2$O for thermal storage

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Abstract. In the present paper, the preparation and characterization of composite material Na$_2$SO$_4\cdot$10H$_2$O - KAl(SO$_4$)$_2\cdot$12H$_2$O for thermal storage are reported. The co - melting method is employed to perform the preparation. The thermal properties and the step cooling behaviors of the composites are studied. The results show that: the phenomenon of phase separation disappears in the composite system with the mass ratio of 1 : 9 to 3 : 7 (Na$_2$SO$_4\cdot$10H$_2$O: KAl(SO$_4$)$_2\cdot$12H$_2$O), and the optimized mass ratio is about 2 : 8, which results in the lowest phase change temperature, the longest heat releasing platform of 41 min and a higher latent heat of 819.93J/g at 72.7 $^\circ$C; the enthalpy remains higher value after 50 thermal cycles. Thus, this composite material has a potential as the phase change thermal storage material for low temperature application.

1. Introduction

Phase change thermal storage material has the advantage of higher latent heat with endothermic and exothermic processes at almost constant temperatures [1-2]. Therefore, it plays a significant role in some industrial fields, including aerospace, energy-efficient buildings, solar energy utilization, etc.

Inorganic hydrated salts have been the effective phase change thermal storage materials owing to their higher latent heat of fusion and melting point ranging from a few degrees to more than a hundred degree, which includes metallic halide salts of alkali and alkaline earth metals, sulphates, phosphates, vinegar salt and other salt hydrate. However, the problems in these materials are phase separation and supercooling in sole component inorganic hydrated salt once melting. Many scholars are doing research to improve their property in order to solve these problems [3-5]. The effective approaches include doping, thickening agent adding and microencapsulated.

The supercooling phenomena of KAl(SO$_4$)$_2\cdot$12H$_2$O was studied by Song through cold fingering and adding nucleating agent. The results indicated that the supercooling in KAl(SO$_4$)$_2\cdot$12H$_2$O can disappear as the nucleating agent MgCl$_2\cdot$6H$_2$O being added about 2%, in addition to the unchangeable of the phase transition temperature of KAl(SO$_4$)$_2\cdot$12H$_2$O [6]. Kuznik prepared composite materials by combing zeolite and dehydrated MgSO$_4$, the actual thermal storage density of this composite reaches to 45% of the theoretical value, and its property remains unchanged after more than three cycles [7].

Wang et al prepared composite hydrated salts by KAl(SO$_4$)$_2\cdot$12H$_2$O and MgSO$_4\cdot$7H$_2$O, which has stable performance and no phase separation phenomenon [8]. Liang et al studied the melting behaviour of the binary hydrated salts system for cold storage by DSC (Differential Scanning Calorimeter) test, they showed that a higher phase change latent heat with a primary endothermic peak could be obtained through proper combination of multiple salts [9].

Wang et al studied the thermal properties of $KAl(SO_4)_2 \cdot 12H_2O$ experimentally [10]，the results indicate that the endothermic enthalpy is 449 kJ/mol in the temperature range of 60～150℃, and the averaged exothermic enthalpy is 341.7kJ/mol in the temperature range of 25～60℃. The applicable efficiency of energy is 76.1% within 3 times cyclic operation. The mixture of graphite and $KAl(SO_4)_2 \cdot 12H_2O$ could obtain a better the heat conductivity [11].

In the present article, thermal storage composite material of $Na_2SO_4 \cdot 10H_2O$ and $KAl(SO_4)_2 \cdot 12H_2O$ is prepared and characterized. The co-melting is employed to perform the preparation. The characterization includes DTA (Differential Thermal Analysis), step cooling and heating – cooling cyclic tests. It aims to provide a technical support to the study of phase change thermal storage material at low temperature.

2. Fundamental properties of the initial materials

2.1. Initial materials
Experimental material. The main chemicals employed are: $Na_2SO_4 \cdot 10H_2O$, Tianjin Kemiao Chemical Reagent Co. Ltd., Tianjin, purity of 99%; $KAl (SO_4)_2 \cdot 12H_2O$, Zhengzhou Paiey Chemical Reagent, Zhengzhou, purity of 99.5%.

Laboratory instrument. The experimental Instruments are: JJ124BC electronic balance (Max = 120g, Min = 2mg), DF-101S constant temperature heater with magnetic stirrer, a thermometer (apuhua TM-902C, −50 ℃ ~ 1300 ℃, accuracy 0.1 ℃), HCT-1 differential scanning calorimetric balance, DZF-6030 vacuum oven.

2.2. Basic properties of $Na_2SO_4 \cdot 10H_2O$ and $KAl (SO_4)_2 \cdot 12H_2O$
The experimental procedure is as follows,

(1) Pour 10g of $Na_2SO_4 \cdot 10H_2O$ and $KAl (SO_4)_2 \cdot 12H_2O$ into the mill ground milling to fine powder, respectively, and then pour each fine powder into individual test tube;

(2) Place each test tube in the thermostat heating magnetic stirrer with a constant temperature heater, and keep half an hour after the material fully melting;

(3) Remove the test tube from the thermostat heating magnetic stirrer and stand at room temperature, record its temperature data once every 10s, drawing step cooling curve after the temperature tests;

(4) Take about 10mg samples of $Na_2SO_4 \cdot 10H_2O$ and $KAl (SO_4)_2 \cdot 12H_2O$ to conduct DTA tests, respectively, the temperature ranges from room temperature to 150 ℃, and the heating rate is 1 ℃ / min.

The experimental step cooling curve and DTA curve for $Na_2SO_4 \cdot 10H_2O$ are shown in figure 1 and figure 2, respectively.

Figure 1 presents that the temperature is decreasing continuously during step cooling process of $Na_2SO_4 \cdot 10H_2O$. Figure 2 shows that the endothermic peak during heating process appears at 37.8 ℃, with a total phase change latent heat of 870.65J/g, which exhibits a high latent heat of phase change material.

Figure 3 is the step cooling curve of $KAl(SO_4)_2 \cdot 12H_2O$, it shows that the molten of $KAl(SO_4)_2 \cdot 12H_2O$ begins to crystallize till cooling to 63.0℃, then there is a temperature rising to 73.4 ℃ due to the releasing of latent heat, which implies a supercooling of 10.4℃ (= 73.4 ℃ − 63.0 ℃). Figure 4 shows the DTA curve of $KAl(SO_4)_2 \cdot 12H_2O$, it shows a large latent heat of 882.58J/g with the phase transition temperature of 75.7 ℃.
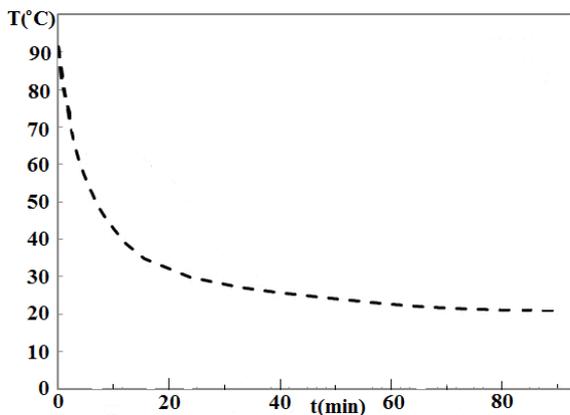
Figure 1. Step cooling curve of $Na_2SO_4 \cdot 10H_2O$　　**Figure 2.** DTA curve of $Na_2SO_4 \cdot 10H_2O$
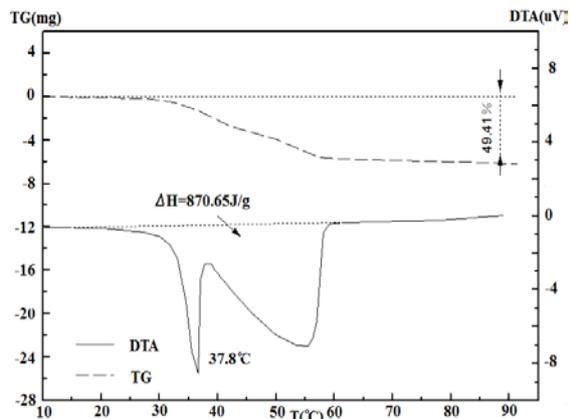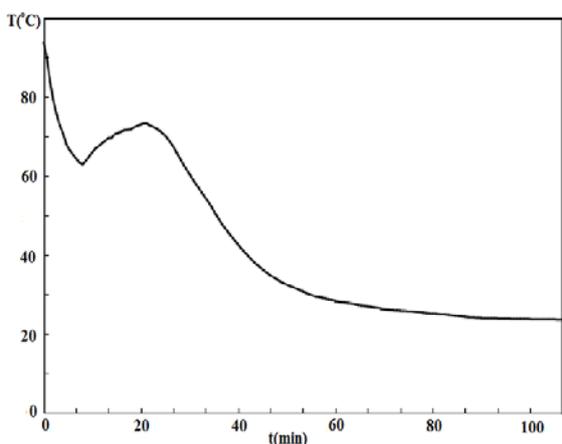
Figure 3. Step cooling curve of $KAl(SO_4)_2 \cdot 12H_2O$　　**Figure 4.** DTA curve of $KAl(SO_4)_2 \cdot 12H_2O$
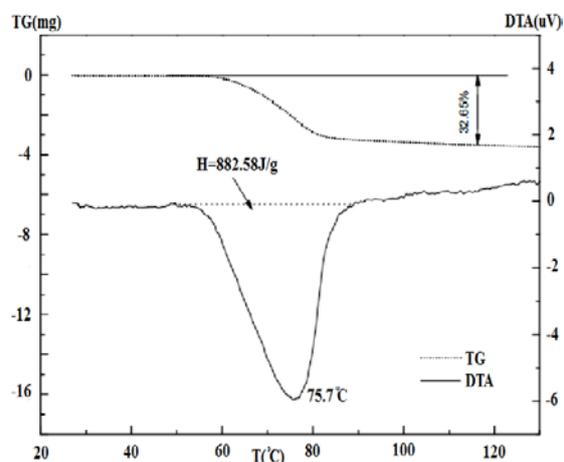
3. Preparation and property test of the composite materials

3.1. Preparation of phase change thermal storage composite material.
The preparation process of composite (or mixture) material is as follows,

(1) Mix and pour the milled $Na_2SO_4 \cdot 10H_2O$ and $KAl(SO_4)_2 \cdot 12H_2O$ powders into a test tube, the mass ratio of the salts is shown in table 1. The total amount is 10g, the test tube is a $\phi20 \times 50$ml plastic tube;

(2) Place the test tube in the thermostat heating magnetic stirrer with a constant temperature heater, and keep half an hour after the material fully melting;

(3) Remove the test tube from the thermostat heating magnetic stirrer and stand at room temperature, record its temperature data once every 10s, drawing step cooling curve after the temperature tests.

Table 1. Mass ratio of $Na_2SO_4 \cdot 10H_2O$ to $KAl(SO_4)_2 \cdot 12H_2O$

No.	S1	S10	S2	S21	S3	S4	S5	S6	S7	S8	S9
$m_1:m_2$	1:9	1.5:8.5	2:8	2.5:7.5	3:7	4:6	5:5	6:4	7:3	8:2	9:1

The heating-cooling test indicates that samples S4-S9 exhibit phase separate, i.e., there is liquid in upper part and solid in the lower part of the test tubes. However, there is no phase separate in S1, S10, S2, S21 and S3.

3.2. Step cooling curve analysis of composite materials.

Figure 5 is the step - cooling curves of the samples with no phase separate. The tested supercooling temperature T_{sc}, the phase transition temperature T_c and the duration of heat releasing platform T_1 for the phase separate free samples are listed in table 2.

Table 2. Variations of T_{sc}, T_c and T_1 v.s. mass ratio

No Contents	S1	S10	S2	S11	S3
T_{sc} /℃	1.8	0	0	4	0
Tc/℃	59.9	64.0	37.6	47.8	43.9
T_1/min	8.0	10.0	41.0	17.0	9.0

As can be seen from table 2, the phase transition temperature T_c behaves a "wavy" shape with the increase of content. The lowest phase transition temperature 37.6 ℃ appears at the mass ratio of 2:8. The samples appear obvious exothermic platform with different lengths during cooling process, the length of exothermic platforms is more than 8 min, and the longest exothermic platforms of S2 lasts 41 min.
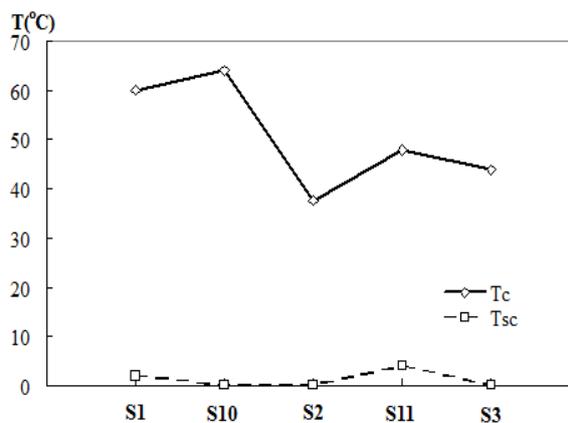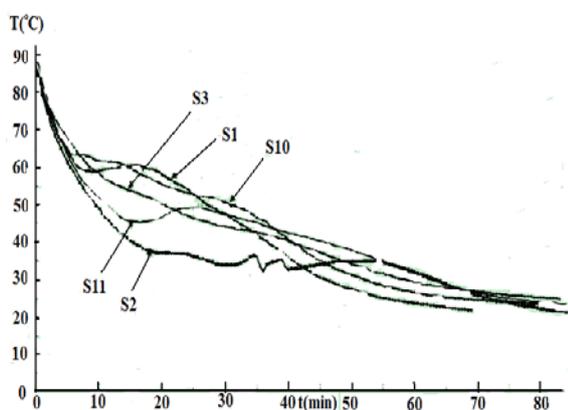

Figure 5. Step cooling curve of some composites

Figure 6. Tc and supercooling of the composites

Figure 6 shows the variation of phase transition temperature Tc and supercooling degree Tsc with respect to the mass ratio of the composite. As can be seen from figure 6, the degree of supercooling of S2 is comparatively smaller. Meanwhile, the thermal releasing platform of S2 is the longest, which lasts about 41 min with the phase transition temperature of 37.6 ℃.

Through above analysis, it can be seen that all the composites behave significant phase transition phenomenon. The composite of the mass ratio of 2:8 behaves a stable phase transition temperature, longer exothermic platform, no phase separation and supercooling during step cooling.

3.3. DTA Analysis of $Na_2SO_4 \cdot 10H_2O$ and $KAl(SO_4)_2 \cdot 12H_2O$ Composite

Take about 10mg composite samples of $Na_2SO_4 \cdot 10H_2O$ and $KAl(SO_4)_2 \cdot 12H_2O$ to conduct their DTA test, the temperature ranges from room temperature to 150 ℃ with heating rate of 1 ℃/min.

3.4. DTA analysis of the composites.

Table 3 lists the test data of phase change temperature and latent heat of the composite materials with respect to content. Figure 7 shows the variation of the latent heat with respect to the mass ratio. As can be seen from table 3 and figure 7 that the biggest phase change latent heat change exhibits at the mass ratio of 1:9 (i.e. S1), its phase change latent heat is 968.26J/g; the lowest phase transition temperature Tcc is at the mass ratio of 2:8 (i.e., S2), 72.7 ℃, which is between those of pure $Na_2SO_4 \cdot 10H_2O$ (37.8 ℃) and $KAl(SO_4)_2 \cdot 12H_2O$ (75.7 ℃).

Table 3. DTA of phase change thermal storage composite materials

Sample No.	mass ratio	latent heat (J/g)	Tcc (℃)
S_1	1:9	968.26	79.7
S_{10}	1.5:8.5	912.22	79.4
S_2	2:8	819.93	72.7
S_{11}	2.5:7.5	830.96	77.6
S_3	3:7	955.86	77.9

Comprehensively, the composite S2 with the mass ratio of 2:8 behaves excellent property, of which the phase change latent heat is 819.93J/g, and the phase transition temperature is 72.7 ℃. The DTA curve of the composite S2 with mass ratio of 2:8 is shown in figure 8.
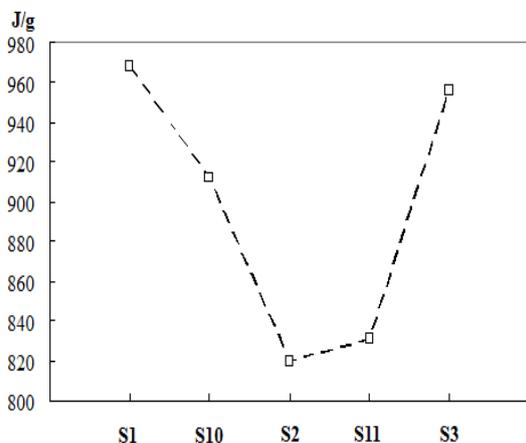

**Figure 7.** Thermal characteristics of the composites   **Figure 8.** DTA curve of composite S2
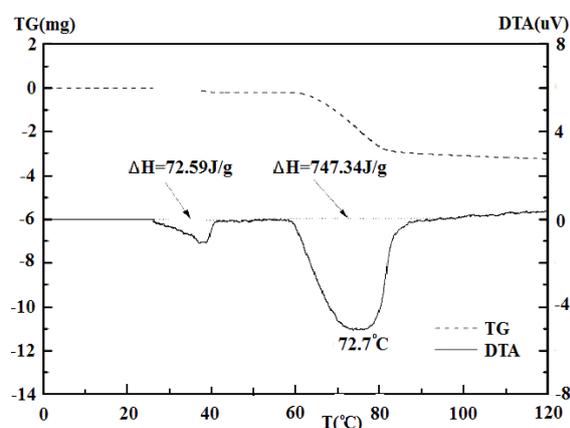
3.5. Cyclic Performance Test of Composite S2

The cyclic performance test of composite S2 is conducted. The procedure of the cyclic performance test is as follows,

Take 10g of the sample material into a test tube, and heat it in a constant-temperature bath at 95 ℃ till melting completely, and then remove the test tube from the bath and cool it in air to room temperature, this is one heating – cooling cycle. A total of 50 cycles was conducted.

DTA test was carried out for the sample of about 10mg after every 10 cycles. The heating process of the DTA test is from room temperature to 150 ℃ with heating rate 1 ℃ / min.

3.6. Results.

From the DTA test, it can be seen that the latent heat of composite S2 decreases slightly with the increase of cyclic number, while the phase transition temperature maintains in the range of 70~80 ℃.

4. Concluding Remarks

Through this study, following conclusion could be obtained:

(1) The step cooling curve analysis shows that the composite sample with the mass ratio of 2 : 8 behaves longer step cooling platform of 41 min and free of supercooling, as well as lower the phase transition temperature of 37.6 ℃ during step cooling process.

(2) DTA analysis shows that the composite sample with the mass ratio of 2 : 8 has latent heat of 819.93J/g and transition temperature of 72.7 ℃ during heating.

(3) The heating – cooling cycle performance testing indicates that the composite sample with mass ratio of 2:8 maintains phase transition temperature within 70 ~ 80℃, stable performance and no stratification process within 50 cycles.

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