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Quaternary chloride eutectic mixture for thermal energy storage at high temperature

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Abstract

For thermal energy storage application at higher temperature, a new quaternary eutectic salt mixture consisting of sodium chloride calcium chloride potassium chloride and magnesium chloride was designed according to the phase diagram. DSC technology was used to confirm the actual eutectic point of this quaternary salt mixture and the result turned to be 385^{o}C. Then, thermo-physical properties of this quaternary salt mixture were measured. Heat of fusion was up to 151.1J/g. Heat capacity of the eutectic salt mixture was calculated from DSC curves as function of temperature in the reference of sapphire standard material. The calculated heat capacity was consistent with theoretical value in the solid state and increased with increasing temperature in liquid state. After thermal circling of 10 circles at 280-500^{o}C, negligible change were seen in the melting point and freezing point of this quaternary salt mixture which showed excellent thermal circling stability. Meanwhile, mass loss curves under isothermal conditions were determined and the result showed that the thermal stability of this novel quaternary eutectic salt mixture was excellent under 650^{o}C, which means this new quaternary eutectic salt mixture was a good thermal energy storage and transfer media.

Keywords: quaternary eutectic salt mixture; thermal-physical properties; thermal stability

1. Introduction

As a renewable and green energy, solar thermal utilization technologies have developed quickly in recent years. Concentrated solar power (CSP) technology uses the concentrated heat of sun to generate electricity and it's promising to be combined with efficient thermal energy storage technology.

Several materials have been investigated to be used as potential thermal energy storage and transfer media. Among these materials, molten salts have been widely used as thermal energy storage and heat transfer fluid in solar power generation system due to their wider working temperature, lower vapor pressure, moderate heat capacity and good thermal stability etc. Solar salt composed of sodium nitrate and potassium nitrate (60-40 wt%, m.p.221^{o}C) was the popular salt mixture and had been used successfully as thermal energy storage medium in the solar two central receiver project and a commercial plant of Gemasolar in Spain [1-3]. HITEC, which is a ternary salt mixture of $NaNO_3$, KNO_3 and $NaNO_2$ (7-53-40 wt%, m.p.142^{o}C) had a wider operating temperature up to 454^{o}C, and may be used up to 538^{o}C for short periods [4-7]. The Rankine cycle efficiency should rise with the increasing maximum output temperature of the fluid. Unfortunately, these nitrate salts are not stable enough at high temperature [8-10] and that restricts their application in higher temperature over 500^{o}C.

Molten chloride salts have long been applied by industry for heat transfer, heat treatment, high temperature electrochemical coatings, and other processes [11]. Chlorides are attractive due to their low cost, abundant, high latent heat, appropriate operating temperature (400-850^{o}C), good thermal stability. Peiwen Li [12] developed three ternary chloride molten salt systems ($AlCl_3$-NaCl-KCl, $ZnCl_2$-NaCl-KCl and $FeCl_3$-NaCl-KCl). But the low boiling point and high vapor pressure of $AlCl_3$ and $FeCl_3$ restricted its application. A binary chloride molten salt system consisting of NaCl and $CaCl_2$ had been developed and its thermal-properties had been tested [13]. The NaCl-$CaCl_2$-$MgCl_2$ ternary system with lower melting point 424^{o}C was also designed and its thermal stabilities and properties were measured [14].

In order to further reduce the melting point and broaden the operating temperature, a novel quaternary chloride system of KCl-NaCl-$CaCl_2$-$MgCl_2$ was prepared according to the phase diagram and the eutectic point ware also validated by differential scanning calorimetry (DSC). Then, all of the relevant properties of this mixture such as heat

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capacity, thermal circling stability and thermal stability at high temperature were determined in order to examine whether this salt mixture was suitable for the solar thermal energy storage application.

2. Experimental

2.1 Materials and synthesis

Potassium chloride, sodium chloride and calcium chloride were all bought with A.R. grade without further purification and they were dried in an oven at 120^{o}C for 48h. Anhydrous magnesium chloride was at least 99% pure. The quaternary eutectic salt mixtures for determining the actual eutectic composition were prepared by mixing the four salts according to the compositions obtained from the eutectic phase area. The salt mixture was static heated to 550^{o}C in an alumina crucible, held for 3h to ensure a homogeneous mixture and then cooled to ambient temperature. Then the solidified salt mixture was ground into powder using mechanical rolling, sealed and kept in desiccators.

2.2 Apparatus and procedure

STA 449C differential scanning calorimeter (DSC, Germany NETZSCH Company) was used to determine the melting point and fusion heat of this quaternary system. About 5-10mg samples were put into alumina crucible with a reference empty one. The measurements were conducted under purified nitrogen atmosphere with a flow rate of 100mL/min and at a heating rate of 20K/min to 700^{o}C.

Subsequently, thermal-physical properties of the confirmed eutectic molten salt mixture were obtained. Heat capacity was measured from DSC curves both in solid state and liquid state in the reference of sapphire standard materials. The thermal circle curves of temperature versus time were recorded by PICO data collection instrument. About 40g quaternary salt mixtures were put in alumina crucible to test the thermal stability, the crucible was covered with a lid in order to avoid the moisture and reduce the volatilization of chloride during the test.

3. Results and discussion

3.1 Determination of the eutectic quaternary salt mixture

The phase diagram [15] of this quaternary system is presented in Fig 1 and it shows a 400^{o}C eutectic phase area. In order to determine the actual eutectic composition, two quaternary salt mixtures are prepared in this phase area and the DSC curves between 300^{o}C and 500^{o}C are presented in Fig 2~3. Molten salt 1's DSC curve shows single endothermic peak whereas the other one presents overlapped peaks, which means that molten salt 1 is in the eutectic region with correct compositions. Therefore, thermal-properties of this quaternary salt mixture are measured.

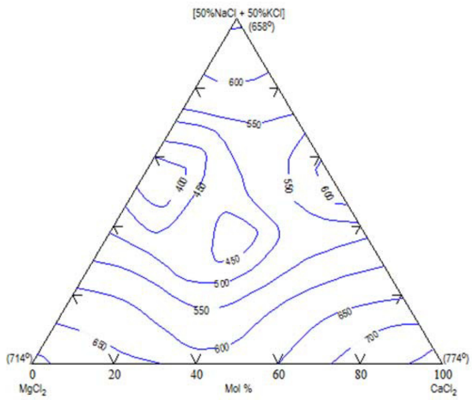

Fig. 1. Phase diagram of the KCl-NaCl-$CaCl_2$-$MgCl_2$ system

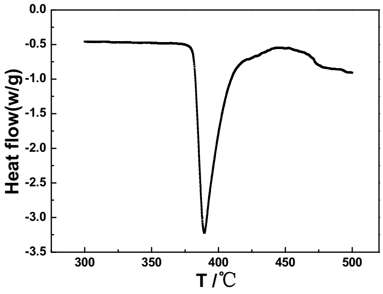

Fig. 2. DSC curves of molten salt 1.

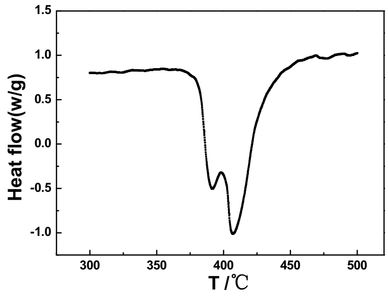

Fig. 3. DSC curves of molten salt 2.

TG-DSC curves of this quaternary eutectic salt mixture were presented in Fig 4. The large weight loss accompanied with variation of heat flow from room temperature to 200°C was mainly attributed to the presence of moisture which was picked up from atmosphere during the process of sample loading and thermal decomposition of hydrous magnesium chloride [16]. Between 250°C and 700°C, TG curves showed little weight loss which meant this salt mixture had good thermal stability. DSC curves appeared only one big endothermic peak which was considered as the melting peak. The melting point of this quaternary salt mixture was identified 385°C and the enthalpy of fusion was determined super high 151.1J/g. Compared to the NaCl-$CaCl_2$-$MgCl_2$ ternary system (424°C, 191J/g), the melting point reduced 40°C, but the heat of fusion decreased 40J/g.

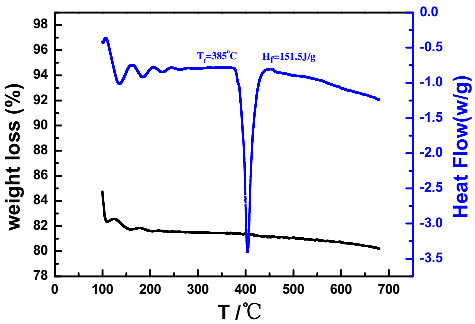

Fig. 4. TG-DSC curves of the quaternary salt mixture.

3.2 Heat capacity

DSC equipment was used to measure the heat capacity of this quaternary salt mixture from 230°C to 680°C in the reference of standard sapphire materials. The heat flow of salt sample and sapphire were all determined by subtracting that baseline curve of an empty crucible. Heat capacity of the quaternary eutectic salt mixture in nitrogen was presented in Table 1 and Fig 5 and compared with the available data in the literature [17]. The sharp peak in heat capacity plot was observed between 386.85 and 466.85°C which was the melting peak of this quaternary salt mixture. The experimental determined results can be divided into two sections: solid state (236.85-366.85°C) and liquid state (476.85-686.85°C). The heat capacity data of each state can fit to a polynomial equation.

The heat capacity data for this quaternary salt mixture in the solid state in the temperature range of 236.85 to 366.85°C is fit to a second order polynomial equation:

$$Cp\ (\text{Solid}) = 8.0507\times10^{-6}T^2 - 0.004287T + 1.4522\ (\text{J/g·°C})$$

The R^2 value for this fit was greater than 0.96. The average heat capacity of the quaternary solid salt was 0.9084 J/g·K.

The heat capacity data for this quaternary salt mixture in the liquid state in the temperature range of 476.85 to 686.85°C can be also fit to a liner equation:

$$Cp\ (\text{liquid}) = 3.5322\times10^{-3}T - 0.6342\ (\text{J/g·°C})$$

The R^2 value was greater than 0.97. The average heat capacity of the quaternary liquid salt is 1.42 J/g·K.

The heat capacity data of the quaternary eutectic salt mixture shows a steady increase with temperature both in solid and liquid state. The heat capacity data for solid quaternary salt mixture is very close to the sum of pure salts' heat capacity from literature. The heat capacity of liquid quaternary salt mixture is bigger than that of the solid state because of disorder for ions in liquid state. The additional energy stored inside the liquid state salt contributes to the increase part of heat capacity comparing solid state salt. When the temperature was over 600°C, the value of heat capacity for the salt increases quickly because of the volatilization of the molten salt under N_2 current and it is distortion in measuring condition. In a word, the average heat capacity of this quaternary salt mixture was bigger than the NaCl-$CaCl_2$-$MgCl_2$ ternary salt (average solid heat capacity 0.83 J/g·°C, liquid 1.19 J/g·°C).

Table.1. Heat capacity of NaCl-KCl-$CaCl_2$-$MgCl_2$ quaternary eutectic salt mixture in solid and liquid state

Solid state				Liquid state			
T (°C)	*Cp* (J/g·k)	*T* (°C)	*Cp* (J/g·k)	*T* (°C)	*Cp* (J/g·k)	*T* (°C)	*Cp* (J/g·k)
236.85	0.89205	296.85	0.88881	476.85	1.11402	586.85	1.3868
246.85	0.8825	306.85	0.89286	486.85	1.116	606.85	1.51379
256.85	0.87976	316.85	0.8975	506.85	1.12585	626.85	1.5962
266.85	0.87986	326.85	0.91961	526.85	1.2689	646.85	1.67032
276.85	0.88324	346.85	0.92714	546.85	1.27313	666.85	1.75302
286.85	0.8868	356.85	0.94785	566.85	1.32418	686.85	1.77969

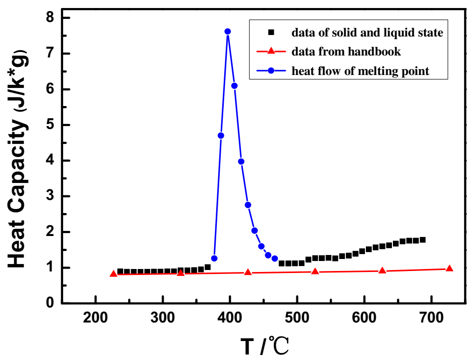

Fig. 5. Heat capacity of the NaCl-KCl-$CaCl_2$-$MgCl_2$ quaternary eutectic salt mixture.

3.3 thermal circling of molten salt

To the best of our knowledge, a good thermal energy storage material should be used repeatedly and its corresponding properties such as melting point and heat of fusion would not be changed after circles. Heat storage performance of this quaternary eutectic salt mixture at 280-480°C could reveal its ability of resisting changes in temperature cycling and the circle curves were presented in Figs 6 and 7. As can be seen from the heating curves, the melting point of this quaternary eutectic mixture was 385°C, which was consistent with the DSC test results. The cooling curves presented two endothermic positions. The point 393°C was speculated as the peritectic point of formed compound and the other one 384°C was sure to be the freezing point of the quaternary eutectic salt mixture. After 10 circles of thermal cycling, the changes of melting point and freezing point were all negligible.

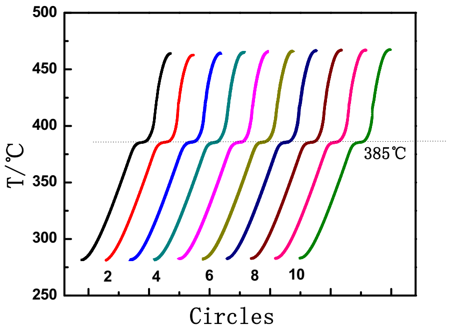

Fig. 6. Heating curves of quaternary salt mixture (10 circles)

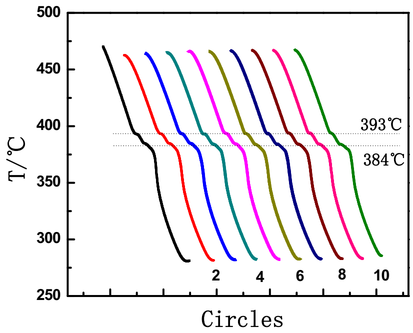

Fig. 7. Cooling curves of quaternary salt mixture (10 circles)

3.4 Thermal stability

Thermal stability which determined how long the molten salt can be used is also an important property. In order to test the thermal stability of present quaternary salt under real operation condition and reduce the influence of moisture and purge stream, about 40g salt mixtures were put into alumina crucible with a lid. The mass loss curves of this quaternary salt mixture under isothermal conditions after 15h are given in Fig 8. It was obviously that the mass loss of molten salt accelerated with the augment of temperature. After 15h, less than 1% of the quaternary molten salts were lost below 600^{o}C and nearly 4% were lost below 650^{o}C. In a non-sealed environment, the mass loss increased with increasing temperature, which was mainly attributed to the increases of volatilization molten salts [18]. In a word, the total weight loss at 650^{o}C is still acceptable for the realistic utility of the quaternary eutectic salt mixture as a potential candidate for solar thermal energy storage applications.

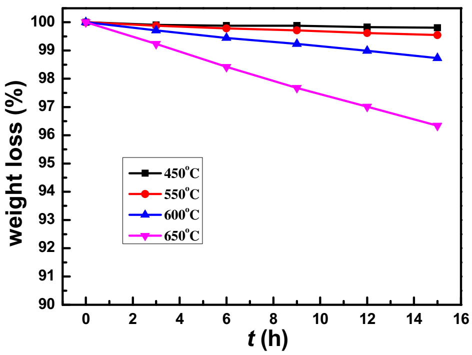

Fig. 8. Mass loss curves of quaternary salt mixture under isothermal conditions

Conclusions

Novel KCl-NaCl-$CaCl_2$-$MgCl_2$ quaternary system was determined according to the phase diagram and DSC technology. The melting point was confirmed 385^{o}C. Besides, all of the relevant thermal-physical properties of the quaternary molten salt were measured. The heat of fusion was 151.1J/g. The heat capacity of the eutectic salt mixture was close to the literature data. Thermal circle curves of salt showed negligible change of melting and freezing point. The mass change curves showed quaternary molten salt had a good thermal stability below 650^{o}C. So, appropriate operating temperature, lager heat capacity, excellent thermal circling ability and good thermal stability all indicated that this quaternary chloride salt mixture was suitable for heat transfer-thermal storage material.

Acknowledgment

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References

[1] Pacheco J E. Final test and evaluation results from the solar two project. Sandia National Laboratories. SAND2002-0120, January (2002).

[2] Herrmann U, Kelly B, Price H. Two–tank molten salt storage for parabolic trough solar power plants. Energy, **29**(6): 883–893 (2004).

[3] Kearney D, Herrmann U, Nava P, et al. Assessment of a molten heat transfer fluid in a parabolic trough solar field [J]. Journal of Solar Energy Engineering, 125(2): 170-176 (2003).

[4] Badger Energy Corp. Design, handling, operation and maintenance procedures for Hitec molten salt. Sandia National Laboratories, SAND81-8179, January (1981).

[5] Kearney D, Kelly B, Herrmann U, et al. Engineering aspects of a molten salt heat transfer fluid in a trough solar field [J].Energy, 29 (5/6): 861-870 (2004).

[6] Tofield B C. Materials for energy conservation and storage. Appl Energy, 8: 89–142 (1981).

[7] Tamme R, Laing D, Steinmann WD, Steinmann WD. Advanced thermal energy storage technology for parabolic trough. J Sol Energy Eng, 126(2): 794–800 (2004).

[8] Alexander J J, Hindin S G. Phase relations in heat transfer salt systems. Ind Eng Chem, 39: 1044-1049 (1947).

[9] Kirst WE, Nagle WM, Castner JB. A new heat transfer medium for high temperatures. Trans AIChE; 36: 371-390 (1940).

[10] Silverman MD, Engel JR. Survey of technology for technology for storage of thermal energy in heat transfer salt. Oak Ridge National Laboratory. Report ORNL/TM-5682; (1977).

[11] Sohal M S, Ebner M A, Sabharwall P, et al. Engineering database of liquid salt thermophysical and thermochemical properties[J]. Idaho National Laboratory, Idaho Falls, (2010).

[12] PHOENIX A. CONCENTRATING SOLAR POWER PROGRAM REVIEW 2013[J]. 2013.

[13] Baohua Hu, Jing Ding, Xiaolan Wei, et al. Test of thermal physics and analysis on thermal stability of high temperature molten salt[J]. Inorganic Chemicals Industry, (2010).

[14] Xiaolan Wei, Ming Song, Qiang peng, et al. New ternary chloride eutectic system for solar thermal energy storage[A]. The 6th International Conference on Applied Energy [C], Taibei, Taiwan, (2014).

[15] J. B. Belavadi, N. Rajagopalan, P. S. Desikan, and U. Sen, J. Appl. Electrochem., **12** [5] 501-503 (1982).

[16] Qiongzhu Huang, Guiming Lu, Jin Wang, et al. Thermal Decomposition Mechanism of $MgCl_2 \cdot 6H_2O$ [J]. Journal of Inorganic Materials, 3: 015 (2010).

[17] David R L. Handbook of chemistry and physics. 84th ed. Florida: CRC Press. p. 1038–65 (2004).

[18] G.J.Janz, C.B.Allen, N.P. Bansal, et al. Physical Properties data compilations relevant to energy storage. II. molten salts: data on single and multi-component salt systems [A]. U.S. Government Printing Office, Washington, (1981).