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Design and thermal properties of a novel ternary chloride eutectics for high-temperature solar energy storage

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HIGHLIGHTS

- A new ternary chloride salt mixture was designed for solar energy storage over 550 °C.
- The eutectic points and composition of salts were predicted from calculated phase diagrams.
- Thermal properties of heat capacity, density and viscosity at high temperature were measured.

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ABSTRACT

A new ternary chloride salt mixture, named SYSU-4, was developed composed of NaCl, $CaCl_2$ and $MgCl_2$ to meet the needs of solar energy storage over 550 °C. The eutectic point and composition of SYSU-4 was predicted from the calculated phase diagram and also validated by differential scanning calorimetry (DSC). SYSU-4 was prepared experimentally by static melting method and its thermo-physical properties including heat capacity, density and viscosity at high temperature were measured, which were determined by DSC, Archimedes and vibration–rotation methods, respectively. According to the calculated ternary phase diagram, the lowest eutectic temperature was 424.05 °C, in good agreement with experimental results of 424 °C measured by DSC. Heat capacity of SYSU-C4 was averaged as 0.83 and 1.19 J/g K for solid and liquid phase, respectively referred to sapphire standard material. Density of SYSU-C4 decreased linearly from 2.5 g/cm^3 to 1.9 g/cm^3 with the increase of temperature from 500 to 750 °C. Viscosity of SYSU-C4 also decreased from 4.0 cp to 3.0 cp as the temperature increased. Negligible changes on the melting and freezing points of SYSU-C4 in 50 thermal cycles at 370–550 °C indicates excellent thermal cycling stability. Moreover, the thermal stability of SYSU-C4 was excellent under 700 °C. The developed ternary chloride salt mixture SYSU-4 can be a promising eutectic mixture for high-temperature solar thermal energy storage.

1. Introduction

Solar energy has attracted great attention as it is a readily available, renewable and concentrated resource. The technologies for solar energy utilization has developed quickly in recent years, among which concentrated solar power (CSP) technology combined with inexpensive thermal energy storage (TES) media is as one of the most promising technologies for electricity generation.

Molten salts have been used widely as thermal energy storage (TES) media and heat transfer fluid (HTF) in solar power generation system due to their wide working temperature range, low vapor pressure, moderate heat capacity and high thermal stability etc. Molten salt composed of sodium nitrate and potassium nitrate (60–40 wt%, m.p. 221 °C) is the most popular salt mixture and has been employed 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 °C), has operating temperature up to 454 °C, or as high as 538 °C for short periods [4–7]. In our previous work, multi-component molten salt with additive A [8] was prepared and its thermal–physical properties were investigated between 150 °C and 550 °C. In the power generation system, the Rankine cycle efficiency rises with the maximum output temperature of the fluid. Unfortunately, these nitrate salts

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are not stable enough at high temperature [9–12], which restricts the high-temperature application over 500 °C.

Chlorides are attractive for high-temperature thermal energy storage due to their low cost, high latent heat, appropriate operating temperature (400–850 °C), and high thermal stability, although slightly corrosive [13]. However, numerous time-consuming experiments were required to resolve the eutectic point corresponding to the optimized composition of salt mixtures. Effective methodology is required essentially to resolve the eutectic point of salt mixtures.

In this work, a new ternary chloride molten salt system consisting of NaCl, $CaCl_2$ and $MgCl_2$ was designed through calculating its phase diagram and predicting its eutectic point [14]. The melting point was obtained from TG–DSC curves of the predicted salt mixture, which was used to verify the accuracy of calculated phase diagram. Ternary salt mixtures with different compositions near the predicted eutectic point were prepared experimentally and the true eutectic salt mixture was confirmed. The eutectic salt mixture used as high-temperature solar energy storage media was prepared based on the confirmed eutectic composition. The relevant thermal properties of this mixture including heat capacity, density and viscosity were determined. Moreover, the thermal cycling performance and thermal stability were investigated for practical solar thermal energy storage application.

2. Experimental and methodology

2.1. Calculation of chloride salt's phase diagram

According to CIS theory [15,16], NaCl–$CaCl_2$–$MgCl_2$ can be defined as AX–BX_2–CX_2 ternary system containing the cations $A^{q_A^+}, B^{q_B^+}, C^{q_C^+}$ and the common anion X^-. The total excess free energy of mixing (ΔG^E) of this system is calculated by the following equation:

$$\Delta G^E = \Delta G^E_{AB} + \Delta G^E_{AC} + \Delta G^E_{BC} \tag{1}$$

ΔG^E_{ij} is the excess free energy of mixing of the binary mixture of the salts i and j where A is AX, B is BX_2 and C is CX_2. The excess Gibbs free energy of mixing can be calculated by the following equation:

$$\Delta G^E_{ij} = X_i X_j \lambda_{ij} \tag{2}$$

where X_i [17] is the equivalent fraction of component, i, $X_i = q_i x_i / \sum_i q_i x_i$, q_i is the charge of that cation and x_i is the mole fraction of that component.

The binary interaction parameter λ_{ij} can be calculated from the three binary phase diagrams (NaCl–$CaCl_2$, NaCl–$MgCl_2$, $CaCl_2$–$MgCl_2$) by the following expression at a given eutectic temperature:

$$\lambda_{ij} = \frac{(\Delta H_i/T_i)T - RT\ln X_i - \Delta H_i + \Delta C_{p(i)}(T_i - T - T\ln(T_i/T))}{q_i X_j^2} = \frac{(\Delta H_j/T_j)T - RT\ln X_j - \Delta H_j + \Delta C_{p(j)}(T_j - T - T\ln(T_j/T))}{q_j(1-X_j)^2} \tag{3}$$

The excess chemical potential of a component can be calculated by differentiating the total excess free energy of the system with respect to the component amount. Hence, for the component AX_{qA}

$$\mu^E_A = RT\ln\gamma_A = \frac{\partial}{\partial n_A}(q_A n_A + q_B n_B + q_C n_C)\Delta G^E \tag{4}$$

incorporating Eqs. (1) and (2), the following equation can be obtained:

$$RT\ln\gamma_A = q_A X_B(X_B + X_C)\lambda_{AB} - q_A X_B X_C \lambda_{BC} + q_A X_C(X_B + X_C)\lambda_{AC} \tag{5}$$

Similarly for BX_{qB} and CX_{qC}

$$RT\ln\gamma_B = q_B X_A(X_A + X_C)\lambda_{AB} - q_B X_A X_C \lambda_{AC} + q_B X_C(X_A + X_C)\lambda_{BC} \tag{6}$$

$$RT\ln\gamma_C = q_C X_A(X_A + X_B)\lambda_{AC} - q_C X_A X_B \lambda_{AB} + q_C X_B(X_A + X_B)\lambda_{BC} \tag{7}$$

where γ_i is the activity coefficient of component i.

Besides, for an ideal mixture of non-electrolytes, the liquidus temperature T_i of the phase field of salt i can be calculated using the following expression [18]:

$$RT_i\ln a_i = RT_i\ln x_i\gamma_i = -\Delta H^o_i(1 - T_i/T^o_i) + \Delta C_{p(i)}[T^o_i - T_i + T_i\ln(T_i/T^o_i)] \tag{8}$$

where T_i, T^o_i and ΔH^o_i are liquid temperature, melting point and the enthalpy of fusion of component i, $\Delta C_{p(i)} = \Delta C^l_{p(i)} - \Delta C^s_{p(i)}$ is the difference between the heat capacity of liquid and solid state. According to the calculated liquid temperature over a grid of liquid compositions, the phase diagram can be obtained.

2.2. Materials and synthesis

Sodium chloride and calcium chloride were bought with A.R. grade without further purification and they were dried in an oven at 120 °C for 48 h. Four ternary salt mixtures for determining the actual eutectic composition were prepared by mixing three salt components according to the compositions near the predicted eutectic point. The salt mixtures were respectively heated to 600 °C, held for 3 h to ensure a homogeneous mixture and then cooled to ambient temperature. The solidified salt mixture was ground into powder using mechanical rolling, sealed and kept in desiccators.

2.3. Measurements and procedure

STD 449C differential scanning calorimeter (DSC, Germany NETZSCH Company) was utilized to confirm the actual eutectic point of ternary system. About 5–10 mg samples were put into alumina crucible with a reference empty one. The measurements were conducted in purified nitrogen atmosphere with a flow rate of 100 mL/min and at a heating rate of 20 K/min to 800 °C.

Subsequently, the thermal–physical properties of the ternary eutectic molten salt at high operation temperature were obtained. Heat capacity was measured from DSC curves both in solid and liquid state in the reference of sapphire standard materials; Density of the molten salt was gained by Archimedes theory in RSD-06 synthetic test instrument for the physical characteristics of fused object; Viscosity of the molten salt was measured with vibration–rotation high temperature melt viscosity instrument (Japan Tokyo Kabushiki Kaisha); The thermal circle curves of temperature versus time were recorded by PICO data collection instrument. About 40 g molten salts were put in alumina crucible to test the thermal stability, the crucible was covered with a lid in order to avoid the effects of moisture and the volatilization of chloride during the test.

3. Results and discussion

3.1. Determination of the lowest eutectic point on molten salts

The calculated ternary phase diagram according to Eqs. (1)–(8) is graphically presented in Fig. 1. The predicted eutectic point was validated by experimental tests. The amplified DSC curve of predicted eutectic mixture between 350 °C and 500 °C is given in Fig. 2. The curve shows two overlapped endothermic peaks, which indicates that the lowest eutectic point predicted by calculated phase diagram had a little deviation. Therefore, four molten salts (named MS_I, MS_II, MS_III and MS_IV) are prepared near the