

Experimental investigation and thermodynamic modeling of an innovative molten salt for thermal energy storage (TES)

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HIGHLIGHTS

- A novel method is used to design and develop thermal energy storage (TES) materials.
- An innovation molten salt (NaCl–NaF–Na₂CO₃) is successfully designed via computational thermodynamic approach.
- Thermal-physical properties of the NaCl–NaF–Na₂CO₃ eutectic salt are determined experimentally using thermal analysis.
- The eutectic salt NaCl–NaF–Na₂CO₃ as TES materials will be used for next generation CSP plants.

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ABSTRACT

A novel computational thermodynamic approach based on thermodynamic principles was applied to design and develop innovative molten salt mixtures for thermal energy storage. In this work, the eutectic composition of the NaCl–NaF–Na₂CO₃ ternary system was predicted based on experimental data via computational thermodynamic approach. Substitutional solution model (SSM) was used to describe the Gibbs energies for all liquid phases. Thus, a set of self-consistent thermodynamic model parameters was obtained for three subsystems and the parameters were used to predict the eutectic composition of the NaF–NaCl–Na₂CO₃ ternary system. Results manifested that the predicted eutectic point of the ternary system were located at $T = 849\text{ K}$ and $X_{\text{NaF}} = 21.66\text{ mol\%}$, $X_{\text{NaCl}} = 41.87\text{ mol\%}$ and $X_{\text{Na}_2\text{CO}_3} = 36.47\text{ mol\%}$. By means of Differential Scanning Calorimetry method, the predicted results were verified experimentally and the agreement between the measured and predicted values was satisfactory. Thermal-physical properties for eutectic salt mixtures, such as enthalpies of fusion, heat capacity, density and thermal stability, were also determined experimentally via thermal analysis methods in this work. Through computational thermodynamics approach, an innovative eutectic salt was designed and developed as thermal energy storage (TES) materials at high temperatures, especially it can be serve as candidate thermal energy storage materials for next generation concentrated solar power (CSP) plants.

1. Introduction

In recent years, energy consumption has grown continuously with the decrease of non-renewable energy, and the development and utilization of renewable energy has become significant and urgent. However, one primary challenge facing renewable energies, such as wind and solar, is that they are intermittent, making them unavailable as steady and credible energy supplies [1–4]. Thermal energy storage (TES) materials, including sensible heat material and latent heat material, have been used as potential thermal energy storage and transfer media for energy recovery and storage applications. Consequently, molten salts as sensible heat materials have been widely used as TES

materials for nuclear and concentrated solar power (CSP) applications because they have numerous advantages, such as high heat capacity, low melting point, high thermal stability, and low cost [5].

For CSP plants, solar salt (NaNO₃–KNO₃ 60–40 wt%) and HITEC (NaNO₃–KNO₃–NaNO₂ 7–53–40 wt%) are the most general and practical TES materials, and they have been widely used in the industry [6]. However, these salts still have some deficiencies, including weak thermal stability and high melting point, which need to be improved [7,8]. Thus, designing and developing innovative molten salts for TES materials with thermal stability and specific heat capacity is highly important. Through massive experimental screening of various compositions in multi-component systems, Justin et al. [9] discovered

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nitrate mixtures, which have melting points that can be lowered to 60 °C. Calcium nitrate mixtures were taken into account by Fernandez et al. [10] as energy storage materials with low melting point and high thermal stability, and the $\text{LiNO}_3\text{-NaNO}_3\text{-KNO}_3\text{-Ca(NO}_3)_2$ quaternary system exhibited better thermal-physical properties (specific heat capacity, thermal stability and viscosity) than solar and HITEC salts. Mantha and Reddy [11,12] designed high-temperature stable molten salts ($\text{LiNO}_3\text{-NaNO}_3\text{-KNO}_3\text{-NaNO}_2$ and $\text{LiF-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$) using thermodynamic calculation based on Gibbs energy of fusion for improved energy conversion efficiency. Moreover, the thermal-physical properties of these multi-component molten salts have been determined experimentally via thermal analysis.

However, the CSP plants are not still economically competitive when compared with the conventional power plants under present circumstances. Further efforts are devoted to improve the system efficiency and reduce the cost [13]. Latterly, Supercritical steam and supercritical CO_2 Brayton cycles are designed to replace the conventional water/steam Rankine cycle, and it has been identified as a promising path to increase the efficiency and reduce the cost for the next generation of CSP plants. The schematic of a heat transfer and storage system coupled to supercritical steam and CO_2 cycles was shown in Fig. 1. One major challenge facing supercritical steam or CO_2 Brayton cycles, is that the operating temperature range from 600 to 800 °C which higher than those of the current CSP plants [14]. The heat transfer and storage materials, such as nitrate salts, are sufficient for current CSP plants, but they are inadequate for the next generation of CSP plants which were operated at higher temperatures. At higher operating temperatures achievable in next generation of CSP plants, mixture salts are promising candidates as heat transfer and storage materials, owing to their higher thermal stability and lower cost compared to nitrate salts. Thus, the design and development of novel mixture salts as TES materials are highly important for next generation CSP applications.

Trial-and-error is costly, time-consuming, and thus inefficient for designing and developing innovative multi-component systems for TES. However, advanced computational materials, such as the atomistic simulation and CALPHAD (Calculation of Phase Diagram), can be powerful tools in designing the required materials with the specific applicable targets. In the present work, we aimed to design and develop innovative molten salt systems using CALPHAD. A multi-component thermodynamic database is a prerequisite when performing CALPHAD-type predictions of invariant points in these systems. The database of multi-component systems mainly comprised all the subsystem excess parameters, and limited ternary parameters are sometimes required to calculate results as accurately as possible. Therefore, the initial work of the present serials is to execute thermodynamic evaluation and optimization on the $\text{NaF-NaCl-Na}_2\text{CO}_3$ subsystems via computational thermodynamics. The detailed process of computational thermodynamics approach is outlined in the following sections.

2. Thermodynamic modeling

2.1. Literature evaluation

The phase diagram of the NaF-NaCl binary system have been experimentally investigated by several research groups [15,16]. All researchers proved that this system only contain one eutectic reaction, and no solid solubility has been reported on the end-member components. The complete phase diagram of the NaF-NaCl system was initially measured for the entire range of compositions by Grjotheim et al. [15] through thermal analysis. The eutectic point was placed at 953 K and 33.5 mol% NaF . Later, Johnson et al. [16] experimentally determined the liquidus using thermal analysis. And the eutectic point was located at 953 K and 33.0 mol% NaF . Using the thermal analysis and visual-polythermal methods, several researchers [17–21] established the temperature of the eutectic type ranged from 948 K to 953 K, and the composition of eutectic point ranges from 33.0 to 35.0 mol% NaF . However, no reported information exists of the mixing enthalpies of the liquid phase.

For the $\text{NaF-Na}_2\text{CO}_3$ binary system, two research groups [22,23] investigated the phase equilibrium of solid-liquid for the whole range of compositions using thermal analysis. Likewise, no intermediate compound and solid solubility were reported on this system. Two research groups validated that this system is simple and just of the eutectic reaction. Amadori et al. [22] first measured the phase diagram of the $\text{NaF-Na}_2\text{CO}_3$ system using thermal analysis. The eutectic point was located at 963 K and 39.7 mol% NaF . Later, Schmitz-Dumont et al. [23] experimentally determined the liquidus for the entire range of compositions; the invariant point was placed at 973 K and 40.0 mol% NaF . Moreover, Volkov and Bergman [24–26] measured the temperature of the eutectic type ranges from 959 K to 973 K with the composition ranging from 38.7 to 40.0 mol% NaF .

Phase Equilibrium relations for the $\text{NaCl-Na}_2\text{CO}_3$ binary system have been investigated by three research groups. All investigations confirmed that this system only includes one eutectic reaction and has no intermediate compound. Using thermal analysis, Amadori et al. [22] initially measured the liquidus for the whole range of compositions, and the eutectic point was placed at 909 K and 41.0 mol% Na_2CO_3 . Niggli et al. [27] experimentally investigated the phase diagram of the $\text{NaCl-Na}_2\text{CO}_3$ system with the invariant point located at 914 K and 44.0 mol% Na_2CO_3 . Later, Belyaev et al. [28] experimentally determined the solid-liquid curves of the $\text{NaCl-Na}_2\text{CO}_3$ system using the visual-polythermal method, and the eutectic point was verified at 905 K and 45.0 mol% Na_2CO_3 . Beyond that, several researchers have experimentally studied the compositions of the eutectic type range from 41.0 to 47.0 mol% Na_2CO_3 at the range of 905–918 K. No solid solubility was reported on both of the end-member components.

2.2. Pure components

As shown in Table 1, the stable solid NaF , NaCl and Na_2CO_3 are halite phase. For these pure chemical species, it is reasonable to describe the Gibbs energies as a function of temperature such as Eq. (1):

$${}^0G_i^p(T) = G_i^p(T) - H^{\text{SER}} = a + bT + cT \ln(T) + dT^2 + eT^3 + fT^{-1} \quad (1)$$

where $G_i^p(T)$ the Gibbs energy function of all phases refer to the molar enthalpy of pure elements in their stable state at 298.15 K (H^{SER} is the stable element reference), a , b , c , d , e , and f are coefficients, and T is the absolute temperature. Coefficients in Eq. (1) were obtained from literature [29] for solid- NaF and liquid- NaF ; those for solid- NaCl and liquid- NaCl were obtained from literature [30]; and solid- Na_2CO_3 and liquid- Na_2CO_3 were obtained from literature [31,32]. Table 2 displays thermodynamic data for the corresponding pure components.

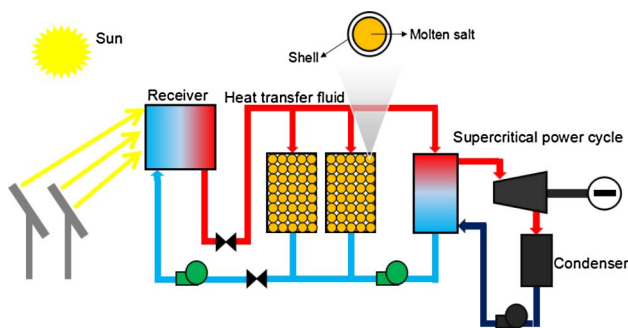


Fig. 1. The schematic of a heat transfer and storage system coupled to supercritical steam and CO_2 cycles.

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