Novel High Thermal Stability LiF-Na₂CO₃-K₂CO₃ Eutectic Ternary System for Thermal Energy Storage Applications

Tao Wang¹, Divakar Mantha¹, Ramana G. Reddy^{1*}

¹*Department of Metallurgical and Materials Engineering,
The University of Alabama, Tuscaloosa, AL 35487-0202, USA*

Abstract

A novel eutectic composition in the LiF-Na₂CO₃-K₂CO₃ ternary system was predicted using thermodynamic modeling based on Gibbs energy of fusion and designed for thermal energy storage or metal heat treatment. Differential Calorimetry Scanning (DSC) technique was used to experimentally measure the melting point of the eutectic composition in the ternary system which was determined to be 694.40 K. Heat capacity of the eutectic composition of the ternary system was also measured using DSC from solid to liquid state and the results were plotted as function of temperature. The upper temperature limit for thermal stability of the eutectic mixture was determined in different atmospheres using Thermogravimetric Analyzer (TGA). The high upper temperature limit for thermal stability ensures the large working temperature range of the LiF-Na₂CO₃-K₂CO₃ ternary system. Thermal conductivity of the ternary system was also studied by using simplified inverse method. The relatively high thermal conductivity indicates its high efficiency of energy storage. Based on the measured thermodynamic properties, physical properties and its high energy storage density, this ternary system can be used as heat transfer fluid for thermal energy storage application.

Key words: Melting point, Heat Capacity, Enthalpy of Fusion, Thermal Stability, Heat Conduction, Molten Salts, Thermodynamic Properties.

1. Introduction

Thermal energy storage and collection has been emphasized nowadays as the energy consumption and demand increases significantly. Different types of materials such as phase

* Corresponding Author, E-mail: rreddy@eng.ua.edu; Tel: +1 (205) 348-4246, Fax: +1 (205) 348-2164

change materials (PCM) and sensible heat materials have been proposed to be used as potential heat transfer media for the energy storage application. For the PCM, the thermal energy is absorbed and released in the charging and discharging process accompanied by fusion [1-5]. However, the sensible heat storage materials were utilized based on its change in heat capacity as function of temperature to store and release thermal energy. Due to its higher efficiency, the sensible heat materials have been actively studied and applied to energy storage applications.

Molten nitrate salts as one type of sensible heat materials have been used as heat transfer fluid for energy storage systems, coolant for metal heat treatment, and residual heat collection medium for steelmaking industry [6-8] due to their low melting points, high heat capacity and excellent thermal stability at 773.15K.

For the solar thermal energy storage application, molten nitrate systems can work perfectly as energy transfer fluid in parabolic trough system which has relatively low maximum working temperature (673.15K to 773.15K). Currently, there are another two major methods being used to take advantage of the solar energy and both of them have much higher maximum working temperature ranges. As one of the methods, solar tower is constructed with thousands of small mirrors surrounded. The radiation from the sun is focused and transferred to the top of the tower which is located in the middle of heliostats. The heat transfer fluid within the tower is heated to high temperature and transferred to energy storage tank. The upper limit of working temperature of solar tower is in the range from 773.15 – 1223.15K. The other method, solar dish, is a large reflective parabolic dish which has a receiver set on its focal point. The radiation is concentrated onto the focal point and transferred to other forms of useful energy. The working upper limit temperature of solar dish is between 973.15 and 1473.15K. Unfortunately, due to the thermal decomposition at temperature above 773.15K, molten nitrate systems are not recommended to be used in those high temperature solar tower and solar dish applications [11].

In order to achieve higher energy conversion efficiency, the current working temperature limit due to the thermal instability of nitrate salts has to be increased. As a result of that, some new high temperature stable molten salt systems were designed in our laboratory that address the thermal stability aspect of thermal energy storage and heat transfer

fluids. In the pursuit of high temperature stable molten salt systems, alkaline fluoride and alkaline carbonate salts were considered as promising candidates due to their excellent high temperature thermal stability.

Several fluoride and carbonate salts have been previously studied [12-17] and their melting points and heat capacity values are given in Table 1. It is observed that most of the salt systems have melting points close to 773.15K, although the highest value is 983.15K and lowest value is 670.15K. All the listed systems present similar heat capacities in liquid state (in the range of 1.6 – 1.7 J/g.K).

Although a number of studies have been done based on either carbonate salt mixtures or fluoride salt mixtures, the systems involving two different anions were relatively less commonly tested. Inspired by the properties of carbonate and fluoride salts, a novel eutectic mixture in the LiF-Na₂CO₃-K₂CO₃ ternary salt system was modeled and synthesized in our laboratory. By mixing a high thermal stability fluoride salt with carbonate salts, the stability of the mixture is expected to be further enhanced.

The eutectic composition of a novel mixture in the ternary system was modeled based on the Gibbs energies of fusion of the individual salt components and the Gibbs energies of mixing of constituent binary systems. The detailed methodology used in developing the thermodynamic model to predict eutectic point in ternary salt mixtures is described elsewhere [18]. The Gibbs energy of fusion for a salt component in a salt mixture is given by the following expression:

$$\Delta G_i^o = -RT \ln(X_i) - \bar{G}_i^{xs} \quad [1]$$

where ΔG_i^o is the Gibbs energy of fusion of salt component ‘i’ in the mixture and $\bar{G}_i^{xs}$ is the partial excess Gibbs energy ‘i’ in the mixture. X_i is the mole fraction of salt ‘i’ and T is absolute temperature. In a ternary system, the summation of Gibbs energies of the three constituent binary systems yields the expression for the integral molar excess Gibbs energy. The partial molar excess Gibbs energy of each constituent salt component in the mixture is then determined from the integral molar excess Gibbs energy expression.

In the ternary system, three equations can be generated for the Gibbs energy of fusion for the three salt components. Newton – Raphson method in three variables is employed to solve

the three Gibbs energies of fusion equations in the three variables which include two composition variables and one temperature variable. The convergence of the solution vector is subject to an error of 10^{-12} . The eutectic composition is then checked for its thermodynamic stability by means of the standard stability function for multi-component solutions. On the basis of the thermodynamic model, the eutectic composition in the LiF-Na₂CO₃-K₂CO₃ ternary salt system was predicted as 17.69 wt% LiF, 28.11 wt% Na₂CO₃ and 54.20 wt% K₂CO₃.

The relevant properties to the thermal energy storage such as melting point, heat capacity, enthalpy of fusion, density, thermal stability, thermal conductivity and energy storage density have been experimentally determined for this eutectic composition. In this paper, we present the results of the experimental determination of the above mentioned properties of this novel eutectic composition in the LiF-Na₂CO₃-K₂CO₃ ternary salt system.

2. Experimental

2.1 Materials and salt preparation

Eutectic composition in the LiF-Na₂CO₃-K₂CO₃ ternary system was synthesized by mixing corresponding amounts of lithium fluoride (>99.0% pure), sodium carbonate (>99.5% pure) and potassium carbonate (purity 99.0% min) obtained from Alfa Aesar®. All the three salts were pre-dried at 423.15K for at least 24hrs using vacuum oven. The quantity of each component salt was weighted according to the eutectic composition and the salt mixtures were mechanically mixed inside the crucible for 15 – 20 minutes continuously under controlled argon atmosphere. Subsequently, the salt mixtures were carefully distributed and sealed in DSC sample pans which were weighted before experiments.

2.2 Apparatus and procedure

Perkin-Elmer Diamond differential scanning calorimeter was used to measure the melting point and heat capacity of the eutectic composition in the ternary salt system. The accuracies of the temperature and heat flow measurements are 0.01K and 0.0001 mW, respectively. Before the measurements, the instrument was calibrated using indium, zinc standard samples

and the acceptable deviations from the standard temperature and heat flow were defined as $\pm 0.2\text{K}$ and $\pm 0.5\text{J/g}$, respectively. After the calibration, the measurements were conducted in highly purified argon atmosphere and carbon dioxide atmosphere with flow rate of 20 – 30 ml/min.

One sample was taken at each time for the melting point determination. Once the temperature inside the DSC reaches equilibrium, the powder was heated from ambient temperature to 873.15K to ensure complete melting. In the process of experimental determination of melting point, a temperature range of 573.15 K to 873.15 K was set with heating and cooling cycles at different heating rates from 0.5 to 20 K/min. The heating-cooling cycles were repeated 6 times to ensure homogeneous mixing of the salt mixture and reproducibility of results. The even distribution of the eutectic salt mixture and uniform mixing was evident from the fact that same melting point was obtained by four sets of measurements.

The heat capacity of the eutectic salt mixture was measured using the similar procedure as that followed in melting point measurement. However, additional “iso-scan-iso” steps were employed in the program cycles with a step width of 25 K in each “scan” step and the sample was held at the set temperature for 5 minutes at each “iso” step. The upper limit for the heat capacity (C_p) measurement was set to 873.15 K in the experiments. To obtain the value of heat capacity of the eutectic mixture, the heat absorbed in the blank experiment with empty sample pan and reference pan was obtained after calibration.

The thermal stabilities were measured using TGA apparatus. Before the measurements, the temperature of instrument was calibrated using indium and zinc samples, and the weight balance was calibrated using 20mg standard platinum calibration materials. The weight calibration material was heated up to multiple temperatures from 373K to 1273K to generate a flat baseline for weight change measurement. In the experiment, 35 – 45mg eutectic salt mixture was placed inside a small platinum crucible. The crucible was then put on the sample pan attached to one of the dual arm horizontal balances, with an empty platinum pan sitting on the reference pan. The sample was heated continuously from 773.15 K to 1223.15 K with 10 K/min heating rate in argon and carbon dioxide atmosphere and the flow rate of the gas was maintained at approximately 50ml/min for the duration of the experiments. Before starting the thermal stability experiment, the salt mixture was kept at 723.15 K for 10

minutes to remove the residual moisture which the salt mixture could have possibly absorbed during the loading process.

The density of the ternary molten salt system was measured using apparatus based on Archimedean principle of buoyancy of immersed bodies and the experimental set-up is shown in Fig.1. In the measurement, the density of molten salt was determined from the buoyancy force exerted on the spherical alumina sinker which was completely immersed in the molten salt and suspended by a platinum wire attached to the electrical balance. The A&D Model GR-202 balance with 0.1mg accuracy was used to weigh the sinker. The under-hook attached to balance allows the sinker to be suspended below the balance. A Thermo Scientific 3-zone tube furnace with a detached controller was used to heat the molten salt inside the alumina container. Two vacuum flanges were added to both ends of the alumina tube to maintain the inert gas atmosphere. Argon gas was used to purge the test chamber throughout the entire process. Any residual air can be removed through the gas outlet hole located in the center of the upper flange. In the experiment, the temperature inside the molten salt was continuously monitored using K-type thermocouple inserted in the salt mixture. By using the crucible holder, the alumina container was kept in the uniform temperature zone (UTZ) of the furnace tube to minimize thermal gradient inside the molten salt. Thermal insulation was placed on both sides of the furnace to avoid any heat loss and heating the balance during the measurement.

Thermal conductivity of salt mixture in solid state was measured using simplified inverse method and the detailed procedure was described elsewhere [19]. Based on the variation of thermal conductivity with temperature in solid state, the value of the studied ternary system in liquid state can be extrapolated.

3. Results and discussion

3.1 Melting point

The melting point is the most critical parameter for high temperature molten salt systems and is measured by DSC technique. In the melting point determination process, different scanning rates in the range of 0.5 – 20 K/min were chosen to measure the change of heat flow

as function of temperature of the ternary system. In each experiment, the eutectic salt mixture was freshly prepared and the measurements were carried out with identical procedure to ensure reproducibility of the result. It is found that only at the scanning rate lower than 5 K/min, the sensitivity of small endothermic peak detection and homogeneity of the temperature distribution inside the DSC chamber can be enhanced [6, 18].

3.1.1 Melting point determination

One representative DSC plot in the heating cycle with scanning rate of 5 K/min in argon atmosphere for the melting point determination experiment is given in Fig. 2. Two endothermic peaks were identified where the first peak corresponds to solid state phase transition. After the solid phase transformation peak, the heat absorption started to increase drastically again at approximately 689 K and this melting peak eventually ended at approximately 703 K. The average peak temperature value of the melting peak was determined to be 694.56 K. The main reason of the wide phase transition temperature range is the low thermal conductivity of salt mixture which is a few orders of magnitude lower than that of metals [19]. As a result, at the onset temperature of endothermic peak, large thermal gradient was present inside the salt mixture and resulted in fluid flow and rapid mixing. This phenomenon is indicated by the rapid increase in endothermic heat after the onset temperature. At the summit temperature of endothermic peak, the last fraction of solid has been transitioned into liquid. Therefore, the peak temperature is emphasized and is considered as the melting point of the eutectic salt mixture. In Fig. 2, the heat flow after the melting peak shows stable reading and no other endothermic peak was detected.

3.1.2 Effect of purge gas on melting point

The typical DSC plots in the heating cycle with scanning rate of 5 K/min in carbon dioxide atmosphere for the $\text{LiF-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ ternary system is given in Fig. 3(a). Similar to the DSC plots (Fig. 3(b)) collected in the argon atmosphere, two endothermic peaks were identified. The average onset and peak temperature values of the melting peak were located at 690.16 K and 694.88 K, respectively. Compared to the experiment using argon purging gas, the current experiment using carbon dioxide purging gas reproduced the melting peak value

with a deviation less than 0.10%. Due to the excellent thermal stability of the ternary system in carbon dioxide atmosphere which will be discussed later in the paper, the almost identical DSC plots under two different inert gases atmosphere demonstrate the reliability and reproducibility of the detected melting point.

3.1.3 Effect of sample pan on melting point

Different sample pans were used in the melting point determination experiments to examine the effect of sample pan on melting point. Five commercially available sample pans (Aluminum pan, copper pan, platinum pan, gold pan and graphite pan) were used to contain salt mixtures and corresponding DSC plots were given in Fig. 4(a) – Fig. 4(e). It is demonstrated that the melting points detected in the measurements using platinum, graphite, gold and copper pans are very close to each other, the deviations are smaller than 0.30% as listed in Table 2. However, the DSC plot collected when using aluminum sample pan was significantly different from the other tests. As illustrated in Fig.4(e), right after the melting peak, the heat flow curve dropped as the temperature increased, which was abnormal in the melting point determination process. After the first heating-cooling cycle, the aluminum pan was taken out of the DSC chamber and the surface was observed to turn into black color, which explains the abnormal heat flow behavior was contributed to the corrosion attack of the molten salt to the aluminum sample pan.

On the basis of the observations, it can be concluded that all the selected pans except aluminum pan can be used as sample containers in the melting point determination. The identical melting peak points throughout all the measurements with different sample pans further verify the reproducibility of the results.

3.1.4 Effect of scanning rate on melting point

In the DSC measurement, the scanning rate of the heat flow plays a significant role in determining the melting point. At a high scanning rate of 20 K/min, the peak is seen shifted slightly to the right. As a result, the melting point detected in this case is higher in comparison to that measured at low scanning rate. The higher melting point value is mainly attributed to the large thermal resistance between the testing sample and sample holder under rapid heating

which reduces the extent of homogeneous temperature distribution within the sample holder. When the heating rate is lowered to 5 K/min or smaller as shown in Fig. 5, the variation of peak temperature is less than 2.7 K. On the basis of values collected at low scanning rates, the average melting point of the eutectic composition in the LiF-Na₂CO₃-K₂CO₃ ternary system was determined to be 694.40 ± 1.60K.

The experimentally determined melting point of the LiF-Na₂CO₃-K₂CO₃ ternary system is listed in Table 1 and compared with some existing carbonate and fluoride multi-component salt mixtures. The lower melting point of the present salt mixture compared to most of the existing systems indicates a large working temperature range that makes this mixture an excellent candidate heat transfer and coolant fluid for the solar thermal energy storage application.

3.2 Enthalpy of fusion

The enthalpy of fusion was determined by collecting the area under the phase transition endothermic peak. The average value of the area under the endothermic peak was measured to be 227.3J/g. In the eutectic salt mixture, the enthalpy of fusion follows the simple mixture rule and can be expressed by equation (2) below if only mechanical mixing is considered: [20]

$$\Delta_{fusion}H_{eutectic} = \sum_{i=1}^n x_i \Delta_{fusion}H_{component_i} \quad (2)$$

Where $\Delta_{fusion}H_{eutectic}$ is enthalpy of fusion of eutectic salt mixture, $\Delta_{fusion}H_{component_i}$ and x_i are the enthalpy of fusion and mole fraction of constituent salt, respectively. The enthalpies of fusion of LiF, Na₂CO₃, K₂CO₃ and the ternary mixture are listed in Table 3 along with the calculated value using mixture rule. The experimental determined enthalpy of fusion is 38.7% lower than the calculated value which reveals that the studied system is not a simple mechanical mixture of three salts. The deviation is possibly contributed due to the formation of cluster in the eutectic mixture [21].

3.3 Heat Capacity

In the DSC equipment, the heat flow through the sample is tested as function of temperature. In the heating process, the temperature profile can be expressed as:

$$T_t = T_o + \beta t \quad (3)$$

where T_o is the initial temperature in K, β is the set heating rate (K/min) and T_t is the temperature in K at a certain time t (min). Based on the thermodynamic definition, heat capacity is the amount of heat required to change a body's temperature by a given amount. Combined with the equation above, the expression for C_p can be shown as follows: [22]

$$C_p = \frac{1}{m} \left(\frac{dH}{dT} \right) = \frac{1}{m} \left(\frac{\frac{dH}{dt}}{\frac{dT}{dt}} \right) = \frac{1}{m} \left(\frac{\Delta P}{\beta} \right) \quad (4)$$

where the ΔP is the actual DSC heat flow signal which has the unit as mW, m is the mass for the sample of interest. This way the heat capacity with the DSC heat flow data is calculated.

The specific heat capacity of the $\text{LiF-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ eutectic salt mixture was measured by the DSC equipment from 623.15 K to 748.15 K. The heat flow is recorded as a function of temperature in “iso-scan-iso” steps at intervals of 25 K. This is a standard procedure followed in the measurement of heat capacity of materials using the DSC equipment. The ‘iso stage’ refers to isothermal holding at a particular temperature, ‘scan stage’ refers to the heat flow recording at a heating rate of 5 K min^{-1} up to an increment of 25 K, followed by another isothermal holding stage. This procedure of heat capacity measurement has two advantages; (i) any heat fluctuations during the recording are avoided by the isothermal steps and (ii) any phase transition can be highlighted by the choice of temperature range. The absolute heat flow to the sample is determined by subtracting the heat flow collected by running a baseline curve with an empty pan. Fig. 6 shows the heat capacity of the $\text{LiF-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ eutectic salt mixture measured as function of temperature in the studied temperature range. Since the heat capacity measurement is equivalent to the heat flow collection against time, the shape of the smoothed heat capacity curve is identical to that in the melting point determination process as illustrated in Fig. 2.

The heat capacity data can be divided into three sections; (i) solid state α (590.15 – 648.15 K) (ii) solid state β (669.15 – 681.15 K) (iii) liquid state (725.15 – 823.15 K). Accordingly, the heat capacity data are fit to three separate equations corresponding to the phases of the eutectic salt mixture.

3.3.1 Heat capacity of solid state α : 590.15 – 648.15 K

The heat capacity data for the LiF-Na₂CO₃-K₂CO₃ eutectic salt mixture in the solid state α in the temperature range of 623.15 to 648.15 K can be fit to a second order polynomial equation. Equation (5) gives the polynomial equation along with the least square fit parameter (R^2) in the temperature range for the solid state α of the eutectic salt mixture.

$$Cp(\text{solid state } \alpha)(\frac{J}{g \cdot K}) = 1.690 \times 10^{-4} T^2 - 2.039 \times 10^{-1} T + 62.9830 \quad (5)$$

(590.15 – 648.15 K)

$$R^2 = 0.9366$$

3.3.2 Heat capacity of solid state β : 669.15 – 681.15 K

The heat capacity data for the LiF-Na₂CO₃-K₂CO₃ eutectic salt mixture in the solid state β in the temperature range of 671.15 to 678.15 K can be fit to a second order polynomial equation. Equation (6) gives the polynomial equation along with the least square fit parameter (R^2) in the temperature range for the solid state β of the eutectic salt mixture.

$$Cp(\text{solid state } \beta)(\frac{J}{g \cdot K}) = 1.162 \times 10^{-2} T^2 - 15.5707 T + 5220.544 \quad (6)$$

(669.15 – 681.15 K)

$$R^2 = 0.9812$$

3.3.2 Heat capacity of liquid state: 725.15 – 823.15 K

The heat capacity data for LiF-Na₂CO₃-K₂CO₃ eutectic salt mixture in the liquid state doesn't vary much as function of temperature. Consequently, the value can be assumed to be constant throughout the liquid state and expressed as Equation (7). The deviation range includes all the liquid state heat capacity values throughout all the four measurements.

$$Cp(\text{liquid state})(\frac{J}{g \cdot K}) = 1.90 \pm 0.04 \quad (7)$$

(725.15 – 823.15 K)

The heat capacity of LiF-Na₂CO₃-K₂CO₃ in the liquid state is listed in Table 1 along with

other existing carbonate and fluoride salt mixtures. On the basis of comparison, the present ternary system shows larger heat capacity in liquid state. Also it is noticed that the heat capacity of $\text{LiF-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ ternary system is 13.8% larger than that of $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ system. Although the melting point is approximately 3.7% higher, the much larger heat capacity compared to the $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ system still demonstrates its better energy storage capacity of the $\text{LiF-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ ternary system.

3.4 Thermal stability

3.4.1 Upper limit of thermal stability in argon atmosphere

In order to determine the accurate upper limit of the working temperature of the ternary salt, the salt mixture was heated continuously from 773.15 K to 1223.15 K with 10 K/min heating rate in argon atmosphere. The measurements were repeated at least three times with fresh prepared samples to ensure the accuracy and reproducibility. One of the collected weight change curve as function of temperature is illustrated in Fig. 7 along with the rate of weight loss dTG. The temperature with approximately 0.01mg/min of dTG trace is defined to be the upper limit of thermally stable working temperature of the $\text{LiF-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ salt and the average value was measured to be 1070.15 ± 35 K.

3.4.2 Upper limit of thermal stability in carbon dioxide atmosphere

The ternary salt was heated continuously from 773.15 K to 1273.15 K with 10 K/min heating rate to determine the upper limit of the working temperature in carbon dioxide atmosphere. One of the weight change curve and the rate dTG trace as function of temperature of the $\text{LiF-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ ternary system is illustrated in Fig. 8 which demonstrates significant improvement of thermal stability compared to that detected in argon atmosphere. The upper limit of thermally stable working temperature of the $\text{LiF-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ salt was measured to be 1194.15 ± 40 K in this case. At 1273.15K, relatively small amount of weight losses (< 1.5 wt%) were observed with approximately 0.06 mg/min dTG trace. It is notable that the upper limit of thermally stable working temperature measured in the carbonate dioxide atmosphere is approximately 124K higher than that detected in argon atmosphere. What's more, the rate of weight loss detected at high

temperature with carbonate dioxide purge gas is lower than that measured in argon atmosphere. The phenomenon is most likely attributed to the presence of carbon dioxide suppresses the decomposition of carbonate salts. Therefore, the extent of weight loss at working temperature was diminished.

On the basis of the experimentally measured upper limit of stable temperature and the thermal weight loss rate dTG, it can be concluded that LiF-Na₂CO₃-K₂CO₃ ternary system can be operated more stably in carbon dioxide atmosphere than other inert gas at high temperature. Consequently, a large working temperature range is achieved given the great thermal stability.

3.5 Density measurement

The density of the ternary system was determined using Archimedean principle of buoyancy of immersed alumina sinker. The weight change indicated from electrical balance represents the buoyancy force exerted on the sinker with known volume. By using the equation below, the density of the molten salt can be calculated:

$$\rho = (M_0 - M_i) / \{V_s [1 + 3C(T - T_0)]\} \quad (8)$$

where M_0 and M_i are the masses of sinker suspended at ambient temperature T_0 and immersed in molten salt, respectively. V_s is the volume of the spherical sinker, C is the linear thermal expansion coefficient of the sink.

The accuracy of the apparatus was evaluated prior to the actual density measurement of novel LiF-Na₂CO₃-K₂CO₃ using some standard pure nitrate salt such as LiNO₃. The density of LiNO₃ determined using current apparatus was plotted against temperature and compared to the values reported in the previous literature. As shown in Fig 9, the density of LiNO₃ salt was measured from 573.15K to 773.15K. The excellent agreement between the current and literature density value verifies the accuracy of density measurement of the apparatus. In the liquid state, the temperature dependence of the density follows a linear equation as shown below:

$$\rho = A - BT \quad (9)$$

where A and B are density value coefficients, T is temperature of salt in liquid state. Based on the regression analysis, the A and B coefficient values for LiNO₃ were determined as

2.055g/cm³ and 5.24×10⁻⁴g/cm³/K, respectively.

The density of LiF-Na₂CO₃-K₂CO₃ was measured using the same apparatus after calibration. The temperature was accurately monitored using the K-type thermocouple inserted to the molten salt and flow rate of purging gas was controlled to have minimum effect on the mass of sinker when suspended in the argon atmosphere above the molten salt. The density of novel LiF-Na₂CO₃-K₂CO₃ molten salt system was plotted as function of temperature and shown in Fig. 10. Similar to the pure standard molten salt, the density of LiF-Na₂CO₃-K₂CO₃ ternary system decreases linearly with temperature in molten state. As a result of that, the density of the molten ternary system can also be expressed in the form of equation (9), where A and B are calculated to be 2.447g/cm³ and 4.83×10⁻⁴g/cm³/K, respectively. On the basis of the linear temperature dependence, the density of LiF-Na₂CO₃-K₂CO₃ at its upper limit temperature of thermal stability can be extrapolated as 1.871g/cm³ and applied to the calculation of energy storage density.

3.6 Thermal conductivity

Thermal conductivity of heat transfer fluid determines the efficiency of thermal energy transfer and therefore has been considered as a very significant parameter for the practical application. The energy transfer medium with high thermal conductivity can collect and release energy rapidly. Thermal conductivity of LiF-Na₂CO₃-K₂CO₃ salt in solid state was measured using simplified inverse method and the result is shown in Fig. 11. Similar to the LiNO₃-NaNO₃-KNO₃ system, the thermal conductivity of studied system decreases as temperature increases. As the sample is heated up to the temperature close to its melting point, the thermal conductivity tends to reach a constant value [19]. Even though the thermal conductivities in the liquid state of salt mixture cannot be determined directly from inverse method, it can still be roughly estimated based on the extrapolated values at melting point. On the basis of that, the value of LiF-Na₂CO₃-K₂CO₃ in liquid state is estimated to be approximately 1.17W/m.K which is much higher than the value of LiNO₃-NaNO₃-KNO₃ (0.60W/m.K), indicating that the studied system can transfer and store energy in a more efficient manner.

3.7 Energy storage density

Energy storage density is considered as the most significant parameter in the energy storage application which directly determines the capacity and efficiency of molten salt used in the heat transfer process. By using the equation below, the energy storage density of any heat transfer medium can be calculated after obtaining its melting point, heat capacity, density and upper limit of working temperature under recommended atmosphere.

$$E = C_p \cdot \rho \cdot (T_{lim} - T_{mp}) \quad (10)$$

where T_{lim} and T_{mp} are the upper limit of thermal stability and melting point for salt mixture, respectively; C_p is the extrapolated heat capacity at upper limit temperature, ρ is the density value at upper limit temperature.

The calculated energy storage density of $\text{LiF-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ ternary system was compared to some existing solar energy storage molten salts such as solar salt, HITEC salt, and $\text{LiNO}_3\text{-NaNO}_3\text{-KNO}_3\text{-NaNO}_2$ under their recommended atmosphere as listed in Table 4. To achieve the maximum energy storage density and stable chemistry of $\text{LiF-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ salt mixture, carbon dioxide atmosphere is recommended for its practical application in thermal energy storage. For nitrate/nitrite salt mixtures, oxygen-free atmosphere is recommended to maintain the stable chemistry of mixture at high temperature [23]. Therefore, the maximum thermal stabilities as well as energy storage densities of nitrate/nitrite salts were achieved under nitrogen, argon or carbon dioxide atmosphere. The energy storage densities of nitrate/nitrite systems in Table 4 were measured under nitrogen atmosphere and very similar values should be expected under argon and carbon dioxide atmosphere due to the same oxygen-free properties of these gases.

Based on the comparison of maximum energy storage density under recommended atmosphere in the long-term operation, the novel ternary molten salt system shows excellent energy storage capacity, which is 135.1% higher than that of the solar salt, 133.5% higher than the HITEC[®] salt and 87.1% higher than the quaternary salt. As illustrated in Fig.12, the energy storage densities of different molten salt systems were plotted again their upper limit temperatures of thermal stability. For the novel $\text{LiF-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ system, the great energy storage density and high maximum working temperature reveals that high melting point

(HMP) systems can potentially be used in solar tower and solar dish energy storage systems which have higher conversion efficiency than solar parabolic trough.

Although the nitrate/nitrite systems have much lower melting points compared to the $\text{LiF-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$, they still show the smaller energy storage capacity given by the effect of low working temperature range. The conclusion can be drawn from this observation that the energy storage capacity is a property affected by multiple parameters and every part plays an important role in determining the capacity of energy storage of salt mixtures. As a result of large working temperature range, high heat capacity and density, the novel HMP systems consisting of fluoride/carbonate salts such as the $\text{LiF-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ can be considered as promising candidate energy storage materials which provide high energy storage capacity at high temperature. Therefore, the future replacement of LMP with HMP can be possible.

4. Conclusions

Melting point and heat capacity of the $\text{LiF-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ eutectic salt mixture were experimentally determined as 694.40 K and 1.90 J/g·K, respectively. The relatively low melting point and high heat capacity of the ternary salt mixture compared to most of the existing systems indicates its better capability as the heat transfer fluid for the solar thermal energy storage application. The experimentally determined enthalpy of fusion is 38.7% lower than the calculated value which reveals that the studied system involves the formation of clusters in the phase transformation process. The upper temperature limit for thermal stability of the eutectic mixture was determined to be 1194.15 K in carbon dioxide atmosphere, which is higher than the value determined in argon atmosphere. The high upper temperature limit for thermal stability ensures the larger working temperature range of the $\text{LiF-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ ternary system. The thermal conductivity of the studied ternary system was measured and compared to the existing thermal energy storage salts. The higher thermal conductivity for $\text{LiF-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ system indicates that the studied system can transfer and store energy in a more efficient manner. As a result of large working temperature range, high heat capacity and density, the novel HMP $\text{LiF-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ can be considered as promising candidate energy storage materials which provide high energy storage density at high temperature.

Acknowledgements

The authors are pleased to acknowledge the financial support from Department of Energy (DOE) Grant No. DE-FG36-08GO18153 for this research project. We also thank the University of Alabama for providing the experimental facilities.

References

- [1] Oró E, Gracia A, Castell A, Farid MM, Cabeza LF. Review on phase change materials (PCMs) for cold thermal energy storage applications. *Applied Energy* 2012; 99: 513 – 33.
- [2] Zhou D, Zhao CY, Tian Y. Review on thermal energy storage with phase change materials (PCMs) in building applications. *Applied Energy* 2012; 92: 593-605.
- [3] Wang LJ, Meng D. Fatty acid eutectic/polymethyl methacrylate composite as form-stable phase change material for thermal energy storage. *Applied Energy* 2010; 87: 2660 – 5.
- [4] Cai YB, Ke HZ, Dong J, Wei QF, Lin JL, Zhao Y, et al. Effects of nano-SiO₂ on morphology, thermal energy storage, thermal stability, and combustion properties of electrospun lauric acid/PET ultrafine composite fibers as form-stable phase change materials. *Applied Energy* 2011; 88: 2106 – 12.
- [5] Zhang ZG, Zhang N, Peng J, Fang XM, Gao XN, Fang YT. Preparation and thermal energy storage properties of paraffin/expanded graphite composite phase change material. *Applied Energy* 2012; 91: 426 – 31.
- [6] Reddy RG, Wang T, Mantha D. Thermodynamic properties of potassium nitrate-magnesium nitrate compound [2KNO₃·Mg(NO₃)₂]. *Thermochimica Acta* 2012; 531: 6-11.
- [7] Wang T, Mantha D, Reddy RG. High thermal energy storage density LiNO₃-NaNO₃-KNO₃-KNO₂ quaternary molten salt for parabolic trough solar power generation. In: Salazar-Villalpando MD, Neelameggham NR, Guillen DP, Pati S, Krumdick GK, editors. *Energy Technology 2012: Carbon Dioxide Management and Other Technologies*; March 11 – 15; Orlando, FL. TMS Warrendale; 2012. P. 73-84.
- [8] Bradshaw RW, Siegel NP. Molten nitrate salt development for thermal energy storage in parabolic trough solar power systems. *ASME Proceedings of Energy Sustainability*; August 10-14; Jacksonville, FL; 2008.
- [9] Wang T, Mantha D, Reddy RG. Thermal stability of the eutectic composition in LiNO₃-NaNO₃-KNO₃ ternary system used for thermal energy storage. *Solar Energy Materials and Solar Cells* 2012; 100: 162 – 8.

- [10] Wang T, Reddy RG. Thermal stability of low melting point $\text{NaNO}_3\text{-NaNO}_2\text{-KNO}_3$ ternary system for thermal storage. Proceedings of 2012 SME Annual Meeting & Exhibit; February 19-22; Seattle, WA; 2012. P. 1-6.
- [11] Forsberg CW, Peterson PF, Zhao HH. High temperature liquid fluoride salt closed brayton cycle solar power tower. Journal of Solar Energy Engineering 2007; 129: 141 – 6.
- [12] Petri RJ, Ong ET. High temperature composite thermal energy storage (TES) systems for industrial applications. Proceedings of 21st intersociety energy conversion engineering conference; August 25-29; San Diego, CA; 1986. P. 873 – 80.
- [13] Marianowski LG, Maru HC. Latent heat thermal energy storage systems above 450°C, Proceedings of 12th intersociety energy conversion engineering conference; August 28-September 2, Washington, D.C.; 1977. P. 555 – 66.
- [14] Heidenreich GR, Parekh MB. Thermal energy storage for organic Rankine cycle solar dynamic space power systems. Proceedings of 21st intersociety energy conversion engineering conference; August 25-29; San Diego, CA; 1986. P. 791 – 7.
- [15] Mayo KE. Heat source systems. United States Patent US 3605720. 1971.
- [16] Eichelberger JJ, Gillman HD. Investigation of metal fluoride thermal energy storage material. Proceedings of 12th intersociety energy conversion engineering conference; August 28-September 2; Washington, D.C.; 1977. P.567 – 74.
- [17] Whittenberger JD, Misra AK. Identification of salt – Alloy combinations for thermal energy storage applications in advanced solar dynamic power systems. Journal of Materials Engineering 1987; 9(3): 293 – 302.
- [18] Mantha D, Wang T, Reddy RG. Thermodynamic modeling of eutectic point in the $\text{LiNO}_3\text{-NaNO}_3\text{-KNO}_3$ ternary system. Journal of Phase Equilibrium and Diffusion 2012; 33: 110 – 4.
- [19] Wang T, Viswanathan S, Mantha D, Reddy RG. Thermal conductivity of the ternary eutectic $\text{LiNO}_3\text{-NaNO}_3\text{-KNO}_3$ salt mixture in the solid state using a simple inverse method. Solar Energy Material and Solar Cells 2012; 102: 201 – 7.
- [20] Rai US, Singh OP, Singh NP, Singh NB. Excess thermodynamic functions for a simple eutectic: m-Aminophenol—pyrogallol systems. Thermochimica Acta 1983; 71: 373 - 5.
- [21] Rai US, George S. Thermochemical studies on the eutectics and addition compounds in the binary systems of benzidine with p-nitrophenol, m-aminophenol and resorcinol. Thermochimica Acta 1994; 243: 17-25.
- [22] Zhang MM, Reddy RG. Thermodynamic properties of $\text{C}_4\text{mim}[\text{Tf}_2\text{N}]$ ionic liquids. Transactions of Institution of Mining and Metallurgy, Section C: Mineral Processing and Extractive Metallurgy 2010; 119: 71 – 6.
- [23] Olivares RI, The thermal stability of molten nitrite/nitrates salt for solar thermal energy storage in different atmospheres. Solar Energy 2012; 86: 2576 - 83.

Fig.1 Schematic of density measurement experimental set-up

Fig.2 Representative DSC heat flow curve for the melting point determination of $\text{LiF-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ eutectic ternary system in argon atmosphere

Fig.3 Effect of purge gas on melting point determination under a) carbon dioxide atmosphere
b) argon atmosphere

Fig. 4 Effect of sample pan on melting point determination using a) graphite pan b) copper pan c) gold pan d) platinum pan e) aluminum pan

Fig.5 DSC heat flow curves for the melting point determination of $\text{LiF-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ eutectic ternary system at different scanning rates

Fig.6 Heat capacity of $\text{LiF-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ eutectic ternary system as function of temperature

Fig.7 Weight change of $\text{LiF-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ system as function of temperature in argon atmosphere

Fig.8 Weight change of $\text{LiF-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ system as function of temperature in carbon dioxide atmosphere

Fig. 9 Density of molten LiNO_3 salt as function of temperature

Fig.10 Density of molten $\text{LiF-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ ternary system as function of temperature

Fig.11 Thermal conductivity of $\text{LiF-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ ternary system as function of temperature

Fig.12 Energy storage densities of both LMP and HMP systems

Fig.1 Schematic of density measurement experimental set-up

Fig.2 Representative DSC heat flow curve for the melting point determination of $\text{LiF-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ eutectic ternary system in argon atmosphere

(a)

(b)

Fig. 3 Effect of purge gas on melting point determination under a) carbon dioxide atmosphere
b) argon atmosphere

(a)

(b)

(c)

(d)

(e)

Fig. 4 Effect of sample pan on melting point determination using a) graphite pan b) copper pan c) gold pan d) platinum pan e) aluminum pan

Fig.5 DSC heat flow curves for the melting point determination of LiF-Na₂CO₃-K₂CO₃ eutectic ternary system in different scanning rates

Fig.6 Heat capacity of $\text{LiF-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ eutectic ternary system as function of temperature

Fig. 7 Weight change of $\text{LiF-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ system as function of temperature in argon atmosphere

Fig.8 Weight change of $\text{LiF-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ system as function of temperature in carbon dioxide atmosphere

Fig. 9 Density of molten LiNO_3 salt as function of temperature

Fig.10 Density of molten LiF-Na₂CO₃-K₂CO₃ ternary system as function of temperature

Fig.11 Thermal conductivity of $\text{LiF-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ ternary system as function of temperature

Fig.12 Energy storage densities of both LMP and HMP systems

Table 1. Melting points and heat capacities of fluoride and carbonate salt systems

Table 2. Melting points determined using different sample pans

Table 3. Calculated and experimental enthalpy of fusion $\Delta_{\text{fusion}}H$

Table 4. Energy storage densities of different molten salt systems under recommended atmospheres for energy storage application

Table 1. Melting points and heat capacities of fluoride and carbonate salt systems

Eutectic mixture	Melting Point (K)	Heat capacity (J/g.K)
$\text{Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$	983.15	1.56
$\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$	778.15	1.76
$\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3\text{-Na}_2\text{CO}_3$	670.15	1.67
LiF-KF	715.15	1.63
LiF-NaF-KF	727.15	1.55
LiF-NaF-KF-MgF_2	722.15	1.55
$\text{LiF-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ (Present work)	694.56	1.90 ± 0.04

Table 2. Melting points determined using different sample pans

Sample pan	Melting point/(K)
Graphite	695.71
Copper	693.79
Gold	693.62
Platinum	694.27
Aluminum	N/A

Table 3. Calculated and experimental enthalpy of fusion $\Delta_{\text{fusion}}H^\circ$

System	$\Delta_{\text{fusion}}H^\circ$
	J/g
LiF	1041.2
Na ₂ CO ₃	279.9
K ₂ CO ₃	199.8
LiF-Na ₂ CO ₃ -K ₂ CO ₃ (Calc.)	371.1
LiF-Na ₂ CO ₃ -K ₂ CO ₃ (Expt.)	227.3±12.3

Table 4 Energy storage densities of different molten salt systems under recommended atmospheres for energy storage application

System	Energy storage density (MJ/m ³)
NaNO ₃ -KNO ₃ (Solar Salt)	756
NaNO ₃ -NaNO ₂ -KNO ₃ (HITEC)	761
LiNO ₃ -NaNO ₃ -KNO ₃ -NaNO ₂	950
LiF-Na ₂ CO ₃ -K ₂ CO ₃	1777