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Mixed metal carbonates/hydroxides for concentrating solar power analyzed with DSC and XRD

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ABSTRACT

Li_2CO_3–Na_2CO_3–K_2CO_3 molten salt mixtures are potentially suitable for high temperature thermal energy storage in the concentrating solar power. We investigated the LiNaK carbonate salt with hydroxides of lithium (LiOH), potassium (KOH), or calcium ($Ca(OH)_2$) by using differential scanning calorimetry (DSC) and X-ray diffraction (XRD). From the repeated heating DSC curves, lower melting points with excellent reproducibility were found when 10 wt% LiOH or KOH was added into 40 wt%Li_2CO_3–20 wt%Na_2CO_3–40 wt%K_2CO_3. Based on the characterization of XRD patterns, the molten eutectic mixtures consisted of $LiKCO_3$, $LiNaCO_3$, and residual Li_2CO_3 when the ternary carbonate salt was heated at the temperature above the melting point and cooled rapidly. In the system of LiNaK carbonate salt with additives of LiOH or KOH, more $LiKCO_3$ and $LiNaCO_3$ with lower melting point can be formed by substitution reaction. Thus, optimal molar ratio for the mixed molten salts with low melting point could be quickly obtained by studying the composition of the resulting eutectic mixtures.

1. Introduction

Concentrating solar power (CSP) has been considered to be an important and efficient approach to provide dispatchable solar power conversion, and to replace fossil burning power stations in current electricity grids [1]. Thermal energy storage (TES) is the crucial part of CSP plants, which allowing solar power to be produced at times of lesser irradiation in the mornings, evenings or during cloudy days [2,3]. It can also contribute to reduce the cost of electricity generation due to more operating hours per year, and less part-load operation [1,4]. Molten salts have already been chosen as thermal energy storage media in CSP plants. So far, several available mixed molten salts composed of nitrates and nitrites have been first used successfully in commerical CPS plants [5,6]. Among of them, Solar Salt, a binary nitrate salt ($NaNO_3$:KNO_3=60:40 wt%), has been used at Solar Two in the USA, at Andasol 1, 2, 3 in Spain, and etc. [7–9]. Solar Salt melts at 220° C, and decomposes at 600 °C [10,11]. Hitec, a ternary molten salt ($NaNO_3$:KNO_3:$NaNO_2$=7:53:40 wt%), is also one of the most common thermal energy storage media, which has a freezing point of 142 °C and a decomposition temperature of 454 °C [12,13]. Hitec XL ($NaNO_3$:KNO_3:$Ca(NO_3)_2$=7:45:48 wt%) has been developed as another commercial ternary molten salt with increased decomposition temperature. The melting point of Hitec XL is about 120 °C, and the decomposition temperature can be up to 500 °C [14]. Better than mixed nitrates, the decomposition temperatures of mixed carbonates are reported as close to 1000 °C [15], which can well meet the requirements of high temperature solar thermal power generation [16–19]. Our research group at B.J.U.T. [20,21] has prepared 36 kinds of ternary carbonate salts and investigated in detail their thermophysical properties. It is found that the melting point of the ternary carbonates with optimized composition can be as low as 400 °C, and the decomposition temperature can be maintained at 800 °C and above. In order to find the optimized composition, in our research we have studied multi-component salt mixtures and permutation thereof.

In studies on preparation aspects of mixed molten salts with lower melting points, knowledge of the melting processes or mechanisms for molten salts systems is absolutely essential. Although the phase diagram can help to obtain the composition and melting points of the eutectic mixtures, it is still difficult to clarify the inner essence and nature of the mixed molten salts with lower melting points. Multicomponent phase diagrams in reality are very complex and often based on a large number of experiments or calculations [22]. Relatively few phase diagrams of mixed molten salts have been reported so far [22].

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Table 1
The melting points of raw materials.

Chemicals	K_2CO_3	Li_2CO_3	Na_2CO_3	LiOH	KOH
Melting point(°C)	898	720	852	471	360

Table 2
Formulation of the mixed molten salts.

Samples	Formulation
LiNaK	40 wt%Li_2CO_3–20 wt%Na_2CO_3–40 wt%K_2CO_3
LiNaK–Li	40 wt%Li_2CO_3–20 wt%Na_2CO_3–40 wt%K_2CO_3–10 wt%LiOH
LiNaK–K	40 wt%Li_2CO_3–20 wt%Na_2CO_3–40 wt%K_2CO_3–10 wt%KOH
LiNaK–Ca	40 wt%Li_2CO_3–20 wt%Na_2CO_3–40 wt%K_2CO_3–10 wt%$Ca(OH)_2$
LiK (11)	*n* (Li_2CO_3):*n* (K_2CO_3)=1:1 (molar ratio)
LiNa (11)	*n* (Li_2CO_3):*n* (Na_2CO_3)=1:1 (molar ratio)
LiNaK (211)	*n* (Li_2CO_3):*n* (Na_2CO_3):*n* (K_2CO_3)=2:1:1 (molar ratio)

There are two main factors that affect the melting point of crystals: pressure and impurity. Under constant pressure, the goal of mixing salts is to have lower melting points than the single component. It has been shown that the melting points of the binary carbonates with different component proportions are in the range of 480–770 °C [22,23], which are lower than that of pure carbonate (see Table 1). The melting point of ternary carbonates is around 400 °C, which is again lower than that of binary carbonates [20]. In addition, the melting point of ternary carbonates could continue to decrease when using additives [18]. In the present work, a series of hydroxides, LiOH, KOH, and $Ca(OH)_2$ were chosen as additives and mixed with the ternary LiNaK carbonates. The melting points of the mixed molten salts were tested by differential scanning calorimetry (DSC). In addition, based on X-ray diffraction (XRD) analysis of the mixed molten salts, the changes in components and the formation of the eutectics were elucidated. Better preparation methods, based on mass ratio or molar ratio, were discussed.

2. Experimental

2.1. Preparation of mixed molten salts

The materials used in the presented experiments were lithium carbonate, sodium carbonate, potassium carbonate, lithium hydroxide, potassium hydroxide, and calcium hydroxide. All carbonates and hydroxides were anhydrous and analytical reagent grade chemicals. The melting points of raw materials are shown in Table 1.

The mixed molten salts were prepared through the direct mixing preparation method [17,18] according to mass ratio or molar ratio shown in Table 2. During the preparation process, the raw materials were dried at 150 °C for 24 h, to remove the adsorbed water in these salts as much as possible.

2.2. Characterization of mixed molten salts

Melting point, initial crystallization point, and decomposition temperature were analyzed with differential scanning calorimetry (DSC) and thermogravimetry (TG). Simultaneous Thermal Analyzers (STA-409PC, NETZSCH) were used to obtain the DSC curves and TG curves with an operating temperature range of 25–1550 °C, with the maximum working temperature of 1500 °C and a weighing precision of 0.001 mg. The precision of the experimental apparatus was validated by measuring DSC with industrial-grade lithium nitrate in platinum–rhodium (Pt–Rh) crucible. The error between the measured value and the literature value on the melting point was 1.6% [20]. The small sample (5–15 mg) was put in a platinum–rhodium (Pt–Rh) crucible (25 μl) with lid during measurement. Using nitrogen (gas purity > 99.999%) as protective gas at 20 ml/min, the heating and cooling experiments of the samples for DSC curves were performed by cycling six times from 25 °C to 700 °C at 10 K/min. For TG curves, the samples were heated from 25 °C to 1000 °C.

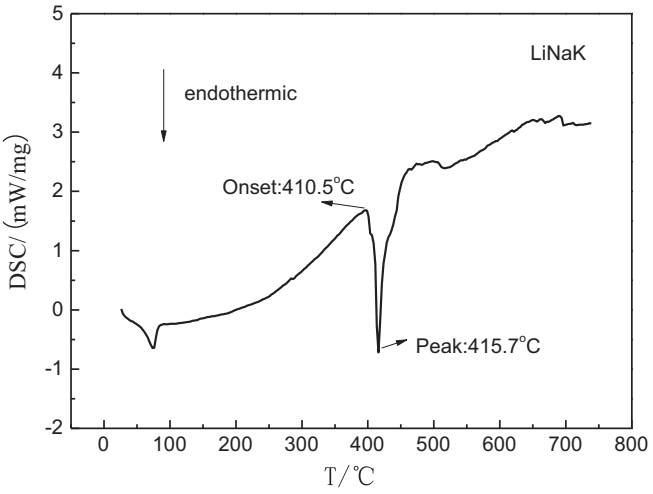

Fig.1. Heating DSC curve of the sample LiNaK (40 wt%Li_2CO_3–20 wt%Na_2CO_3–40 wt%K_2CO_3).

The compositions of the prepared samples were determined by an X-ray diffraction meter (D8 Advance Bruker/AXS). The samples were prepared by using a rapid quenching technique. At first, the materials were mixed fully and heated at 500 °C for 30 min in muffle furnace. Then, the obtained samples were dumped into the steel plate and rapidly cooled. Finally, the resultant samples were grinded and recorded to get diffraction pattern using a Cu Kα target.

3. Results and discussions

3.1. DSC curves of mixed molten salts

The melting point is the most basic thermophysical property of molten salts, which can be obtained by analyzing the heating DSC curve. Fig. 1 shows the heating DSC curve of the ternary carbonates (40 wt%Li_2CO_3–20 wt%Na_2CO_3–40 wt%K_2CO_3). Before measuring the DSC curve, lithium, sodium and potassium carbonates were mixed directly and stirred. As temperature rise, a single endothermic melting sharp peak with onset temperature of 410.5 °C appears in the sample LiNaK in Fig. 1, which is due to an "invariant reaction" of eutectic transformation [24]. The shape of this sharp peak is similar to that obtained for the melting of pure component with an invariant melting point [24]. At this point, the eutectic composition played an important role on reaching the lowest possible temperature under liquidus equilibrium. In addition, the melting point of ternary carbonates could continue to decrease when using additive [18]. Moreover, the melting point of these mixed molten salts must be kept unaltered over multiple heating/cooling cycles. So, the sample LiNaK was further studied by adding a series of hydroxides, LiOH, KOH and $Ca(OH)_2$. The heating and cooling cycle experiments of the resultant samples were carried out six times in sequence to analyze their melting process and melting points, as well as the repeatability of the melting point. Fig. 2 shows DSC repeated heating curves of ternary carbonates with different hydroxides.