Experimental and theoretical research on the thermal properties of carbonate mixtures

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Abstract. In this paper, Na₂CO₃, Li₂CO₃ and K₂CO₃ were selected to prepare carbonate mixtures according to different proportions. The thermal property and stability of the samples were tested by differential scanning calorimeter (DSC). The phase change temperature and latent heat of carbonate mixtures were calculated by theoretical formula, and compared with the experimental data to verify whether the theoretical formula are applicable in the field of high temperature molten salt. The results show that the melting point of carbonates which melted together is about 400°C. And the melting point of ternary carbonates is lower than the single component. The initial crystallization points of some samples are higher than the melting points. The differences between the melting point and the primary crystallization temperature are 5~20°C. The phase change latent heat of the carbonate mixtures is lower than the single component’s. The latent heat of melting is more than the latent heat of solidifying. The DSC testing curves of the carbonate mixtures are almost coincident. The stability of mixed carbonate is very good. This experiment will provide reference and basis for its application in solar thermal power generation.

1. Introduction

High temperature heat transfer and heat storage technology of solar energy is a core technology in solar thermal power generation system. It is very important to select a suitable high-temperature heat storage medium. In recent years, molten salts have been a good choice as high temperature heat transfer and heat storage medium of solar energy, because they have wide temperature range, low viscosity, high liquidity, low vapor pressure, low pressure resistance to the pipeline, large relative density, high specific heat capacity, good heat storage capacity and low cost, etc..

The American Oak Ridge National Laboratory studied the physical and chemical properties of various molten salts and their compatibility with the container materials [1]. American Sandia National Laboratory has been engaged in studying the thermal properties of mixed molten salt and developing new low melting point mixed molten salts [2]. Araki et al studied the thermal conductivity of molten carbonate [3]. Kourkova et al fitted the specific heat curve of Li₂CO₃ at 303.15~563.15K [4]. Ma Zhongfang and Wu Yuting prepared hundreds of mixed molten salts, especially a number of molten salts with low melting point to reduce the cost of molten salts [5]. The team of Professor Ding Jing of Zhongshan University has made a deep research on the aspect of preparation of new molten
salt, reducing the melting point and increasing the boiling point [6]. Ren Nan et al prepared and researched ternary mixed carbonates with different proportions [7].

We selected Na$_2$CO$_3$, Li$_2$CO$_3$ and K$_2$CO$_3$ to prepare 36 kinds of mixed molten salts according to different proportions. Thermal properties of the samples were studied by differential scanning calorimeter (DSC). The melting point, phase change latent heat and the initial crystallization points were studied and carried out cyclic experiment. The 36 kinds of mixed carbonates were optimized according to the standard of low melting point, high latent heat and wide using temperature.

2. Experimental methods

2.1. Experimental materials and experimental equipment
The carbonates used in the experiment were sodium carbonate(Na$_2$CO$_3$), lithium carbonate(K$_2$CO$_3$) and potassium carbonate(Li$_2$CO$_3$), which produced by Sinopharm Group Chemical Reagent Co., Ltd. level are analytically pure. The main instruments used in the experiment included vacuum drying box, electronic balance, muffle furnace and differential scanning calorimeter (DSC).

2.2. Experimental processes
The three kinds of carbonates were placed in the vacuum drying box for 24 hours at 120°C, and then mixed according to different quality ratio to prepare 36 kinds of samples (showed in Table 1). Put them into the muffle furnace to melt, the temperature of the muffle furnace was set to 600°C, and heating time was 2 hours. Then the sample was taken out and solidified in the air. And then ground into a powder in a mortar. There were 6 kinds of samples not to melt in the muffle furnace, and they were number 08, 15, 31, 34, 35 and 36.

Differential scanning calorimeter (DSC) was used to test the mixed carbonate with different proportions, the phase change temperature and phase change latent heat of the samples during the heating process and the crystallization point of the sample during cooling were determined. The proportions of the different components are shown in Table 1.

| NO. | Na$_2$CO$_3$ | Li$_2$CO$_3$ | K$_2$CO$_3$ | NO. | Na$_2$CO$_3$ | Li$_2$CO$_3$ | K$_2$CO$_3$ | NO. | Na$_2$CO$_3$ | Li$_2$CO$_3$ | K$_2$CO$_3$ |
|-----|-------------|-------------|-------------|-----|-------------|-------------|-------------|-----|-------------|-------------|-------------|
| 01  | 10%         | 10%         | 80%         | 13  | 20%         | 50%         | 30%         | 25  | 40%         | 40%         | 20%         |
| 02  | 10%         | 20%         | 70%         | 14  | 20%         | 60%         | 20%         | 26  | 40%         | 50%         | 10%         |
| 03  | 10%         | 30%         | 60%         | 15  | 20%         | 70%         | 10%         | 27  | 50%         | 10%         | 40%         |
| 04  | 10%         | 40%         | 50%         | 16  | 30%         | 10%         | 60%         | 28  | 50%         | 20%         | 30%         |
| 05  | 10%         | 50%         | 40%         | 17  | 30%         | 20%         | 50%         | 29  | 50%         | 30%         | 20%         |
| 06  | 10%         | 60%         | 30%         | 18  | 30%         | 30%         | 40%         | 30  | 50%         | 40%         | 10%         |
| 07  | 10%         | 70%         | 20%         | 19  | 30%         | 40%         | 30%         | 31  | 60%         | 10%         | 30%         |
| 08  | 10%         | 80%         | 10%         | 20  | 30%         | 50%         | 20%         | 32  | 60%         | 20%         | 20%         |
| 09  | 20%         | 10%         | 70%         | 21  | 30%         | 60%         | 10%         | 33  | 60%         | 30%         | 10%         |
| 10  | 20%         | 20%         | 60%         | 22  | 40%         | 10%         | 50%         | 34  | 70%         | 10%         | 20%         |
| 11  | 20%         | 30%         | 50%         | 23  | 40%         | 20%         | 40%         | 35  | 70%         | 20%         | 10%         |
| 12  | 20%         | 40%         | 40%         | 24  | 40%         | 30%         | 30%         | 36  | 80%         | 10%         | 10%         |

3. Experimental results and analysis

3.1. Test and analysis of phase change temperature
In the solar thermal power generation system, the lower the melting point of the mixed molten salt which used as heat transfer and heat storage medium is, the lower the operation cost is, the better the economy. Simultaneously, the lower the freezing point of the mixed molten salt is, the safer the system is. The melting point and the initial crystallization temperature of the mixed molten salts are
very important for the optimization of mixed molten salts. The melting starting point and the ending point of each sample are shown in Table 2.

| Number | Starting point (℃) | Ending point (℃) | Number | Starting point (℃) | Ending point (℃) |
|--------|-------------------|-----------------|--------|-------------------|-----------------|
| 01     | 444.6             | 466.8           | 19     | 401.6             | 410.4           |
| 02     | 428.9             | 471.7           | 20     | 396.8             | 405.9           |
| 07     | 400.9             | 408.1           | 21     | 393.8             | 403.6           |
| 09     | 428.5             | 447.0           | 22     | 408.8             | 423.3           |
| 10     | 424.6             | 445.0           | 24     | 397.0             | 405.8           |
| 12     | 399.6             | 407.4           | 25     | 399.7             | 406.2           |
| 13     | 398.4             | 406.4           | 27     | 403.1             | 412.4           |
| 14     | 402.4             | 409.3           | 28     | 398.8             | 406.0           |
| 16     | 428.2             | 437.7           | 29     | 393.9             | 402.3           |
| 17     | 403.1             | 412.4           | 30     | 397.4             | 406.3           |
| 18     | 398.6             | 407.1           |        |                   |                 |

The DSC curves of the 36 kinds of samples are shown in Figure 1. The melting point of most mixed molten salts is concentrated at 400℃. In all 36 kinds of samples, there were 9 kinds of samples didn’t form regular melting peak in the melting process, and they are number 03, 04, 05, 06, 11, 23, 26, 32 and 33. Figure 2 shows an irregular DSC curve of sodium carbonate, lithium carbonate, and potassium carbonate at a mass ratio of 1: 3: 6. The curve has two melting peak, and the melting temperature range is about 100℃. This not only increases the cost of system operation, but also makes it easy to separate part of the group when the temperature changes, increasing the probability of pipeline plugging, and it is detrimental for the solar power generation system.

According to the experimental results, 15 kinds of ratio with low melting point and regular melting peak regular were preliminarily preferred. DSC curve of sample number 13 is shown in Figure 3. From the figure, we can see that it has typical melting peak. It’s phase change latent heat is 147.1J/g, the starting melting temperature is 398.4℃, and the ending melting temperature is 406.4℃, the melting temperature range is 8℃. The mixed molten salt with the ratio can be completely melted in a small temperature range. It is more suitable for solar power generation and is conducive to the initial operation of the power generation system.

In all 9 kinds of samples with irregular melting peaks, 6 kinds of samples have a same characteristic that one of the components accounted for a small mass ratio, and only 10%, such as sample 03, 04, 05, 06, 26 and 33. They were not eutectic in the heating process, maybe because minor component reduce the interaction with other components and can't melt together at the same temperature.
3.2. Test and analysis of initial crystallization point
When the mixed molten salt changed from a molten state to a solid state, the precipitation of each component was in order. So we can obtain the primary crystallization temperature (initial crystallization point) by analyzing the DSC curve of the cooling process. The heating curve is compared with the cooling curve.

The DSC curves of sample 07 and 30 appeared two exothermic peaks, the components of mixed molten salts were precipitated in two phases, and it can increase the risk of pipeline clogging. They are not suitable to be used as thermal storage medium. Figure 4 is the heating and cooling curve of sample 07. From the figure, we can see that its melting point is 400.9℃, the first crystallization temperature is 407.9℃, and the second crystallization temperature is 389.9℃. The melting points and the primary crystallization temperatures are shown in Table 3.

![Figure 4. Heating and cooling curves of No. 07](image1)

![Figure 5. Heating and cooling curve of sample 14](image2)

| Number | Melting point (℃) | Primary crystallization temperature (℃) | Number | Melting point (℃) | Primary crystallization temperature (℃) |
|--------|-------------------|----------------------------------------|--------|-------------------|----------------------------------------|
| 01     | 444.6             | 432.7                                  | 19     | 401.6             | 385.5                                  |
| 02     | 428.9             | 413.6                                  | 20     | 396.8             | 385.7                                  |
| 09     | 428.5             | 420.7                                  | 21     | 390.8             | 381.1                                  |
| 10     | 424.6             | 404.8                                  | 22     | 408.8             | 390.2                                  |
| 12     | 399.6             | 389.5                                  | 24     | 397.0             | 384.0                                  |
| 13     | 398.4             | 389.0                                  | 25     | 399.7             | 385.2                                  |
| 14     | 402.4             | 387.6                                  | 27     | 403.1             | 381.6                                  |
| 16     | 428.2             | 413.4                                  | 28     | 398.8             | 378.8                                  |
| 17     | 403.1             | 398.2                                  | 29     | 393.9             | 384.6                                  |
| 18     | 398.6             | 385.7                                  |        |                   |                                        |

From the table, we can see that the primary crystallization temperatures of samples are lower than the melting points. The differences between the melting point and the primary crystallization temperature are 5~20℃. Figure 5 is the heating and cooling curve of sample 14. From the figure, we can see that the starting melting point of the sample is 402.4℃, the ending melting point is 409.3℃. When the sample is cooled, the components precipitate at 387.6℃.

3.3. The stability of mixed carbonate
The sample of No.18 was selected to study the stability. The sample was heated to melt and cooled to solidify continuously for 5 times. And the phase change temperature and latent heat after melting and solidifying each time were tested. The results of repeated melting are shown in the Figures 7 and Table 5. The results of repeated solidifying are shown in the Figures 8 and Table 6.
Table 4. The repeated melting experimental results of mixed carbonate (sample 18)

| Experimental order(times) | Starting point (℃) | Ending point (℃) | Latent heat of melting (J/g) |
|---------------------------|--------------------|------------------|-----------------------------|
| 1                         | 398.6              | 407.1            | 263.7                       |
| 2                         | 397.2              | 406.2            | 261.4                       |
| 3                         | 397.2              | 406.2            | 262.6                       |
| 4                         | 397.3              | 406.1            | 263.2                       |
| 5                         | 397.4              | 406.3            | 263.4                       |
| Average value             | 397.54             | 406.38           | 262.86                      |

Table 5. The repeated solidifying experimental results of mixed carbonate (sample 18)

| Experimental order(times) | Primary crystallization temperature (℃) | Latent heat of solidification (J/g) |
|---------------------------|----------------------------------------|------------------------------------|
| 1                         | 385.7                                  | 244.4                              |
| 2                         | 384.5                                  | 243.9                              |
| 3                         | 384.5                                  | 241.5                              |
| 4                         | 384.8                                  | 243.9                              |
| 5                         | 384.4                                  | 242.6                              |
| Average value             | 384.8                                  | 243.3                              |

Figure 6. DSC comparison curves for repeated heating of mixed carbonate

Figure 7. DSC comparison curves for repeated cooling of mixed carbonate

From the figures and tables, we can see that the stability of mixed carbonates is very good. The DSC testing curves are almost coincident. The DSC testing curve in the first time has a little deviation compared with others. The reason is that the sample contact incompletely with the bottom of the crucible in the first time. The phase change temperature and latent heat in the heating and cooling process are almost equal. The biggest differences in the phase change temperatures are about 1℃ (relative difference 0.25%) and in the latent heat are 3J/g (relative difference 1.2%).

4. Theoretical calculation of mixed carbonate

It is assumed that several inorganic salts are completely immiscible in the solid state and they are completely miscible in the liquid state. Zhang Yiping deduced the theoretical formulas for calculating the phase change temperature and latent heat of eutectic system according to the second law of thermodynamics and phase equilibrium theory.

\[
T_m = \left[ \frac{1}{T_i} \cdot \frac{R \ln X_i}{H_i} \right]^{-1} \quad H_m = T_m \sum_{i=1}^{n} \frac{X_i H_i}{T_i} \quad (i=A, B)
\]

\(T_m\) - The melting point of the binary mixture (K);  
\(H_m\) - The melting latent heat of the binary mixture (J/mol);  
\(T_i\) - The melting point of single component (A or B) (K);  
\(H_i\) - The melting latent heat of
single component (A or B) (J/mol); \( X_i \) - The mole percentage of A or B in the mixture; \( R \) - Gas constant (8.315 J/mol.K).

According to the above formulas, several binary mixed chloride salts prepared in this experiment were calculated theoretically and compared with the experimental values. The results are shown in Table 8. Basic Calculation parameters of this two kinds of carbonates are shown in Table 7.

### Table 6. Basic calculation parameters of three kinds of carbonates

| Type         | Melting point (°C) | Melting latent heat (J/g) | Molecular weight |
|--------------|--------------------|----------------------------|-----------------|
| Na\(_2\)CO\(_3\) | 851                | 138                        | 105.99          |
| Li\(_2\)CO\(_3\) | 723                | 506                        | 73.89           |
| K\(_2\)CO\(_3\) | 891                | 197                        | 138.21          |

### Table 7. Theoretical values and experimental values of phase change temperature and latent heat of ternary mixed carbonate

| Sample Number | Phase change temperature (°C) | Phase change latent heat (J/g) |
|---------------|--------------------------------|-------------------------------|
|               | Experimental value             | Theoretical value             |
| 13            | 398.4                          | 467.76                        |
| 14            | 402.4                          | 397.63                        |
| 18            | 398.6                          | 539.20                        |
| 19            | 401.6                          | 474.29                        |
| 20            | 396.8                          | 402.68                        |
| 22            | 408.8                          | 612.94                        |
| 24            | 397.0                          | 481.20                        |
| 25            | 399.7                          | 408.00                        |
| 28            | 398.8                          | 488.54                        |

Results in the Table 8 shows that the theoretical calculation and the experimental value have a large difference. So the above assumptions do not hold and the above formulas are not suitable for the calculation of ternary mixed carbonate.

### 5. Conclusion

1. In all the ternary carbonate mixtures prepared by Na\(_2\)CO\(_3\), Li\(_2\)CO\(_3\) and K\(_2\)CO\(_3\), some samples are not eutectic, and some samples’ DSC curves have not regular melting peak. For other samples, the melting points of the mixtures are lower than that of the single component and between 393°C and 445°C. From starting to ending, the melting temperature range are between 7°C and 43°C.

2. The primary crystallization temperature of the ternary carbonate mixtures are less than the melting points. The differences between the melting point and the primary crystallization temperature are 5~20°C.

3. The phase change temperature and latent heat in the heating and cooling process are almost equal. The biggest differences in the phase change temperatures are about 1°C and in the latent heats are about 3J/g. The stability of the mixtures is good.

4. The theoretical formula for calculating phase change temperature and latent heat of the eutectic is not suitable for the theoretical calculation of ternary mixed carbonate.

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