Experimental research on latent heat characteristics of binary mixed molten salt

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Abstract. At present, thermal storage is considered as one of the key technologies to alleviate the problem of instability and intermittence for renewable energy. Due to relatively high latent heat, latent heat storage by molten salt is considered to a potential technology. Because of the restriction of different thermophysical parameters, the application of latent heat storage by molten salt has many technical obstacles. So, it is an urgent work to find a better mixed molten salt formula with comprehensive thermophysical properties. In this paper, we selected halogen salts (NaCl, NaF) and alkali (NaOH) to prepare binary mixed molten salts. From the results, for the mixed molten salt of NaCl-NaOH, NaCl:NaOH=1:9 has a maximum latent heat value of 301.2J/g. The initial melting temperature is about 200°C. With the increase of the mass ratio of NaCl, the termination melting temperature increases firstly then decreases. For mixed molten salt of NaF-NaOH, NaF:NaOH=1:9 has a maximum latent heat value of 199.5J/g, the initial and termination melting temperatures are about 265°C and 380°C, repectively. The latent heat value of NaCl-NaOH and NaF-NaOH mixed molten salts decreased with the increase of the mass ratio of halogen salts.
Keywords: Heat storage; Molten salt; Melting point; Latent heat.

1 Introduction

Energy is the foundation of modern society and economic development. Today, China has changed from traditional fossil energy to developing renewable energy, but one of the key technologies to achieve large-scale application of renewable energy is energy storage technology. Molten salt because of its excellent characteristics are widely used as high-temperature storage in the heat storage medium. Nowadays, the sensible heat of molten salt is used for heat storage, and the preparation of molten salt mostly considers the characteristics of low melting point, high specific heat, high decomposition temperature, low viscosity, high thermal conductivity, and low corrosion. However, the specific heat of molten salt is generally 1~3J/(g·K), and the thermal conductivity is generally less than 1W/(m·K). Obviously, sensible heat storage has disadvantages such as low heat storage

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density, large volume, and low heat storage efficiency [1]. Compared with the latent heat storage, the latent heat value of the phase change of molten salt can be between tens to hundreds (unit: J/g). Under the same heat storage volume, molten salt undergoes a solid-liquid phase transition, and its latent heat storage is 5-14 times that of sensible heat storage [2]. At the same time, latent heat storage has the advantages of compact device size, high energy storage density, smaller storage temperature range, low vapor pressure and small pressure change of the heat storage medium, and It is considered to be one of the most promising energy storage technologies at this stage [3]. However, latent heat storage also has some challenges, such as improving the thermal conductivity of molten salt, increasing the heat transfer area, improving the uniformity of heat transfer, and preparing economical high latent heat and low melting point homogeneous mixed molten salt.

Nowadays, the large-scale molten salt used in commercial solar thermal power plants is nitrate, including Solar salt(60% $NaNO_3$ + 40% KNO_3, wt %), Hitec(53% KNO_3 + 7% $NaNO_3$ + 40% $NaNO_2$, wt %) and Hitec XL(45% KNO_3 + 7% $NaNO_3$ + 48% $Ca(NO_3)_2$, wt %). Among them, Solar salt has a melting point of 222.8°C and a latent heat value of 110.7J/g; Hitec has a melting point of 142°C and a latent heat value of 80J/g; Hitec XL has a melting point of 120°C and a latent heat value of 55.4J/g[4-6]. The new quaternary nitrate molten salt studied by Wu Yuting et al. has a melting point of 83.1°C and a latent heat value of 71.75J/g [7]. It can be seen that the latent heat value of these mixed nitrate molten salts is very small. Murat et al[8-12] summarized the thermophysical data of melting point and latent heat from unit to multi-component molten salt. the mixed molten salt with high latent heat value is mostly obtained by mixing lithium salt, or the mixed molten salt with high latent heat value is accompanied by a higher melting point, which cannot meet the requirements of economy and low use temperature. In the mixed molten salt of alkali and salt, low melting point and higher latent heat value can be obtained, which is a method worth trying.

In this paper, starting from the demand for latent heat, while considering economy, first select the unit salt with high latent heat (NaCl, NaF), and then choose the unit salt with low melting point (NaOH). Prepare the binary molten salt with the same cation mixed with salt (NaCl, NaF) and alkali (NaOH), and explore high latent heat molten salt.

2 Experimental scheme

The researcher first selects NaCl, and then selects NaF, which has a higher latent heat than NaCl, and then prepares binary mixed molten salt with NaOH to obtain binary mixed molten salt with the same cations of NaCl and NaOH, NaF and NaOH. The thermal properties of the reagents are shown in Table 1 below.

Table 1. Thermophysical parameters of reagents.

Salt name	Melting temperature(°C)	Heat of fusion (J/g)	Purity %	Specification
NaCl	800	481.8	≧99.5%	AR
NaF	996	794.2	≧98.0%	AR
NaOH	320	159.0	≧96.0%	AR

The specific experimental methods are as follows:

(1) Weigh. Use a high-precision balance to weigh the mixed molten salt according to the mass ratio, a total of 20g.

(2) Preparation by melting method. Choose NaCl and NaOH, NaF and NaOH to mix in a mass ratio of 1:9 to 9:1 to prepare binary mixed molten salt. And in a muffle furnace at a rate of 10K/min heated to 650 °C, keep for 24H to make the mixture completely melt and uniformly mixed. Finally, it is cooled and ground, sealed and stored for the next test.

(3) DSC measurement. Use STA-409PC synchronous thermal analyzer to measure,

weigh 5~10mg of sample and place it in an alumina crucible. The heating process is set to 30~650°C, the heating rate is 10K/min. The cooling process is set to 650~30°C, and the cooling rate is 8K/min. Nitrogen is used as a shielding gas, and the gas flow rate is 30 mL/min. Finally, the DSC curve of the measured sample is obtained, and the melting point and latent heat value of the binary mixed molten salt are obtained. See Fig. 1.

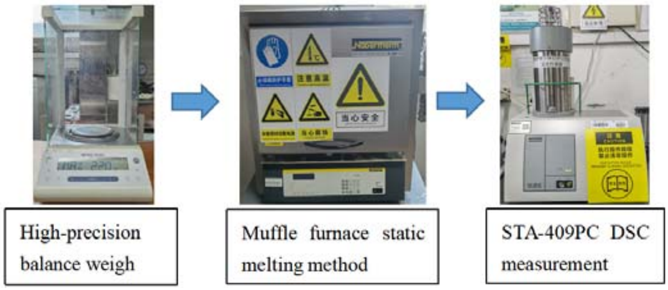

Fig. 1. Experimental flow chart.

3 Results and discussion

In the muffle furnace heated to 650°C, the mass ratio of NaCl and NaOH to the molten state has 8 groups of 1:9 to 8:2. And NaCl: NaOH=9:1 has not reached the communicative state, it is solid. The mass ratio of NaF and NaOH to the molten state has 3 groups of 1:9 to 3:7, and the remaining 7 groups are solid in the muffle furnace at 650°C. During the DSC measurement, after each measurement, the alumina crucible sticks to the thermocouple, causing salt creep. Three DSC measurements were taken for each group, and the average value of melting point and latent heat value was taken to reduce the experimental error.

3.1 NaCl-NaOH binary mixed molten salt

3.1.1 *DSC curve clusters under different mass ratios*

The mass ratio of 8 sets of NaCl-NaOH binary molten salt is measured. Measure three times in each group to get the measured DSC curve cluster, see Figs.2-9 below. The melting point and latent heat value of each measurement are shown in Table 2 below.

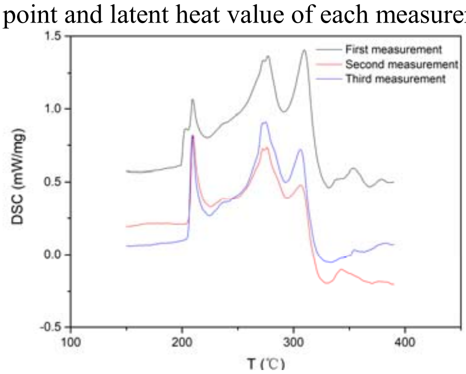

Fig. 2. DSC curve clusters of NaCl: NaOH=1: 9 three measurements.

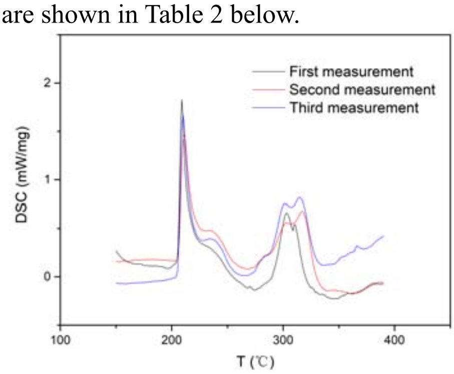

Fig. 3. DSC curve clusters of NaCl: NaOH=2: 8 three measurements.

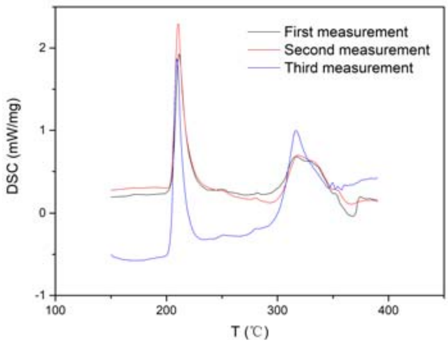

Fig. 4. DSC curve clusters of NaCl: NaOH=3: 7 three measurements.

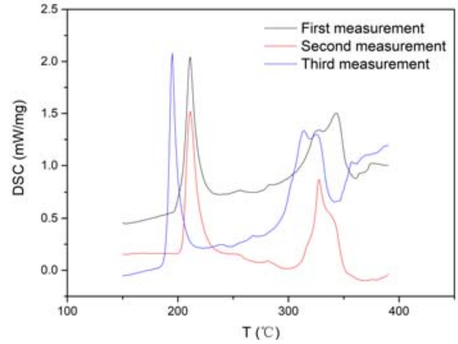

Fig. 5. DSC curve clusters of NaCl: NaOH=4: 6 three measurements.

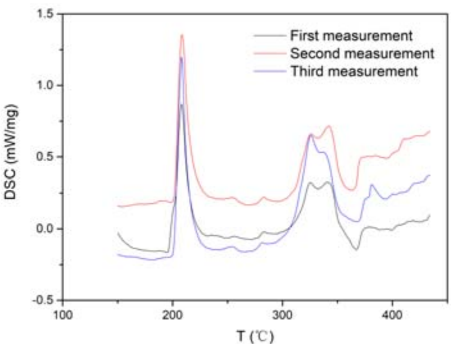

Fig. 6. DSC curve clusters of NaCl: NaOH=5: 5 three measurements.

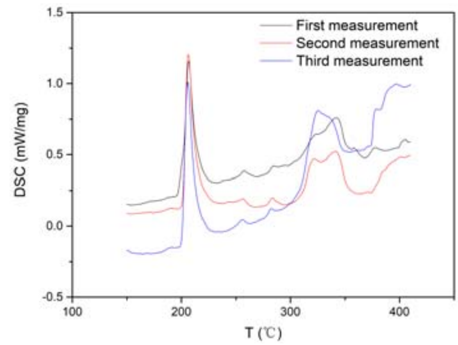

Fig. 7. DSC curve clusters of NaCl: NaOH=6: 4 three measurements.

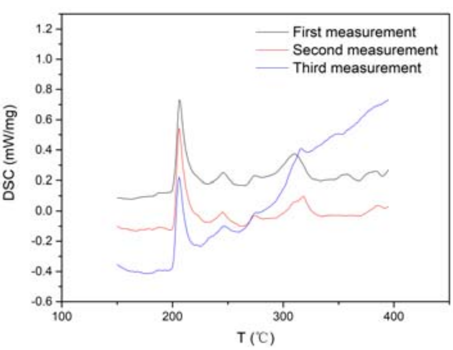

Fig. 8. DSC curve clusters of NaCl: NaOH=7: 3 three measurements.

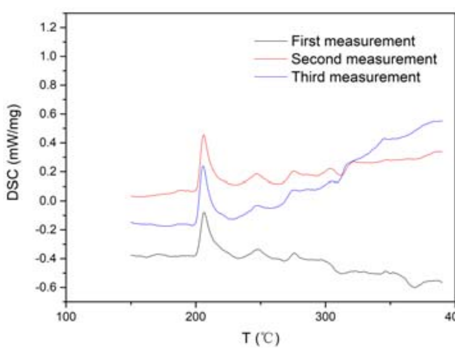

Fig. 9. DSC curve clusters of NaCl: NaOH=8: 2 three measurements.

Table 2. Melting point and latent heat value data of three measurements of NaCl-NaOH molten salt.

NaCl: NaOH mass ratio	Number of experiments	Starting melting temperature °C	End melting temperature °C	Latent heat value J/g
1: 9	1	199.6	332.0	332.7
	2	206.5	330.5	271.1
	3	205.9	333.7	299.8
	average value	204.0	331.9	301.2
2: 8	1	205.9	344.6	224.5
	2	206.2	339.9	248.2
	3	205.9	336.7	274.4
	average value	206.0	340.4	249.0
3: 7	1	205.5	367.0	227.0
	2	205.2	367.2	227.3
	3	204.2	361.7	244.4
	average value	205.0	365.3	232.9
4: 6	1	204.4	361.0	195.3
	2	204.4	368.5	190.1
	3	189.8	361.0	211.4
	average value	199.5	363.5	198.3
5: 5	1	201.2	367.0	146.8
	2	201.9	363.8	152.1
	3	201.4	368.5	182.1
	average value	201.5	366.4	160.3
6: 4	1	201.4	369.0	95.6
	2	201.6	364.7	115.8
	3	200.9	352.9	125.1
	average value	201.3	362.2	112.2
7: 3	1	201.5	330.0	42.3
	2	201.6	334.9	51.5
	3	201.0	323.6	32.8
	average value	201.4	329.5	42.2
8: 2	1	201.3	323.0	16.2
	2	201.5	312.1	29.5
	3	200.7	310.0	24.3
	average value	201.1	315.0	23.3

In the 8 sets of mass ratio DSC curves of the binary molten salt of NaCl-NaOH, only NaCl:NaOH=1:9 is a large melting peak formed after three cycles of melting and crystallization, as shown in Fig. 1. The remaining 7 groups of NaCl-NaOH mixed molten salts change from one large melting peak to two or more independent melting peaks as the mass ratio of NaCl increases. And only the first melting peak is regular and orderly, and the remaining melting peaks are mostly irregular or small. The appearance of more than two independent melting peaks in the DSC curve indicates that the component cannot reach the eutectic state, and each component in the component undergoes phase change independently. The melting peak starting temperature of the three measured DSC curves for each mass ratio in Figs.2-9 is basically the same. In Figs.7-9, starting from NaCl:NaOH=6:4, the quality of NaCl begins to exceed the quality of NaOH, and the melting peak at 300°C began to decrease sharply, until the melting peak at 300°C of NaCl:NaOH=8:2 nearly disappeared. The highest temperature measured by DSC in this experiment is 650°C. As the quality of NaCl increases, there may be a melting peak above 650°C. Each mass ratio is measured three times, and the DSC curves of the three measurements are more consistent. Because the alumina crucible is used to measure the mixed molten salt, the DSC curve is relatively drifting.

3.1.2 *Melting point and latent heat*

Because there are multiple melting peaks, the melting point is divided into the initial melting temperature and the ending melting temperature. It can be seen in Table 1 that the mass ratios of the 8 groups of binary molten salts of NaCl-NaOH all start to melt around 200°C, with a maximum difference of 6.5°C, which is basically the same. The melting point of the mixed molten salt is lower than the melting point of the lowest unit component NaOH. The termination melting temperature first increases with the increase of the NaCl mass ratio, then basically remains unchanged, and finally decreases. The termination melting temperature of NaCl: NaOH=1:9 to 3:7 is continuously increased from 331.9°C to 365.3°C, and the termination melting temperature of NaCl:NaOH=3:7 to 6:4 is about 365°C, which basically remains unchanged. NaCl:NaOH=6:4 to 8:2 The termination melting temperature began to drop from 362.2°C to 315°C. The latent heat value is the sum of the melting peak area of the DSC curve. In Table 1, the average latent heat value of the three measurements of NaCl:NaOH=1:9 is 301.2J/g. And the latent heat value decreases as the mass ratio of NaCl increases.

3.2 NaF and NaOH binary mixed molten salt

3.2.1 *DSC curve clusters under different mass ratios*

The mass ratios of the three groups of NaF-NaOH binary mixed molten salt were measured. The mass ratios of each group were measured three times to obtain the measured DSC curve clusters, as shown in Figs. 10-12. The melting point and latent heat value are shown in Table 3 below

Table 3. Melting point and latent heat value data of three measurements of NaF-NaOH molten salt.

NaF: NaOH mass ratio	Number of experiments	Starting melting temperature °C	End melting temperature °C	Latent heat value J/g
1: 9	1	264.5	387.0	212.9
	2	264.9	379.0	174.3
	3	265.1	381.0	211.3
	average value	264.8	382.3	199.5
2: 8	1	265.1	377.0	182.1
	2	265.1	385.0	186.1
	3	265.1	380.0	182.0
	average value	265.1	380.7	183.4
3: 7	1	264.4	382.0	164.7
	2	265.0	394.0	167.4
	3	265.1	384.0	155.3
	average value	264.8	386.7	162.5

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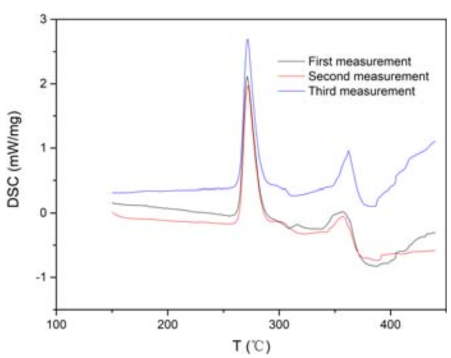

Fig. 10. DSC curve clusters of NaF: NaOH=1: 9 three measurements.

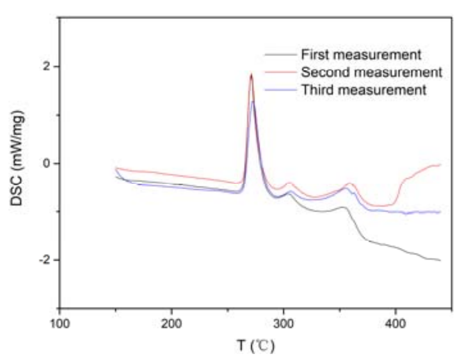

Fig. 11. DSC curve clusters of NaF: NaOH=2: 8 three measurements.

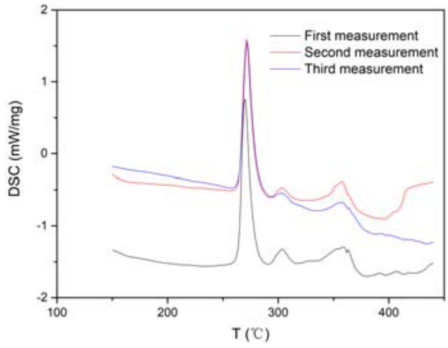

Fig. 12. DSC curve clusters of NaF: NaOH=3: 7 three measurements.

It can be seen that the mass ratio of the three groups of NaF-NaOH binary molten salt has not reached the eutectic. There are two obvious melting peaks in the DSC curves in Fig. 10. There are three melting peaks in Fig. 11 and 12, and one more small melting peak at 300°C. The three sets of average values of the initial melting temperature and the ending melting temperature remain basically unchanged. The mass ratio of each group of NaF and NaOH mixed molten salt is measured three times, and the DSC curves of the three measurements are basically the same. As the alumina crucible was used in the experiment, the curve after the melting peak drifted.

3.2.2 *Melting point and latent heat*

In Table 2, the average value of the initial melting temperature of the mixed molten salt of NaF-NaOH is 265°C, which is consistent, and the ending melting temperature is 380°C, which is basically the same. The melting point of the mixed molten salt is lower than the melting point of the lowest unit component NaOH. NaF:NaOH=1:9 has a maximum latent heat value of 199.5J/g, and the latent heat value of the three groups of NaF-NaOH mixed molten salt decreases as the mass ratio of NaF increases.

3.3 Comparative analysis

The initial melting temperature of the mixed molten salt of NaCl-NaOH is lower than that of the mixed molten salt of NaF-NaOH, with a difference of about 65°C. Under the same mass ratio, the latent heat value of the unit salt NaF is higher than that of NaCl, but the latent heat value of the mixed molten salt of NaCl-NaOH is higher than that of the mixed molten salt of NaF-NaOH. The latent heat value of the two groups of mixed molten salts decreases with the increase of the mass ratio of the salt (NaCl, NaF).

4 Conclusions

In this experiment, a binary molten salt with the same cation is prepared by mixing salt (NaCl, NaF) and alkali (NaOH), measuring its melting point and latent heat value, exploring the change of latent heat value of salt-alkali mixing, and providing basic mixed molten salt thermal physical property data.

In the binary mixed molten salt of NaCl-NaOH, the measured initial melting temperature is about 200°C, which is basically the same. The ending melting temperature increases firstly, then remains unchanged and finally decreases as the mass ratio of NaCl increases. The average latent heat value of NaCl:NaOH=1:9 is at most 301.2J/g, and the latent heat value decreases as the mass ratio of NaCl increases.

In the binary mixed molten salt of NaF-NaOH, the measured initial melting temperature is 265°C, which is consistent, and the final melting temperature is 380°C, which is basically the same. NaF:NaOH=1:9 has a maximum latent heat value of 199.5J/g, and the latent heat value decreases as the mass ratio of NaF increases.

Under the same mass ratio, the latent heat value of the unit salt NaCl is smaller than that of NaF, but the latent heat value of the mixed molten salt of NaCl-NaOH is higher than that of the mixed molten salt of NaF-NaOH.

Acknowledgments

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