Study on the preparation and thermal properties of binary mixed chloride salts

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Abstract. Nitrate phase change materials (PCMs) are the most widely used PCMs in solar thermal power generation technology. The maximum service temperature of Nitrate phase change materials is only 600°C. Therefore, to find a phase change material with large heat capacity, wide temperature range, low heat loss and low price is the focus of current research. According to different mass ratios, nine binary molten salt mixtures were prepared by mixing lithium chloride and sodium chloride. The phase change temperature and latent heat of phase transition of them were studied by differential scanning calorimeter (DSC). The experiment results showed that since the melting point of sodium chloride was high, when the content of sodium chloride in the binary mixture of lithium chloride and sodium chloride was large, a small amount of lithium chloride could not reduce the melting point of the mixture below 600°C, the mixture could not be melted. Meanwhile, when sodium chloride and lithium chloride were melted, the phase transition temperature of lithium chloride and sodium chloride remained at about 540°C and floated at ±15°C. The melting temperature and crystallization temperature of the binary mixture of 90% lithium chloride and 10% sodium chloride were quite different, and the latent heat of phase transformation was relatively high. Therefore, the binary mixed molten salt can be used in the heat transfer and storage technology of solar power generation.

1. Introduction

With the rapid development of society and economy, the consumption of conventional energy has reached an unprecedented level. The development and utilization of renewable energy has developed. Solar energy, as a kind of renewable energy, has been developed rapidly in power generation technology. Phase change energy storage materials have been widely used in solar thermal power generation technology, among which nitrate phase change materials are the most widely used in solar thermal power generation technology. Although nitrate is widely used in solar thermal power generation technology because of its economy and reliability, its maximum operating temperature is only 600°C. Therefore, finding a phase change heat storage material with large heat capacity, wide operating temperature range, low heat loss and cheap price is the focus of current research. Wang[1] has studied the ternary eutectic mixture of lithium nitrate, sodium nitrate and potassium nitrate, which can be used in thermal energy storage technology. The phase change temperature of the mixture is
118.1 °C, which can be used in solar thermal power generation technology in parabola tank. Jiang et al. [2] measured that the phase transition temperature of sodium carbonate-sodium chloride binary eutectic mixture is 637 °C and the latent heat of phase transformation is 283.3 J/g by DSC. The binary molten salt has good thermal stability and may become an ideal high temperature energy storage phase change material. Guo Chaxiu et al. [3] measured the latent heat of phase transformation, thermal conductivity, volume expansion coefficient and melting point of nitrate mixture. Baohua Hu et al. [4] used sodium chloride and anhydrous calcium chloride to prepare mixed chloride. The phase change temperature and latent heat of the mixed chloride were measured to be 497.67 °C and 86.85 J/g by static melting method. Qiang Peng et al. [5] prepared ternary mixed nitrate with mass ratio of 53% potassium nitrate and 40% sodium nitrite and 7% sodium nitrate, and added 7% (mass fraction) additive to it. The experimental data show that the ternary mixed nitrate with additive has stronger thermal stability and wider operating temperature range in high temperature environment. Wanyu He [6] prepared the binary mixture of potassium chloride and anhydrous magnesium chloride. The binary mixture could not melt at any mass ratio in the range of 600 °C. In the binary mixture prepared by potassium chloride and lithium chloride, only the mass ratio of potassium chloride to lithium chloride was 9:1, and there was no co-melting. When the mass ratio is 5:5, the latent heat of phase transformation is 219.9 J/g and the temperature of phase transition is 354.9 °C. The binary mixed chloride salt with this ratio has higher latent heat of phase transformation and lower temperature of phase transformation, which can be used in the field of solar thermal power generation technology. Min Liao et al. [7] prepared binary mixed carbonate with mass ratio of 50% sodium carbonate and 50% potassium carbonate by static melting method, and modified it with high melting point materials such as sodium chloride. When the mass fraction of sodium chloride reached 22.81%, a good improved molten salt was obtained. The phase transition temperature was 133 °C lower than that of carbonate, and the latent heat of phase transformation was twice as much as that of binary carbonate. When the temperature is about 850 °C, the mixed molten salt with sodium chloride has better thermal stability. Nine kinds of binary mixed molten salt samples were obtained by selecting two kinds of inorganic salt phase change materials lithium chloride and sodium chloride according to different mass ratios. The phase transition temperature and phase transformation latent heat of the nine samples were measured and analyzed by DSC.

2. Experiment

2.1. Experimental equipment and materials
Materials: lithium chloride (purity > 97.0%, melting point 603 °C), sodium chloride (purity > 99.5%, melting point 801 °C).

Equipment: differential scanning Calorimeter, vacuum drying box, dryer, muffle furnace, Electronic scales, etc.

2.2. Experimental methods

2.2.1. Experimental basis. Binary chloride composite phase change energy storage materials were prepared by static melting. The basic principle of energy storage is that the heat storage material absorbs heat when the temperature rises, and the accompanying state changes from solid state to liquid state; on the contrary, when the temperature decreases, the heat storage material releases heat, and the accompanying state changes from liquid state to solid state.

2.2.2. Preparation method of sample. A certain amount of lithium chloride and sodium chloride were put into two pallets respectively, and then dried at 120 °C for more than 24h in a vacuum drying box to remove the moisture from the material. After drying, the tray is taken out and the two materials are poured into the mortar to grind. The ground material is placed in two beakers, sealed in the bag and
put in the dryer for spare time. Nine kinds of samples were prepared by mixing the two materials according to different mass ratios, and the total mass of the mixed materials was 10g. The muffle temperature was set to 600°C and preheated for 20 minutes. After preheating, three kinds of samples (No.1~3) were added to muffle furnace and continuously heated for 3h, and taken out after heating. The remaining six kinds of samples (No.4~9) were heated by the same method. The sample number and composition are shown in table 1.

| Number | m(LiCl):m(NaCl) | Number | m(LiCl):m(NaCl) |
|--------|-----------------|--------|-----------------|
| 1      | 1:9             | 6      | 6:4             |
| 2      | 2:8             | 7      | 7:3             |
| 3      | 3:7             | 8      | 8:2             |
| 4      | 4:6             | 9      | 9:1             |
| 5      | 5:5             |        |                 |

2.2.3. Sample test. Among the 9 kinds of samples heated in muffle furnace, 1, 2 and 3 samples were not melted, and the other six samples were melted. The six melted samples were poured into the tray and solidified at room temperature. When the sample is cooled to room temperature, it is ground in a mortar and the ground sample is put into a sealed bag. The molten salt of about 10mg was weighed and put into the crucible of aluminum, and the pressure was pressed by the capping machine to be used. The phase transition temperature and phase transformation latent heat of the samples were tested by DSC. Each sample was tested at least three times, and the average value was taken as the final test result.

2.2.4. Sample characterization. The phase transition temperature and phase transformation latent heat of binary mixed chloride PCMs were measured by 200PC differential scanning Calorimeter.

3. Experimental results and analysis

3.1. Analysis of unmelted samples

A picture of the unmelted sample is shown in figure 1 (sample No. 1). It can be seen from figure 1 that only a small part of the mixed chloride melts, while the rest are still white crystals. The reason why the three samples are not melted may be that the mass fraction of sodium chloride is large, but the melting point of sodium chloride is already on the high side (801°C), and trace lithium chloride cannot reduce its melting point below 600°C.

Figure 1. Photo of unmelted mixed chloride (sample 1)

3.2. Analysis of completely melted sample

A picture of the completely melted sample is shown in figure 2 (sample No. 5). As can be seen in Figure 2, the completely melted solid mixed chloride has a smooth, white, insipid surface and low hardness.
Several lithium chloride and sodium chloride binary molten salt mixtures with different mass ratios were selected for DSC analysis, and the results are shown in figure 3. From figure 3, it can be seen that the fluctuation of DSC curve of sample No. 4 increases with the increase of temperature, and the DSC curve reaches the maximum value when the temperature is at 580°C; the DSC curve fluctuates greatly, and there is no definite peak value. This is because the mass ratio of No. 4 sample is 40% LiCl+60% NaCl. Even if the radius of Na+ is larger than the radius of Li+, the proportion of Na+ in the sample is larger than that of Li+, and the effect of Na+ is stronger radius, so that the temperature of the mixture cannot be reduced, and the sample is not completely melted, then the phase transition temperature and phase transformation latent heat of the binary mixture cannot be measured.

The DSC curve of sample No. 5 has better regularity than that of No. 4 sample, which indicates that the two materials in sample No. 5 have been melted and the phase transition temperature is 523.5°C. However, there is only the starting point temperature of the melting peak in the DSC curve of sample No. 5, and there is no end point temperature of the melting peak, that is the melting temperature. The reason is that although the proportion of Na and Li are the same, the melting point of NaCl is higher than that of LiCl, and the effect of Na+ is stronger than Li+. Therefore, the crystallization process can only be achieved in the range of heating temperature. The melting process is reached, so the melting temperature is not shown on the DSC curve. Therefore, if the area of DSC curve cannot be calculated, the latent heat of phase change of the sample cannot be measured. Although the DSC curve of No. 6 sample is the same as that of No. 5 sample, the proportion of Li+ in No. 6 sample is larger than that of Na+. LiCl can reduce the melting point of NaCl, so the melting process of the two materials in No. 6 sample reaches the melting process in the range of heating temperature. The starting point temperature of melting peak of sample No. 6 is 523.5°C, the termination point temperature is 554.1°C, the peak value is 534.4°C, and the area is 277.1J/g. It can be seen that the crystallization temperature of sample No. 6 is 523.5°C. That is the phase transition temperature is 523.5°C, the melting temperature is 554.1°C, and the latent heat of phase transformation in the crystallization process is 277.1J/g.

The crystal temperature of No. 8 was 524.3°C, which means that the phase change temperature was 524.3°C; the melting temperature is 560.6°C, and the latent heat of phase transformation in the crystallization process is 205.7J/g. The crystallization temperature of sample No. 9 is 542.0°C, that is, the phase transition temperature is 542.0°C, the melting temperature is 576.2°C, and the latent heat of phase transformation in the crystallization process is 370.6 J/g.
Figure 3. DSC curve (samples 4, 5, 6, 8, 9).

Figure 4 shows the phase transition temperature and phase transformation latent heat of the completely melted samples (5, 6, 8, 9). It can be seen from Figure 4 that the phase transition temperature of sample 5 and No. 6 is the lowest, which is 523.5°C, and that of sample 8 is the lowest, the latent heat of phase transformation is the highest, the phase transition temperature is 542.0°C, and the latent heat of phase transformation is 370.6 J/g, the phase transition temperature is 542.0°C, and the latent heat of phase transformation is 370.6 J/g. The phase transition temperature of several chloride mixtures is lower than the melting point of a single substance. It can be seen that the mixture of lithium chloride and sodium chloride can reduce the melting point of any substance. Because of the mixing of lithium chloride and sodium chloride, the higher the content of lithium chloride is, the higher the phase transition temperature of the mixture is. The maximum phase transition temperature of No. 9 sample is 542.0°C.

Figure 5 shows the melting temperature and crystallization temperature of 6, 8, 9 samples. It can be
seen from Figure 5 that the melting temperature and crystallization temperature of No. 8 sample are quite different from those of No. 9 sample, and the melting temperature is higher than the crystallization temperature, and the difference is about 35°C. The mixed molten salt of the two samples is hot in solar energy. The heat transfer and heat storage technology of electricity has certain advantages. This is because the more the crystallization temperature of molten salt is lower than the melting temperature, the less freezing and blocking will occur in the pipeline and system, and the more stable the system will be.

At present, the temperature required in the field of solar high-temperature heat storage is generally at 540°C, the phase transition temperature of the sample prepared in the experiment is at about 540°C. The difference between the melting temperature of the sample No. 9 and the crystallization temperature is large. Therefore, the latent heat of phase change is high and the damage to pipeline is reduced. Meanwhile, the price of the chloride salt is low and the comparison is easy to obtain. And the sample 9 is a phase change material suitable for the field of solar high-temperature energy storage.

![Figure 5. Melting temperature and crystallization temperature (samples 6, 8, 9).](image)

### 4. Conclusion

1. Sodium chloride has a high melting point. When the binary mixture of lithium chloride and sodium chloride has a high content of sodium chloride, a small amount of lithium chloride cannot lower the melting point of the mixture below 600°C and the mixed material cannot be melted.

2. When sodium chloride and lithium chloride are melted, the phase change temperature remains around 530°C with a float of ±15°C; 80% LiCl-20% NaCl has the lowest latent heat of phase change at 205.7 J/g and 90% LiCl-10% NaCl has the highest latent heat of phase change with a value of 370.6 J/g.

3. The melting temperature of the sample No. 9, that is, 90% LiCl-10% NaCl, is different from that of the crystallization temperature, and the latent heat of the phase change is high. So the binary mixed molten salt can be applied to the heat transfer and heat storage technology of the solar power generation.

The melting point of a mixed binary molten salt differs from that of a single molten salt by almost 200°C. Mixing binary molten salts will change the properties of the molten salt considerably, so a mixture of binary molten salts of sodium chloride and lithium chloride can be used as a high temperature thermal storage phase change material.
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