The promotional effect of sodium chloride on thermophysical properties of nitrate

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Abstract. Nitrate are the excellent phase change materials (PCMs) for thermal energy storage. Nitrate has no phase separation during phase transition and has good chemical stability. The present study concentrates on improving the latent heat of phase change and of heat absorption rate by adding various proportions NaCl into the nitrate/mixed nitrate. Sodium nitrate and sodium chloride were selected to prepare binary mixture by static melting method. The melting point and latent heat of phase change were measured by differential scanning calorimetry (DSC). Compared with pure sodium nitrate, the melting point and solidification point of binary molten salt containing 5% NaCl are reduced by 9°C and 16°C, respectively. On the other hand, the latent heat of melting and solidification increased by 12J/g and 10J/g, respectively.

1. Introduction
The International Energy Agency, based on the latest global Energy consumption projections, predicts that global demand for Energy will continue to increase over the next 20 to 30 years [1]. Solar thermal power generation is an important aspect of solar thermal utilization, which is regarded as the most promising generator of renewable energy equipment [2-4]. Among many inorganic salts, nitrate has excellent heat transfer and fluidity. Its melting point is about 300°C, and the upper limit temperature is about 600°C. When it exceeds 600°C, it will decompose into other substances. At present, the widely used molten salt still has the problems of high melting point, poor thermal stability and high risk of system freezing and plugging, which cannot meet the requirements of advanced solar thermal storage. Therefore, the development of new mixed molten salt with better stability, lower melting point and wider temperature range has become the main research direction and hot spot.

The chloride system has a wide variety of applicable temperature range (150-900°C) [5]. It has high latent heat and specific heat capacity, but high temperature chlorine salt has strong corrosiveness. Sodium chloride (NaCl) could be used as the additive to promote nucleation [6]. This paper aims to study the effect of adding NaCl particles on the thermal properties of binary nitrate and improve the performance of heat storage materials. The thermal properties of mixed molten salt were measured by DSC, and the phase and crystallization of the material were analysed by XRD. Through the experimental results, the performance of nitrate was improved, the application range of nitrate molten salt in phase change heat storage and solar power generation was widened and its reliability was improved.
2. Experimental methods and materials

Sodium nitrate (melting point 306.8 °C, latent heat 162.5 J/g) and sodium chloride (melting point 801 °C, latent heat 482 J/g) are provided by Shanghai Feng Shun Fine Chemicals Co China.

2.1. Preparation of Materials
Two kinds of pure salt were dried in a drying oven for 24h at a drying temperature of 120 °C, and the crystal water in the sample was removed. Mixed molten salt was prepared by static melting method, sodium chloride solids with different mass fractions of 5%, 10% and 15% were added to pure sodium nitrate to prepare 4 kinds of mixed molten salts with different proportions. Place the 4 groups of mixed salt in a stain steel mortar and grind them until they are completely powdered. Put them into a corundum crucible, then place them in a muffer furnace to heat and melt. The heating time is 2h and the heating temperature is 400 °C. After cooling, remove, grind and dry.

2.2. Method
DSC synchronous thermal analyzer (METTLER TGA/DSC2 1600LF) was used to measure the melting point and phase change latent heat of the samples. Samples to be tested after drying were sealed in an aluminum crucible. Place crucible in instrument furnace, at the rate of 10 K/min, the temperature rises from 50 °C to 400 °C. The temperature is kept at 400 °C for 10 min. Then the temperature is cooled from 400 °C to 50 °C, and the cooling rate is 10 K/min. Nitrogen was used as experimental protective gas during the measurement, and the flow rate was 25 ml/min.

3. Results

3.1. Thermal performances of NaCl with various addition proportion
The DSC curves of samples mixture with various weight rates of NaCl are shown in Fig. 1. It shows that both endothermic and exothermic peaks of the heat flow curve of binary molten salt decreased. The melting point, solidification point and latent heat of sodium nitrate and three mixed molten salts containing different mass fractions of NaCl are listed in Tables 1 and 2. The graph shows that the melting point and solidification point of sodium nitrate can be reduced by adding sodium chloride. However, there is no linear relationship between the amount of sodium chloride added and the value of increase/decrease.

Compared with pure sodium nitrate, the melting point and solidification point of binary molten salt containing 5% NaCl are reduced by 9 °C and 16 °C, respectively. On the other hand, the latent heat of melting and solidification increased by 12J/g and 10J/g, respectively. However, the melting point and solidification point of the mixed molten salt decreased, the latent heat also decreased after adding higher mass fraction of NaCl. This is consistent with the known literature results. When adding a small amount of NaCl into PCMs, the latent heat tends to increase. It can be explained that the crystallization of the two salts is always imperfect due to natural reasons. An appropriate amount of NaCl can be uniformly dispersed in the interior of sodium nitrate as a nucleus, which promotes nucleation and contributes to the increase of latent heat. However, latent heat does not increase with the increase of NaCl. There is no linear relationship between them and there is an optimal eutectic ratio.

Fig.2a, b show the starting and ending temperatures of phase change during heating/cooling, and D-value represents the difference between the starting and ending points. The smaller the D-value is, the sharper the endothermic/exothermic peak is, which indicates that the faster the endothermic and exothermic rate of molten salt is, the better the performance of molten salt is. Supercooling is a common phenomenon in the crystallization process of molten salt. Metastable state near the melting point will affect the crystallization process. From Table 1 and 2, it can be seen that in order to increase the latent heat of phase transformation of nitrate, the supercooling degree of molten salt increases slightly. According to nucleation theory [7, 8], NaCl promotes the transformation of molten salts from
homogeneous nuclei to heterogeneous nuclei, which improves the latent heat of phase transformation and shortens the time of phase transformation.

![Figure 1. DSC curves of samples with various addition rates of NaCl](image)

**Table 1.** Heat of fusion, melting temperature, peak temperature of sodium nitrate and mixed salt

|                     | Heating process | Cooling process |
|---------------------|-----------------|----------------|
| Materials           | NaNO3           | 0.05NaCl       | 0.1NaCl       | 0.15NaCl       |
| Enthalpy (J/g)      | 224.1           | 236.4          | 198.5         | 174.2          |
| Onset (°C)          | 309.0           | 300.7          | 299.4         | 300.8          |
| Peak (°C)           | 316.8           | 305.2          | 307.7         | 305.8          |
| End set (°C)        | 324.5           | 313.1          | 313.9         | 312.4          |
| D-value             | 15.5            | 12.4           | 14.6          | 11.6           |

**Table 2.** Heat of fusion, melting temperature, peak temperature of sodium nitrate and mixed salt

|                     | Heating process | Cooling process |
|---------------------|-----------------|----------------|
| Materials           | NaNO3           | 0.05NaCl       | 0.1NaCl       | 0.15NaCl       |
| Enthalpy (J/g)      | 218.3           | 228.7          | 190.6         | 155.6          |
| Onset (°C)          | 308.1           | 292.5          | 295.4         | 295.2          |
| Peak (°C)           | 300.1           | 286.7          | 289.2         | 289.6          |
| End set (°C)        | 293.5           | 280.7          | 282.8         | 284.0          |
| D-value             | 14.5            | 11.8           | 12.6          | 11.2           |
Figure 2. (a) phase change temperature during heating process (b) phase change temperature during cooling process (c) latent heat

3.2. X-ray diffraction

Fig. 3 shows the XRD results of sodium nitrate, sodium chloride and mixed salts after five thermal cycles. The spectral peaks of mixed salt correspond to the positions of two pure salt peaks one by one, and there are no irregular peaks. This indicates that the two molten salts are physically mixed and no chemical reaction occurs to produce new substances. The peak strength of each component can indicate the relative crystalline strength of the crystal. Thermal and cold cycles have little effect on the final phase change of phase change materials, showing good thermal stability and chemical compatibility.
4. Conclusion
Appropriate sodium chloride particles can increase the latent heat of phase change of nitrate, accelerate its heat absorption and exothermic rate, and improve the performance of PCMs. However, there is no linear relationship between the amount of NaCl and its properties, and there is an optimum eutectic ratio between sodium chloride and sodium nitrate. The results show that eutectic can be achieved when the ratio of sodium chloride to sodium nitrate is less than 1:9. Compared with pure sodium nitrate, the melting point and solidification point of binary molten salt containing 5% NaCl are reduced by 9°C and 16°C, respectively. On the other hand, the latent heat of melting and solidification increased by 12J/g and 10J/g, respectively.

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