

Thermal Characterization of inorganic salts as phase change materials for thermal energy storage systems

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Abstract. There is a lag between the demand and supply of energy in today's global scenario. Apart from that, the world is facing serious environmental challenges like global warming due to increased burning of fossil fuels. To mitigate this, people are focusing towards the renewable based energy technology. But harnessing energy from the renewable sources has its own challenges. They are intermittent sources of energy hence, some energy storage medium is necessary for the continuous supply of energy. The present study aims to evaluate the various characteristics of the phase change materials used as energy storage mediums. Various thermo physical properties like melting temperature, enthalpy values and specific heats capacities are calculated using Differential Scanning Calorimetry technique for high temperature PCM materials. In this study, Sodium nitrate and Potassium nitrate are taken as the PCMs because of their high melting temperature above 300 °C and they are widely used in concentrated solar powerplants as a heat transfer fluids.

Keywords: Phase change materials(PCMs), thermophysical properties, NaNO_3 , KNO_3

1. Introduction

The present study includes characterization study of phase change materials for thermal energy storage systems. For accessing the performance of PCMs used in different applications like solar distillation, passive storage, cooling systems etc. the knowledge of properties of PCMs is very essential. For the control of the performance of the PCM based material which is used in Thermal energy storage systems, inherent properties and characters of the material should be known to us. In this study, evaluation of the thermo physical properties of some selected PCMs (Sodium Nitrate and Potassium Nitrate) is done through an experimental set up using Differential Scanning Calorimetry (DSC) technique.

2. Experimental Setup

The experimental set up for determination of thermo physical properties consists of a Differential Scanning calorimeter. The DSC Q-2000 model by TA instruments is used for the thermal characterization of PCM materials. The principle of DSC is based upon the difference in thermal response when a temperature program is applied for the PCM sample and the reference material [1]. The DSC works on two modes, the first is step mode and the other one is dynamic mode. Different modes are recommended in various papers for different PCMs like for salt hydrates step mode is there and for paraffins both the modes can be operated [1]. In the present work, dynamic mode of operation is used. In the setup, Indium is used as the reference material.

2.1 Software used for the analysis of the result

There are a number of software packages supported by DSC Q-2000 model by TA instruments like TRIOS, DSC Run, Advantage /Ultimate Analysis. For thermal analysis Ultimate Analysis is good as it



can be used for multiple calibrations on integration with the autosampler [2]. In the context of present study, Ultimate analysis 2000 is used in the analysis of the DSC data.

2.2 Weighing and preparation of samples

Proper weighing and preparation of samples of known masses of Potassium Nitrate (KNO_3) and sodium nitrate (NaNO_3) is done using the electronic weighing balance and DSC crimping press. At the time of preparation of the samples handling of the PCM salt samples should be done with utmost care as they are hygroscopic in nature and any moisture in the samples will cause deviations in the experimental results. For the removal of the inherent moisture present in the samples, they were dried in the oven at about 90-100 °C.

2.3 DSC Calibration

Firstly, DSC is calibrated for measuring the thermo physical properties. Calibration is necessary for good sensitivity. There are three types of measurements:

- DSC Baseline measurement using both the empty pans.
- Using reference material i.e indium in this case.
- The actual PCM material measurements.

The two modes of operations are dynamic mode and step mode: In dynamic mode constant heating and cooling rate while in step mode small ramps are there. After calibration, the sample is prepared and kept inside the DSC pan for measurements.

3. Results

3.1 DSC measurements for potassium nitrate samples

Firstly a sample of potassium nitrate having mass of 28.3 mg is prepared and tested at different heat rates which are 10 °C/ min, 15 °C/ min and 20 °C/ min respectively. The DSC is operated in dynamic mode at the given heat rates and the data is recorded for each of the heat rates.

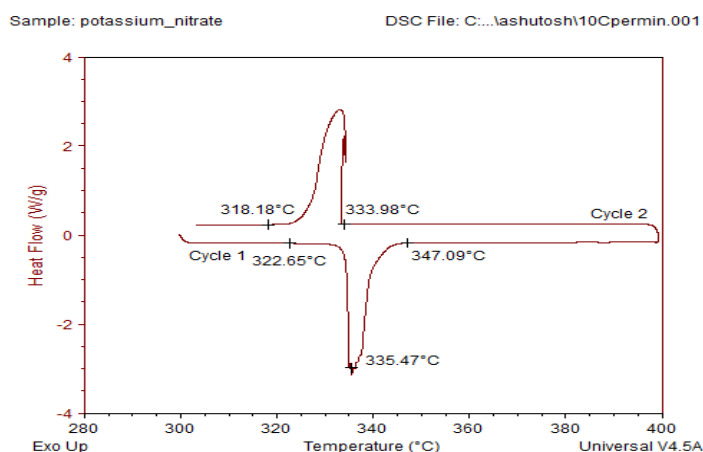


Figure 1. DSC heat flow graph for KNO_3 at heat rate of 10 °C/ min for sample mass 28.3 mg

Similarly, DSC heat flow graph is plotted for heat rates of rate of 15°C/ min and 20°C/ min for sample mass 28.3 mg. The nature of the DSC graphs for heat rates of 15°C/ min and 20°C/ min are similar to that of 10°C/ min, hence they are not shown as it would be of repetitive in nature. But all the thermophysical property values are given in the tabular form for appreciating the deviation in values. After plotting the DSC heat flow graph for sample mass of 28.3 mg, the mass of the potassium nitrate sample is changed for knowing the effect of decrease of sample mass on the DSC characteristic curves. The mass of the sample taken is 13.3 mg. In the heat flow curve in the melting region figure 1, the point of maximum slope on the leading side and then extrapolation of heat flow curve gives melting onset temperature [3]. In this way the melting temperature and onset temperature is measured. The integration of the curve within the melting range gives Latent heat of fusion of the sample (J/gm).

3.1. Effect of temperature rate and sample mass on thermophysical properties of KNO_3 in DSC measurements

Table 1. Potassium Nitrate (KNO_3) Sample mass: 28.3 mg

S.No	Temperature Rate	Onset Temperature (in $^{\circ}\text{C}$)	Melting temperature (in $^{\circ}\text{C}$)	Latent heat (in J/g)
1	10 $^{\circ}\text{C}/\text{min}$	334.65	335.58	98.71
2	15 $^{\circ}\text{C}/\text{min}$	334.46	336.01	97.69
3	20 $^{\circ}\text{C}/\text{min}$	334.45	336.75	96.76

Table 2. Potassium Nitrate (KNO_3) Sample mass: 13.3 mg

S.No	Temperature Rate	Onset Temperature (in $^{\circ}\text{C}$)	Melting temperature (in $^{\circ}\text{C}$)	Latent heat (in J/g)
1	10 $^{\circ}\text{C}/\text{min}$	334.62	334.86	94.83
2	15 $^{\circ}\text{C}/\text{min}$	334.47	336.18	94.38
3	20 $^{\circ}\text{C}/\text{min}$	334.38	335.88	93.72

For the sample mass 28.3 mg the melting temperature increases on increasing the heat rate while in the second case sample having mass 13.3 mg the melting temperature is maximum for 15 $^{\circ}\text{C}/\text{min}$ heat rate. The onset melting temperature is approximately the same for both the sample masses while the melting temperature differs for both. The latent heat decreases slightly with the decrease in sample mass of KNO_3 taken for experimental testing. It decreases slightly with the increase in heat rate.

3.2 DSC measurements for sodium nitrate samples

The melting onset temperature does not differ much (306.55 ± 0.25 $^{\circ}\text{C}$) for both the NaNO_3 sample masses while the melting temperature shows variation in both the cases. In first case the melting temperature is maximum at 15 $^{\circ}\text{C}/\text{min}$ while for sample mass 11.6 mg it is maximum for 20 $^{\circ}\text{C}/\text{min}$.

Table 3. Sodium nitrate (NaNO_3) Sample mass: 24 mg

S.No	Temperature Rate	Onset Temperature (in $^{\circ}\text{C}$)	Melting temperature (in $^{\circ}\text{C}$)	Latent heat (in J/g)
1	10 $^{\circ}\text{C}/\text{min}$	306.42	309.38	173.50
2	15 $^{\circ}\text{C}/\text{min}$	306.38	309.95	177.30
3	20 $^{\circ}\text{C}/\text{min}$	306.51	308.62	175.50

Table 4. Sodium nitrate (NaNO_3) Sample mass: 11.6 mg

S.No	Temperature Rate	Onset Temperature (in $^{\circ}\text{C}$)	Melting temperature (in $^{\circ}\text{C}$)	Latent heat (in J/g)
1	10 $^{\circ}\text{C}/\text{min}$	306.55	307.76	172.06
2	15 $^{\circ}\text{C}/\text{min}$	306.43	310.50	176.50
3	20 $^{\circ}\text{C}/\text{min}$	306.48	310.81	175.00

This deviation can be due to the impurities present in the samples. The latent heat decreases slightly with the decrease in sample mass taken for experimental testing. But the latent heat is maximum at the heat rate of 15 °C/min for both the sample masses.

The heat flow graphs for Sodium nitrate samples have almost similar nature as that of potassium nitrate in figure 1. But there are some deviations in the solidification curves which is explained in the section 3.2.2. Solidification curve is the portion of the curve when the PCM starts solidifying from the melted stage and reverses its direction in the heat flow graph.

3.2.1 Heat flow graph for sodium nitrate sample for different heat rates

The peaks of the DSC melting curves shift due to the different heat rates for the NaNO_3 sample as shown in figure 2. On increasing the heat rates the peak shifts towards the right. It is at minimum temperature for a heat rate of 10 °C/min and increases on increasing the heat rates. This is due to the kinetics of the melting process. Larger the heat rate broader the melting curve will be and the peak is shifted towards the right. Slower heating rate gives less noise in the signal and the resolution will be better than higher heating rates.

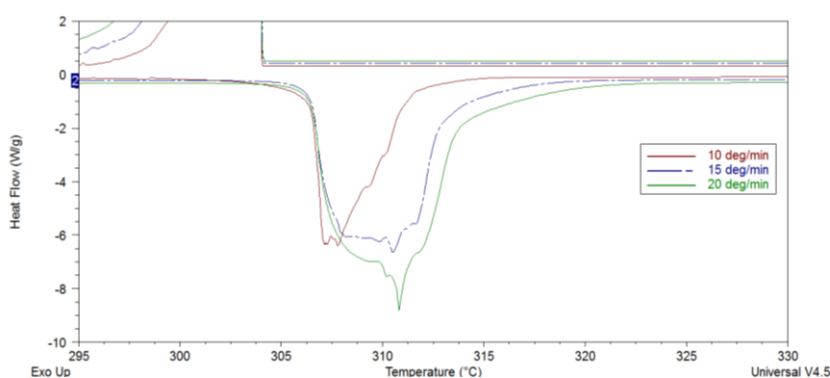


Figure 2. Combined DSC Heat flow graph for Sodium Nitrate (NaNO_3) for sample mass 11.6 mg

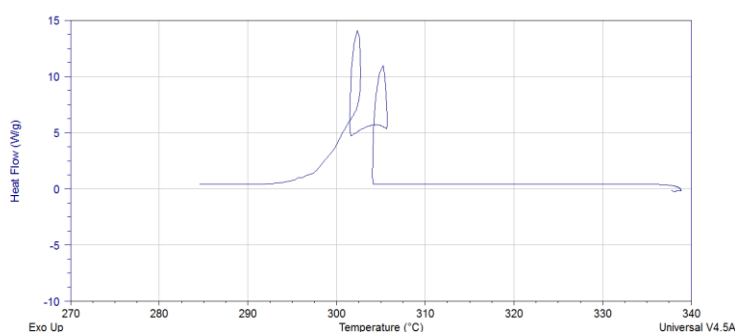


Figure 3. Solidification curve for Sodium Nitrate (NaNO_3) having sample mass 11.6 mg

3.2.2 Solidification Curve for Sodium Nitrate sample

The solidification curve for Sodium Nitrate (NaNO_3) is shown in figure 3. There is deviation from the ideal solidification graphs in this case. Normally the solidification graph consists of 1 peak but here there are 2 peaks in the solidification curve. This is due to a phenomenon known as polymorphism. This is because of the occurrence of different crystalline form of sodium nitrate in that range of temperature. The reason can be hygroscopic nature of the salt and humidity acts as catalyst for the polymorphism behaviour.

3.3 Variation in Specific heat capacity of Sodium Nitrate above the melting temperature

Using the DSC measurement data, the specific heat capacity of sodium nitrate at different temperature points is found out. The temperature points at which the specific heat (C_p) values are taken are above the melting temperatures. The specific heat values show an interesting behaviour in the vicinity of the melting temperature. The function of specific heat with respect to temperature is an increasing one but the nature of increase is different for different heat rates. The variation is analysed for three heat rates

which are 10 °C/min, 15 °C/min and 20 °C/min respectively, as shown in figure 4. On increasing the heat rates the specific heat of the sodium nitrate in the melted form decreases.

3.4 Empirical relationship between Specific heat (C_p) and Temperature (t) above melting temperature

Using the curve fitting technique, the set of experimental data points is fitted to a polynomial curve in accordance with the method of least square error.

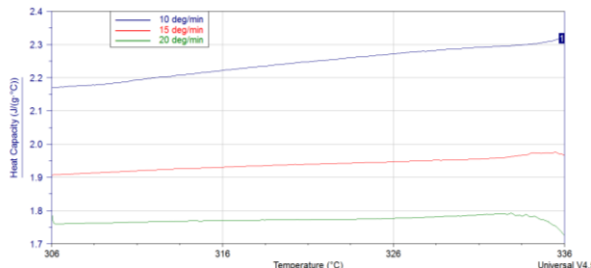


Figure 4. Variation of specific heat above melting temperature for NaNO₃ sample

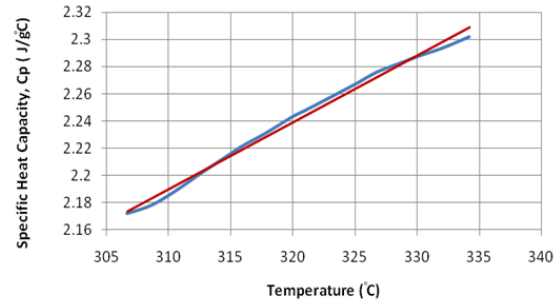


Figure 5. Fitting of curve for NaNO₃ at 10 °C/ min

For minimising the errors, and accurately predicting the degree of polynomial equation which is to be fitted to the data points, regression coefficients (R^2) are checked accordingly. Curves having R^2 values near to one are termed as ‘Good fit’ and in our scope of calculations the R^2 values are in the range of 0.98-0.99. The mathematical relationship developed for specific heat (C_p) and temperature is of utmost importance when we have to predict the sensible heat storage capacity of the thermal energy storage reservoir and in its designing above the melting range of sodium nitrate.

In Figure 5, the variation of specific heat with temperature is plotted at a heat rate of 10 °C/ min.

The curve is fitted with a linear polynomial curve having equation

$$C_p = 0.004 t + 0.665 \quad \text{.....(1)}$$

Similarly, the variation of specific heat with temperature is plotted at the heat rates 15 °C/ min and 20 °C/ min. The curve is fitted with a 3rd order polynomial for 15 °C/ min heat rate having equation

$$C_p = 4 \times 10^{-6} t^3 - 0.003 t^2 + 1.254 t - 132.2 \quad \text{....(2)}$$

The curve is fitted with a 4th order polynomial for 20 °C/ min heat rate having equation

$$C_p = -3 \times 10^{-7} t^4 + 0.000 t^3 - 0.173 t^2 + 37.10 t - 2967 \quad \text{....(3)}$$

Where, C_p = Specific heat (in J/gm °C) and t = temperature in °C

$R^2 = 0.992$ for (1), $R^2 = 0.994$ for (2) and $R^2 = 0.982$ for (3) where, R^2 = Regression coefficient

4. Conclusion

The results are well in conformance with the theoretical data available within the error range of 5%. The sensitivity of DSC is high for smaller heat rates and 10 °C/ min heat rate gives the most accurate result among all. The present study provides valuable database regarding characteristics and properties of PCMs over varying experimental conditions. Also, there are no defined national or international standards for the characterization of PCMs. Every researcher applies his own methodology and approach for problem solving and the analysis of results.

References

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