Conference Paper

Thermal Properties of $(Na_{0.6}K_{0.4})NO_3$ Thermal Storage System in the Solid-Solid Phase

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Abstract: The thermal behaviour for the DTA, DSC and TGA measurements have been carried on the solid phase transformation for the binary eutectic mixture of 60 wt% sodium nitrate ($NaNO_3$) and 40 wt% potassium nitrate (KNO_3). Thermal energy storage materials are important for the technology that is applied to reduce cost solar thermal power generation. The $NaNO_3$-KNO_3 system is a binary inorganic salt system and it is one of the most promising thermal storage materials. The methods are based on the principle that a change in the physical state of a material is accompanied by the liberation or absorption of heat. The various techniques of thermal analysis are designed for the determination of the enthalpy accompanying the changes in the physical properties of the material. The thermal measurements showed a reversible phase transition at ~114°C during heating process and at ~108°C during cooling process. It has been shown also the presence of thermal hysteresis during this transformation with a magnitude of the hysteresis temperature ~8°C. The thermogravimetery analysis (TGA) indicated that the eutectic system $(Na_{0.6}K_{0.4})NO_3$ is thermally stable up to the melting point at $\cong 225°C$. This means that the sample under study is structurally stable. DTA measurements were also carried out for the sample at different heating rates of (2, 5, 10, 15 and 20°C/min). Some thermal parameters such as the transition point, enthalpy and the activation energy for the transformation process were estimated at each heating rate. It has been also shown that these parameters are affected by the heating rate. The noticeable effect of heating rate on the thermal parameters means that the heating rate is a main factor to change the thermal interaction potential of the Na and K atoms around the nitrate group (NO_3^-) during the phase conversion for the eutectic $(Na_{0.6}K_{0.4})NO_3$ system.

Keywords: Phase Change Material, Thermal Storage, Calorimetry

1. Introduction

Thermal energy storage systems are a key technology for reduced cost solar thermal power generation [1, 2]. Also, they are one possibility for solar thermal power plants to compensate temporary divergences between the availability of sunlight and the demand for electricity. This high temperature application requires storage operation above 100°C. Therefore, thermal energy storage at high temperature (>120°C) is an efficient way for energy saving in industrial process. Several mixtures of alkali nitrates and nitrites have been used as a heat transfer medium because of its low cost and good compatibility with common structural materials [3]. Additionally, significant attention has been given to using salts as a phase change storage media (using encapsulation and otherwise) [4]. The $NaNO_3$-KNO_3 system is one of the most extensively investigated binary inorganic salt systems [3, 4]. Mixture of $NaNO_3$ and KNO_3 is promising from the

viewpoints of cost and thermal stability and can be used for sensible heat storage. The application of this mixed salt to thermal storage, for load leveling, and for solar thermal electric power generation were postulated to be promising [7]. The effect of the thermal history has been investigated by DSC and X-ray diffraction and the enthalpy change has been measured for quenched and annealed samples of 50 mole% $NaNO_3$-50 mole% KNO_3 by a high-temperature calorimeter of the twin type [7, 8]. A binary mixture of 30 wt.% potassium nitrate (KNO_3) and 70 wt.% sodium nitrate ($NaNO_3$) has been studied by Martin et al [8]. The measurement systems include a differential scanning calorimeter, a melting point apparatus, a custom-built adiabatic calorimeter and a lab-scale storage unit. Recently, salt has been considered for use in trough and linear fresnel based solar collectors and has been shown to offer a reduction in levelized cost of energy as well as increased availability [10]. The phase diagram of $NaNO_3$-KNO_3 is determined by DSC and high-temperature x-ray diffractometry [11] Thermal and mechanical properties of three representative salts for use in thermal storage systems have been evaluated as a function of temperature, thermal conductivity, specific heat, and the apparent heat of fusion were obtained using a differential scanning calorimeter [9]. Using additives such as graphite to $NaNO_3$-KNO_3 mixture leads to insignificant thermal conductivity improvement in overall application and hence the thermo physical properties for energy storage will be improved [10]. The system KNO_3-$NaNO_3$ was also discussed in detail in terms of their thermo-physical properties in the liquid and solid phase [11]. Recent measurements of the electrical conductivity of the solidified KNO_3-$NaNO_3$ 50: 50 mole% composition and of the melting enthalpy have suggested that the solid consists of alternating areas of sodium nitrate-rich and potassium nitrate-rich composition [12]. Also, a detailed calorimetric study of the $NaNO_3$/KNO_3 phase behaviour as a function of cation composition was presented [13].

In spite of the interest, no or very few examples of commercial high temperature thermal energy storage were realized and the KNO_3-$NaNO_3$ system is still has the attention of researchers. Therefore, we studied in this work the thermal properties of 40 wt.% potassium nitrate (KNO_3) and 60 wt.% sodium nitrate ($NaNO_3$) by the measurements of DSC, DTA and TGA.

2. Experimental Details

Chemically pure $NaNO_3$ and KNO_3, Aualar from BDH, were used as constituent compounds for the mixture (NaK)NO_3 by the molecular ratio 60% $NaNO_3$ and 40% KNO_3. The binary system was formed by the pre-annealing of the pure nitrates up to 400°C in a muffle furnace for three hours. The mixture was then allowed to be equilibrated in air at 400°C before casting into a stainless steel mould to quench and solidify to form the eutectic system $(Na_{0.6}K_{0.4})NO_3$. Differential Scanning Calorimetry (DSC) and Differential Thermal Analysis (DTA) measurements were performed using a DSC-DTA apparatus (model Shimadzu DSC-50).

However Thermogravimetry Analysis (TGA) was performed using TGA apparatus (model Shimadzu TGA-50). It was found that this eutectic system has a melting point of $\cong 225°C$ which is less than melting points of both $NaNO_3$ and KNO_3. The thermal measurements for the eutectic $(Na_{0.6}K_{0.4})NO_3$ system were carried out by using (DSC) during heating and cooling at rate of 10°C/min, (TGA) and Differential Thermal Analysis (DTA) at heating rates of 2, 5, 10, 15 and 20°C/min.

3. Results and Discussion

3.1. Differential Scanning Calorimetry (DSC)

Differential Scanning calorimetry (DSC) technique is used in a wide range for the thermal investigation. Usually, a material such as (NaK)NO_3 will show definite and characteristic effects on heating which relate to its nature, composition and history. These observations are informative about its properties. The program may involve heating or cooling at a fixed rate of temperature change, or holding the temperature constant, or any sequence of these. Differential techniques involve the measurements of a difference in the property between the sample and a reference material. Thermal analysis is now generally recognized as one of the basic analytical tools for characterizing the compounds. The nature of phase transitions even in complex compounds and their thermal stability is often studied by DTA and DSC. Endothermic or exothermic band may be due to chemical or physical or physical reaction. DTA and DSC are completely to each other. Both of them provide a rapid method for studying the thermal kinetics of the material under test.

DSC which is performed in the present work for the eutectic $(Na_{0.6}K_{0.4})NO_3$ samples was recorded during heating and cooling process. Various kinetic parameters controlling such phase transitions and thermal information are to be determined by such thermal analyses.
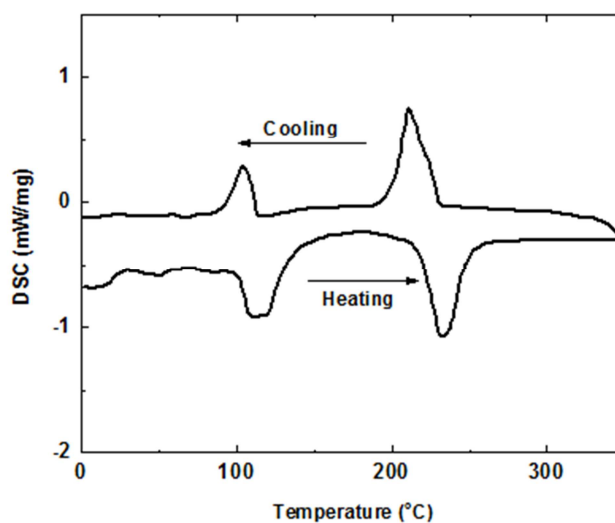

Figure 1. DSC thermogram record during heating and cooling of the eutectic system of $(Na_{0.6}K_{0.4})NO_3$ sample.

The differential scanning thermal analysis curve shown in figure 1 was recording during heating and cooling process at a rate of 10°C /min. It is clear that it supports the presence of thermal hysteresis phenomena. This figure indicates that the endothermic peak of transformation for eutectic $(Na_{0.6}K_{0.4})NO_3$ system takes place at ~114°C during heating. However the reversibility of the exothermic peak of this transformation appeared at ~106°C. The difference in the peak height, in the forward and reverse direction i.e. during heating and cooling runs, is due to the difference in the heat of transformation (ΔH) during heating and the heat evolved during cooling. However, it is clear that there is a pronounced thermal hysteresis during the reversible transformation of the eutectic $(Na_{0.6}K_{0.4})NO_3$ system [14].

3.2. Thermogravimetry Analysis (TGA)

The thermogravimetry analysis (TGA) is basically quantitative in nature where the mass-changecan be accurately determined. This method is a useful technique for studying the ability of a substance to maintain its mass under a variety of conditions [17]. Figure 2 a, b show a high accurate thermal gravimetric analysis measurement for $(Na_{0.6}K_{0.4})NO_3$ sample during its phase transformation. It is note the analysis of this curve and its derivative that there is no nearly any mass loss in the temperature range (30 – 20°C) i.e. during the transformation process for this sample. This means that the $(Na_{0.6}K_{0.4})NO_3$ sample is structurally stable contributing to ant mass loss during the transformation process. It demonstrated also this transformation to have a thermal stability up to the melting point [18].
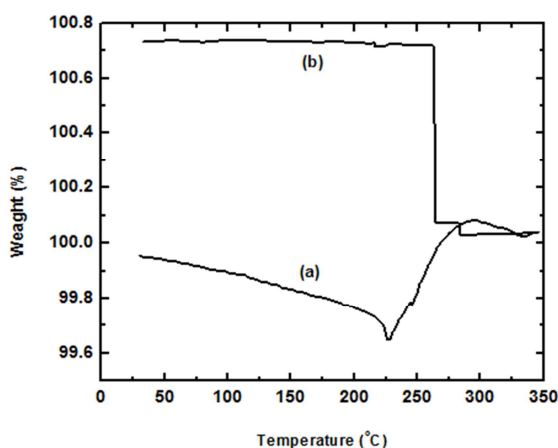

Figure 2. TGA analysis (TGA and derivative curves) for thermal stability of the phase transition for $(Na_{0.6}K_{0.4})NO_3$ sample. (a) TGA curve, (b) Derivative curve.

3.3. Differential Thermal Analysis (DTA)

Differential Thermal Analysis (DTA) was also successfully used, in the present work for the eutectic $(Na_{0.6}K_{0.4})NO_3$ samples, to characterise the kinetic parameters controlling such phase transitions. Figure 3 shows the DTA thermograms for $(Na_{0.6}K_{0.4})NO_3$ samples at different heating rates (2, 5, 10, 15, and 20°C /min) during heating run up to 250°C. An endothermic peak at approximately 114°C is shown in figure

for the measurements that recorded at 2°C/min. The calculated thermal energy of transformation was found to be 26.32 J/g. Further, heating of $(Na_{0.6}K_{0.4})NO_3$ sample up to 220°C gives no change indicating to the sample stability against the thermal agitation up to 220°C. As the temperature increases, an endothermic peak near to ~225°C which is due to melting process of the sample. The DTA thermograms recorded at 5°C/min represented also an endothermic peak at ~114°C and the thermal energy of transformation was found to be 18.87 J/g. The endothermic peak that appeared with The DTA thermograms recorded at 10°C/min was found to be at ~112°C and the thermal energy of transformation was found to be 41.3 J/g. However the endothermic peak that appeared with the DTA thermograms recorded at 15°C/min was found to be at ~117°C and the thermal energy of transformation was found to be 11.9 J/g. For the DTA thermograms recorded at 15°C /min, the endothermic peak that appeared at ~118°C and the thermal energy of transformation was found to be 9.52 J/g.
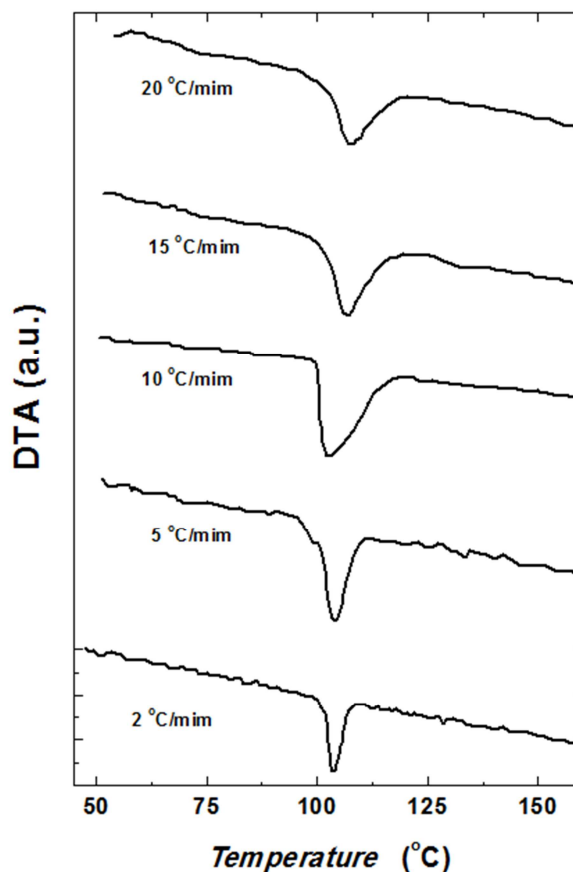

Figure 3. The variation of DTA thermogram with different heating rates (2, 5, 10, 15 and 20°C/min).

The effect of the heating rate on the band shape of the DTA curves for the phase-phase transformation process of $(Na_{0.6}K_{0.4})NO_3$ sample is clearly seen in figure 3. It could be observed from these curves that the increasing of the heating rate of the transformation process leading to increase of the band width and the maximum differential temperature ΔT_{max} up to heating rate of 10°C/min. After this rate i.e. at rates of 15°C/min and 20°C/min, the area under the DTA curves does not nearly change. While the phase transition point is varied

according to the heating rate on the sample during the transformation process. It is also clear from the superimposed thermograms that represented in figure 3 that the peak symmetry is sensitive to the change of the heating rate. It is observed that the transformation peak at heating rate of 10°C/min has a large symmetry differ from the peaks obtained with the other heating rates. This can be attributed to the increase of the different dynamical situations of Na^+ and K^+ ions around the (NO_3^-) group. This is because the (NO_3^-) group has a large relaxation time, high enthalpy and approximately low transition point [19].

Figure 4 shows the relation between the rate of heating and peak position of transition point. It is shown that the peak position is changed with increasing the heating rate. The location of the peak can be related to the activation energy provided to the phase transformation in the eutectic $(Na_{0.6}K_{0.4})NO_3$ system at different heating rates. The activation energy at each heating rate was calculated and listed in table 1. The variation of the activation energy with the heating rate for the $(Na_{0.6}K_{0.4})NO_3$ sample seems to be consistent with the expectation that the temperature dependence of the activation energy is mainly caused by the lattice thermal expansion. The temperature dependence is also caused by the formation of polarizability arising from the cationic Na^+ and K^+ ions sphere around the (NO_3^-) group [19, 21].
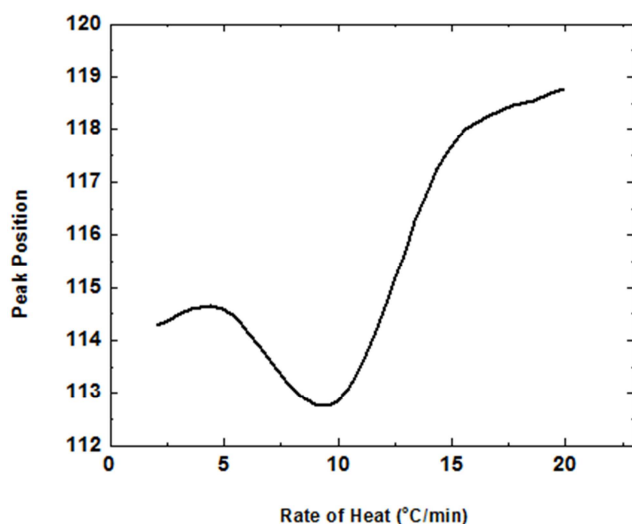

Figure 4. *Variation of the peak position (transition point) of $(Na_{0.6}K_{0.4})NO_3$ sample with heating rate.*

Figure 5 shows the relation between the enthalpy, ΔH, and the heating rate. It is clear that the enthalpy increasing with increasing the heating rate reaching a maximum of value equals to 41.3 J/g at heating arte of 10°C/min. Then the enthalpy decreases with increasing the heating rate.

The effect of heating rate on the thermal characteristic behaviour can be clearly observed. This indicates to the presence of a certain dependence on the heating rate for the thermal phase-phase transformation of $(NaK)NO_3$ sample which was detected by the DTA measurements. This means that the effect of heating rate is mainly associated with changes of the thermal interaction potential of Na^+ and K^+ ions around the (NO_3^-) group during the phase transformation. This

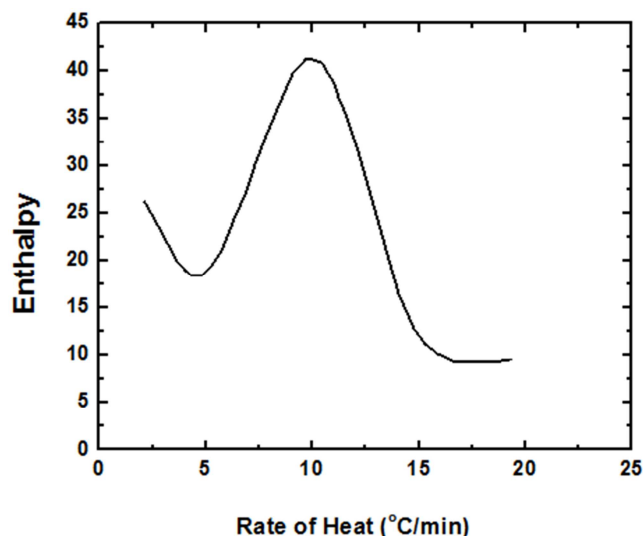leads to a change in both the transition point and the enthalpy for the $(NaK)NO_3$ sample [20].

Figure 5. *Variation of the enthalpy (ΔH) of $(Na_{0.6}K_{0.4})NO_3$ sample with heating rate.*

Table 1. *The activation energy at different heating rate of the $(NaK)NO_3$ sample.*

Heating Rate (°C/min)	E x 10^{23} eV/mole
2	49.109
5	13.261
10	14.183
15	23.970
20	8.456

4. Conclusion

A mixture $(Na_{0.6}K_{0.4})NO_3$ eutectic system of molecular ratio 60% $NaNO_3$ and 40% KNO_3 was prepared from chemically pure $NaNO_3$ and KNO_3. The various techniques of thermal analysis such as Differential Thermal Analysis (DTA), Differential Scanning calorimetry (DSC) and Thermogravimetry Analysis (TGA) were applied to study the thermal properties of the prepared mixture. The DSC measurements showed a thermal hysteresis during this transformation with a magnitude of the hysteresis temperature ~8°C. Where the measurements showed a reversible phase transition at ~114°C during heating process and at ~108°C during cooling process for the solid phase transformation for the eutectic $(NaK)NO_3$ system. The thermogravimetery analysis (TGA) indicated and demonstrated the phase transition inside this eutectic system having thermal stability up to the melting point at $\cong$225°C indicating to the structural stability of the sample under study. It has been also shown from the DTA measurements that the thermal parameter such as the transition point, enthalpy and the activation energy for the transformation process are affected by the heating rate of (2, 5, 10, 15 and 20°C/min). The noticeable effect of heating rate on the thermal parameters means that the heating rate is a main factor to change the thermal interaction potential of the Na and K atoms around the nitrate group (NO_3^-) during the phase conversion for the eutectic $(Na_{0.6}K_{0.4})NO_3$ system.

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