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Phase equilibria in the reciprocal NaCl–KCl–$NaNO_3$–KNO_3 system

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ABSTRACT

Differential thermal analysis of the various compositions in the KCl–$NaNO_3$ and NaCl–KNO_3 systems has been performed. Temperatures of phase transitions were obtained. The relative content of NaCl, KCl, $NaNO_3$, and KNO_3 compounds was determined by the use of X-ray diffraction analysis. These results together with the experimental data from literature were used for optimization of thermodynamic parameters for all available phases and compounds to obtain the Gibbs energy dataset which can be used for the calculation and prediction of the phase diagrams and other thermodynamic properties of these systems.

1. Introduction

Thermal energy storage (TES) is one of the promising issues of the energy-saving technologies. The primary principles of TES are based on the use of the sensible- and the latent-heat of materials. Salt systems as TES are used in industry and solar thermal power plants because of low price and suitable temperature range [1–3]. For the selection of suitable systems in application, it is of considerable importance to know their thermodynamic properties and phase diagrams. Systems based on NaCl, KCl, $NaNO_3$, and KNO_3 salts are at reasonable price and already widely used in industry.

The phase diagrams and thermodynamic properties of the binary systems $NaNO_3$–KNO_3[4–9], NaCl–KCl [10–15], $NaNO_3$–NaCl [16,17], and KNO_3–KCl [16–20] were studied experimentally by different authors. Moreover, the liquidus projection of the reciprocal NaCl–KCl–$NaNO_3$–KNO_3 system was published in Ref. [21]. To complete this system the sections NaCl–KNO_3 and KCl–$NaNO_3$ have to be studied for optimizing the thermodynamic parameters of all available phases and compounds to generate the Gibbs energy dataset, which can be used for the calculation and prediction the phase diagrams and other thermodynamic properties of the whole system.

This work is focussed on studying the sections NaCl–KNO_3 and KCl–$NaNO_3$ of the reciprocal NaCl–KCl–$NaNO_3$–KNO_3 system by the use of differential thermal analysis (DTA) and X-ray diffraction (XRD) in connection with the critical assessment and optimisation of the complete salt system following the Calphad method.

2. Experimental

2.1. Instruments

2.1.1. Differential thermal analysis (DTA)

DTA measurements were performed using a STA 449C Jupiter (Netzsch) with a silicon carbide oven (0–1600 °C) and a perpendicular sample holder with type S thermocouple (Pt/(Pt10Rh)). The temperature calibration was conducted using the structure and phase transitions temperatures of In (156.6 °C), Zn (419.6 °C), SiO_2 (574 °C), K_2CrO_4 (673 °C), and Ag (961.8 °C). The experiments were carried out with a scan rate of 5 K/min and 4 cycles of heating and cooling. Single phase transitions were obtained from the extrapolated onset construction in the heating curve and for cooling from the extrapolated end temperature under consideration of the undercooling effect. The onset was used for the solidus and the end temperature for the liquidus transition. All the values were determined with Proteus Analysis software from Netzsch. The results showed good reproducibility from the second cycle.

2.1.2. X-ray diffractometer (XRD)

A Bruker D4 Endeavour diffractometer (Bruker AXS GmbH) with Cu-Kα radiation (40 kV, 40 mA) and a NaI scintillation

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Table 1
Sample information.

Chemical name	Source	Purity[a]	Melting temperature[b] (°C)		Transition temperature[b] (°C)	
			Heating[c]	Cooling[c]	Onset	Peak
NaCl	Alfa (AESAR)	99.99%, ultra dry	805	803	–	–
KCl	Alfa (AESAR)	99.99%, ultra dry	773	771	–	–
$NaNO_3$	Sigma-Aldrich	99.995%	301	303	–	273
KNO_3	Sigma-Aldrich	99.999%	331	335	127	134

[a] On metal basis.
[b] The standard uncertainty (u) is $u(T) = 3$ °C.
[c] Based on the onset of peak.

counter detector was used for the XRD analysis. The phase identification was deduced from the inorganic crystal structure database (ICSD, FIZ Karlsruhe) with the software HighScore Plus 3.0 (PANanalytical B.V.). Rietveld refinement was performed using TOPAS 4.2 software (Bruker AXS GmbH).

2.2. Samples

The specifications of the compounds used for the preparation of mixtures are described in Table 1. Melting and structure transition temperatures of pure compounds were determined by the authors using DTA (Table 1, Fig. 1). in closed glass ampoules. These values show that undercooling effects on the cooling curves do nearly not see. This conclusion was used for determination of liquidus temperatures of the studied mixtures. All mixtures were prepared in a glass ampoule under purified argon inside of a glove box. The sample was heated carefully under vacuum to remove any residual moisture and then the glass ampoule was sealed. To achieve homogeneity prior to examination, the mixtures in the ampoules were sequentially melted and crystallized 3 times at a rate of 5 K/min.

3. Experimental results

3.1. Differential thermal analysis

3.1.1. KCl–$NaNO_3$

The 24 compositions of KCl–$NaNO_3$ system were synthesized in closed glass ampoules and studied by DTA. Figs. 2 and 3 show the main DTA-curves on heating and cooling, which characterize all important points of this system. The pure $NaNO_3$ has one structural transition at 273 °C (Table 1, Fig. 1). Therefore, it was difficult to distinguish and separate the peaks of melting point and structure changing for the compositions 5KCl–95$NaNO_3$, 6KCl–94$NaNO_3$, and 7.5KCl–92.5$NaNO_3$ (Fig. 2a). To solve this problem, additional measurements with a low heating rate of 1 K/min were carried out. However, the signal was in this case lower and it still did not allow separating the temperature transitions. For the mixtures 10KCl–90$NaNO_3$ and 15KCl–85$NaNO_3$ the crystallization peak could only be seen on the cooling curves (Fig. 2a). It allowed finding out the eutectic composition 7.5KCl–92.5$NaNO_3$ which exhibits the lowest temperature of crystallization, i.e. at 275 °C (Fig. 2a). Along with these peaks there was a small one at 110 °C (Table 2, column 3), which is also seen for other compositions (Fig. 2b). The DTA-curves of 20KCl–80$NaNO_3$, 25KCl–75$NaNO_3$, 30KCl–70$NaNO_3$, 35KCl–65$NaNO_3$, and 40KCl–60$NaNO_3$ mixtures outline transitions related to the eutectoid transformation. It has a temperature of 209 °C and the composition 35KCl–65$NaNO_3$ (Table 2, column 2). In addition, a small deviation from the base-line was seen in the region of 130–200 °C (Fig. 2b, in circles) for heating and cooling curves. This line is labelled in Table 2 as column 4.

Fig. 3a shows the changes of two transition signals in the concentration range of 50:50 compositions (Table 2, columns 1–3). The peak temperature of the first transition is 110 °C (onset 100 °C) for the 42.5KCl–57.5$NaNO_3$ to 50KCl–50$NaNO_3$ compositions and is changed to 120 °C (onset 110 °C) for 55KCl–45$NaNO_3$ (Table 2, column 3). The second transition has a maximum onset at 242 °C for the heating and cooling curves of the 55KCl–45$NaNO_3$ composition. This temperature is constant for compositions with higher KCl concentration (Table 2, columns 1 and 2). For KCl concentrations lower than 55 mol%, the onset is continuously changing to lower temperature and ends in two transitions with an onset at 205 °C for the first peak.

Fig. 3b illustrates peaks of the liquidus line for mixtures with KCl higher than 50 mol% (Table 2). The transition temperatures were taken from the so-called end-set determination that represents the beginning of crystallization on the cooling curves. An additional peak (in circles) was observed (Table 2, column 5). All transition temperatures related to the various compositions are tabulated in Table 2.

3.1.2. NaCl–KNO_3

Nineteen compositions in the NaCl–KNO_3 system were studied by DTA in closed glass ampoules in the same way as described before for the KCl–$NaNO_3$ system. Fig. 4 shows the DTA-curves of some compositions from 5% to 40% NaCl in the temperature range 200–400 °C. In the range of NaCl concentrations below 40 mol% more than two transitions have been observed. Three transitions

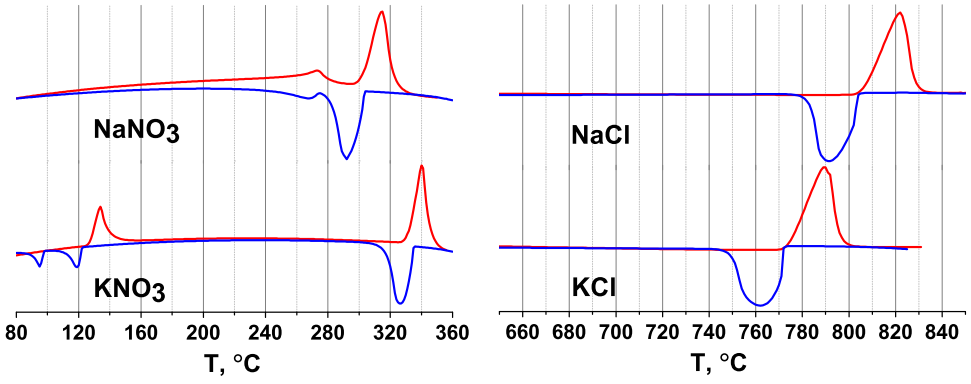

Fig. 1. Heating (red/upper) and cooling (blue/lower) DTA-curves of KNO_3, $NaNO_3$, KCl, and NaCl compounds. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)