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Revised Phase Diagram of the System NaF–$NaBF_4$

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Summary. The phase diagram of the binary system NaF–$NaBF_4$ was determined using the thermal analysis method. Subsequent coupled analysis of the thermodynamic and phase diagram data was carried out to calculate the thermodynamically consistent phase diagram. The system NaF–$NaBF_4$ forms a simple eutectic phase diagram with the calculated coordinates of the eutectic point: 8.1 mol% NaF, 91.9 mol% $NaBF_4$, and 385.7°C. The probable inaccuracy in the calculated binary phase diagram is 9°C.

Keywords. Thermal analysis; Phase diagram; Sodium fluoroborate; Excess molar *Gibbs* energy.

Introduction

The system NaF–$NaBF_4$ has been considered as a heat carrier for the secondary circuits of nuclear power plants with a Molten Salt Reactor (MSR) [1, 2] or as buffer salt in an Advanced High Temperature Reactor project [3].

Two papers have dealt with the investigated system. *Selivanov* and *Stender* [4] have measured the phase diagram of this system using the thermal analysis method. The cooling curves were registered at the cooling rate of 6–8°C · min^{-1}. The temperatures of primary crystallization were checked using the visual observation of formation of the first crystals in the melts. For the temperature of fusion of NaF the authors reported the value of 1026°C, which was significantly higher than that one given in the thermodynamic tables of Refs. [5, 6]. For the temperature of fusion of $NaBF_4$ *Selivanov* and *Stender* [4] have indicated the value of 368°C, which is significantly lower than that one given by *Barton et al.* [7]. Also the coordinates of the eutectic point given in Ref. [4] are substantially different from those indicated in Ref. [7].

Barton et al. [7] has indicated for the temperature of fusion of sodium fluoride the value of 997°C, which is in accordance with the values given in the present thermodynamic tables. For the temperature of fusion of $NaBF_4$ these authors have published the value of 408°C. The phase diagram is simple eutectic one and the proposed coordinates of the eutectic point are 8 mol% NaF and 384°C. These authors have prepared very pure $NaBF_4$ by recrystallisation from the water solution of HF and subsequent treatment of its melt by bubbling with BF_3, HF, and He. The temperature of fusion of the final product was (408 ± 1)°C.

The use of the DTA technique and the details of its use have been described in Ref. [8].

From the above mentioned survey it follows that the phase diagram according to *Barton et al.* [7] is more likely to be correct than the one measured by *Selivanov* and *Stender* [4].

In the present work the phase diagram of the system NaF–$NaBF_4$ was measured using the thermal analysis method followed by coupled analysis of the

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thermodynamic and phase diagram data which was performed in order to obtain a thermodynamically consistent phase diagram.

Results and Discussion

The thermodynamically consistent and optimized phase diagram of the system NaF–$NaBF_4$ together with the data according to *Barton et al.* [7] is shown in Fig. 1 (Table 1). The liquidus curves and the scatter of the experimental points near the eutectic point are shown in the insertion of Fig. 1. The standard deviation of the experimental values of the temperatures of primary crystallization from the calculated ones is $SD(T_{pc}) = \pm 9.0°C$. The comparison of the eutectic point coordinates obtained in this work with the results of *Barton et al.* [7] is as follows: 8.1 mol% NaF, 91.9 mol% $NaBF_4$, and 385.7°C this work, 8 ± 1 mol% NaF, 92 ± 1 mol% $NaBF_4$, and 384 ± 2°C *Barton et al.* [7].

It can be seen that very good agreement was attained, in spite of serious difficulties with the decomposition of $NaBF_4$. Because our measurements were not performed in closed ampoules, the pure $NaBF_4$ decomposed. This was the reason that we could not determine its temperature of fusion and in the calculation the value given in thermodynamic tables [6] was used (see Table 2). By the addition of NaF the decomposition was suppressed. Reliable data were thus obtained, however, at the pressure different from atmospheric one.

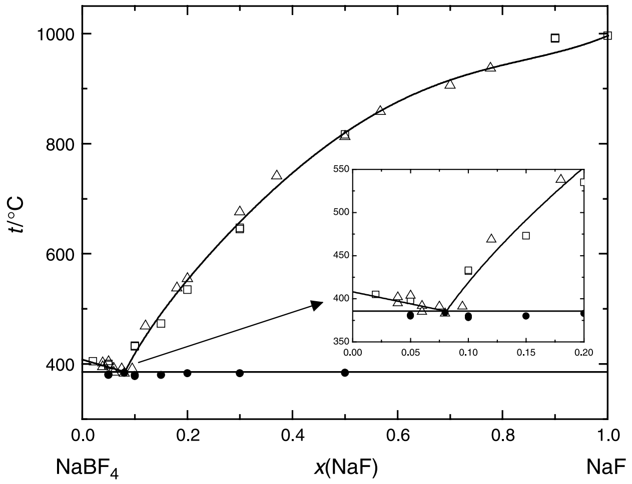

Fig. 1. Phase diagram of the system NaF–$NaBF_4$. □ – our data; Δ – *Barton et al.* [7]; ● – eutectic temperature (our data); – optimized calculation according to Eq. (8)

Table 1. The measured values of the temperature of primary and eutectic crystallization in the system NaF–$NaBF_4$

x(NaF)	$x(NaBF_4)$	t/°C	t_{eut}/°C
1.00	0.00	996	–
0.90	0.10	992	–
0.90	0.10	991	–
0.50	0.50	817	384
0.30	0.70	647	383
0.30	0.70	645	383
0.20	0.80	535	383
0.15	0.85	473	380
0.10	0.90	432	380
0.10	0.90	433	378
0.08	0.92	–	384
0.05	0.95	400	380
0.05	0.95	398	381
0.02	0.98	405	–

Table 2. The enthalpy and the temperature of fusion of pure compounds used in the calculation

Component	T_{fus}/K	$\Delta_{fus}H°/\mathrm{J\cdot mol^{-1}}$	Ref.
NaF	1269	33137	[9]
$NaBF_4$	681	13602	[6]

Table 3. Coefficients G_i of the excess molar *Gibbs* energy of mixing in the system NaF–$NaBF_4$

Coefficient	$G_i/\mathrm{J\cdot mol^{-1}}$
G_0	$(10.8 \pm 0.9) \times 10^3$
G_1	$-(25.0 \pm 2.5) \times 10^3$
G_2	$(14.8 \pm 1.9) \times 10^3$

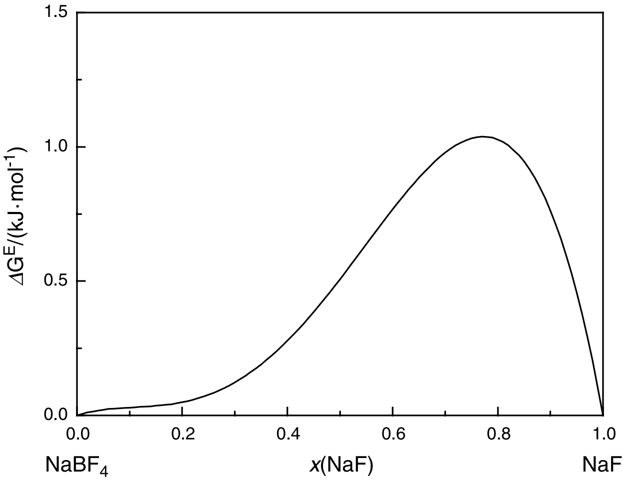

Fig. 2. Excess molar *Gibbs* energy of mixing in the system NaF–$NaBF_4$

The excess molar *Gibbs* energy in the system NaF–$NaBF_4$ is shown in Fig. 2 and was calculated using coefficients given in Table 3. For details see Data Processing. It follows that there is a slight endothermic reaction in the whole composition range of the system, most pronounced in the region of high content of NaF. This effect may have the following origin. At low content of NaF in the melt small anions F^- can easy randomly distribute among relatively large anions $BF_4{}^-$. Thus, nearly ideal behaviour is expected. On the other side, addition of large anions $BF_4{}^-$ among large number of small F^- causes disorder in the melt and larger deviation from ideal behaviour is expected.

On the cooling curves of the investigated sample with the high content of $NaBF_4$, additional temperature discontinuity was found which corresponds to the transformation from the α to the β modification. According to the thermodynamic tables, the temperature of this phase transformation is 243°C [6], while *Barton et al.* [7] gave the transformation temperature of 283°C. In this work it was found that the transformation takes place at approx. 246°C, which is very close to the tabulated value [6].

Data Processing

The calculation of the phase diagrams of the condensed systems using the coupled analysis of the thermodynamic and phase diagram data is based on the solution of the set of equations of the following type, where each of the equation describes the field of primary crystallization of the component i

$$\Delta_{\mathrm{fus}} G_i^{\varnothing}(T) + RT \ln \frac{a_{l,i}(T)}{a_{s,i}(T)} = 0 \qquad (1)$$

$\Delta_{\mathrm{fus}} G_i^{\varnothing}$ is the standard molar *Gibbs* energy of fusion of the component i at the temperature T, R is gas constant, and $a_{s,i}(T)$ and $a_{l,i}(T)$ are the activities of the component i in the solid and liquid phase at the temperature T, respectively. The molar excess *Gibbs* energy of mixing in the liquid phase of the binary systems was described by the following general equation

$$\Delta G^{\mathrm{E}} = \sum_{j=0}^{n} x_1 x_2^j G_j \qquad (2)$$

G_j is a coefficient of interaction. It is supposed, that parameter G_j does not depend on the composition and in the field interesting for the investigation of the phase diagram is independent on the temperature.

The used model deals only with solidus–liquidus equilibria, solid phase transformation is not involved in the model.

The coupled thermodynamic analysis, *i.e.* the calculation of the coefficients G_j in the Eq. (2) has been performed using multiple linear regression analysis omitting the statistically non-important terms in the excess molar *Gibbs* energy of mixing on the 0.99 confidence level according to the Student's test. As the optimizing criterion for the best fit between the experimental and calculated temperatures of the primary crystallization the following condition was used for all measured points

$$\sum_n (T_{\mathrm{pc,exp},n} - T_{\mathrm{pc,calc},n})^2 = \min \qquad (3)$$

In the calculation the measured temperatures of primary crystallization (see Table 1) and the thermodynamic data on the enthalpies and temperatures of fusion of both components given in Table 2 were used.

The crystallization area of NaF takes place within a temperature range of more than 600°C. Therefore, the enthalpy of fusion of NaF was assumed to be dependent on temperature by using the thermal capacity:

$$\frac{\Delta c_p^{\mathrm{l/s}}}{\mathrm{J \cdot mol^{-1}}} = \mathrm{a} + \mathrm{b}T + \mathrm{c}T^2 + \mathrm{d}T^{-2} \qquad (4)$$

where $\mathrm{a} = 17.261$; $\mathrm{b} = -7.043 \times 10^{-3}\,\mathrm{K^{-1}}$; $\mathrm{c} = -6.442 \times 10^{-6}\,\mathrm{K^{-2}}$; $\mathrm{d} = 104.587 \times 10^5\,\mathrm{K^2}$ [9].

It is known that $NaBF_4$ decomposes according to the reaction

$$\mathrm{NaBF_4(l) = NaF(l) + BF_3(g)} \qquad (5)$$

The formed BF_3 escapes from the melt, while NaF remains in the melt. NaF and $NaBF_4$ are ionic liquids. It can be assumed that on the basis of coulombic electrostatic forces specific preferred arrangement of ions to ion pairs will be present in the melt [10, 11]. It is supposed that ions Na^+, F^-, and BF_4^- form preferred ion pairs $[Na^+ \cdot F^-]$ and $[Na^+ \cdot BF_4^-]$ [11].

For the dependence of the excess molar *Gibbs* energy on composition the following equation was assumed

$$\Delta G^{\mathrm{E}} = x_1 x_2 (G_0 + G_1 x_2 + G_2 x_2^2) \qquad (6)$$

It should be noted that subscripts 1 and 2 represent ion pairs $[Na^+ \cdot F^-]$ and $[Na^+ \cdot BF_4^-]$.

The calculated values of the regression coefficients G_j as well as their standard deviations are given in Table 3.

Experimental

For the preparation of the samples the following chemicals were used: NaF (Merck 99.9%), dried for 2 h at 500°C, and $NaBF_4$ (Fluka, p.a.), dried in a vacuum furnace at 100°C for 5 h. All handling of the salts was done under dry nitrogen atmosphere (Messer 99.990%) in a glove box.

The temperatures of individual phase transitions were determined by means of thermal analysis, recording the cooling and heating curves of the investigated mixtures at the rate of 3–4°C $\cdot$ $\mathrm{min^{-1}}$. The closed platinum crucible containing 10.0 g of the samples was placed into the resistance furnace provided by an Ar atmosphere and adjustable cooling rate. The melt was kept *ca.* 30 min 20°C above the expected temperature of primary crystallization. Then the lid of the crucible was removed and thermocouple was immersed into the melt. The temperature control and the data processing were performed using a computerized measuring device. The temperature was measured using a Pt-PtRh10 thermocouple calibrated to the melting points of NaCl, KCl, and Na_2SO_4. The measured transition temperatures were reproducible within ±2°C. The measured values of the temperature of primary (t/°C) and eutectic

($t_{eut}/°C$) crystallization in the system NaF–$NaBF_4$ are given in Table 1.

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