Journal of Thermal Analysis and Calorimetry, Vol. 76 (2004) 763–773

PHASE DIAGRAM OF THE SYSTEM NaF–KF–AlF_3

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(Received November 27, 2003; in revised form January 7, 2004)

Abstract

The phase diagrams of the binary system KF–AlF_3 as well as the ternary system NaF–KF–AlF_3 in the range up to 50 mol% AlF_3, were measured using the thermal analysis method.

In the system KF–AlF_3 the coordinates of the eutectic points are: E_1: 8.0 mol% AlF_3, 821.2°C, and E_2: 45.5 mol% AlF_3, 565.0°C.

In the investigated concentration range of the ternary system 2 eutectic points have been found with the calculated coordinates: E_1: 36.3 mol% NaF, 62.7 mol% KF, 1.0 mol% AlF_3; t=711.2°C; and E_2: 51.9 mol% NaF, 27.4 mol% KF, 20.7 mol% AlF_3; t=734.5°C. Other eutectic points lie most probably beyond the investigated part of the system.

Keywords: aluminium fluoride, coupled analysis, cryolite, phase equilibria, sodium fluoride

Introduction

Part of the investigated system Na–KF–AlF_3 represents an interest from technical point of view as a possible low-melting electrolyte for an alternative process of aluminium electrowinning.

The phase diagram of the binary system NaF–KF was published in [1, 2]. It is an eutectic system with solid solution on the KF side up to 5 mol% NaF at the eutectic temperature. Coordinates of the eutectic point are 40 mol% NaF and 721°C [2].

The phase diagram of the binary system NaF–AlF_3 was studied in [3–8]. The complex compounds Na_3AlF_6, melting congruently at 1011.6°C, and $Na_5Al_3F_{14}$, melting incongruently at 740°C, exist in the system. Solheim and Sterten [9] have collected all available experimental data and published the optimized phase diagram. They supposed that Na_3AlF_6 is slightly non-stoichiometric compound Na_xAlF_{3+x}. Peritectic point has coordinates 42.5 mol% AlF_3, 740°C. The eutectic points in the system are: E_1: 13 mol% AlF_3, 891°C; E_2: 46 mol% AlF_3, 698°C.

The phase diagram of the binary system KF–AlF_3 was investigated by Fedotieff and Timofeeff [10] and Phillips *et al*. [11]. In the system, the complex compound

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1388–6150/2004/ $ 20.00

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Kluwer Academic Publishers, Dordrecht

K_3AlF_6, melting congruently at 1020°C [10] or 985°C [11], exists. Coordinates of eutectic points are: E_1: 5 mol% AlF_3, 840°C [10] or 7.5 mol% AlF_3, 830°C [11]; E_2: 45 mol% AlF_3, 570°C [10] or 560°C [11].

In monograph [12] phase diagram of the system NaF–KF–AlF_3 up to 60 mol% AlF_3 has been presented. The data in the quoted work [12] are not detailed enough. Even crystallization fields of Na_3AlF_6 and K_3AlF_6 are not separated. In the published part of the phase diagram, there is only one eutectic point: 37 mol% NaF, 60 mol% KF, 3 mol% AlF_3 with the temperature below 750°C.

Gabčová *et al*. [13] published the cryolite corner of the system NaF–KF–AlF_3. Quasi-binary system Na_3AlF_6–K_3AlF_6 was studied in [14–16]. The eutectic point of the system Na_3AlF_6–K_3AlF_6 was found at 40 mol% K_3AlF_6, 938°C which represents concentration coordinates 45 mol% NaF, 30 mol% KF and 25 mol% AlF_3 in the system NaF–KF–AlF_3.

This work deals with the measurement of the phase diagram of the binary system KF–AlF_3 and the ternary system NaF–KF–AlF_3. Thermodynamically consistent phase diagram was calculated using the coupled analysis of the thermodynamic and equilibrium phase diagram data.

Experimental

The temperatures of individual phase transitions (primary, secondary and eutectic crystallization) were determined by means of thermal analysis method, recording the cooling and heating curves of the investigated mixtures at the rate of 2–5°C min^{-1}. The platinum crucible containing 30 g of the sample was placed into the resistance furnace provided by an adjustable cooling rate. 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 NaF, $BaCl_2$, NaCl, KCl, LiF and Na_2SO_4.The measured transition temperatures were reproducible within ±2°C.

For the preparation of the samples, the following chemicals were used: NaF (Lachema, analytical grade), AlF_3, KF (Mikrochem, pure) and P_2O_5 (Mikrochem, analytical grade). NaF was dried at 600°C for 2 h, AlF_3 was purified by sublimation and KF was dried in vacuum drying oven in the presence of P_2O_5.

The liquidus temperature in the binary system KF–AlF_3 were measured up to 60 mol% AlF_3. The phase transition temperatures in the ternary system NaF–KF–AlF_3 were measured in different cross-sections with constant mole fraction of one component. The measured transition temperatures are given in Table 1.

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 a set of equations of the following type

Table 1 Measured (t_{exp}) and calculated (t_{calc}) temperatures of primary crystallization and their differences (Δt) of the investigated mixtures in the system NaF–KF–AlF_3

x(NaF)	x(KF)	x(AlF_3)	t_{exp}/°C	t_{calc}/°C	Δt/°C	Crystallizing phase
0.00	0.65	0.35	921	920	1	K_3AlF_6
0.00	0.70	0.30	965	987	–13	K_3AlF_6
0.00	0.71	0.29	975	985	–10	K_3AlF_6
0.00	0.72	0.28	989	990	–1	K_3AlF_6
0.00	0.73	0.27	991	993	–2	K_3AlF_6
0.00	0.74	0.26	994	995	–1	K_3AlF_6
0.00	0.75	0.25	995	996	–1	K_3AlF_6
0.00	0.76	0.24	991	995	–4	K_3AlF_6
0.00	0.77	0.23	984	993	–9	K_3AlF_6
0.00	0.78	0.22	979	990	–11	K_3AlF_6
0.00	0.79	0.21	975	985	–10	K_3AlF_6
0.00	0.80	0.20	972	979	–7	K_3AlF_6
0.00	0.85	0.15	916	929	–13	K_3AlF_6
0.00	0.90	0.10	862	854	8	K_3AlF_6
0.00	0.91	0.09	830	837	–7	K_3AlF_6
0.00	0.92	0.08	828	823	5	KF
0.00	0.93	0.07	827	829	–2	KF
0.00	0.94	0.06	826	835	–9	KF
0.00	0.95	0.05	833	840	–7	KF
0.00	0.96	0.04	836	844	–8	KF
0.80	0.10	0.10	918	913	5	NaF
0.70	0.20	0.10	908	900	8	NaF
0.60	0.30	0.10	853	868	–15	NaF
0.50	0.40	0.10	834	834	0	K_3AlF_6
0.40	0.50	0.10	854	851	3	K_3AlF_6
0.30	0.60	0.10	864	863	1	K_3AlF_6
0.20	0.70	0.10	866	866	0	K_3AlF_6
0.10	0.80	0.10	861	862	–1	K_3AlF_6
0.45	0.30	0.25	935	936	–1	Na_3AlF_6
0.25	0.50	0.25	966	959	7	K_3AlF_6
0.35	0.30	0.35	907	910	–3	Na_3AlF_6
0.25	0.40	0.35	898	888	10	Na_3AlF_6
0.15	0.45	0.40	838	850	–12	Na_3AlF_6
0.45	0.50	0.05	811	814	–3	K_3AlF_6
0.40	0.60	0.05	824	822	2	K_3AlF_6

Table 1 Continued

x(NaF)	x(KF)	x(AlF$_3$)	t_{exp}/°C	t_{calc}/°C	Δt/°C	Crystallizing phase
0.35	0.60	0.05	791	803	–12	K3AlF6
0.30	0.65	0.05	801	803	–2	K_3AlF_6
0.05	0.90	0.05	813	818	–5	KF
0.05	0.85	0.10	866	851	15	K_3AlF_6
0.75	0.10	0.15	871	871	0	Na_3AlF_6
0.75	0.05	0.20	961	961	0	Na_3AlF_6
0.70	0.05	0.25	992	992	0	Na_3AlF_6
0.65	0.05	0.30	985	985	0	Na_3AlF_6
0.60	0.05	0.35	923	926	–3	Na_3AlF_6
0.70	0.10	0.20	943	943	0	Na_3AlF_6
0.65	0.10	0.25	976	973	3	Na_3AlF_6
0.60	0.10	0.30	970	969	1	Na_3AlF_6
0.55	0.10	0.35	913	919	–6	Na_3AlF_6
0.65	0.15	0.20	927	927	0	Na_3AlF_6
0.60	0.15	0.25	961	961	0	Na_3AlF_6
0.55	0.15	0.30	951	952	–1	Na_3AlF_6
0.50	0.15	0.35	901	908	–7	Na_3AlF_6
0.60	0.20	0.20	924	887	37	Na_3AlF_6
0.55	0.20	0.25	950	945	5	Na_3AlF_6
0.50	0.20	0.30	944	944	0	Na_3AlF_6
0.45	0.20	0.35	895	917	–22	Na_3AlF_6
0.40	0.20	0.40	814	816	–2	Na_3AlF_6

$$\Delta_{\text{fus}} G_{\text{i}}^{0}(T) + RT \ln \frac{a_{\text{l,i}}(T)}{a_{\text{s,i}}(T)} = 0 \tag{1}$$

where $\Delta_{\text{fus}} G_{\text{i}}^{0}$ is the standard molar Gibbs energy of fusion of the component *i* at the temperature *T*, *R* is gas constant and $a_{\text{s,i}}(T)$ and $a_{\text{l,i}}(T)$ are the activities of the component *i* in the solid and liquid phase at the temperature *T*, respectively. Equation (1) describes a crystallization field of the component *i*.

In the case that molar enthalpy of mixing of the system is known, the molar excess Gibbs energy of mixing in the liquid phase of the *i*-th boundary binary systems can be described by the following general equation

$$\Delta G_{\text{bin,i}}^{\text{E}} = \Delta H_{\text{bin,i}}^{\text{M}} - T\Delta S_{\text{bin,i}}^{\text{E}} \tag{2}$$

$$\Delta H^{\mathrm{M}}_{\mathrm{bin,i}} = \sum_{\mathrm{j=1}}^{\mathrm{n}} x_1 x_2^{\mathrm{j}} H_{1,\mathrm{j}} \qquad (3)$$

$$\Delta S^{\mathrm{E}}_{\mathrm{bin,i}} = \sum_{j=1}^{\mathrm{n}} x_1 x_2^{\mathrm{j}} S_{1,\mathrm{j}} \qquad (4)$$

The molar excess Gibbs energy of mixing in the ternary system was calculated according to equation

$$\Delta G^{\mathrm{E}}_{\mathrm{ter}} = \sum_{\mathrm{i=1}}^{3} \Delta G^{\mathrm{E}}_{\mathrm{bin,i}} + \sum_{\mathrm{b,c,d=1}}^{\mathrm{n}} x_1^{\mathrm{b}} x_2^{\mathrm{c}} x_3^{\mathrm{d}} G_{\mathrm{b,c,d}} \qquad (5)$$

where the first term on the right side of the Eq. (5) is the sum of the molar excess Gibbs energies of mixing in the binary systems and the second term represents the ternary interaction. Detailed description can be found in [17].

However, subsolidus areas of the phase diagram cannot be calculated using this method. Curves in subsolidus area can be estimated by methods shown in [18, 19].

Result and discussion

Constants H_{j} of molar enthalpy of mixing have been calculated using multiple linear regression analysis omitting the statistically non-important terms in Eq. (3) on the 0.99 confidence level according to the Students test. As the optimizing criterion for the best fit between experimental and calculated data the following condition was used for all measured points

$$\sum_{\mathrm{n}} (\Delta H^{\mathrm{M}}_{\mathrm{exp}} - \Delta H^{\mathrm{M}}_{\mathrm{calc}})^2 = \mathrm{min} \qquad (6)$$

The coupled thermodynamic analysis, *i.e.* the calculation of the coefficients S_{j} in Eq. (2) and G_{j} in Eq. (5) has been performed using multiple linear regression analysis omitting the statistically non-important terms in the excess molar entropy and excess molar Gibbs energy of mixing on the 0.99 confidence level according to the Student test, respectively. 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

$$\sum_{\mathrm{n}} \left(T_{\mathrm{pc,exp,n}} - T_{\mathrm{pc,calc,n}} \right)^2 = \mathrm{min} \qquad (7)$$

The values of the enthalpy of fusion of individual components used in the calculation are summarized in Table 2. The temperatures of primary crystallization in the system NaF–KF used for the calculation were taken from [2] and those for the system NaF–AlF_3 from [9], respectively. The data on enthalpy of mixing of all binary systems were taken from [20–23]. Sangster and Pelton [20] published an equation describing of molar enthalpy of mixing of the system NaF–KF. The experimental data on molar

Table 2 Enthalpy and temperature of fusion of pure compounds used for the calculation

Component	T_{fus}/K	$\Delta_{fus}H^0$/kJ mol^{-1}
NaF	1269.0 [25]	33.137 [25]
KF	1131.0 [25]	28.260 [25]
Na_3AlF_6	1284.8 [9]	106.700 [25]
K_3AlF_6	1269.0 [this work]	122.620 [25]

enthalpy of mixing of the system NaF–AlF_3 and its subsystems were studied in [21, 22]. In paper by Hong and Kleppa [23] the data on molar enthalpy of mixing were presented for both systems NaF–AlF_3 and KF–AlF_3.

System NaF–KF

The equation describing the molar enthalpy of mixing of the system NaF–KF was taken from [20]. The calculated phase diagram of NaF–KF system is shown in Fig. 1. Formation of solid solution of NaF in KF was taken into account. The calculated eutectic point of this binary system is 40 mol% NaF and 722.3°C, which is very close to that in [2].

The values of interaction coefficients H_i, S_i are given in Table 3. The standard deviation of the approximation is $\sigma(t_{calc}) = \pm 1.9°C$.

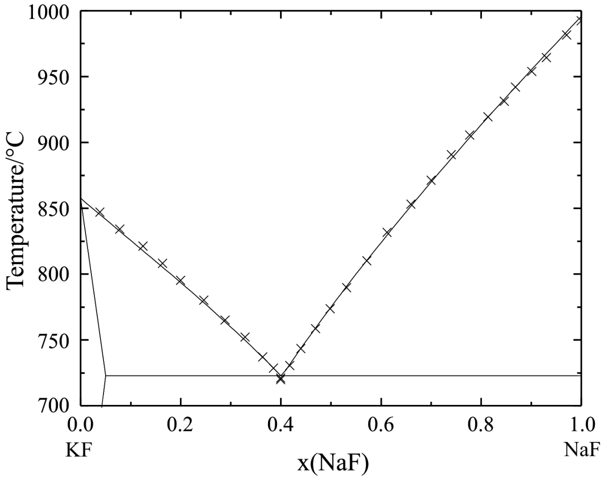

Fig. 1 Phase diagram of the system NaF–KF; crosses – Holm [2], full line – calculated

System NaF–AlF_3

The calculated activities of NaF, Na_3AlF_6 and $NaAlF_4$ and phase diagram of the system NaF–AlF_3 are shown in Figs 2 and 3, respectively. The calculated coordinates of the peritectic and eutectic points (P: 42 mol% AlF_3, 741.0°C; E_1: 13 mol% AlF_3, 892.1°C;

E_2: 45.5 mol% AlF_3, 699.9°C) are very close to those given in [9]. Liquidus curve of $Na_5Al_3F_4$ was calculated according to the thermodynamic data by Solheim and Sterten [9] and Bruno *et al*. [24].

Table 3 Coefficients H_i, S_i, G_i of Eqs (3) – (5) in the system NaF–KF–AlF_3

System	Coefficient	H_i, $S_i^{a)}$, G_i /J mol^{-1}	SD^a /J mol^{-1}
NaF–KF	$H_{1,1}$	–355 [18]	–
	$S_{1,1}$	–1.58	0.11
NaF–AlF_3	$H_{1,1}$	$-69\cdot10^3$	$1.3\cdot10^3$
	$H_{1,2}$	$-184\cdot10^3$	$11\cdot10^3$
	$H_{1,3}$	$883\cdot10^3$	$21\cdot10^3$
	$S_{1,1}$	109	4
	$S_{1,3}$	634	15
	$S_{1,4}$	196	8
KF–AlF_3	$H_{1,1}$	$-69\cdot10^3$	$1.9\cdot10^3$
	$H_{1,2}$	$-309\cdot10^3$	$15\cdot10^3$
	$H_{1,3}$	$885\cdot10^3$	$25\cdot10^3$
	$S_{1,1}$	156	11
	$S_{1,3}$	491	32
	$S_{1,4}$	544	11
NaF–KF–AlF_3	$G_{1,1,1}$	$-26.7\cdot10^3$	$3.9\cdot10^3$

[a] Unit for the S_i coefficient is J mol^{-1} K^{-1}

The values of interaction coefficients H_i and S_i are given in Table 3. The standard deviation of the approximation for molar enthalpy of mixing and phase diagram is $\sigma(\Delta_{mix}H) = \pm500$ J mol^{-1} and $\sigma(t_{calc}) = \pm3.8$°C, respectively.

System KF–AlF_3

The calculated activities of KF, K_3AlF_6 and $KAlF_4$ and phase diagram of the system KF–AlF_3 are shown in Figs 4 and 5, respectively. The calculated coordinates of the eutectic points are E_1: 8 mol% AlF_3, 821.2°C; E_2: 45.5 mol% AlF_3, 565.0°C. Temperature of fusion of K_3AlF_6 was measured as 996°C. The obtained values are closer to the data published by Phillips *et al*. [11] than data by Fedotieff and Timofeeff [10]. However, there is difference about 10°C for the temperature of fusion of pure K_3AlF_6 between value from this work and [11]. Because of better experimental technique for preparation of pure non-aqueous KF we assume that our data are more correct.

The values of interaction coefficients H_i and S_i are given in Table 3. The standard deviation of the approximation for molar enthalpy of mixing and phase diagram is $\sigma(\Delta_{mix}H) = \pm433$ J mol^{-1} and $\sigma(t_{calc}) = \pm7.6$°C, respectively.

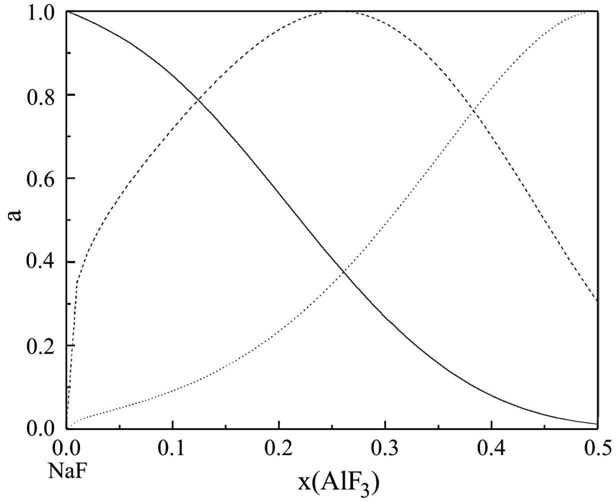

Fig. 2 Activities of NaF, Na_3AlF_6 and $NaAlF_4$ in the system NaF–AlF_3; full line – NaF, dashed line – Na_3AlF_6, dotted line – $NaAlF_4$

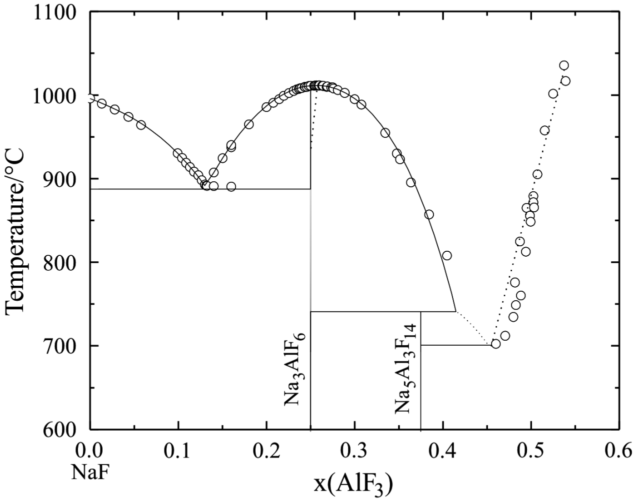

Fig. 3 Phase diagram of the system NaF–AlF_3; circles – Solheim and Sterten [9], full line – calculated

Comparison between experimental and calculated data in the system KF–AlF_3 is in Table 1.

System NaF–KF–AlF$_3$

The calculated phase diagram of NaF–KF–AlF_3 system up to 40 mol% AlF_3 is shown in Fig. 6. Four crystallization fields are presented in the calculated part of the phase

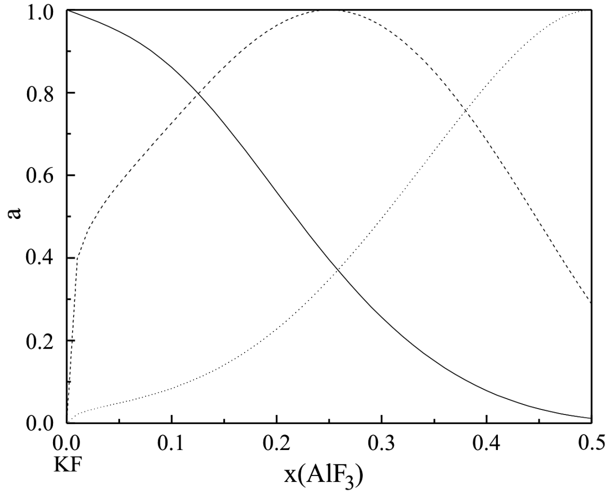

Fig. 4 Activities of KF, K_3AlF_6 and $KAlF_4$ in the system KF–AlF_3; full line – KF, dashed line – K_3AlF_6, dotted line – $KAlF_4$

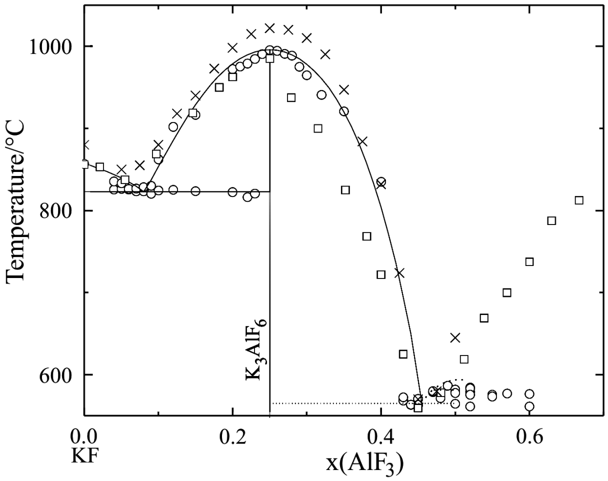

Fig. 5 Phase diagram of the system KF–AlF_3; circles – this work, squares – Phillips *et al*. [11], crosses – Fedotieff and Timofeeff [10], full line – calculated

diagram corresponding to the primary crystallization of NaF, KF, Na_3AlF_6 and K_3AlF_6. The calculated coordinates of the ternary eutectic points are E_1: 36.3 mol% NaF, 62.7 mol% KF, 1.0 mol% AlF_3; 711.2°C; and E_2: 51.9 mol% NaF, 27.4 mol% KF, 20.7 mol% AlF_3; 734.5°C. Other eutectic points lie most probably beyond the investigated part of the system.

Calculated phase diagram in the section of quasi-binary system Na_3AlF_6–K_3AlF_6 is in excellent agreement with previous published ones [14–16].

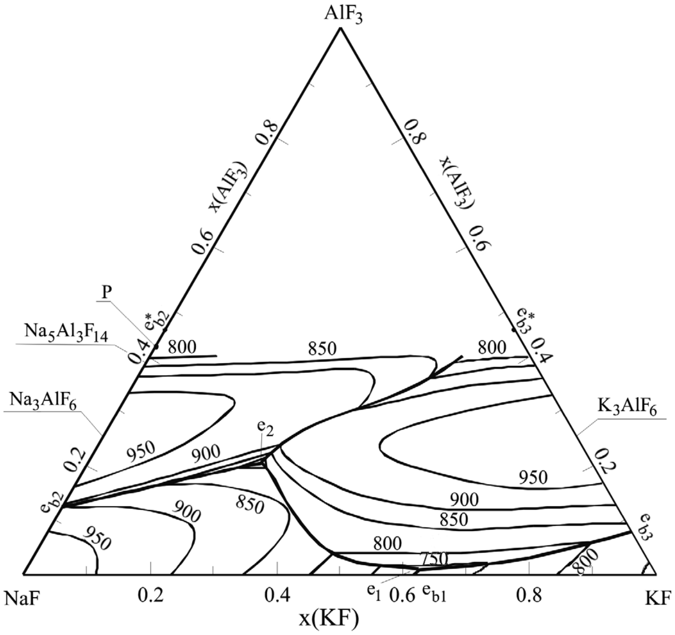

Fig. 6 Calculated phase diagram of the system NaF–KF–AlF$_3$

Comparison between experimental and calculated data in the system NaF–KF–AlF$_3$ is in Table 1. The values of interaction coefficients G_i are given in Table 3. The standard deviation of the approximation is $\sigma(t_{calc}) = \pm 9.0°C$.

From the thermodynamic point of view the expression of ΔG^E (Eq. (5)) is correct. Of course, the equation is valid only for the investigated concentration area and there is, unfortunately, no value for the activity, or the temperature of primary crystallization, of AlF$_3$ available. Thus the activity of AlF$_3$ cannot be calculated from this equation since it can lead to non-realistic values. In order to get a valid ΔG^E equation for the whole ternary system, measurements should be performed in a broader concentration area, *i.e.* where also AlF$_3$ is the primary crystallization phase.

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The present work was financially supported by the courtesy of the Slovak Grant Agency (VEGA 1/9406/02).

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