

## Phase diagram of the system $\text{KF-KBF}_4\text{-K}_2\text{TiF}_6$

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### Abstract

The phase diagrams of the binary system  $\text{KBF}_4\text{-K}_2\text{TiF}_6$  and of the ternary system  $\text{KF-KBF}_4\text{-K}_2\text{TiF}_6$  were determined using the thermal analysis method. The subsequent coupled analysis of the thermodynamic and phase diagram data was performed to obtain a thermodynamically consistent phase diagram. In the system  $\text{KF-KBF}_4\text{-K}_2\text{TiF}_6$ , the intermediate compound  $\text{K}_3\text{TiF}_7$  is formed. The  $\text{K}_3\text{TiF}_7\text{-KBF}_4$  joint divides the ternary system into two simple eutectic ones. The calculated coordinates of the two ternary eutectic points are:  $e_1$ : 26 mol% KF, 69 mol%  $\text{KBF}_4$ , 5 mol%  $\text{K}_2\text{TiF}_6$ ,  $t_{e1} = 448^\circ\text{C}$ ; and  $e_2$ : 4 mol% KF, 69 mol%  $\text{KBF}_4$ , 27 mol%  $\text{K}_2\text{TiF}_6$ ,  $t_{e2} = 440^\circ\text{C}$ .

The system  $\text{KBF}_4\text{-K}_2\text{TiF}_6$  is a simple eutectic one with the calculated coordinates of the eutectic point being 28 mol%  $\text{K}_2\text{TiF}_6$  and  $448^\circ\text{C}$ . The probable inaccuracy in the calculated ternary phase diagram is  $11.5^\circ\text{C}$ .

*Keywords:* Phase diagram; Thermodynamic analysis

### 1. Introduction

The system  $\text{KF-KBF}_4\text{-K}_2\text{TiF}_6$  is a part of the quaternary system  $\text{KF-KCl-KBF}_4\text{-K}_2\text{TiF}_6$ , which may be used as the electrolyte in the electrochemical synthesis of  $\text{TiB}_2$ , especially when coherent coatings on metallic bases have to be prepared [1]. From the theoretical point of view, this system belongs to the group of systems in which chemical reactions between components take place that affect the real composition and consequently the physico-chemical properties of the electrolyte.

According to Ref. [2], the phase diagram of the boundary system  $\text{KF-KBF}_4$  is a simple eutectic system with the eutectic point at 74.5 mol%  $\text{KBF}_4$  and  $460^\circ\text{C}$ .

The phase diagram of the system KF–K<sub>2</sub>TiF<sub>6</sub> [3] presents the compound K<sub>3</sub>TiF<sub>7</sub>, congruently melting at 775°C, which divides the system into two simple eutectic ones. According to Ref. [3], the coordinates of the respective eutectic points are: 75 mol% KF, 710°C and 30 mol% KF, 740°C. The zero value of the tangent of the K<sub>3</sub>TiF<sub>7</sub> liquidus curve at  $x_{\text{K}_2\text{TiF}_6} = 0.5$  indicates that, on melting, this compound undergoes a considerable thermal dissociation. On the basis of the experimentally determined phase diagram [3], the dissociation degree was calculated [4] as  $\alpha_0 = 0.64$ , in very good agreement with the value obtained on the basis of the density data,  $\alpha_0(727^\circ\text{C}) = 0.6$ ,  $\alpha_0(827^\circ\text{C}) = 0.7$  [4].

In the present work, the phase diagrams of the binary system KBF<sub>4</sub>–K<sub>2</sub>TiF<sub>6</sub> and of the ternary system KF–KBF<sub>4</sub>–K<sub>2</sub>TiF<sub>6</sub> were determined using the thermal analysis method and the subsequent coupled analysis of the thermodynamic and phase diagram data.

## 2. Experimental

The temperatures of individual phase transitions (primary and secondary crystallisation, and the eutectic temperature) were determined from measurements of the cooling and heating curves of the investigated mixtures at a rate of 2–5°C min<sup>-1</sup>. The samples (approx. 40 g) were placed in a platinum crucible in a resistance furnace with an adjustable cooling rate. The temperature control and the data processing were performed using a computerised measuring device. The temperature was measured using a Pt–PtRh10 thermocouple calibrated to the melting points of NaCl, KCl and Na<sub>2</sub>SO<sub>4</sub>. The hot end of the thermocouple was immersed directly in the melt. The measured temperatures of the phase transitions were reproducible in the range of ±5°C.

For the preparation of samples, the following chemicals were used: KF (Lachema), and KBF<sub>4</sub> and K<sub>2</sub>TiF<sub>6</sub> (Fluka), all analytical grade. KF was dried in vacuum at 130°C in the presence of P<sub>4</sub>O<sub>10</sub> for two weeks; KBF<sub>4</sub> and K<sub>2</sub>TiF<sub>6</sub> were dried at 400°C for 2 h.

The phase transition temperatures in the ternary system KF–KBF<sub>4</sub>–K<sub>2</sub>TiF<sub>6</sub> were measured in different cross-sections with constant mole fraction of one component. The samples with high K<sub>2</sub>TiF<sub>6</sub> content showed a tendency to undercooling. Careful adjustment of the cooling rate and registration of the heating curve were used in such cases. The measured transition temperatures of the samples are given in Table 1.

## 3. Data processing

The calculation of the phase diagrams of 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 type

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

where  $\Delta_{fus}G_i^o(T)$  is the standard molar Gibbs energy of fusion of the component  $i$  at the temperature  $T$ ,  $R$  is the gas constant and  $a_{s,i}(T)$  and  $a_{l,i}(T)$  are the activities of component  $i$  in the solid and liquid phase, respectively. Assuming immiscibility of components  $i$  in the solid phase ( $a_{s,i}=1$ ) and that the enthalpy of fusion of the components does not change with temperature, for the thermodynamic temperature of primary crystallisation of the component  $i$ ,  $T_{pc,i}$ , we get

$$T_{pc,i} = \frac{\Delta_{fus}H_i^o + RT_{pc,i} \ln \gamma_{l,i}}{\Delta_{fus}S_i^o - R \ln x_{l,i}} \quad (2)$$

where  $\Delta_{fus}H_i^o$  and  $\Delta_{fus}S_i^o$  are the standard enthalpy and standard entropy of fusion, respectively,  $x_{l,i}$  and  $\gamma_{l,i}$  are the mole fraction and the activity coefficient of component  $i$ , respectively. The activity coefficients can be calculated from the molar excess Gibbs energy of mixing

$$RT_{pc,i} \ln \gamma_{l,i} = \left[ \frac{dn \Delta G_l^E}{dn_i} \right]_{T,p,n_{j \neq i}} \quad (3)$$

where  $n_i$  is the number of moles of component  $i$  and  $n$  is the total number of moles of all components.

In the ternary system A–B–C, the molar excess Gibbs energy of mixing in the liquid phase,  $\Delta G_l^E$  can be described by the following general equation

$$\Delta G_l^E = \sum_j (x_A^{k(j)} x_B^{l(j)} x_C^{m(j)}) G_j \quad (4)$$

where  $x_i$  are the mole fractions of components,  $G_j$  are empirical coefficients in the composition dependence of the molar excess Gibbs energy of mixing and  $k(j)$ ,  $l(j)$ ,  $m(j)$  are adjustable integers.

Using Eq. (2), the following mathematical model for the coupled thermodynamic analysis can be used

$$T_{pc,i} = F_{o,i} + \sum_j F_{j,i} G_j \quad (5)$$

where  $T_{pc,i}$  is obtained from the phase diagram measurement. The first term on the right side represents the ideal behaviour and the second term the deviation from ideal behaviour. For the auxiliary functions  $F_{o,i}$  and  $F_{j,i}$  with respect to the Gibbs–Duhem relation, the following equations hold

$$F_{o,i} = \frac{\Delta_{fus}H_i^o}{\Delta_{fus}S_i^o - R \ln x_{l,i}} \quad (6)$$

$$F_{j,i} = \frac{\left[ \frac{dn x_A^{k(j)} x_B^{l(j)} x_C^{m(j)}}{dn_i} \right]_{n_{j \neq i}}}{\Delta_{fus}S_i^o - R \ln x_{l,i}} \quad (7)$$

Table 1

Measured ( $t_{pc,e}$ ) and calculated ( $t_{pc,c}$ ) temperatures of primary crystallisation, and their difference ( $\Delta t_{pc}$ ), temperatures of secondary crystallisation ( $t_{sc}$ ) and the eutectic temperatures ( $t_e$ ) of the system KF–KBF<sub>4</sub>–K<sub>2</sub>TiF<sub>6</sub>.

$x_{KF}$	$x_{KBF_4}$	$x_{K_2TiF_6}$	$t_{pc,e}/^{\circ}C$	$t_{pc,c}/^{\circ}C$	$\Delta t_{pc}/^{\circ}C$	$t_{sc}/^{\circ}C$	$t_e/^{\circ}C$
System KF–KBF <sub>4</sub> [2]							
1.00	0.00		858	858.0	0.0		
0.90	0.10		828	824.2	–3.8		
0.75	0.25		778	776.8	–1.2		
0.67	0.33		745	743.2	–1.8		
0.60	0.40		715	711.3	–3.7		
0.50	0.50		654	651.8	–2.2		
0.40	0.60		589	578.9	–10.1		
0.30	0.70		505	493.6	–11.4		
0.20	0.80		489	491.1	2.1		
0.15	0.85		512	513.4	1.4		
0.10	0.90		534	533.9	–0.1		
0.05	0.95		551	552.7	1.7		
0.00	1.00		570	570.0	0.0		
System KF–K <sub>2</sub> TiF <sub>6</sub> [3]							
1.00		0.00	858	858.0	0.0		
0.909		0.091	823	819.9	–3.1		
0.851		0.149	800	790.1	–9.9		
0.791		0.209	771	752.3	–18.7		
0.750		0.250	712	721.9	10.1		
0.694		0.306	724	719.3	–4.7		
0.645		0.355	743	743.8	0.8		
0.572		0.428	769	767.5	–1.5		
0.500		0.500	775	775.0	0.0		
0.452		0.548	768	771.8	3.8		
0.409		0.591	762	764.1	2.1		
0.365		0.635	756	752.4	–3.6		
0.262		0.738	799	783.8	–15.2		
0.223		0.777	820	807.0	–13.0		
0.108		0.892	863	855.4	–7.6		
0.000		1.000	899	899.0	0.0		
System KBF <sub>4</sub> –K <sub>2</sub> TiF <sub>6</sub>							
	1.00	0.00	570	570.0	0.0		–
	0.90	0.10	523	533.5	10.5		455
	0.80	0.20	489	489.1	0.1		455
	0.75	0.25	467	463.8	–3.2		455
	0.70	0.30	462	470.4	8.4		455
	0.60	0.40	570	577.7	7.7		456
	0.50	0.50	671	668.8	–2.2		455
	0.40	0.60	753	740.3	–12.7		456
	0.30	0.70	785	791.8	6.9		455
	0.20	0.80	833	827.7	–5.3		455
	0.10	0.90	857	857.8	0.8		455
	0.00	1.00	899	899.0	0.0		–

Table 1 (Continued)

$x_{KF}$	$x_{KBF_4}$	$x_{K_2TiF_6}$	$t_{pc,e}/^{\circ}C$	$t_{pc,c}/^{\circ}C$	$\Delta t_{pc}/^{\circ}C$	$t_{sc}/^{\circ}C$	$t_e/^{\circ}C$
System KF–KBF <sub>4</sub> –K <sub>2</sub> TiF <sub>6</sub>							
1.00	0.00	0.00	858	858.0	0.0	–	–
0.80	0.10	0.10	772	779.3	7.3	650	441
0.70	0.10	0.20	697	713.3	16.3	677	441
0.60	0.10	0.30	711	702.6	–8.4	678	440
0.50	0.10	0.40	733	737.7	4.7	620	441
0.40	0.10	0.50	736	739.4	3.4	650	443
0.30	0.10	0.60	727	711.9	–15.1	667	443
0.20	0.10	0.70	750	773.3	23.3	667	443
0.10	0.10	0.80	830	824.8	–5.2	649	441
0.70	0.20	0.10	737	738.6	1.7	618	441
0.60	0.20	0.20	676	660.0	–16.0	–	441
0.50	0.20	0.30	705	687.7	–17.3	620	441
0.40	0.20	0.40	713	708.7	–4.3	–	441
0.30	0.20	0.50	707	694.2	–12.8	635	441
0.20	0.20	0.60	684	711.2	27.2	647	442
0.10	0.20	0.70	788	784.6	–3.4	602	442
0.50	0.40	0.10	618	627.0	9.0	576	442
0.40	0.40	0.20	612	607.9	–4.1	540	442
0.30	0.40	0.30	621	633.7	12.7	469	–
0.20	0.40	0.40	597	616.6	19.6	540	441
0.10	0.40	0.50	658	652.0	–6.0	520	441
0.40	0.50	0.10	526	553.3	27.3	–	442
0.10	0.50	0.40	575	557.2	–17.8	480	442
0.30	0.60	0.10	520	508.0	–12.0	478	440
0.20	0.60	0.20	532	543.3	11.3	472	–
0.10	0.60	0.30	541	516.2	–24.8	–	442
0.20	0.70	0.10	465	476.7	11.7	–	441
0.10	0.70	0.20	472	480.3	8.3	460	440
0.10	0.80	0.10	512	500.7	–11.3	469	–

If an intermediate compound  $Z = A_p B_q C_r$  ( $p+q+r < 1$ ) is formed in the ternary system, Eqs. (4), (6) and (7) for this compound must be modified [5,6]

$$\Delta G_l^E = \sum_j (x_A^{k(j)} x_B^{l(j)} x_C^{m(j)} - p^{k(j)} q^{l(j)} r^{m(j)}) G_j \quad (8)$$

$$F_{o,Z} = \frac{\Delta_{fus} H_Z^o}{\Delta_{fus} S_Z^o - R \ln K x_A^p x_B^q x_C^r} \quad (9)$$

$$F_{j,Z} = \frac{p \left[ \frac{dG'}{dn_A} \right]_{n_B, n_C} + q \left[ \frac{dG'}{dn_B} \right]_{n_A, n_C} + r \left[ \frac{dG'}{dn_C} \right]_{n_A, n_B}}{\Delta_{fus} S_Z^o - R \ln K x_A^p x_B^q x_C^r} \quad (10)$$

where

$$K = (p^{k(j)} q^{l(j)} r^{m(j)})^{-1} \quad (11)$$

and

$$G' = n(x_A^{k(j)} x_B^{l(j)} x_C^{m(j)} - p^{k(j)} q^{l(j)} r^{m(j)}) \quad (12)$$

Two different procedures can be used for the calculation of the molar excess Gibbs energy of mixing of a three-component system:

A. In the first step the molar excess Gibbs energy of mixing is calculated separately for the individual binary boundary systems using the binary phase diagram data

$$\Delta G_{bin}^E = \sum_j x_1 x_2^j G_j \quad (13)$$

In the second step the resulting coefficients  $G_j$  are used for the calculation of the molar excess Gibbs energy of mixing in the ternary system using the ternary phase diagram data only

$$\Delta G_{ter}^E = \sum_{i=1}^3 \Delta G_{bin,i}^E + \sum_j (x_A^{k(j)} x_B^{l(j)} x_C^{m(j)}) G_j \quad (14)$$

In this case for the auxiliary functions  $F_{o,i}$ , it holds that

$$F'_{o,i} = \frac{\Delta_{fus} H_i^o + \left[ \frac{dn \sum \Delta G_{bin,j}^E}{dn_i} \right]_{n_j \neq i}}{\Delta_{fus} S_i^o - R \ln x_{i,i}} \quad (15)$$

The other relations remain unchanged.

B. The calculation of the molar excess Gibbs energy of mixing is performed in one step using Eq. (4). Then, for the binary systems, one of the integers  $k, l, m$  equals zero.

In the calculation of the phase diagrams of ternary systems using the coupled analysis of thermodynamic and phase diagram data, the former approach is frequently used [5, 6]. However, when it is applied to ternary systems in which there are considerable differences in the deviation of the binary systems from ideal behaviour (so-called unsymmetrical systems), this approach describes the binaries well, but does not yield a reliable ternary diagram. For such cases the latter approach is more convenient. In the present work, both ways of calculation were used for comparison.

#### 4. Results and discussion

The coupled thermodynamic analysis, i.e. the calculation of the coefficients  $G_j$  in Eqs. (4) and (8), has been performed using the multiple linear regression analysis omitting the statistically non-important terms on the given confidence level according to the Student test. As the optimising criterion for the best fit between the experimental and calculated temperatures of primary crystallisation, the following condition was used for all  $n$  measured points

$$\sum_n (T_{pc,exp,n} - T_{pc,calc,n})^2 = \min \quad (16)$$

The values of the enthalpy of fusion of individual components were taken from the literature and are summarised in Table 2. The experimentally determined temperatures

Table 2

Temperatures and enthalpies of fusion of compounds in the system  $\text{KF-KBF}_4\text{-K}_2\text{TiF}_6$  used for the phase diagram calculation

Compound	$\Delta_{fus}H^\circ/\text{kJ mol}^{-1}$	$T_{fus}/\text{K}$	Ref.
KF	27.196	1131	[7]
$\text{KBF}_4$	17.656	843	[7]
$\text{K}_2\text{TiF}_6$	21.000	1172	[8]
$\text{K}_3\text{TiF}_7$	57.000	1048	[9]

of primary crystallisation for the system  $\text{KF-KBF}_4$  were taken from Ref. [2] and those for the system  $\text{KF-K}_2\text{TiF}_6$  from Ref. [3]. In addition to condition (16), for the calculation of the molar excess Gibbs energy of mixing the minimum necessary  $G_j$  coefficients for attaining a thermodynamically consistent phase diagram and a reasonable standard deviation of approximation were required.

The phase diagram of the system  $\text{KF-KBF}_4\text{-K}_2\text{TiF}_6$  calculated using the approach B is shown in Fig. 1. Four crystallisation fields are present in the phase diagram corresponding to the primary crystallisation of KF,  $\text{KBF}_4$ ,  $\text{K}_2\text{TiF}_6$  and the intermediate compound  $\text{K}_3\text{TiF}_7$ . The calculated coordinates of the two ternary eutectic points are:  $e_1$ : 26 mol% KF, 69 mol%  $\text{KBF}_4$ , 5 mol%  $\text{K}_2\text{TiF}_6$ ,  $t_{e1} = 448^\circ\text{C}$ ,  $e_2$ : 4 mol% KF, 69 mol%  $\text{KBF}_4$ , 27 mol%  $\text{K}_2\text{TiF}_6$ ,  $t_{e2} = 440^\circ\text{C}$ .

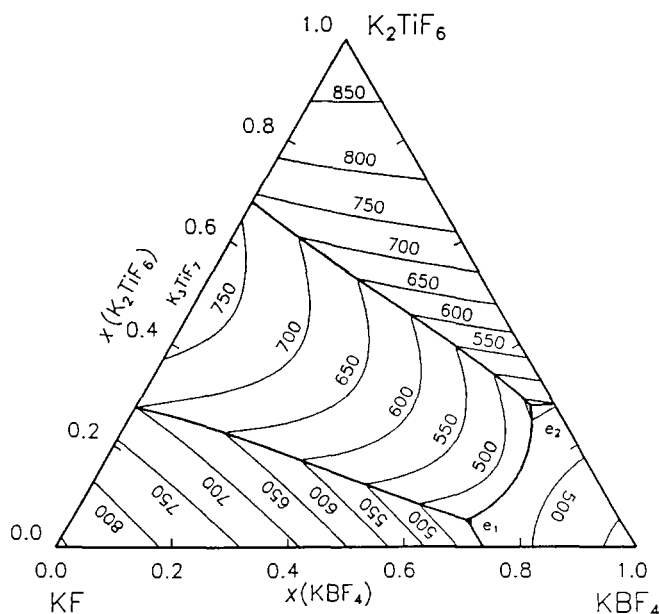


Fig. 1. Optimalised phase diagram of the system  $\text{KF-KBF}_4\text{-K}_2\text{TiF}_6$ . Isotherm values in  $^\circ\text{C}$ .

The deviations of the experimental temperatures of primary crystallisation from the calculated ones are listed in Table 1. The probable inaccuracy in the calculated ternary phase diagram is  $\pm 11.5^\circ\text{C}$ .

For the molar excess Gibbs energy of mixing, the following equation was obtained

$$\Delta G_{\text{ter}}^E = x_1x_2(G_{12,1} + G_{12,2}x_2 + G_{12,3}x_2^2) + x_1x_3(G_{13,1} + G_{13,2}x_3 + G_{13,3}x_3^2) + x_2x_3(G_{23,1} + G_{23,2}x_3^2) + G_{123}x_1^2x_2x_3 \quad (17)$$

The first term represents the molar excess Gibbs energy of mixing in the binary system KF–KBF<sub>4</sub>, the second the molar excess Gibbs energy of mixing in the binary system KF–K<sub>2</sub>TiF<sub>6</sub> and the third in the binary system KBF<sub>4</sub>–K<sub>2</sub>TiF<sub>6</sub>. The last term represents the interaction contribution in the ternary system. The coefficients  $G_{ijk}$  are given in Table 3. The molar excess Gibbs energy of mixing in the ternary system KF–KBF<sub>4</sub>–K<sub>2</sub>TiF<sub>6</sub> is shown in Fig. 2.

The calculation of the phase diagram of the system KF–KBF<sub>4</sub>–K<sub>2</sub>TiF<sub>6</sub> was also performed using procedure A. The corresponding coefficients  $G_j$  together with the standard deviation in the temperatures of primary crystallisation are given in Table 4. For the ternary interaction term the integers in Eq. (14), as in the B approach (Eq. (17)), were  $k=2$  and  $l=m=1$ . It may be seen that even when the standard deviation is low in the individual binary systems, it is substantially higher for the ternary diagram compared with procedure B.

The phase diagram of the boundary system KF–KBF<sub>4</sub> is shown in Fig. 3. The third-order polynomial was obtained for the concentration dependence of the molar excess Gibbs energy of mixing in this system. A third-order polynomial for this quantity was also obtained using approach A (see Table 4); however, the standard deviation of the approximation is substantially lower.

The calculated coordinates of the eutectic point 74 mol% KBF<sub>4</sub> and 460°C, agree well with those given in Ref. [2]. The significant inflex course of the liquidus curve of KF in the region of low KBF<sub>4</sub> concentration is most probably due to the decreasing

Table 3

Coefficients of the concentration dependence of the molar excess Gibbs energy of mixing and the standard deviation of the temperature of primary crystallisation of the ternary system calculated according to the B approach

Coefficient	$\{G_{ijk}\} \pm \{\text{SD in coefficient}\}$
$G_{12,1}/(\text{J mol}^{-1})$	$3569 \pm 1164$
$G_{12,2}/(\text{J mol}^{-1})$	$-15930 \pm 3979$
$G_{12,3}/(\text{J mol}^{-1})$	$8347 \pm 4009$
$G_{13,1}/(\text{J mol}^{-1})$	$-13319 \pm 1758$
$G_{13,2}/(\text{J mol}^{-1})$	$-14859 \pm 5447$
$G_{13,3}/(\text{J mol}^{-1})$	$26989 \pm 5113$
$G_{23,1}/(\text{J mol}^{-1})$	$-3688 \pm 689$
$G_{23,2}/(\text{J mol}^{-1})$	$-11864 \pm 1205$
$G_{123}/(\text{J mol}^{-1})$	$-26897 \pm 8839$
SD in $t_{\text{pc}}/^\circ\text{C}$	11.5



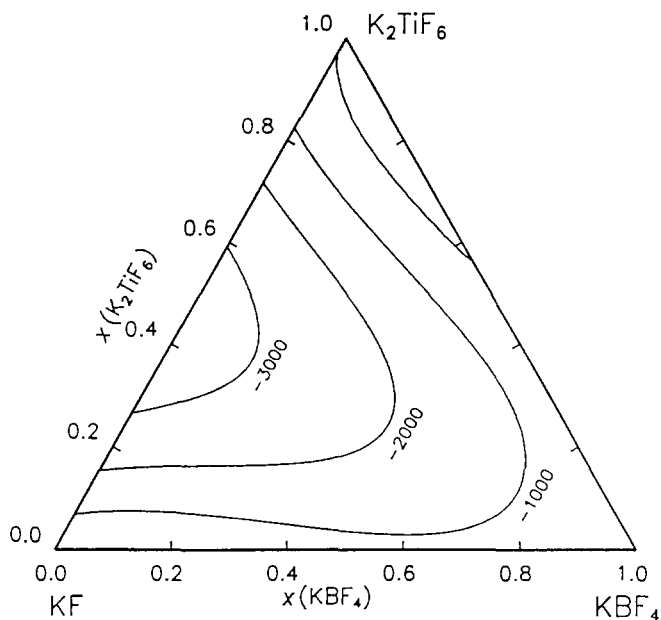


Fig. 2. Molar excess Gibbs energy of mixing ( $\text{J mol}^{-1}$ ) of the system  $\text{KF-KBF}_4\text{-K}_2\text{TiF}_6$ .

Table 4

Coefficients of the concentration dependence of the molar excess Gibbs energy of mixing and the standard deviation of the temperature of primary crystallisation of the binary and ternary systems calculated according to the A approach

System	$G_1/(\text{J mol}^{-1})$	$G_2/(\text{J mol}^{-1})$	$G_3/(\text{J mol}^{-1})$	SD in $t_{pc}/^\circ\text{C}$
$\text{KF-KBF}_4$	$3836 \pm 233$	$-14434 \pm 790$	$6625 \pm 833$	1.9
$\text{KF-K}_2\text{TiF}_6$	$-11507 \pm 1743$	$-19918 \pm 6050$	$33344 \pm 5830$	6.5
$\text{KBF}_4\text{-K}_2\text{TiF}_6$	$-4430 \pm 425$	-	$12905 \pm 713$	6.1
$\text{KF-KBF}_4\text{-K}_2\text{TiF}_6$	$-25220 \pm 7880$	-	-	16.1

stability of  $\text{KBF}_4$  with increasing temperature. At higher temperatures  $\text{KBF}_4$  probably decomposes partly at the formation of gaseous  $\text{BF}_3$ .

The phase diagram of the boundary system  $\text{KF-K}_2\text{TiF}_6$  is shown in Fig. 4. The third-order polynomial for the molar excess Gibbs energy of mixing was obtained regardless of the calculation approach used. However, as in the previous case, the standard deviation of approximation is lower for approach A (see Tables 3 and 4). The coordinates of both eutectic points ( $e_1$ : 28 mol%  $\text{K}_2\text{TiF}_6$ ,  $701^\circ\text{C}$  and  $e_2$ : 68 mol%  $\text{K}_2\text{TiF}_6$ ,  $738^\circ\text{C}$ ) differ from those given in Ref. [3], probably due to the appreciable inaccuracy in the determination of the liquidus temperature in Ref. [3].

Similar results, as in the previous cases, were also obtained for the boundary system  $\text{KBF}_4\text{-K}_2\text{TiF}_6$ . The phase diagram is shown in Fig. 5. The system  $\text{KBF}_4\text{-K}_2\text{TiF}_6$  is

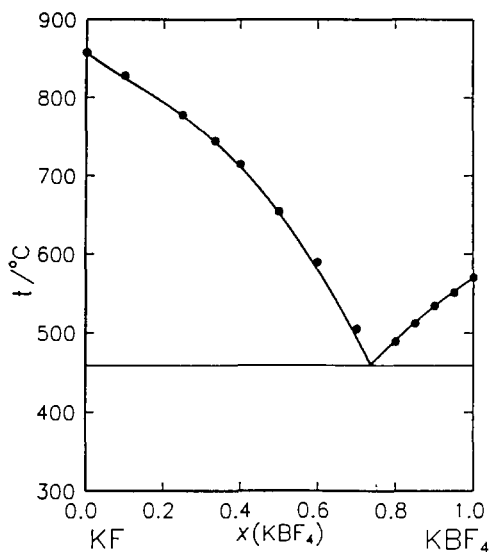


Fig. 3. Phase diagram of the system KF–KBF<sub>4</sub>. Solid circles, Ref. [2]; solid line, calculated.

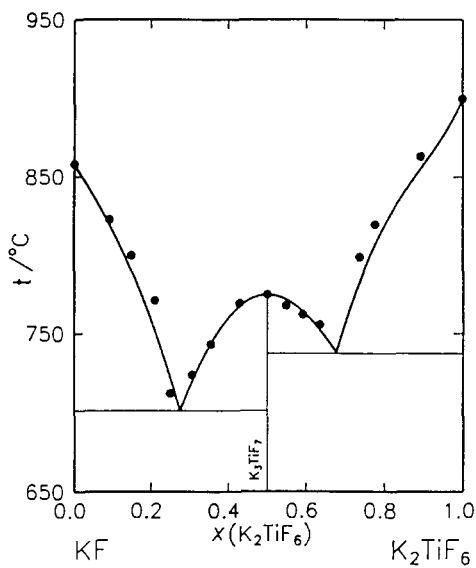


Fig. 4. Phase diagram of the system KF–K<sub>2</sub>TiF<sub>6</sub>. Solid circles, Ref. [3]; solid line, calculated.

a simple eutectic one with the coordinates of the eutectic point being 28 mol% K<sub>2</sub>TiF<sub>6</sub> and 448°C. As in the system KF–KBF<sub>4</sub>, the significant inflex course of the K<sub>2</sub>TiF<sub>6</sub> liquidus curve is most probably due to the partial decomposition of KBF<sub>4</sub> and escape of gaseous BF<sub>3</sub>.

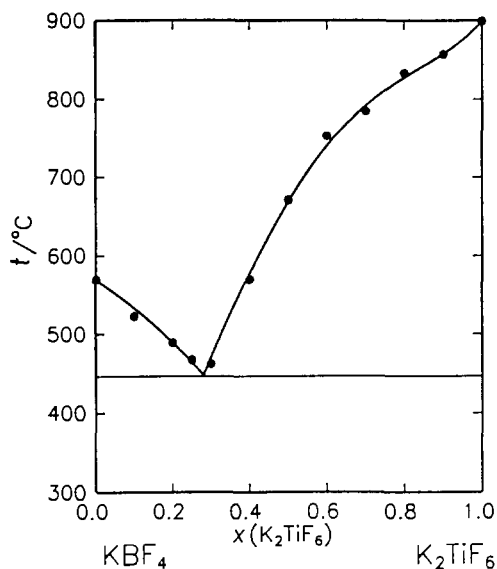


Fig. 5. Phase diagram of the system  $\text{KBF}_4\text{-K}_2\text{TiF}_6$ . Solid circles, experimental; solid line, calculated.

The coefficients of the molar excess Gibbs energy of mixing and the standard deviations of the approximations for both calculation procedures are given in Tables 3 and 4, respectively.

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