Phase Diagram of the System KCl—KBF$_4$—K$_2$TiF$_6$

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The phase diagram of the ternary system KF—KBF$_4$—K$_2$TiF$_6$ was determined using the thermal analysis method. The subsequent coupled analysis of the thermodynamic and phase equilibrium data was performed to obtain thermodynamically consistent phase diagram. In the system KCl—KBF$_4$—K$_2$TiF$_6$ the intermediate compound K$_3$TiF$_6$Cl is formed. The K$_3$TiF$_6$Cl—KBF$_4$ joint divides the ternary system into two simple eutectic systems. The calculated coordinates of the two ternary eutectic points are as follows:

e$_1$: 24.1 mole % KCl, 62.1 mole % KBF$_4$,
13.8 mole % K$_2$TiF$_6$, $\theta_{e_1} = 447.1$ °C
e$_2$: 6.5 mole % KCl, 62.5 mole % KBF$_4$,
31.0 mole % K$_2$TiF$_6$, $\theta_{e_2} = 414.5$ °C

The standard deviation of the temperature of primary crystallization in the calculated ternary phase diagram is ±17.1 °C.

The system KCl—KBF$_4$—K$_2$TiF$_6$ is a part of the quaternary system KF—KCl—KBF$_4$—K$_2$TiF$_6$, which may be used as electrolyte in the electrochemical synthesis of 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 affecting the real composition and consequently the physicochemical properties of the electrolyte.

Only the phase diagrams of the boundary binary systems have been measured till now. The phase diagram of the system KCl—KBF$_4$ was studied in [2]. The authors of this work found out that it is a simple eutectic system with the coordinates of the eutectic point 75 mole % KBF$_4$ and 464 °C.

The phase diagram of the system KCl—K$_2$TiF$_6$ was studied in [3]. The congruently melting compound K$_3$TiF$_6$Cl with the melting temperature of 691 °C, formed in this system, divides the above system into two simple eutectic systems. The coordinates of the respective eutectic points are: 30.7 mole % K$_2$TiF$_6$, 652 °C and 64.8 mole % K$_2$TiF$_6$, 670 °C. The zero value of the tangent of the K$_3$TiF$_6$Cl liquidus curve at x(K$_3$TiF$_6$Cl) = 0.5 indicates that this compound undergoes at melting a considerable thermal dissociation. The dissociation degree calculated on the basis of the experimentally determined phase diagram is α = 0.78, which is in a very good accordance with the value obtained on the basis of the density data, α_0(727 °C) = 0.71, α_0(827 °C) = 0.81 [4].

The phase diagram of the system KBF$_4$—K$_2$TiF$_6$ was measured in [5]. The authors found that it is a simple eutectic system with the coordinates of the eutectic point 28 mole % K$_2$TiF$_6$ and 448 °C.

In the present work the phase diagram of the ternary system KCl—KBF$_4$—K$_2$TiF$_6$ was determined using the thermal analysis method and the subsequent coupled thermodynamic analysis and the analysis of equilibrium diagram data.

EXPERIMENTAL

The temperatures of individual phase transitions (primary and secondary crystallization and the eutectic temperature) were determined by means of the thermal analysis, registrating the cooling and heating curves of the investigated mixtures at a rate of 2—5 °C min^{-1}. The samples (ca. 40 g) were placed in a platinum crucible in the resistance furnace with 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 NaCl, KCl, and Na$_2$SO$_4$. The hot end of the thermocouple was immersed directly in the melt. The measured temperatures of phase transitions were reproducible in the range of ±10 °C.

For the preparation of samples, KCl (Lachema), KBF$_4$ and K$_2$TiF$_6$ (both Fluka), all anal. grade, were used. All chemicals were dried at 400 °C for 2 h.

The phase transition temperatures in the ternary system KCl—KBF$_4$—K$_2$TiF$_6$ were measured in different cross-sections with constant mole fraction of one component. The samples with high K$_2$TiF$_6$ content showed tendency to undercooling. Careful adjusting of

Table 1. Measured ($\theta_{pc,e}$) and Calculated ($\theta_{pc,c}$) Temperatures of Primary Crystallization, their Difference ($\Delta\theta_{pc}$), Temperatures of Secondary Crystallization (θ_{sc}) and the Eutectic Temperatures (θ_e) of the Melts of the System $KCl—KBF_4—K_2TiF_6$

Composition			$\dfrac{\theta_{pc,e}}{°C}$	$\dfrac{\theta_{pc,c}}{°C}$	$\dfrac{\Delta\theta_{pc}}{°C}$	$\dfrac{\theta_{sc}}{°C}$	$\dfrac{\theta_e}{°C}$
x_{KCl}	x_{KBF_4}	$x_{K_2TiF_6}$					
System $KCl—KBF_4$ [2]							
1.00	0.00	0.00	772	772.0	0.0		
0.70	0.30	0.00	667	666.9	−0.1		
0.60	0.40	0.00	629	629.9	0.9		
0.40	0.60	0.00	542	547.4	5.4		
0.30	0.70	0.00	491	497.9	6.9		
0.20	0.80	0.00	490	504.5	14.5		
0.10	0.90	0.00	519	537.0	18.0		
0.00	1.00	0.00	570	570.0	0.0		
System $KCl—K_2TiF_6$ [3]							
1.000	0.000	0.000	772	772.0	0.0		
0.967	0.000	0.033	748	760.4	12.4		
0.928	0.000	0.072	736	747.0	11.0		
0.883	0.000	0.117	725	730.8	5.8		
0.828	0.000	0.172	698	710.2	12.2		
0.763	0.000	0.237	657	682.6	25.6		
0.682	0.000	0.318	682	661.9	−20.1		
0.580	0.000	0.420	687	689.0	2.0		
0.518	0.000	0.482	697	695.6	−1.4		
0.500	0.000	0.500	696	696.0	0.0		
0.446	0.000	0.554	694	692.5	−1.5		
0.362	0.000	0.638	684	671.8	−12.2		
0.264	0.000	0.737	684	679.7	−4.3		
0.000	0.000	1.000	899	899.0	0.0		
System $KBF_4—K_2TiF_6$ [5]							
0.00	1.00	0.00	570	570.0	0.0		
0.00	0.90	0.10	523	532.3	9.3		
0.00	0.80	0.20	489	483.7	−5.3		
0.00	0.75	0.25	467	455.4	−11.6		
0.00	0.70	0.30	462	439.3	−22.7		
0.00	0.60	0.40	570	559.6	−10.4		
0.00	0.50	0.50	671	661.9	−9.1		
0.00	0.40	0.60	753	741.2	−11.8		
0.00	0.30	0.70	785	796.3	11.3		
0.00	0.20	0.80	833	831.9	−1.1		
0.00	0.10	0.90	857	859.5	2.5		
0.00	0.00	1.00	899	899.0	0.0		
System $KCl—KBF_4—K_2TiF_6$							
0.80	0.10	0.10	708	702.3	−5.7	613	438
0.70	0.10	0.20	676	663.0	−13.0	620	
0.60	0.10	0.30	648	630.7	−17.3	629	−
0.50	0.10	0.40	662	656.8	−5.2	577	
0.40	0.10	0.50	667	657.4	−9.6		432
0.20	0.10	0.70	736	694.3	−41.7	620	437
0.10	0.10	0.80	806	792.2	−13.8	600	436
0.70	0.20	0.10	678	666.0	−12.0	587	449
0.60	0.20	0.20	644	623.0	−21.0	590	432
0.50	0.20	0.30	612	605.6	−6.4	590	
0.40	0.20	0.40	628	623.3	−4.7		460
0.30	0.20	0.50	622	606.8	−15.2	515	432
0.20	0.20	0.60	630	628.3	−1.7		430
0.10	0.20	0.70	770	745.7	−24.3	560	432
0.50	0.40	0.10	580	586.3	6.3	482	445
0.40	0.40	0.20	535	527.4	−7.6	535	444
0.30	0.40	0.30	568	547.8	−20.2		444
0.20	0.40	0.40	552	531.0	−21.0		433
0.10	0.40	0.50	550	598.2	48.2	527	433
0.10	0.50	0.40	457	496.5	39.5	432	
0.30	0.60	0.10	476	488.5	12.5		449
0.20	0.60	0.20	456	469.8	13.8		450
0.10	0.60	0.30	465	447.9	−17.1		439
0.20	0.70	0.10	450	472.3	22.3		443
0.10	0.70	0.20	455	463.0	8.0	447	433
0.10	0.80	0.10	496	502.9	6.9	450	

the cooling rate and registration of the heating curve were used in such cases. The measured phase transition temperatures of the investigated samples are given in Table 1.

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 the set of equations of the following type

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

where $\Delta_{\text{fus}}G_i^0(T)$ 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 the immiscibility of components in the solid phase ($a_{s,i} = 1$) and that the enthalpy of fusion of the components does not change with temperature, for the temperature of primary crystallization of the component i, $T_{\text{pc},i}$, we get

$$T_{\text{pc},i} = \frac{\Delta_{\text{fus}}H_i^0 + RT \ln \gamma_{l,i}}{\Delta_{\text{fus}}S_i^0 - R \ln x_{l,i}} \qquad (2)$$

where $\Delta_{\text{fus}}H_i^0$ and $\Delta_{\text{fus}}S_i^0$ is the standard enthalpy and standard entropy of fusion, respectively, $x_{l,i}$ and $\gamma_{l,i}$ is the mole fraction and the activity coefficient of the component i, respectively. The activity coefficient can be calculated from the molar excess Gibbs energy of mixing

$$RT_{\text{pc},i} \ln \gamma_{l,i} = \left(\frac{\partial n \Delta G_l^E}{\partial n_i} \right)_{T,p,n_{j \neq i}} \qquad (3)$$

where n_i is the amount of substance of component i and n is the total amount of substance of all components.

In the ternary system A—B—C the molar excess Gibbs energy of mixing in the liquid phase, ΔG_l^E, can be described by the following general equation

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

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 eqn (2), the following mathematical model for the coupled thermodynamic analysis can be used

$$T_{\text{pc},i} = F_{0,i} + \sum_j F_{j,i} G_j \qquad (5)$$

where $T_{\text{pc},i}$ is obtained from the phase equilibrium measurement. The first term on the right side represents the ideal behaviour and the second one the

deviation from the ideal behaviour. For the auxiliary functions $F_{0,i}$ and $F_{j,i}$, with respect to the Gibbs—Duhem relation, the following equations hold

$$F_{0,i} = \frac{\Delta_{\text{fus}}H_i^0}{\Delta_{\text{fus}}S_i^0 - R \ln x_{l,i}} \qquad (6)$$

$$F_{j,i} = \frac{\left(\dfrac{\partial n x_A^{k(j)} x_B^{l(j)} x_C^{m(j)}}{\partial n_i} \right)_{n_{j \neq i}}}{\Delta_{\text{fus}}S_i^0 - R \ln x_{l,i}} \qquad (7)$$

If an intermediate compound $Z = A_pB_qC_r(p + q + r = 1)$ is formed in the ternary system, eqns (4), (6), and (7) for this compound must be modified [6, 7]

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

$$F_{0,z} = \frac{\Delta_{\text{fus}}H_Z^0}{\Delta_{\text{fus}}S_Z^0 - R \ln K x_A^p x_B^q x_C^r} \qquad (9)$$

where K is the normalization factor.

$$F_{j,z} =$$
$$\frac{p \left(\dfrac{\partial G_j'}{\partial n_A} \right)_{n_B,n_C} + q \left(\dfrac{\partial G_j'}{\partial n_B} \right)_{n_A,n_C} + r \left(\dfrac{\partial G_j'}{\partial n_C} \right)_{n_A,n_B}}{\Delta_{\text{fus}}S_Z^0 - R \ln K_j x_A^p x_B^q x_C^r} \qquad (10)$$

where

$$K_j = \left(p^{k(j)} q^{l(j)} r^{m(j)} \right)^{-1} \qquad (11)$$

and

$$G_j' = n \left(x_A^{k(j)} x_B^{l(j)} x_C^{m(j)} - p^{k(j)} q^{l(j)} r^{m(j)} \right) \qquad (12)$$

The calculation proceeds in one step introducing all the binary and ternary data. Then for the binary systems with a binary compound one of the integers $k(j), l(j), m(j)$ equals zero.

RESULTS AND DISCUSSION

The coupled thermodynamic analysis, i.e. the calculation of the coefficients G_j in eqn (4), resp. (8), has been performed using the multiple linear regression analysis omitting the statistically unimportant terms on the 0.95 confidence level according to the Student test. As the optimizing criterion for the best fit between the experimental and calculated temperatures of primary crystallization the following condition was used for all the n measured figurative points

$$\sum_n (T_{\text{pc,exp},n} - T_{\text{pc,calc},n})^2 = \min \qquad (13)$$

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

Table 2. Temperatures and Enthalpies of Fusion of Compounds in the System KCl—KBF$_4$—K$_2$TiF$_6$ Used for the Phase Diagram Calculation

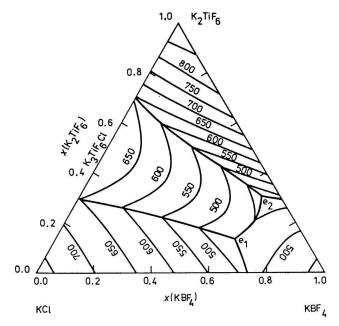| Compound	$\dfrac{\Delta_{fus}H^0}{kJ\ mol^{-1}}$	$\dfrac{T_{fus}}{K}$	Ref.
KCl	26.154	1045	[8]
KBF$_4$	17.656	843	[8]
K$_2$TiF$_6$	21.000	1172	[9]
K$_3$TiF$_6$Cl	47.000	969	[10]

Fig. 1. Optimalized phase diagram of the system KCl—KBF$_4$—K$_2$TiF$_6$. Isotherm values in °C.

the system KCl—KBF$_4$ were taken from [2], those in the system KCl—K$_2$TiF$_6$ from [3] and in the system KBF$_4$—K$_2$TiF$_6$ from [5]. Besides condition (13) for the calculation of the molar excess Gibbs energy of mixing the minimum necessary G_j coefficients for attaining thermodynamical consistent phase diagram and a reasonable standard deviation of approximation were required.

The phase diagram of the system KCl—KBF$_4$—K$_2$TiF$_6$ calculated using the coupled analysis of thermodynamic and phase diagram data is shown in Fig. 1. Four crystallization fields are present in the phase diagram corresponding to the primary crystallization of KCl, KBF$_4$, K$_2$TiF$_6$ and the intermediate compound K$_3$TiF$_6$Cl. The calculated coordinates of the two ternary eutectic points are as follows:

e_1: 24.1 mole % KCl, 62.1 mole % KBF$_4$, 13.8 mole % K$_2$TiF$_6$, $\theta_{e_1} = 447.1$ °C

e_2: 6.5 mole % KCl, 62.5 mole % KBF$_4$, 31.0 mole %

K$_2$TiF$_6$, $\theta_{e_2} = 414.5$ °C

The deviations of the experimental temperatures of primary crystallization from the calculated ones are listed in Table 1. The standard deviation of the temperature of primary crystallization in the calculated ternary phase diagram is ±17.1 °C.

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

$$\Delta G_{ter}^E = x_1 x_2 G_{12,1} + x_1 x_3 (G_{13,1} + G_{13,2} x_3) + \\ + x_2 x_3 (G_{23,1} + G_{23,2} x_3^2) + G_{123} x_1^2 x_2 x_3 \qquad (14)$$

The first term represents the molar excess Gibbs energy of mixing in the binary system KCl—KBF$_4$, the second one in the binary system KCl—K$_2$TiF$_6$, and the third one in the binary system KBF$_4$—K$_2$TiF$_6$. The last term represents the interaction contribution in the ternary system. The coefficients $G_{ij,k}$ are given in Table 3. The molar excess Gibbs energy of mixing in the ternary system KCl—KBF$_4$—K$_2$TiF$_6$ is shown in Fig. 2.

The phase diagram of the boundary system KCl—KBF$_4$ is shown in Fig. 3. The concentration dependence of the molar excess Gibbs energy of mixing in this system is symmetrical, which indicates that simple regular solutions are formed in this system. The calculated concentration coordinates of the eutectic point 72.9 mole % KBF$_4$ and 27.1 mole % KCl are relatively close to those given in [2], while the calculated eutectic temperature 481.7 °C is substantially higher.

The phase diagram of the boundary system KCl—K$_2$TiF$_6$ is shown in Fig. 4. The second-order polynomial for the molar excess Gibbs energy of mixing was obtained. The coordinates of eutectic points are: e_1: 29.7 mole % K$_2$TiF$_6$, 654.0 °C; e_2: 70.0 mole % K$_2$TiF$_6$, 642.3 °C. The value of e_2 differs from that given in [3], probably due to the appreciable inaccuracy in the determination of the liquidus temperature.

Similar results, like in the previous work [5], were obtained also for the boundary system KBF$_4$—K$_2$TiF$_6$, where the third-order polynomial for the molar excess Gibbs energy of mixing was found. The

Table 3. Coefficients of the Concentration Dependence of the Molar Excess Gibbs Energy of Mixing and the Standard Deviation of the Temperature of Primary Crystallization of the Ternary System KCl—KBF$_4$—K$_2$TiF$_6$

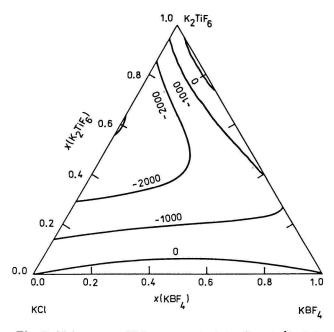| Coefficient	$\{G_{ij,k}\} \pm \{$SD in coefficient$\}$
$G_{12,1}/(J\ mol^{-1})$	1745 ± 686
$G_{13,1}/(J\ mol^{-1})$	−6906 ± 2475
$G_{13,2}/(J\ mol^{-1})$	−10055 ± 2646
$G_{23,1}/(J\ mol^{-1})$	−6092 ± 1086
$G_{23,2}/(J\ mol^{-1})$	14202 ± 1803
$G_{123}/(J\ mol^{-1})$	−36401 ± 9885
SD in $\theta_{pc}/$°C	17.1

Fig. 2. Molar excess Gibbs energy of mixing ($J\ mol^{-1}$) of the system KCl—KBF₄—K₂TiF₆.

Fig. 4. Phase diagram of the system KCl—K₂TiF₆. Full circles: [3], solid line: calculated.

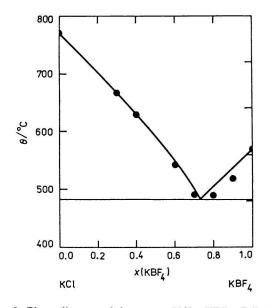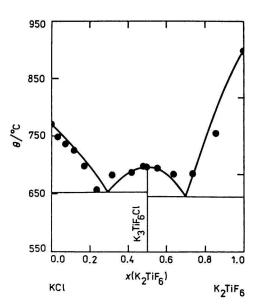**Fig. 3.** Phase diagram of the system KCl—KBF₄. Full circles: [2], solid line: calculated.

Fig. 5. Phase diagram of the system KBF₄—K₂TiF₆. Full circles: [5], solid line: calculated.

phase diagram is shown in Fig. 5. The system KBF_4—K_2TiF_6 is a simple eutectic one with the coordinates of the eutectic point 29.2 mole % K_2TiF_6 and 429.9 °C. The significant inflex course of the K_2TiF_6 liquidus curve is most probably due to the decomposition of KBF_4 and escape of gaseous BF_3.

REFERENCES

1. Matiašovský, K., Grjotheim, K., and Makyta, M., *Metall 42*, 1192 (1988).
2. Daněk, V., Votava, I., Chrenková-Paučírová, M., and Matiašovský, K., *Chem. Zvesti 30*, 841 (1976).
3. Aotani, K., Hasegawa, K., and Miyazawa, Y., *J. Electrochem. Soc. Jpn. 27*, 117 (1959).
4. Daněk, V. and Matiašovský, K., *Z. Anorg. Allg. Chem. 570*, 184 (1989).

5. Chrenková, M., Patarák, O., and Daněk, V. *Thermochim. Acta*, in press.
6. Lin, P.-L., Pelton, A. D., and Bale, C. W., *J. Am. Ceram. Soc. 62*, 414 (1979).
7. Sangster, J. and Pelton, A. D., *J. Phase Equil. 12*, 511 (1991).
8. Knacke, O., Kubachewski, O., and Hesselmann, K., *Thermochemical Properties of Inorganic Substances.* 2nd Edition. Springer-Verlag, Berlin, 1991.
9. Adamkovičová, K., Kosa, L., Nerád, I., Proks, I., and Strečko, J., *Thermochim. Acta 258*, 15 (1995).
10. Adamkovičová, K., Kosa, L., Nerád, I., and Proks, I., *Thermochim. Acta*, submitted for publication.

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