

Phase Diagram of the System $\text{KF—KCl—KBF}_4\text{—K}_2\text{TiF}_6$

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The phase diagram of the quaternary system $\text{KF—KCl—KBF}_4\text{—K}_2\text{TiF}_6$ was determined using the thermal analysis method. Subsequent coupled analysis of the thermodynamic and phase diagram data was performed to obtain thermodynamically consistent phase diagram.

In the ternary system $\text{KF—KCl—K}_2\text{TiF}_6$ two intermediate compounds, K_3TiF_7 and $\text{K}_3\text{TiF}_6\text{Cl}$, are formed. The calculated coordinates of the three ternary eutectic points are e_1 : 13 mole % KF, 25 mole % KCl, 62 mole % K_2TiF_6 , $t_{e1} = 635^\circ\text{C}$, e_2 : 21 mole % KF, 50 mole % KCl, 29 mole % K_2TiF_6 , $t_{e2} = 620^\circ\text{C}$, and e_3 : 46 mole % KF, 44 mole % KCl, 10 mole % K_2TiF_6 , $t_{e3} = 586^\circ\text{C}$. The phase diagram was calculated from the binary boundary ones and from the measured quaternary mixtures.

Three quaternary eutectic points were found in the quaternary phase diagram $\text{KF—KCl—KBF}_4\text{—K}_2\text{TiF}_6$. Their coordinates are e_1 : 2.8 mole % KF, 5.8 mole % KCl, 64.5 mole % KBF_4 , 26.9 mole % K_2TiF_6 , $t_{e1} = 413^\circ\text{C}$, e_2 : 4.9 mole % KF, 13.7 mole % KCl, 73.9 mole % KBF_4 , 7.5 mole % K_2TiF_6 , $t_{e2} = 389^\circ\text{C}$, and e_3 : 14.0 mole % KF, 11.2 mole % KCl, 74.0 mole % KBF_4 , 0.8 mole % K_2TiF_6 , $t_{e3} = 336^\circ\text{C}$. The inaccuracy in the calculated phase diagram is $\pm 20.7^\circ\text{C}$.

The study of physicochemical properties of the molten system $\text{KF—KCl—KBF}_4\text{—K}_2\text{TiF}_6$ is important because of its potential use as an electrolyte for electrodeposition of titanium diboride [1]. The phase diagrams of the individual ternary boundary systems were already studied previously.

The phase diagram of the ternary system KF—KCl—KBF_4 was measured in [2]. It was found that the system is a simple eutectic one with the coordinates of the eutectic point of 19.2 mole % KF, 18.4 mole % KCl, 61.4 mole % KBF_4 and the temperature of the eutectic crystallization of 422°C .

In the ternary system $\text{KF—KCl—K}_2\text{TiF}_6$ [3] two intermediate compounds, K_3TiF_7 and $\text{K}_3\text{TiF}_6\text{Cl}$, are formed. The authors found two ternary eutectic points with the coordinates e_1 : 9.6 mole % KF, 32.2 mole % KCl, 58.2 mole % K_2TiF_6 , $t_{e1} = 640^\circ\text{C}$, e_2 : 38.8 mole % KF, 47.7 mole % KCl, 13.5 mole % K_2TiF_6 , $t_{e2} = 562^\circ\text{C}$, and one peritectic point with the coordinates 39.1 mole % KF, 35.0 mole % KCl, 25.9 mole % K_2TiF_6 , $t_p = 600^\circ\text{C}$.

In the ternary system $\text{KF—KBF}_4\text{—K}_2\text{TiF}_6$, measured in [4], it was found that the intermediate compound K_3TiF_7 divides the system into two simple eutectic systems. The calculated coordinates of the two ternary eutectic points are as follows: e_1 : 26 mole %

KF, 69 mole % KBF_4 , 5 mole % K_2TiF_6 , $t_{e1} = 448^\circ\text{C}$ and e_2 : 4 mole % KF, 69 mole % KBF_4 , 27 mole % K_2TiF_6 , $t_{e2} = 440^\circ\text{C}$. The inaccuracy in the calculated ternary phase diagram was $\pm 11.5^\circ\text{C}$.

According to [5], in the ternary system $\text{KCl—KBF}_4\text{—K}_2\text{TiF}_6$ the intermediate compound $\text{K}_3\text{TiF}_6\text{Cl}$ divides the ternary system into two simple eutectic ones. The calculated coordinates of the two ternary eutectic points are e_1 : 24.1 mole % KCl, 62.1 mole % KBF_4 , 13.8 mole % K_2TiF_6 , $t_{e1} = 447.1^\circ\text{C}$ and e_2 : 6.5 mole % KCl, 62.5 mole % KBF_4 , 31.0 mole % K_2TiF_6 , $t_{e2} = 414.5^\circ\text{C}$. The standard deviation of the temperature of primary crystallization in the calculated ternary phase diagram was $\pm 17.1^\circ\text{C}$.

In the present work the phase diagram of the quaternary system $\text{KF—KCl—KBF}_4\text{—K}_2\text{TiF}_6$ was calculated using the coupled analysis of thermodynamic and previously published binary and ternary, as well as in this work measured quaternary equilibrium phase diagram data.

THEORETICAL

The calculation of the phase diagram using the coupled analysis of the thermodynamic and phase diagram data is based on the solution of a set of equations

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of the following type

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

where $\Delta_{\text{fus}}G_i^{\circ}$ 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 $a_{1,i}(T)$ are the activities of component i in the solid and liquid phase at the temperature T , respectively. For $T \equiv T_{\text{pc},i}$ and assuming $\Delta C_{p,s/l} = 0$ and the immiscibility of components in the solid phase $a_{s,l} = 1$, the thermodynamic temperature of primary crystallization of the component i is then

$$T_{\text{pc},i} = \frac{\Delta_{\text{fus}}H_i^{\circ} + RT_{\text{pc},i} \ln \gamma_{1,i}}{\Delta_{\text{fus}}S_i^{\circ} - R \ln x_{1,i}} \quad (2)$$

where $\Delta_{\text{fus}}H_i^{\circ}$ and $\Delta_{\text{fus}}S_i^{\circ}$ is the standard enthalpy and standard entropy of fusion, respectively, $x_{1,i}$ and $\gamma_{1,i}$ is 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, ΔG^{E} , according to the relation

$$RT_{\text{pc},i} \ln \gamma_{1,i} = \left[\frac{\partial (n\Delta G^{\text{E}})}{\partial n_i} \right]_{T,P,n_j \neq i} \quad (3)$$

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

The molar excess Gibbs energy of mixing in the liquid phase in the quaternary system KF—KCl—KBF₄—K₂TiF₆ was calculated as the sum of the molar excess Gibbs energies of mixing in the binary systems, of the molar excess Gibbs energies of mixing in the ternary systems and of the quaternary interaction terms.

The molar excess Gibbs energy of mixing in the boundary binary systems was described using the following general equation

$$\Delta G_{i,\text{bin}}^{\text{E}} = \sum_k x_1^{b(k)} x_2^{c(k)} G_k \quad (4)$$

and in the ternary systems

$$\Delta G_{j,\text{ter}}^{\text{E}} = \sum_{i=1}^3 \Delta G_{i,\text{bin}}^{\text{E}} + \sum_k x_1^{b'(k)} x_2^{c'(k)} x_3^{d'(k)} G'_k \quad (5)$$

For the molar excess Gibbs energy of mixing in the quaternary system the final equation is then

$$\Delta G_{\text{quat}}^{\text{E}} = \sum_{j=1}^4 \Delta G_{j,\text{ter}}^{\text{E}} + \sum_k x_1^{b''(k)} x_2^{c''(k)} x_3^{d''(k)} x_4^{e''(k)} G''_k \quad (6)$$

where the second term represents the quaternary interactions. Exponents $b''(k)$, $c''(k)$, $d''(k)$, and $e''(k)$ are integers in the range 1—3.

However, in the binary systems KF—K₂TiF₆ and KCl—K₂TiF₆ the intermediate compounds K₃TiF₇ and K₃TiF₆Cl, respectively, are formed. In the calculation this fact was taken into account in the following way.

Let us consider the system AX—AY, in which a compound $m\text{AX} \cdot n\text{AY}$ is formed in the solid state. According to [6], this compound may be written as $(\text{AX})_p \cdot (\text{AY})_q$, where

$$p = \frac{m}{m+n}, \quad q = \frac{n}{m+n} \quad (7)$$

and the Gibbs energy of fusion of $(\text{AX})_p \cdot (\text{AY})_q$ equals to

$$\Delta_{\text{fus}}G^{\circ} [(\text{AX})_p \cdot (\text{AY})_q] = \frac{\Delta_{\text{fus}}G^{\circ} (m\text{AX} \cdot n\text{AY})}{m+n} \quad (8)$$

The activity of $(\text{AX})_p \cdot (\text{AY})_q$ can be expressed in the form

$$a [(\text{AX})_p \cdot (\text{AY})_q] = x [(\text{AX})_p \cdot (\text{AY})_q] \gamma [(\text{AX})_p \cdot (\text{AY})_q] \quad (9)$$

The activities of AX and AY are then

$$a(\text{AX}) = x(\text{AX}) \gamma(\text{AX}), \quad a(\text{AY}) = x(\text{AY}) \gamma(\text{AY}) \quad (10)$$

EXPERIMENTAL

For the preparation of samples the following chemicals were used: KF, KCl (both Lachema), KBF₄ and K₂TiF₆ (both Fluka), all anal. grade. KF was dried in vacuum at 130 °C in the presence of P₄O₁₀ for two weeks, KCl, KBF₄, and K₂TiF₆ were dried at 400 °C for 2 h. All handling of salts was done under a dry inert atmosphere 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 a rate of 2—5 °C min⁻¹. The platinum crucible with the sample (10 g) was placed into the resistance furnace with adjustable cooling rate and a controlled argon atmosphere. The temperature control and the data processing were performed using a computerized measuring device. The temperature was measured using a PtRh10—Pt thermocouple calibrated to the melting points of anal. grade NaCl, KCl, and Na₂SO₄. The measured transition temperatures were reproducible within ± 3 °C.

The thermal analysis in the quaternary system KF—KCl—KBF₄—K₂TiF₆ was performed in cross-sections with constant 10, 20, 30, 40, 50, 60, and 70 mole % K₂TiF₆. The measured temperatures of primary and eutectic crystallization are given in Table 1.

Table 1. Measured ($t_{pc,exp}$) and Calculated ($t_{pc,calc}$) Temperatures of Primary Crystallization, their Difference (Δt_{pc}), and the Temperatures of Secondary Crystallization (t_{sc}) of Individual Mixtures in the Quaternary System KF—KCl—KBF₄—K₂TiF₆

| x_{KF} | x_{KCl} | x_{KBF_4} | $x_{K_2TiF_6}$ | $\frac{t_{pc,exp}}{^{\circ}C}$ | $\frac{t_{pc,calc}}{^{\circ}C}$ | $\frac{\Delta t_{pc}}{^{\circ}C}$ | $\frac{t_{sc}}{^{\circ}C}$ |
|----------|-----------|-------------|----------------|--------------------------------|---------------------------------|-----------------------------------|----------------------------|
| 0.10 | 0.10 | 0.70 | 0.10 | 478 | 451.8 | -26.2 | 467 |
| 0.10 | 0.20 | 0.70 | 0.10 | 455 | 476.3 | 21.3 | 416 |
| 0.20 | 0.10 | 0.60 | 0.10 | 469 | 501.5 | 32.5 | 416 |
| 0.10 | 0.40 | 0.40 | 0.10 | 563 | 556.5 | -6.5 | - |
| 0.40 | 0.10 | 0.40 | 0.10 | 566 | 547.5 | -18.5 | 520 |
| 0.10 | 0.60 | 0.20 | 0.10 | 650 | 620.4 | -29.6 | 625 |
| 0.40 | 0.30 | 0.20 | 0.10 | 590 | 586.1 | -3.9 | 503 |
| 0.60 | 0.10 | 0.20 | 0.10 | 675 | 680.6 | 5.6 | 625 |
| 0.30 | 0.50 | 0.10 | 0.10 | 606 | 605.8 | -0.2 | 530—535 |
| 0.10 | 0.10 | 0.60 | 0.20 | 470 | - | - | 465 |
| 0.10 | 0.10 | 0.60 | 0.20 | 501 | 495.3 | -5.7 | 483 |
| 0.20 | 0.20 | 0.40 | 0.20 | 580 | 576.2 | -3.8 | 434 |
| 0.10 | 0.40 | 0.40 | 0.20 | 570 | 588.2 | 18.2 | - |
| 0.40 | 0.10 | 0.30 | 0.20 | 620 | 631.4 | 11.4 | 576 |
| 0.10 | 0.50 | 0.20 | 0.20 | 585 | 599.4 | 14.4 | - |
| 0.30 | 0.30 | 0.20 | 0.20 | 636 | - | - | 588 |
| 0.30 | 0.30 | 0.20 | 0.20 | 632 | 626.1 | -5.9 | - |
| 0.30 | 0.40 | 0.10 | 0.20 | 640 | 625.3 | -14.7 | 570 |
| 0.50 | 0.20 | 0.10 | 0.20 | 673 | 650.3 | -22.7 | 657 |
| 0.15 | 0.45 | 0.20 | 0.20 | 647 | 600.0 | -47.0 | 643 |
| 0.45 | 0.15 | 0.20 | 0.20 | 618 | 647.7 | 29.7 | 581 |
| 0.10 | 0.30 | 0.40 | 0.20 | 585 | 565.3 | -19.7 | 571 |
| 0.30 | 0.10 | 0.40 | 0.20 | 575 | 600.5 | 25.5 | 561 |
| 0.10 | 0.20 | 0.40 | 0.30 | 556 | 570.8 | 14.8 | 461 |
| 0.20 | 0.10 | 0.40 | 0.30 | 580 | 608.4 | 28.4 | 461 |
| 0.20 | 0.40 | 0.10 | 0.30 | 625 | 627.7 | 2.7 | 605 |
| 0.40 | 0.20 | 0.10 | 0.30 | 680 | 679.3 | -0.7 | 587 |
| 0.10 | 0.10 | 0.40 | 0.40 | 625 | - | - | - |
| 0.10 | 0.10 | 0.40 | 0.40 | 579 | 601.4 | 22.4 | - |
| 0.10 | 0.30 | 0.20 | 0.40 | 611 | 644.3 | 33.3 | - |
| 0.10 | 0.30 | 0.20 | 0.40 | 693 | - | - | 678 |
| 0.30 | 0.10 | 0.20 | 0.40 | 673 | 681.1 | 8.1 | 620 |
| 0.30 | 0.10 | 0.20 | 0.40 | 650 | - | - | - |
| 0.20 | 0.20 | 0.20 | 0.40 | 669 | 653.8 | -15.2 | - |
| 0.10 | 0.10 | 0.30 | 0.50 | 688 | 648.1 | -39.9 | 590 |
| 0.10 | 0.30 | 0.10 | 0.50 | 646 | 656.0 | 10.0 | 607 |
| 0.30 | 0.10 | 0.10 | 0.50 | 710 | 693.3 | -16.7 | 670 |
| 0.10 | 0.10 | 0.20 | 0.60 | 765 | - | - | 558 |
| 0.10 | 0.10 | 0.20 | 0.60 | 640 | 673.0 | 33.0 | 604 |
| 0.20 | 0.10 | 0.10 | 0.60 | 670 | 674.1 | 4.1 | - |
| 0.075 | 0.225 | 0.10 | 0.60 | 684 | 678.8 | 5.2 | - |
| 0.225 | 0.075 | 0.10 | 0.60 | 671 | 679.5 | 8.5 | - |
| 0.10 | 0.10 | 0.10 | 0.70 | 690 | 715.3 | 25.3 | 622 |

RESULTS AND DISCUSSION

The coupled thermodynamic analysis, *i.e.* the calculation of coefficients G_k , G'_k , and G''_k in eqns (4—6), respectively, has been performed using the multiple linear regression analysis omitting the statistically nonimportant terms in the molar excess 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 primary crystallization the following condition was used for all measured points

$$\sum_n (T_{pc,exp,n} - T_{pc,calc,n})^2 = \min. \quad (11)$$

The values of the enthalpy of fusion of individual components used in the calculation are summarized in Table 2. The experimentally determined temperatures of primary crystallization in the ternary system KF—KCl—KBF₄ were taken from [2], those of the system KF—KBF₄—K₂TiF₆ from [4], and those of the system KCl—KBF₄—K₂TiF₆ from [5].

For the excess molar Gibbs energy of mixing in the

Table 2. Temperatures and Enthalpies of Fusion of Compounds Used for the Phase Diagram Calculation

| Compound | $\frac{\Delta_{\text{fus}}H^\circ}{\text{kJ mol}^{-1}}$ | $\frac{T_{\text{fus}}}{\text{K}}$ | Ref. |
|------------------------------------|---|-----------------------------------|------|
| KF | 27.196 | 1131 | [7] |
| KCl | 26.154 | 1045 | [7] |
| KBF ₄ | 17.656 | 843 | [7] |
| K ₂ TiF ₆ | 21.000 | 1172 | [8] |
| K ₃ TiF ₇ | 57.000 | 1048 | [9] |
| K ₃ TiF ₆ Cl | 47.000 | 969 | [10] |

boundary binary systems the general equation

$$\Delta G_{i,\text{bin}}^E = x_1 x_2 (G_1 + G_2 x_2 + G_3 x_2^2) \quad (12)$$

was found to be valid. The values of the coefficients G_i together with the standard deviations of the fits are given in Table 3.

For the excess molar Gibbs energy of mixing in the ternary systems the following equations were obtained

$$\Delta G_{\text{KCl-KF-KBF}_4}^E =$$

$$= \sum_{i=1}^3 \Delta G_{i,\text{bin}}^E + G'_1 x_1 x_2^2 x_3 + G'_2 x_1 x_2^2 x_3^2 \quad (13)$$

$$\Delta G_{\text{KF-K}_2\text{TiF}_6\text{-KBF}_4}^E = \sum_{i=1}^3 \Delta G_{i,\text{bin}}^E + G'_1 x_1^3 x_2 x_3 + G'_2 x_1^3 x_2 x_3^2 \quad (14)$$

$$\Delta G_{\text{KCl-K}_2\text{TiF}_6\text{-KBF}_4}^E = \sum_{i=1}^3 \Delta G_{i,\text{bin}}^E + G'_1 x_1 x_2^3 x_3^2 + G'_2 x_1 x_2 x_3^3 + G'_3 x_1^2 x_2^2 x_3^3 + G'_4 x_1^3 x_2 x_3 \quad (15)$$

$$\Delta G_{\text{KCl-KF-K}_2\text{TiF}_6}^E = \sum_{i=1}^3 \Delta G_{i,\text{bin}}^E + G'_1 x_1 x_2 x_3 + G'_2 x_1 x_2^2 x_3 + G'_3 x_1^3 x_2^2 x_3^3 \quad (16)$$

The calculated coefficients of the concentration dependence of the excess molar Gibbs energy of mixing together with the standard deviations of the fit temperature in the ternary systems are given in Table 4.

Table 3. Coefficients G_i of the Concentration Dependence of the Molar Excess Gibbs Energy of Mixing and the Standard Deviations of the Temperature of Primary Crystallization in the Binary Subsystems of the Quaternary System KF—KCl—KBF₄—K₂TiF₆

| System | $\frac{G_1}{\text{J mol}^{-1}}$ | $\frac{G_2}{\text{J mol}^{-1}}$ | $\frac{G_3}{\text{J mol}^{-1}}$ | $\frac{\sigma}{^\circ\text{C}}$ |
|---|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| KCl—KF | 2144 ± 547 | -7379 ± 284 | 6111 ± 829 | 1.2 |
| KF—KBF ₄ | 3836 ± 233 | -14434 ± 790 | 6625 ± 833 | 1.9 |
| KF—K ₂ TiF ₆ | -11507 ± 1743 | -19918 ± 6050 | 33344 ± 5830 | 6.5 |
| KCl—KBF ₄ | 50 ± 22 | 3725 ± 736 | -7175 ± 2367 | 5.6 |
| KCl—K ₂ TiF ₆ | -7531 ± 2458 | 25700 ± 6335 | -31125 ± 8457 | 5.0 |
| K ₂ TiF ₆ —KBF ₄ | 8475 ± 830 | -25810 ± 1426 | 12905 ± 713 | 6.1 |

Table 4. Coefficients G'_i of the Concentration Dependence of the Molar Excess Gibbs Energy of Mixing and the Standard Deviations of the Temperature of Primary Crystallization in the Ternary Subsystems of the Quaternary System KF—KCl—KBF₄—K₂TiF₆

| Coef. | System | | | |
|----------------------------------|-------------------------|--|--|---|
| | KCl—KF—KBF ₄ | KCl—KF—K ₂ TiF ₆ | KF—K ₂ TiF ₆ —KBF ₄ | KCl—K ₂ TiF ₆ —KBF ₄ |
| $\frac{G'_1}{\text{J mol}^{-1}}$ | -22709 ± 1429 | 36975 ± 2173 | -14718 ± 5725 | -263005 ± 16623 |
| $\frac{G'_2}{\text{J mol}^{-1}}$ | -36041 ± 1843 | -31585 ± 2067 | -198846 ± 16972 | 92415 ± 8284 |
| $\frac{G'_3}{\text{J mol}^{-1}}$ | - | -1241825 ± 89126 | - | 796972 ± 72485 |
| $\frac{G'_4}{\text{J mol}^{-1}}$ | - | - | - | 41055 ± 5182 |
| $\frac{\sigma}{^\circ\text{C}}$ | 6.8 | - | 15.2 | 17.6 |

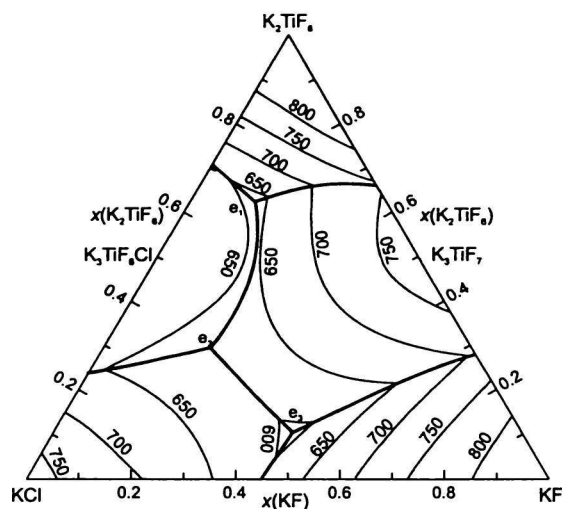


Fig. 1. The calculated ternary phase diagram of the system KF—KCl—K₂TiF₆ (parameter: $t/^\circ\text{C}$).

The ternary system KF—KCl—KBF₄ is a simple eutectic one with the coordinates of the eutectic point 21 mole % KF, 19 mole % KCl, 60 mole % KBF₄ and the temperature of the eutectic crystallization of 409°C. The inaccuracy in the calculated ternary phase diagram is $\pm 6.8^\circ\text{C}$. In the ternary system KF—KBF₄—K₂TiF₆ the intermediate compound K₃TiF₇ divides the system into two simple eutectic ones. The calculated coordinates of the two ternary eutectic points are e_1 : 26 mole % KF, 68 mole % KBF₄, 6 mole % K₂TiF₆, $t_{e1} = 450^\circ\text{C}$ and e_2 : 3 mole % KF, 69 mole % KBF₄, 28 mole % K₂TiF₆, $t_{e2} = 435^\circ\text{C}$. The inaccuracy in the calculated ternary phase diagram is $\pm 15.2^\circ\text{C}$.

In the ternary system KCl—KBF₄—K₂TiF₆ the intermediate compound K₃TiF₆Cl is formed, which divides the ternary system into two simple eutectic systems. The calculated coordinates of the two ternary eutectic points are e_1 : 18 mole % KCl, 66 mole % KBF₄, 16 mole % K₂TiF₆, $t_{e1} = 449^\circ\text{C}$ and e_2 : 6 mole % KCl, 63 mole % KBF₄, 31.0 mole % K₂TiF₆, $t_{e2} = 417^\circ\text{C}$. The inaccuracy in the calculated phase diagram is $\pm 17.6^\circ\text{C}$.

In the ternary system KF—KCl—K₂TiF₆ two intermediate compounds, K₃TiF₇ and K₃TiF₆Cl, are formed. The calculated coordinates of the three ternary eutectic points are e_1 : 13 mole % KF, 25 mole % KCl, 62 mole % K₂TiF₆, $t_{e1} = 635^\circ\text{C}$, e_2 : 21 mole % KF, 50 mole % KCl, 29 mole % K₂TiF₆, $t_{e2} = 620^\circ\text{C}$, and e_3 : 46 mole % KF, 44 mole % KCl, 10 mole % K₂TiF₆, $t_{e3} = 586^\circ\text{C}$. The phase diagram was calculated from the binary boundary ones and from the measured quaternary mixtures, therefore the standard deviation of the fit is not given. The calculated phase diagram of this system is shown in Fig. 1. The experimentally determined [3] phase diagram is probably

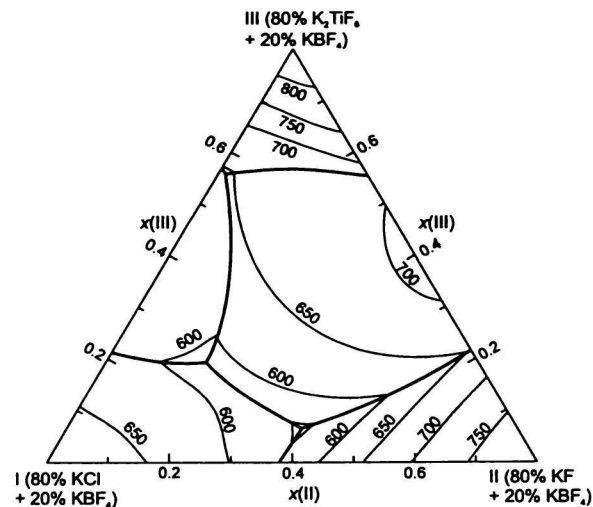


Fig. 2. Cross-section of the quaternary phase diagram KF—KCl—K₂TiF₆—KBF₄ at 20 mole % KBF₄ (parameter: $t/^\circ\text{C}$).

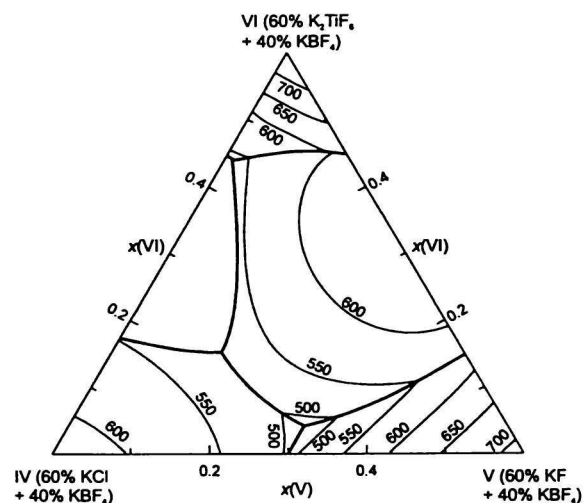


Fig. 3. Cross-section of the quaternary phase diagram KF—KCl—K₂TiF₆—KBF₄ at 40 mole % KBF₄ (parameter: $t/^\circ\text{C}$).

not quite correct because of few experimental data in the region of the presented peritectic point.

Finally, for the excess molar Gibbs energy of mixing in the ternary systems of the quaternary system KF(2)—KCl(1)—KBF₄(4)—K₂TiF₆(3) the following equation was obtained

$$\Delta G_{\text{quat}}^E = \sum_{j=1}^4 \Delta G_{j,\text{ter}}^E + G''_1 x_1 x_2 x_3 x_4^3 + G''_2 x_1^3 x_2 x_3^2 x_4^2 + G''_3 x_1 x_2 x_3^3 x_4 \quad (17)$$

The calculated coefficients of the excess molar Gibbs energy of mixing and the standard deviation of

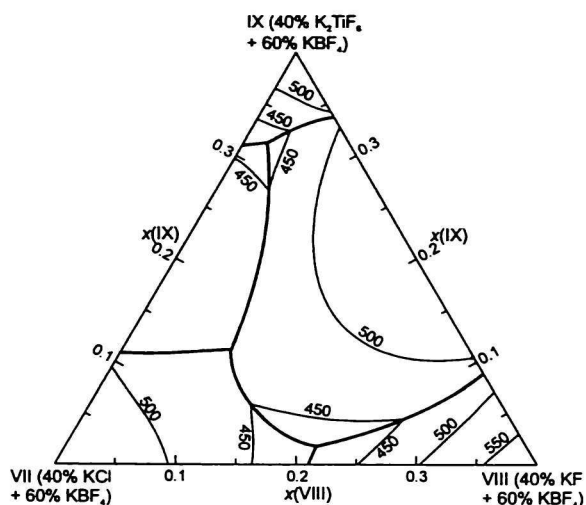


Fig. 4. Cross-section of the quaternary phase diagram KF—KCl—K₂TiF₆—KBF₄ at 60 mole % KBF₄ (parameter: $t/^\circ\text{C}$).

the measured and calculated temperature of primary crystallization for the quaternary system are: $\frac{G_1''}{\text{J mol}^{-1}}$

$$= 2009367 \pm 145628, \quad \frac{G_2''}{\text{J mol}^{-1}} = 15367354 \pm 1123575,$$

$\frac{G_3''}{\text{J mol}^{-1}} = 249546 \pm 20491, \quad \frac{\sigma}{^\circ\text{C}} = 20.7$. Three quaternary eutectic points were found in the quaternary phase diagram KF—KCl—KBF₄—K₂TiF₆. Their coordinates are e_1 : 2.8 mole % KF, 5.8 mole % KCl, 64.5 mole % KBF₄, 26.9 mole % K₂TiF₆, $t_{e1} = 413^\circ\text{C}$, e_2 : 4.9 mole % KF, 13.7 mole % KCl, 73.9 mole % KBF₄,

7.5 mole % K₂TiF₆, $t_{e2} = 389^\circ\text{C}$, and e_3 : 14.0 mole % KF, 11.2 mole % KCl, 74.0 mole % KBF₄, 0.8 mole % K₂TiF₆, $t_{e3} = 336^\circ\text{C}$. The inaccuracy in the calculated phase diagram is $\pm 20.7^\circ\text{C}$. The cross-sections of the quaternary phase diagram KF—KCl—KBF₄—K₂TiF₆ with constant content of 20, 40, and 60 mole % KBF₄ are shown in Figs. 2—4.

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