

Density of the System LiF—KF—K₂NbF₇

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The density of the melts in the system LiF—KF—K₂NbF₇ has been measured using the Archimedean method. On the basis of the determined density values the molar volume, partial molar volume, and excess molar volume of the melts were calculated. In the boundary system KF—K₂NbF₇ the congruently melting compound K₃NbF₈ is formed. This compound exhibits a low thermal stability and at melting it undergoes a thermal dissociation. The degree of the thermal dissociation was calculated on the basis of both the thermal analysis of the phase diagram and the volume properties of the investigated system. It was found that the degree of the thermal dissociation of K₃NbF₈ at the melting point attains the value $\alpha_0 = 0.44$.

The molten system LiF—KF—K₂NbF₇ is interesting from both theoretical and technological points of view. The theoretical interest is associated with the formation of the congruently melting compound K₃NbF₈, which affects the ionic composition of the melt. In practical terms this system is interesting as a potential electrolyte for electrodeposition of niobium [1].

The phase diagram of the system KF—K₂NbF₇ was studied in [2–4]. The congruently melting compound, K₃NbF₈, melting according to different authors in the range 760–770 °C, gives rise to two eutectics. According to different authors, the coordinates of the respective eutectic points are in the range 23–26.5 mole % K₂NbF₇, 719–732 °C, and 80–81 mole % K₂NbF₇, 703–708 °C. The melting point of K₂NbF₇ was determined to lie in the range 730–735 °C.

The phase diagrams of the binary system LiF—K₂NbF₇ and of the ternary system LiF—KF—K₂NbF₇ were determined in [5]. The system LiF—K₂NbF₇ is a simple eutectic one with the eutectic point at 72 mole % K₂NbF₇ and 670 °C. In the binary system KF—K₂NbF₇ the intermediate compound K₃NbF₈ divides the ternary system into two simple eutectic ones. The calculated coordinates of the two ternary eutectic points are: e_1 : 22.3 mole % LiF, 9.4 mole % KF, 68.3 mole % K₂NbF₇; $t_e = 649$ °C, and e_2 : 45.5 mole % LiF, 51.7 mole % KF, 2.8 mole % K₂NbF₇; $t_e = 486$ °C.

In the present work the density of the ternary system LiF—KF—K₂NbF₇ was determined. On the basis of the obtained data the molar volumes, partial molar volumes, and the excess molar volumes were calculated to get information on the interaction of the components and the possible chemical reactions between them. The density values were used in the calculation

of the degree of thermal dissociation of the additive compound K₃NbF₈.

EXPERIMENTAL

The density of the investigated melts was measured using the Archimedean methods. The platinum vessel suspended on a platinum wire has been used as the measuring body. The dependence of the vessel volume on temperature was determined by calibration using molten NaCl and KCl. For the measuring device control and the evaluation of experimental data the on-line PC XT computer was used. The experimental error in the density measurement did not exceed ± 0.4 %. The detailed description of the measuring device used is given in [6].

For the preparation of samples the following chemicals were used: LiF (Lachema), KF (Merck), and K₂NbF₇ (Aldrich), all of reagent quality. LiF was dried at 600 °C for 2 h, KF and K₂NbF₇ were dried in vacuum at 130 °C for one day. All handling of salts was done in a glove box under dry inert atmosphere.

The measurements were carried out in the temperature interval of approximately 150 K starting at 10–20 K above the temperature of primary crystallization. In the ternary system cross-sections with the constant ratio $x(\text{LiF})/x(\text{KF}) = 3, 1, \text{ and } 0.333$ with the constant content of 25 mole %, 50 mole %, and 75 mole % K₂NbF₇ were chosen for the measurement. The density values were automatically registered by the measuring device every 30 s, yielding approximately 30–50 density values for each composition. The density measurement of every melt composition was repeated 2 times. Thus, the temperature dependence of the density was presented in the form of the linear equations

Table 1. Coefficients *a* and *b* in Eqn (1) and the Standard Deviations of the Fit for the Investigated Melts of the System LiF—KF—K₂NbF₇

<i>x</i> _{LiF}	<i>x</i> _{KF}	<i>x</i> _{K₂NbF₇}	<i>a</i> g cm ⁻³	<i>b</i> · 10 ⁴ g cm ⁻³ °C	SD · 10 ³ g cm ⁻³	<i>t</i> °C
1.000	0.000	0.000	2.1968	4.6247	0.36	860—960
0.750	0.250	0.000	2.3319	5.7073	0.62	740—850
0.500	0.500	0.000	2.5955	8.5597	1.67	580—730
0.250	0.750	0.000	2.5539	7.6910	0.48	730—840
0.000	1.000	0.000	2.5579	7.5523	0.25	870—970
0.250	0.000	0.750	3.2028	10.1782	1.65	720—820
0.500	0.000	0.500	3.2572	11.0828	0.28	770—850
0.750	0.000	0.250	3.2347	11.3694	1.65	820—910
0.000	0.000	1.000	3.2791	10.9280	1.15	750—860
0.000	0.250	0.750	3.1754	9.4765	0.36	740—830
0.000	0.500	0.500	3.0491	7.5374	1.00	780—870
0.000	0.750	0.250	2.8509	6.3402	1.03	745—850
0.563	0.187	0.250	3.1116	9.8633	0.73	750—830
0.375	0.375	0.250	3.0146	8.5767	0.74	680—770
0.187	0.563	0.250	2.9296	7.4918	0.68	720—820
0.375	0.125	0.500	3.1465	9.7030	0.38	740—830
0.250	0.250	0.500	3.1195	9.2390	0.85	710—810
0.125	0.375	0.500	3.0357	7.9892	1.02	750—850
0.125	0.125	0.750	3.3307	11.5789	0.99	730—820

$$\rho = a - b \cdot t \quad (1)$$

where ρ is the density in g cm⁻³ and t is the temperature in °C. The values of the constants a and b together with the standard deviations of approximations, obtained by the linear regression analysis of the experimentally obtained data, are given in Table 1. The original density data are available on request at the first author.

RESULTS AND DISCUSSION

System LiF—KF

The density of the system LiF—KF was measured in [7], however the values of the density of pure salts were lower than the data measured in this work (Fig. 1). From the results of this work the density increases monotonically with increasing content of KF. From the values of the molar volume it follows that this system shows very small deviations from ideal behaviour. The maximum deviation of the excess molar volume is in the range of the experimental error.

System LiF—K₂NbF₇

The density of the system LiF—K₂NbF₇ is shown in Fig. 2. The density increases with increasing content of K₂NbF₇. The concentration dependence of the molar volume of this system at 1100 K can be described by the equation

$$V = (14.29 + 105.21x_{\text{K}_2\text{NbF}_7} + 19.41x_{\text{K}_2\text{NbF}_7}^2 - 10.96x_{\text{K}_2\text{NbF}_7}^3) \text{ cm}^3 \text{ mol}^{-1} \quad (2)$$

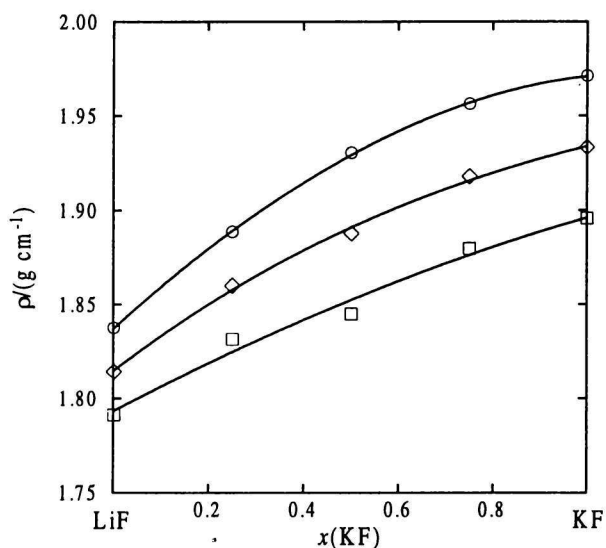


Fig. 1. The density of the system LiF—KF. ○ 1050 K, ◇ 1100 K, □ 1150 K.

$$\text{SD} = 7.17 \times 10^{-2} \text{ cm}^3 \text{ mol}^{-1}$$

From the values of the excess molar volume it follows that this system deviates significantly from the ideal behaviour. The maximum deviation attains $-1.13 \text{ cm}^3 \text{ mol}^{-1}$ (2.7 % at the concentration of 25 mole % K₂NbF₇). Differentiating eqn (2) according to $x(\text{K}_2\text{NbF}_7)$ and introducing into the equation

$$V(\text{K}_2\text{NbF}_7) = V + x_{\text{LiF}} \left(\frac{\partial V}{\partial x_{\text{K}_2\text{NbF}_7}} \right) \quad (3)$$

we get for the partial molar volume of K₂NbF₇ the

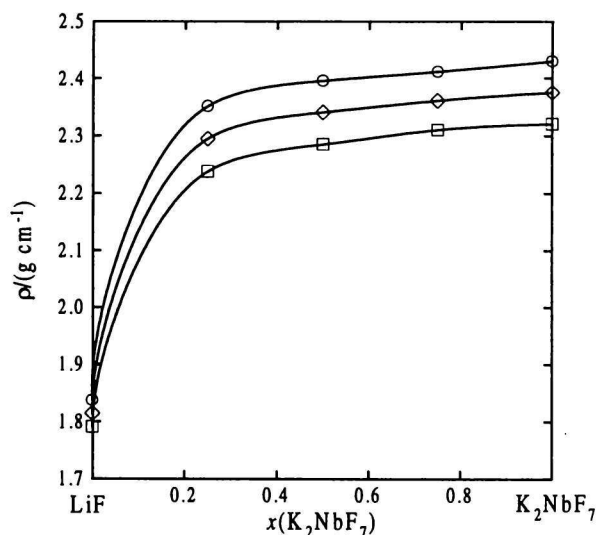


Fig. 2. The density of the system LiF—K₂NbF₇. ○ 1050 K, ◇ 1100 K, □ 1150 K.

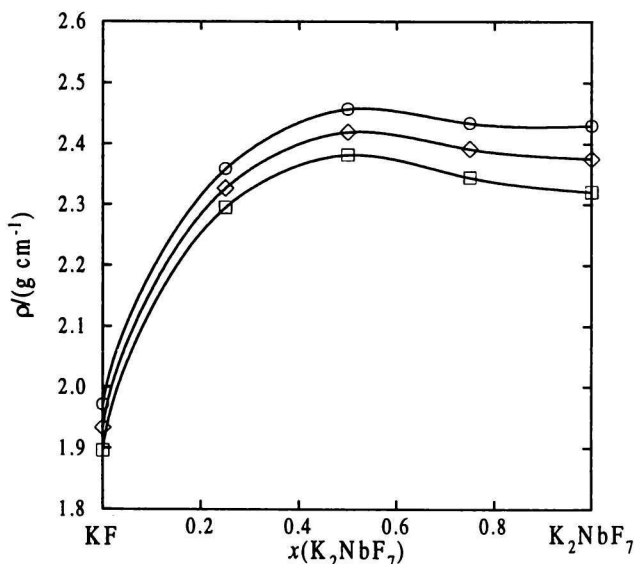


Fig. 3. The density of the system KF—K₂NbF₇. ○ 1050 K, ◇ 1100 K, □ 1150 K.

equation

$$V(\text{K}_2\text{NbF}_7) = (127.96 + 13.48x_{\text{LiF}}^2 - 21.93x_{\text{LiF}}^3) \text{ cm}^3 \text{ mol}^{-1} \quad (4)$$

For $x_{\text{LiF}} \rightarrow 1$ we obtain for the partial molar volume of K₂NbF₇ in the infinitely diluted solution the value $V(\text{K}_2\text{NbF}_7) = 119.51 \text{ cm}^3 \text{ mol}^{-1}$. This value is lower than that of the pure K₂NbF₇, which may refer to the chemical interaction of both components under formation of large [NbF₈]³⁻ anions in the melts of this system.

System KF—K₂NbF₇

The density of the system KF—K₂NbF₇ is shown in Fig. 3. The density course shows a small maximum at 50 mole % K₂NbF₇, which is due to the formation of the additive compound K₃NbF₈. The concentration dependence of the molar volume at 1100 K was described by the polynomial

$$V = (30.06 + 78.83x_{\text{K}_2\text{NbF}_7} + 26.33x_{\text{K}_2\text{NbF}_7}^2 - 7.04x_{\text{K}_2\text{NbF}_7}^3) \text{ cm}^3 \text{ mol}^{-1} \quad (5)$$

$$\text{SD} = 0.34 \text{ cm}^3 \text{ mol}^{-1}$$

The maximum deviation of the excess molar volume at the concentration of 50 mole % K₂NbF₇ attains the value $-3.6 \text{ cm}^3 \text{ mol}^{-1}$, which is 4.8 % of the molar volume of this melt. The partial molar volume can be described by the equation

$$V(\text{K}_2\text{NbF}_7) = (128.18 - 5.23x_{\text{KF}}^2 - 14.07x_{\text{KF}}^3) \text{ cm}^3 \text{ mol}^{-1} \quad (6)$$

and for $x_{\text{KF}} \rightarrow 1$ we obtain for the partial molar volume of K₂NbF₇ in the infinitely diluted solution the value $V(\text{K}_2\text{NbF}_7) = 108.88 \text{ cm}^3 \text{ mol}^{-1}$. This value is again lower than that for the pure K₂NbF₇, which again refers to the formation in the melts of larger [NbF₈]³⁻ anions.

The density values of the system KF—K₂NbF₇ were used in the determination of the degree of thermal dissociation of the additive compound K₃NbF₈. The detailed description of the calculation procedure is given in [8]. The values of the degree of dissociation and densities of the molten nondissociated compound K₂NbF₈ at 1050 K, 1100 K, and 1150 K are summarized in Table 2. The obtained value of the dissociation degree refers to the pronounced thermal dissociation of this compound on melting.

Fig. 4 shows the phase diagram of the system KF—K₂NbF₇. Experimental results according to [4] and the theoretical liquidus curve calculated using the dissociation degree $\alpha = 0.44$ are shown in Fig. 4. The standard deviation of the approximation is 2.5 K. The determined value of the degree of thermal dissociation of the additive compound K₃NbF₈ agrees very well with the value determined by the analysis of the volume properties.

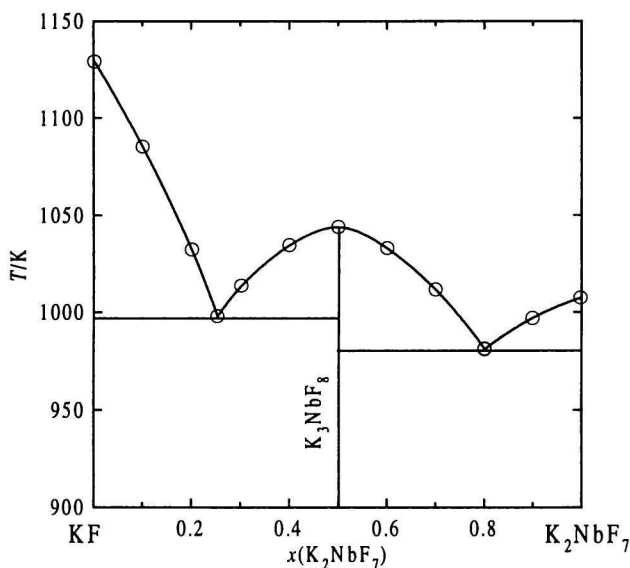
System LiF—KF—K₂NbF₇

The dependence of the molar volume of the ternary system LiF(1)—KF(2)—K₂NbF₇(3) on composition at constant temperature can be described by the equation

$$V = \sum_{i=1}^3 x_i V_i + \sum_{i \neq j}^3 x_i x_j \sum_{n=0}^k A_{nij} x_j^n + B x_1^p x_2^q x_3^r \quad (7)$$

Table 2. Values of the Degree of Thermal Dissociation, the Hypothetical Density of Nondissociated Compound K₃NbF₈, and the Standard Deviations of Approximation in the Theoretical Density Calculation

T/K	α	$\rho_{K_3NbF_8,nd}$	$SD \cdot 10^2$
		g cm ⁻³	g cm ⁻³
1050	0.61	2.65	1.24
1100	0.61	2.65	1.10
1100	0.55	2.60	1.10
1150	0.55	2.60	1.24
1150	0.38	2.50	1.23

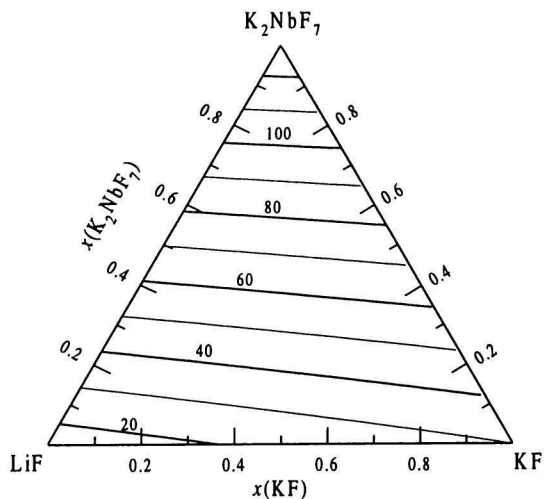
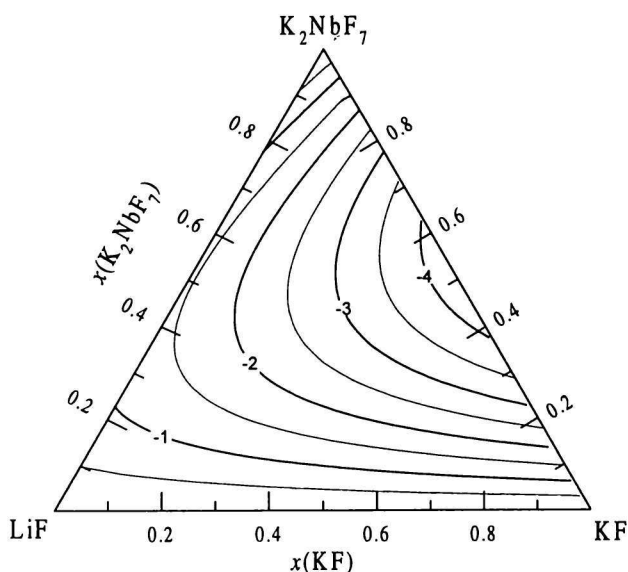
**Fig. 4.** The phase diagram of the system KF—K₂NbF₇. O According to [4], — calculated using the dissociation degree $\alpha = 0.44$.

where p , q , r , and n are adjustable integers. The first term represents ideal behaviour, the second one describes the binary interactions, and the third one the interaction of all three components.

The constants V_i , A_{nij} , and B in eqn (7) were calculated using the multiple linear regression analysis

Table 3. Coefficients V_i and A_{nij} of Eqn (6) and the Standard Deviations of the Fit for the Composition Dependence of the Molar Volume of the System LiF—KF—K₂NbF₇

Constants	1050 K	1100 K	1150 K
$V_1/(\text{cm}^3 \text{ mol}^{-1})$	14.098 ± 0.071	14.302 ± 0.069	14.539 ± 0.173
$V_2/(\text{cm}^3 \text{ mol}^{-1})$	29.432 ± 0.117	30.065 ± 0.114	31.448 ± 0.291
$V_3/(\text{cm}^3 \text{ mol}^{-1})$	126.244 ± 0.502	129.169 ± 0.491	132.475 ± 1.235
$V_{013}/(\text{cm}^3 \text{ mol}^{-1})$	-6.156 ± 1.184	-5.727 ± 1.160	-5.800 ± 2.916
$V_{023}/(\text{cm}^3 \text{ mol}^{-1})$	-14.691 ± 1.305	-17.228 ± 1.274	-22.544 ± 3.198
$SD/(\text{cm}^3 \text{ mol}^{-1})$	0.198	0.193	0.487

**Fig. 5.** The molar volume/ $(\text{cm}^3 \text{ mol}^{-1})$ of the system LiF—KF—K₂NbF₇ at 1100 K.**Fig. 6.** The excess molar volume/ $(\text{cm}^3 \text{ mol}^{-1})$ of the system LiF—KF—K₂NbF₇ at 1100 K.

omitting the statistically nonimportant terms on the 0.95 confidence level. The following equation was obtained

$$V = x_1V_1 + x_2V_2 + x_3V_3 + x_1x_3A_{013} + x_2x_3A_{023} \quad (8)$$

The values of constants V_i and A_{nij} in eqn (8) as well as the standard deviations of approximation for the temperatures 1050 K, 1100 K, and 1150 K are given in Table 3. The molar volume of the system LiF—KF—K₂NbF₇ at the temperature of 1100 K is shown in Fig. 5 and the excess molar volume at the same temperature is in Fig. 6.

From eqn (8) it follows that no interaction of all three components was found in the ternary system LiF—KF—K₂NbF₇. A weak interaction was found in the binary system LiF—KF, which is due to the non-random mixing of both components. The significant interaction in both binary LiF—K₂NbF₇ and KF—K₂NbF₇ systems is obviously due to the formation of more voluminous [NbF₈]³⁻ anions.

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