Phase diagram of the ternary system LiF—NaF—NaCl*

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The phase diagram of the quasi-ternary system LiF—NaF—NaCl was studied using the classical TA method. This system exhibits one ternary eutectic point with these coordinates: 37.6 mole % LiF, 33.4 mole % NaF, 29.0 mole % NaCl, $t_E = 604$°C. The experimental results are compared with the theoretical ones, obtained using various assumptions.

Методом термического анализа была изучена фазовая диаграмма трехкомпонентной системы LiF—NaF—NaCl. Система обладает одной точкой тройной эвтектики с координатами 37,6 мол.% LiF; 33,4 мол.% NaF; 29,0 мол.% NaCl, $t_E = 604$°C. Экспериментальные значения были сравнены с теоретическими результатами, полученными при различных предпосылках.

The system LiF—NaF—NaCl has not been separately studied up-to-now, however, it is a subsystem of the ternary reciprocal system $Li^+, Na^+ \| F^-, Cl^-$ published in 1964 by *Bergman et al.* [1]. These authors have used the visual-polythermic method in their investigation. The rate of cooling, the purity of salts used, and the amount of the samples are not mentioned. The main data from [1] concerning the systems LiF—NaF, LiF—NaCl, NaF—NaCl, and LiF—NaF—NaCl can be seen in Table 1.

The course of monovariant equilibrium curves in the ternary system LiF—NaF—NaCl, as it is demonstrated in [1], is not probable because the angle formed by two monovariant equilibrium curves in ternary eutectic point is excluded to be greater than 180° [2, 3].

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Abbreviations used:

TPC temperature of primary crystallization.
TSC temperature of secondary crystallization.

Experimental

The phase diagrams of two-component systems LiF—NaF, LiF—NaCl, and NaF—NaCl, bounding the concentration triangle of the system LiF—NaF—NaCl and the phase diagram of this system have been investigated using the TA method, in detail described in [4].

The system LiF—NaF is a eutectic system with limited solid solutions of LiF in NaF the extent of which is approx. 8 mole % LiF at the eutectic temperature.

The system LiF—NaCl is a simple eutectic system. On both liquidus curves there are real points of inflection.

The system NaF—NaCl is a simple eutectic system. The main data concerning the mentioned systems can be found in Table 1.

In investigating the phase diagram of LiF—NaF—NaCl system 19 primary sections of the 1st kind of two types have been chosen:

a) the sections 01—09, connecting the NaF vertex with the points on the LiF—NaCl side at 10, 20, 30, 40, 50, 60, 70, 80, 90 mole % LiF;

b) the sections 10—90, connecting the LiF vertex with the points on the NaF—NaCl side at 10, 20, 30, 40, 50, 60, 70, 80, 90 mole % NaF.

The intersection points of these two sets of sections have been chosen as the studied points. To make the course of the monovariant equilibrium curves more accurate a secondary section of the 1st kind has been constructed. This section is connecting the NaCl vertex and the point on the NaF—LiF side at 50 mole % LiF.

Altogether 83 ternary mixtures have been studied using the TA method. Some of them have been re-investigated. The reproducibility of the TPC and TSC measurement of the ternary salt mixtures has made ±3°C. The reproducibility of the measurement of the temperature of the ternary eutectic crystallization of the points in the vicinity of the ternary eutectic point has made ±2°C. The phase diagram of the LiF—NaF—NaCl system with marked isotherms over every 20°C is drawn in Fig. 1.

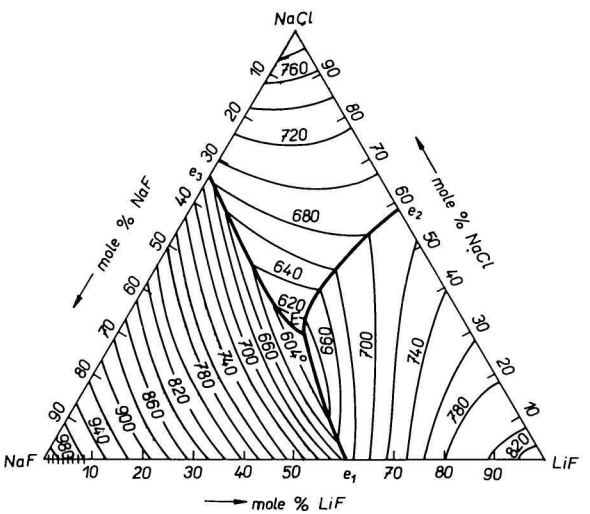

Fig. 1. Phase diagram of the ternary system LiF—NaF—NaCl according to our measurement with marked lines of monovariant equilibrium and of the isotherms.
NaF 993.5°C; LiF 848.3°C; NaCl 800.8°C; e_1 652°C; e_2 686.5°C; e_3 688.5°C.

The LiF—NaF—NaCl system contains one ternary eutectic point. There are three primary crystallization fields of LiF, NaF, and NaCl, respectively, in the corresponding concentration triangle.

The curves of monovariant crystallization intersect in the ternary eutectic point the composition of which is: 37.6 ± 1 mole % (24.0 weight %) LiF, 33.4 ± 1 mole % (34.4 weight %) NaF, 29.0 ± 1 mole % (41.6 weight %) NaCl; the temperature being 604 ± 2°C.

As the LiF—NaF system involves limited solid solutions, the extent of which is approx. 8 mole % LiF in NaF, there exists evidently a narrow range of limited solid solutions also in the ternary LiF—NaF—NaCl system near the NaF vertex. Our points of investigation lie off this region. The investigation of this region has been out of the scope of this paper.

Our experimental data have been compared with those of *Bergman et al.* [1] in Table 1. It is evident that these two sets of data differ substantially more than it corresponds to the accuracy of measurements. Especially the temperature of the ternary eutectic crystallization by *Bergman et al.* [1] appears to be much lower than the correct value of it should be. The course of the monovariant LiF—NaCl crystallization curve [1] can be criticized also.

Theoretical

The experimentally found course of the isotherms and the monovariant equilibrium curves of the ternary LiF—NaF—NaCl system has been compared with the results calculated on the basis of data from the binary systems.

The course of the liquidus curves in binary systems has been calculated under the assumptions:

1. the components form a classical ideal solution $a_i = x_i$ [5—7];
2. the components form an ideal ionic solution — Temkin's model has been used [8];
3. the activity is expressed using the universal relationship [9] in the form $a_i = x_i^k$, where

$$k = \frac{k_{j/i}^{St}}{1 + b(1 - x_i)}$$

$k_{j/i}^{St}$ — the Stortenbeker correction factor,
b — the parameter calculated using the data of the eutectic point.

Then for LiF—NaF system: $b_{LiF} = -0.4685$; $b_{NaF} = -0.3372$;
for LiF—NaCl system: $b_{LiF} = 2.2135$; $b_{NaCl} = 2.2334$;
for NaF—NaCl system: $b_{NaF} = 0.1151$; $b_{NaCl} = 0.3761$.

The values ΔH_i^f, T_i^f, and $\Delta C_{P_i}^{l/s}$ are taken from [10].

Theoretically calculated liquidus curves in binary systems enable the determination of the isotherms in a ternary system. We simply suggest that the composition coordinates of the figurative points of ternary mixtures, the temperatures of which are situated at a certain isotherm, are linear combinations of the composition coordinates of binary mixtures, the calculated values of TPC of which lie on the same isotherm. The isotherms in the ternary system obtained in this way are

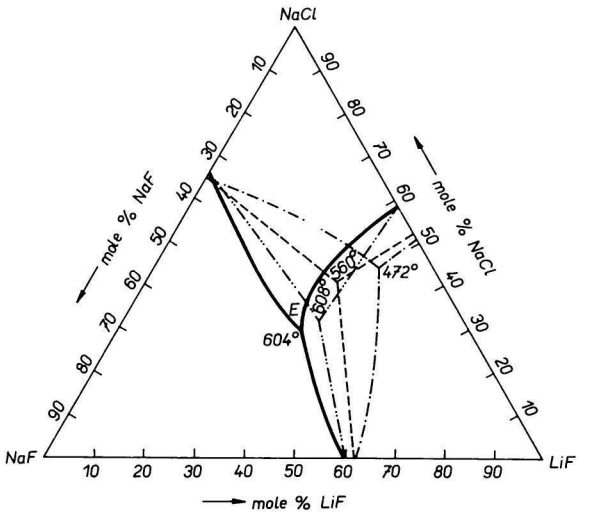

Fig. 2. Concentration triangle of the system LiF—NaF—NaCl with marked lines of monovariant equilibrium.
——— experimental, – – – – $a_i = x_i$, – – – Temkin's model, – – $a_i = x_i^k$.

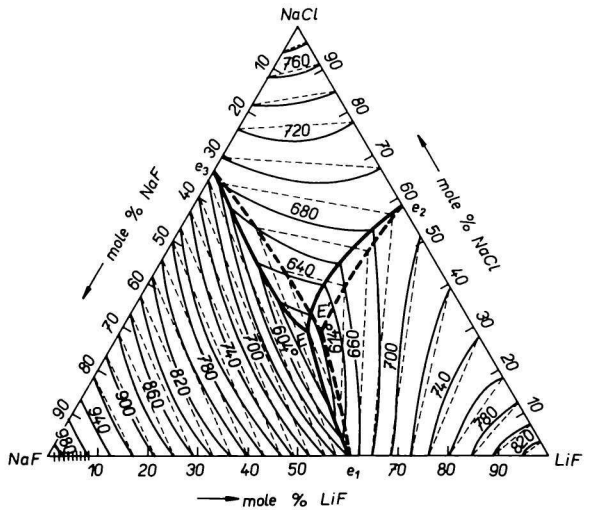

Fig. 3. Phase diagram of the ternary system LiF—NaF—NaCl with marked lines of monovariant equilibrium and of the isotherms.
——— experimental, – – – constructed on the basis of measured binary systems.

straight lines. Connecting the intersection points of the projections of corresponding isotherms we obtain the projection of a monovariant equilibrium curve of LiF—NaF—NaCl system. These results are demonstrated in Fig. 2.

Further, the isotherms and monovariant equilibrium curves have been constructed in the same way using the experimental data of binary systems LiF—NaF, LiF—NaCl, and NaF—NaCl (Fig. 3).

The isotherms and the monovariant equilibrium curves obtained on the basis of the universal relationship are nearest to the experimental data. This relationship is very useful especially for the approximate calculation of the ternary eutectic point, because it enables to obtain the studied coordinates in a relatively simple way.

The course of the isotherms in the phase diagram of the reciprocal system Li^+, $Na^+ \| Cl^-, F^-$ — the subsystem of which is the quasi-ternary LiF—NaF—NaCl

Table 1

The comparison of the data of [1] concerning the systems LiF—NaF, LiF—NaCl, NaF—NaCl, LiF—NaF—NaCl with our results

System	E (eutectic point)		Notes
	mole %	t_E (°C)	
LiF—NaF	61.0 LiF	652.0	[1]
	60.5 LiF	652.0	Our results
LiF—NaCl	41.5 LiF	670.0	[1]
	41.5 LiF	686.5	Our results
NaF—NaCl	34.0 NaF	675.0	[1]
	34.0 NaF	688.5	Our results
LiF—NaF—NaCl	40 LiF; 36 NaF; 24 NaCl	582.0	[1]
	37.6 LiF; 33.4 NaF; 29.0 NaCl	604.0	Our results

Table 2

The comparison of the coordinates of the ternary eutectic point of the system LiF—NaF—NaCl from our experiment and calculation and from the calculation of [11]

Mole %			t_E °C	Notes
LiF	NaF	NaCl		
37.6	33.4	29.0	604	Our results
39.0	29.0	32.0	608	Our calculation for $a_i = x_i^k$
39.6	35.7	24.7	614	According to [11]

system — has been calculated in 1974 by *Saboungi* and *Blander* [11] on the basis of the conformal ionic solution theory (CIS) [12, 13]. This method has some advantages because it does not apply for the knowledge of the stable diagonal for the calculation of the isotherms in quasi-ternary systems. On the other hand, if the liquidus diagrams of all boundary systems are known, the way of calculation used in this paper is much simpler. Moreover, it gives more accurate coordinates of ternary eutectic point than the method of conformal ionic solutions (Table 2).

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