# Phase diagram of the system LiF—NaF—$Na_2SO_4$ and its thermodynamic analysis I. Experimental investigation of the phase diagram

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Phase equilibria solidus—liquidus in the system LiF—NaF—$Na_2SO_4$ were determined by the method of thermal analysis. A congruently melting compound of stoichiometric composition $Na_3FSO_4$ is formed in the system NaF—$Na_2SO_4$. Composition of investigated mixtures was chosen with respect to thermodynamic analysis of the system. From this point of view the systems LiF—$Na_3FSO_4$ and LiF—$Na_2SO_4$ are of special interest. The former one contains a compound which partly dissociates under melting and in the latter system a region of primary crystallization of $Na_3FSO_4$ occurs.

С помощью метода термического анализа определены фазовые равновесия между солидусом и ликвидусом в системе LiF—NaF—$Na_2SO_4$. Конгруэнтно плавящееся соединение стехиометрического состава $Na_3FSO_4$ образуется в системе NaF—$Na_2SO_4$. Состав изучаемых смесей был выбран с учетом термодинамического анализа системы. С этой точки зрения особый интерес представляют системы LiF—$Na_3FSO_4$ и LiF—$Na_2SO_4$. Первая из них содержит соединение частично диссоциирующее при плавлении, а во второй системе наблюдается область первичной кристаллизации $Na_3FSO_4$.

Ternary system LiF—NaF—$Na_2SO_4$ is a part of reciprocal system $Li^+$, $Na^+ \parallel F^-$, $SO_4^{2-}$. It contains a congruently melting compound $Na_3FSO_4$ which partly dissociates under melting [1]. Existence of this compound allows to divide the system in question into two subsystems, *viz.* LiF—NaF—$Na_3FSO_4$ and LiF—$Na_2SO_4$—$Na_3FSO_4$. Special attention was paid to the binary systems LiF—$Na_3FSO_4$ and LiF—$Na_2SO_4$.

Phase diagram of the system LiF—$Na_3FSO_4$ has been studied by *Speranskaya* and *Bergman* [2]. The cited authors used a visual-polythermal method. They found that it is a simple eutectic system, composition of the eutectic point being 61.0 mole % LiF, 39.0 mole % $Na_3FSO_4$ and its temperature $T(E) = 890.15$ K (617 °C).

The system LiF—$Na_2SO_4$ has been studied by *Speranskaya* and *Bergman* [2] as a part of the reciprocal system $Li^+$, $Na^+ \parallel F^-$, $SO_4^{2-}$. According to their opinion it is an unstable diagonal characterized by the existence of two invariant

points $e_1$, $e_2$. The parameters of these points are as follows: $e_1$ – 40.6 mole % LiF, 59.4 mole % $Na_2SO_4$, $T(e_1) = 893.15$ K (620 °C); $e_2$ – 55.6 mole % LiF, 44.4 mole % $Na_2SO_4$, $T(e_2) = 861.15$ K (588 °C).

The ternary system LiF—NaF—$Na_2SO_4$ has not yet been studied in detail. The aim of this work was to obtain experimental data on phase equilibria in the ternary system LiF—NaF—$Na_2SO_4$ and pseudobinary systems LiF—$Na_3FSO_4$, LiF—$Na_2SO_4$ with precision required for thermodynamic analysis of these systems.

## Experimental

Solidus—liquidus equilibrium was determined by the method of thermal analysis (cooling curves method). The chemicals used were of anal. grade (Lachema, Brno). Temperature of the sample was measured by PtRh10—Pt thermocouple. Comparing point (cool junction) of the thermocouple was kept at the temperature (25.00 ± 0.01) °C. Mass of the sample in platinum crucible was 20 g, rate of cooling did not exceed 2 K $min^{-1}$. The thermocouple was calibrated using the melting points of pure salts: NaF, $\theta$(fus) = 993.5 °C (this standard was supplied by the Institute of Inorganic Chemistry, Centre for Chemical Research, Slovak Academy of Sciences, Bratislava); $Na_2SO_4$, $\theta$(fus) = 884.8 °C [3]; NaCl, $\theta$(fus) = 800.8 °C [3]; KCl, $\theta$(fus) = 771.0 °C [3]. Besides, the melting temperatures of eutectic mixtures were used: KCl—$K_2SO_4$, $\theta(E) = 685.0$ °C [4] and NaCl—$Na_2SO_4$, $\theta(E) = 628$ °C [5]. Repeated measurements of temperature of primary crystallization of the same sample were in the interval narrower than 1 K.

## Results and discussion

### *The system* LiF—$Na_3FSO_4$

The results of experimental investigation of the solidus—liquidus equilibrium of the system LiF—$Na_3FSO_4$ are summarized in Table 1. (The experimental phase diagram will be presented in the second part of this series together with the calculated phase diagram.) It was confirmed in accord with paper [2] that the system in question is of simple eutectic type. However, composition of the eutectic point found in this work, *i.e.* 53.0 mole % LiF and 47.0 mole % $Na_3FSO_4$ ($\theta(E) = 619.5$ °C) differs remarkably from the literature data (61.0 mole % LiF, 39.0 mole % $Na_3FSO_4$). The eutectic temperature differs only by 2.5 K.

### *The system* LiF—$Na_2SO_4$

The results of thermal analysis of the system LiF—$Na_2SO_4$ are summarized in Table 2. (The phase diagram will be presented in Part II of this series.) This

*Table 1*

Dependence of the temperature of the primary crystallization $\theta_1$ and of the second thermal arrest $\theta_2$ on the composition of the system LiF—$Na_3FSO_4$

| $x$(LiF)/% | $x$($Na_3FSO_4$)/% | $\theta_1$/°C | $\theta_2$/°C |
|---|---|---|---|
| 100 | 0 | 849.5 | — |
| 99 | 1 | 838.0 | 615.0 |
| 98 | 2 | 831.5 | 615.5 |
| 97 | 3 | 824.0 | 615.5 |
| 96 | 4 | 822.5 | 617.0 |
| 95 | 5 | 812.0 | 619.5 |
| 90 | 10 | 782.0 | 619.0 |
| 85 | 15 | 762.5 | 619.5 |
| 80 | 20 | 732.5 | 619.0 |
| 75 | 25 | 711.5 | 618.0 |
| 70 | 30 | 681.5 | 619.0 |
| 65 | 35 | 669.0 | 619.0 |
| 60 | 40 | 646.5 | 620.0 |
| 57 | 43 | 634.5 | 620.0 |
| 56 | 44 | 632.5 | 618.0 |
| 55 | 45 | 630.0 | 619.0 |
| 54 | 46 | 628.5 | 616.5 |
| 53 | 47 | — | 619.5 |
| 52 | 48 | 620.0 | 619.5 |
| 51 | 49 | 623.0 | 619.5 |
| 50 | 50 | 626.0 | 618.0 |
| 45 | 55 | 648.5 | 620.0 |
| 40 | 60 | 664.5 | 620.0 |
| 35 | 65 | 686.0 | 620.0 |
| 30 | 70 | 693.5 | 620.0 |
| 25 | 75 | 711.5 | 619.0 |
| 20 | 80 | 725.5 | 619.0 |
| 15 | 85 | 737.5 | 615.5 |
| 10 | 90 | 756.0 | 619.0 |
| 5 | 95 | 773.5 | 615.5 |
| 4 | 96 | 777.0 | 615.5 |
| 3 | 97 | 781.0 | 615.0 |
| 2 | 98 | 785.0 | 614.0 |
| 1 | 99 | 789.0 | 614.0 |
| 0 | 100 | 793.5 | — |

system is an unstable diagonal of the ternary reciprocal system $Li^+$, $Na^+ \| F^-$, $SO_4^{2-}$ with three characteristic points:

$e_1$ — 44.5 mole % LiF, 55.5 mole % $Na_2SO_4$, $\theta(e_1) = 604.0$ °C;

$e_2$ — 55.5 mole % LiF, 44.5 mole % $Na_2SO_4$, $\theta(e_2) = 586.0$ °C;

*Table 2*

Dependence of the temperature of the primary crystallization $\theta_1$, of the second thermal arrest $\theta_2$ and third thermal arrest $\theta_3$ on the composition of the system LiF—$Na_2SO_4$

| $x$(LiF)/% | $x(Na_2SO_4)$/% | $\theta_1$/°C | $\theta_2$/°C | $\theta_3$/°C |
|---|---|---|---|---|
| 0 | 100 | 884.0 | — | — |
| 1 | 99 | 873.0 | 705.0 | — |
| 2 | 98 | 866.5 | 698.0 | — |
| 3 | 97 | 859.0 | 692.5 | — |
| 4 | 96 | 851.5 | 682.5 | — |
| 5 | 95 | 842.5 | 674.0 | — |
| 6 | 94 | 837.0 | 667.0 | — |
| 7 | 93 | 831.5 | 660.5 | — |
| 8 | 92 | 826.0 | 659.0 | — |
| 9 | 91 | 818.0 | 654.5 | 569.5 |
| 10 | 90 | 805.0 | 648.5 | 567.5 |
| 20 | 80 | 748.5 | 623.0 | 568.5 |
| 30 | 70 | 685.0 | 613.0 | 568.5 |
| 35 | 65 | 659.0 | — | — |
| 40 | 60 | 628.5 | 606.0 | 569.0 |
| 41 | 59 | 625.5 | 606.2 | 568.5 |
| 42 | 58 | 620.0 | 604.0 | 567.5 |
| 43 | 57 | 613.0 | 605.0 | 568.0 |
| 44 | 56 | 607.0 | 599.5 | 568.0 |
| 45 | 55 | 603.0 | 600.0 | 568.5 |
| 46 | 54 | 603.0 | — | 568.5 |
| 47 | 53 | 601.0 | 600.0 | 567.5 |
| 48 | 52 | 598.5 | 574.0 | 567.5 |
| 49 | 51 | 595.5 | 573.0 | 567.5 |
| 50 | 50 | 592.0 | 571.5 | 567.5 |
| 51 | 49 | 594.5 | 577.5 | 569.5 |
| 52 | 48 | 589.5 | 580.0 | 567.5 |
| 53 | 47 | 588.5 | — | 568.5 |
| 54 | 46 | 585.0 | 583.0 | 567.5 |
| 55 | 45 | 588.5 | 585.0 | 567.5 |
| 56 | 44 | 589.5 | 586.5 | 568.5 |
| 57 | 43 | 595.5 | 586.0 | 570.5 |
| 58 | 42 | 604.0 | 586.5 | 570.5 |
| 59 | 41 | 605.5 | 585.5 | 568.5 |
| 60 | 40 | 613.0 | 586.5 | 569.5 |
| 70 | 30 | 660.0 | 586.5 | 569.0 |
| 80 | 20 | 695.0 | 583.5 | 569.5 |
| 90 | 10 | 766.0 | 581.0 | 568.5 |
| 91 | 9 | 778.5 | 579.5 | 566.0 |
| 92 | 8 | 715.5 | 578.0 | 566.5 |
| 93 | 7 | 782.0 | 577.0 | 565.0 |
| 94 | 6 | 790.5 | 576.0 | 567.0 |
| 95 | 5 | 797.0 | 573.0 | 565.0 |
| 96 | 4 | 805.5 | 569.5 | 565.0 |
| 97 | 3 | 813.0 | 561.0 | 559.0 |
| 98 | 2 | 824.0 | 561.0 | 559.0 |
| 99 | 1 | 837.5 | 559.5 | — |
| 100 | 0 | 845.0 | — | — |

$P$ – 49.0 mole % LiF, 51.0 mole % $Na_2SO_4$, $\theta(P)$ = 568.5 °C.

It was confirmed that this system is of the type reported in literature [2]. However, composition and/or temperature of these points determined in this work differs remarkably from older data, which can be explained by the used experimental technique.

## *The system* LiF—NaF—$Na_2SO_4$

Sections of the phase diagram LiF—NaF—$Na_2SO_4$ were chosen for experimental investigation taking into account the existence of incongruently melting compound $Na_3FSO_4$ in the system. Ten sections of the first kind (constant ratio of components) and eight sections of the second kind (constant content of one component) were studied. Totally 138 mixtures were analyzed. The phase diagram of the system LiF—NaF—$Na_2SO_4$ is presented in Fig. 1. (Detailed tables

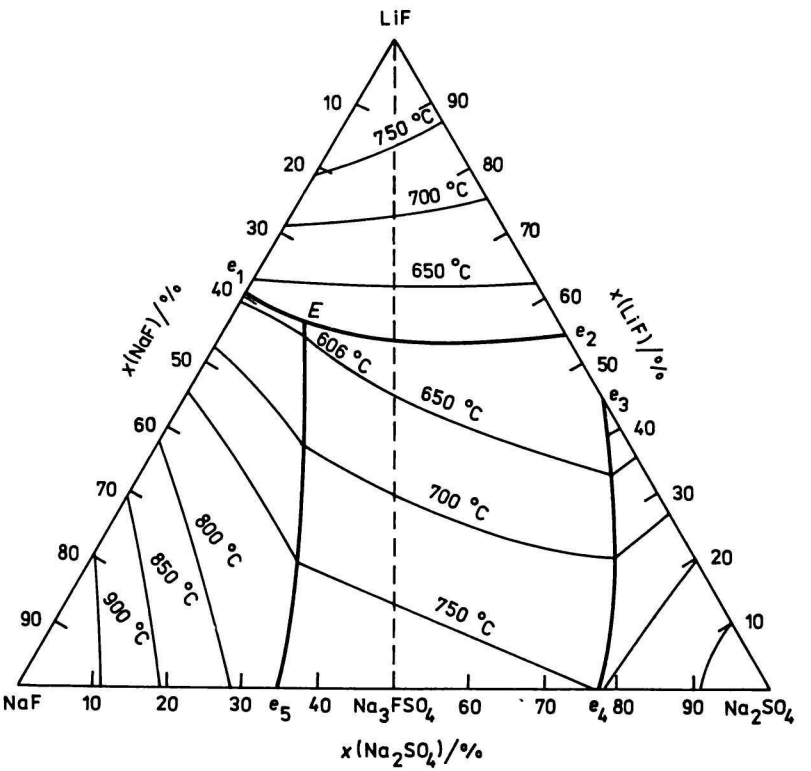


*Fig. 1.* Phase diagram of the system LiF—NaF—$Na_2SO_4$.

of experimental data will be supplied by authors on request.) It can be seen that there are four regions of primary crystallization in this phase diagram:

LiF—$e_1$—$E$—$e_2$ (primary crystallization of LiF);

NaF—$e_1$—$E$—$e_5$ (primary crystallization of NaF);

$Na_2SO_4$—$e_3$—$e_4$ (primary crystallization of $Na_2SO_4$);

$e_2$—$E$—$e_5$—$e_4$—$e_3$ (primary crystallization of $Na_3FSO_4$).

The system LiF—NaF—$Na_2SO_4$ has one eutectic point. Its composition and temperature are as follows: 57.5 mole % LiF, 33.0 mole % NaF, 9.5 mole % $Na_2SO_4$, $\theta(E) = 606\,°C$.

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