Phase diagram of the system LiF—NaCl—KCl*

[a]J. PESCHL and [b]M. MALINOVSKÝ

[a]*Power Research Institute, 884 03 Bratislava*

[b]*Department of Inorganic Technology, Slovak Technical University, 880 37 Bratislava*

Received 27 July 1977

Accepted for publication 5 December 1977

The phase diagram of the three-component system LiF—NaCl—KCl was precised using the classical TA method and X-ray phase analysis. This system is bounded by two simple eutectic systems LiF—NaCl (E: 42 mole % LiF, 58 mole % NaCl, $t_E = 682$°C), LiF—KCl (E: 20 mole % LiF, 80 mole % KCl, $t_E = 714$°C) and one binary system NaCl—KCl formed by continuous solid solution with the temperature minimum (50 mole % NaCl, 50 mole % KCl, $t_{min} = 662$°C). The quasi-ternary system LiF—NaCl—KCl contains one eutectic point (11 mole % LiF, 48 mole % NaCl, 41 mole % KCl, $t_E = 613$°C). On the NaCl—KCl side there exists a continuous solid solution, the decomposition of which begins at 3—4 mole % LiF within the composition triangle. The existence of solid solution was confirmed by means of X-ray phase analysis.

Фазовая диаграмма трехкомпонентной системы LiF—NaCl—KCl была уточнена при помощи классического термического и рентгенографического фазового анализов. Эта система ограничена двумя простыми эвтектическими системами LiF—NaCl (E: 42 мол. % LiF, 58 мол. % NaCl, $t_E = 682$°C), LiF—KCl (E: 20 мол. % LiF, 80 мол. % KCl, $t_E = 714$°C) и одной бинарной системой NaCl—KCl с непрерывным твердым раствором с температурой минимума (50 мол. % NaCl, 50 мол. % KCl, $t_{min} = 662$°C). Квази-тернарная система LiF—NaCl—KCl имеет одну эвтектическую точку (11 мол. % LiF, 48 мол. % NaCl, 41 мол. % KCl, $t_E = 613$°C). На стороне NaCl—KCl существует непрерывный твердый раствор, распад которого начинается при 3–4 мол. % LiF внутри трехугольника состава. Существование твердого раствора было подтверждено рентгенографическим фазовым анализом.

The quasi-binary systems LiF—NaCl and LiF—KCl were investigated by several authors [1—8]. There is a fair agreement as to the general character of phase diagrams of these systems. However, the data on the system NaCl—KCl do not

* Based on a paper presented at the 1st Conference of Socialist Countries on Chemistry and Electrochemistry of Molten Salts, Smolenice, November 24—26, 1975.

allow an unambiguous characterization of the system in spite of the fact that it was investigated by a great number of authors (some selected data are presented in Table 1). The differences between the reported values might be due to an insufficient number of internal mixtures studied in the system. In [8] the number of investigated mixtures was sufficient, but due to the used technique of the hot-stage microscope the accuracy of the results is only ±4°C. Moreover, the reported temperature of the minimum on the liquidus and solidus curves is by 13—15°C lower than in other papers. Therefore it was necessary to reexamine the phase diagram of the system NaCl—KCl.

Table 1

Literature data on the system NaCl—KCl

T^t		Point of temperature minimum		Number of investigated binary mixtures	Ref.
NaCl	KCl	t, °C	mole % NaCl		
800	774	660	50	5	[1]
800	775	658	50	6	[2]
800	775	660	50	6	[3]
800	770	658	50	12	[4]
800	772	660	50	9	[5]
800	772	658	50	14	[6]
805	774	645	50	21	[7]
800.8	772	662	50	41	This work

The phase diagram of the system LiF—NaCl—KCl was described only by *Bergman et al.* [9]; it is a plane diagonal section of the quaternary reciprocal system Li^+, K^+, $Na^+||F^-$, Cl^-. According to [9] the system LiF—NaCl—KCl is bounded by simple eutectic systems: LiF—NaCl (E: 40.5 mole % LiF, 59.5 mole % NaCl, $t_E = 668$°C), LiF—KCl (E: 19 mole % LiF, 81 mole % KCl, $t_E = 710$°C) and the system NaCl—KCl with a temperature minimum (51.5 mole % NaCl, 48.5 mole % KCl, $t_{min} = 658$°C). In [9] seven internal sections in the given system were investigated. One ternary eutectic point, E, was found at 13 mole % LiF, 50 mole % NaCl, 37 mole % KCl, and $t_E = 604$°C. The isotherms were marked over every 50°C. However, the data by *Bergman et al.* [9] concerning the system LiF—NaCl differ substantially from our measurements and therefore it was necessary to reexamine the three-component system, too.

Experimental

In our investigations the following reagents were used: LiF, pure (Lachema, Brno), m.p. 848.3°C; NaCl, anal. grade (Lachema, Brno), m.p. 800.8°C; KCl, anal. grade (Lachema,

Brno), m.p. 771°C. The salts were calcined at 550°C for 2 h and stored in wide-mouth bottles in an desiccator. The salts were weighed in a Pt crucible, the whole amount being 20 g. The samples were melted in an electric resistance furnace, in open atmosphere. The temperature was measured with a PtRh10—Pt thermocouple. The test junction of the thermocouple was inserted directly in the measured melt. The reference junction was maintained at a constant temperature of 25°C with an accuracy of ±0.01°C using an ultrathermostat. The calibration of the thermocouple was performed by means of melting points of the following pure substances: Na_2SO_4 (m.p. 884.8°C [10]), LiF (m.p. 848.3°C [11]), NaCl (m.p. 800.8°C [11]), KCl (m.p. 771°C [11]) and by means of the eutectic point of the system NaCl—Na_2SO_4 (51.9 mole % NaCl, 48.1 mole % Na_2SO_4, $t_E = 628$°C [12]). The data of thermocouple were recorded with a line recorder, type EZ 11. The rate of cooling was 1—4°C/min. In the vicinity of the NaCl—KCl side the rate of cooling was 0.5—2°C/min and also some heating curves were recorded.

The samples for X-ray phase analysis were prepared first by the quenching method using Pt vessels. However, it was impossible to obtain unambiguous results in this way. Therefore the samples were prepared in the following way: A small piece of chemical glass was immersed into the melt and quickly drawn out. A certain amount of fixed melt was peeled off and crushed in an agate mortar. The samples prepared in this way had length of life at least 14 days, and only later the decomposition of the solid solution into NaCl and KCl could be detected.

Results and discussion

In the binary system NaCl—KCl 41 internal mixtures were investigated. It is the system with continuous solid solution and a minimum with the coordinates 50 ±2 mole % NaCl, 50 ±2 mole % KCl, $t_{min} = 662 \pm 2$°C. The data obtained by the

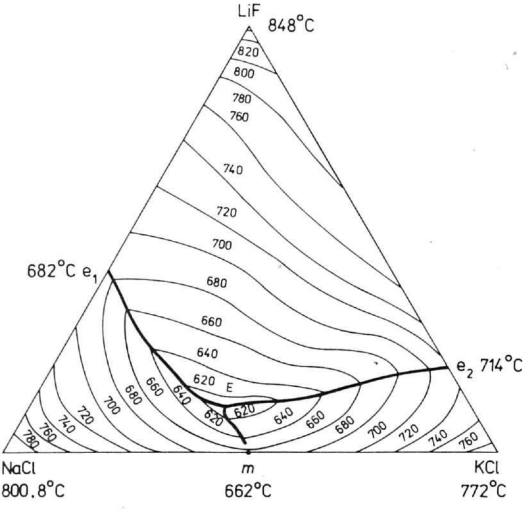

Fig. 1. Phase diagram of the LiF—NaCl—KCl system; *m* = point of temperature minimum.

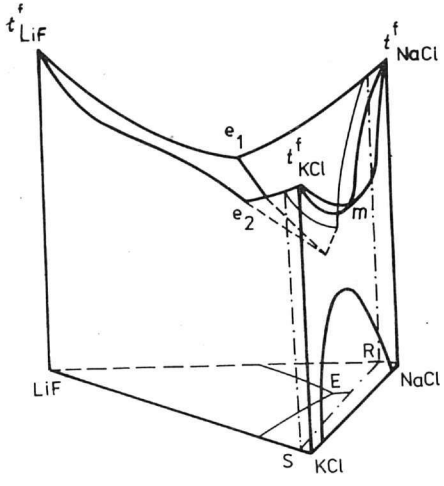

Fig. 2. Vertical section of the second kind of the composition prism of the system LiF—NaCl—KCl.

classical TA method were confirmed by the results of X-ray phase analysis. In the system LiF—NaCl—KCl 110 ternary mixtures were investigated, with the figurative points situated on 22 internal sections. In the studied system one ternary eutectic point was found with the coordinates 11 ±2 mole % LiF, 48 ±2 mole % NaCl, 41 ±2 mole % KCl, $t_E = 613$ ±2°C. On the NaCl—KCl side there exists a continuous solid solution, the decomposition of which starts after addition of 3—4 mole % LiF. Also these data could be confirmed using X-ray phase analysis. A comparison of our data with those presented by *Bergman et al.* [9] shows that our results differ especially with respect to the content of KCl in the ternary eutectic point as well as in the temperature T_E, but the general character of the system LiF—NaCl—KCl agrees with that by *Bergman et al.* [9]. In Fig. 1 the phase diagram of the LiF—NaCl—KCl system is shown. In Fig. 2 the vertical section of the second kind with a constant content of LiF of the investigated system is presented.

References

1. Gabčová, J., Peschl, J., Malinovský, M., and Koštenská, I., *Chem. Zvesti* ***30,*** 796 (1976).
2. Akopov, E. K. and Bergman, A. G., *Zh. Obshch. Khim.* ***24,*** 1524 (1954).
3. Bukhalova, G. A. and Bergman, A. G., *Zh. Prikl. Khim.* ***28,*** 1266 (1955).
4. Bukhalova, G. A. and Mateyko, Z. A., *Zh. Obshch. Khim.* ***25,*** 887 (1955).
5. Rubleva, V. V. and Bergman, A. G., *Zh. Obshch. Khim.* ***26,*** 651 (1956).
6. Belyaev, A. I. Zhemchuzhina, E. A., and Firsanova, L. A., *Fizicheskaya khimiya rasplavlennykh solei.* Metallurgizdat, Moscow, 1957.

7. Bukhalova, G. A., Maslennikova, G. N., and Ryabkin, D. M., *Zh. Neorg. Khim.* **7,** 1640 (1962).
8. Coleman, D. S. and Lacy, P. D. A., *Mater. Res. Bull.* **2,** 935 (1967).
9. Bergman, A. G., Berezina, I. S., and Bakumskaya, E. L., *Zh. Neorg. Khim.* **8,** 2144 (1963).
10. Foster, R. A., Jr., *J. Amer. Ceram. Soc.* **53,** 598 (1970).
11. Stull, D. R. and Prophet, H., *JANAF Thermochemical Tables*, 2nd Ed. U.S. Departm. of Commerce, Natl. Bur. Stand., Washington, 1971.
12. Bergman, A. G. and Bakumskaya, E. L., *Zh. Obshch. Khim.* **25,** 2405 (1955).

Translated by M. Uhrová