

Phase Relations in the Systems NaF-LiF, NaF-KF, and NaF-RbF

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The phase diagrams for the systems NaF-LiF, NaF-KF, and NaF-RbF have been examined by thermal analysis, differential thermal analysis and quenching technique.

The system NaF-RbF was found to be a simple eutectic with no detectable solid solubility greater than 1 mole % on either side, while limited solid solubility was observed on the NaF-side of the system NaF-LiF (4 ± 0.5 mole % at the eutectic temperature 649°C) and on the KF-side of the system NaF-KF (5 ± 0.5 mole % at the eutectic temperature 721°C).

The binary systems NaF-LiF, NaF-KF, and NaF-RbF have been reexamined. A special attention has been paid to the possibility of formation of solid solutions in the systems.

The system NaF-LiF has recently been investigated by Bergman and Dergunov.¹ They reported a simple eutectic system without any solid solubility, with an eutectic point at 40 mole % NaF and 652°C . Kurnakov² who investigated the system NaF-KF found that while there is a considerable solubility of sodium fluoride in potassium fluoride (an eutectic halt was found at $N_{\text{KF}} = 0.80$, but not at $N_{\text{KF}} = 0.85$), the solid solubility of potassium fluoride in sodium fluoride is much less (an eutectic halt was found at $N_{\text{NaF}} = 0.94$). Kurnakov reported an eutectic point in the system at 40 mole % NaF and 700°C . Dergunov³ also reported an eutectic point in the system NaF-RbF at 33 mole % NaF and 644°C .

EXPERIMENTAL

Materials. The chemicals used in the studies were commercially available reagent grade lithium fluoride (Fischer Certified Reagent, Fischer, U.S.A.) m.p. 846.3°C , sodium fluoride (Merck, Darmstadt, Germany) m.p. 994.5°C , potassium fluoride (Baker and Adamson, U.S.A.) m.p. 858.4°C and rubidium fluoride (Light Laboratories Ltd, England) m.p. 793°C . The chemicals were dried in a vacuum furnace at $400-500^\circ\text{C}$ before use. Specially care had to be taken with the potassium fluoride and rubidium fluoride since these materials were found to be very hygroscopic.

Apparatus and methods. The liquidus and solidus data reported were obtained from cooling curves taken by ordinary thermal analysis, differential thermal analysis (DTA) and by using a quenching technique.

The apparatus and technique used for the thermal analysis have been described in previous papers.^{4,5} It is known that this method is not sensitive enough for registrations of eutectic halts at compositions near the pure components. Therefore samples of these compositions were examined by DTA. The cooling curves were recorded by a Speedomax G X—Y recorder and by use of a D.C. Microvolt Amplifier (range 50—2000 microvolt, Leeds and Northrup, U.S.A.). A more detailed description of the apparatus and technique will soon be published.

Samples for the quenching experiments were first homogenized by mixing in 100 % alcohol in a glove box and then dried at 120°C. Small samples were put into platinum containers and heated to different temperatures. After equilibration, the samples were quenched in kerosene oil and examined with a polarizing microscope in order to observe the first appearance of a liquid phase. Because of the steepness of the solidus curve and the small area of solid solution in the systems, it was proved during the experiments that this method only can give a crude determination of the solidus curve near the pure components.

RESULTS AND DISCUSSION

The results from the thermal analysis are given in Tables 1, 2, and 3, while the phase diagrams for the three systems are presented in Figs. 1, 2, and 3.

The system NaF—LiF. The observed eutectic point in the system is at 39 mole % NaF and 649°C. This is in good agreement with the data reported by Bergman.¹

The cooling curves from the DTA examination of samples containing 3, 5 and 98 mole % LiF are given in Figs. 4a, b, and c. A small exothermic peak at 640°C corresponding to the eutectic temperature is observed when the mixture contains 5 mole % LiF (Fig. 4b). By changing the concentration of LiF from 5 to 3 mole % no peak could be observed at this temperature (Fig.

Table 1. The system NaF—LiF. Temperature obtained by thermal and differential thermal analysis.

Comp. mole % LiF	Liquidus curve °C	Solidus curve eutectic temperature °C
0	994.5	—
5.00	974.1	640 *
10.00	954.9	645.0
19.89	908.8	647.0
30.00	858.2	648.0
40.00	801.0	648.7
50.00	732.7	649.0
60.00	652.6	649.2
64.43	672.7	649.1
70.00	705.6	648.8
80.00	760.2	648.3
90.00	806.4	646.0
98.00	—	649 *
100.00	846.3	—

* found by DTA.

Table 2. The system NaF—KF. Temperatures obtained by thermal and differential thermal analysis.

Comp. mole % KF	Liquidus curve °C	Solidus curve eutectic temperature °C
0	994.5	—
5.05	974.5	718 *
10.04	954.6	719.0
19.89	913.2	720.0
29.96	869.5	720.7
38.70	827.8	720.9
43.69	802.7	720.9
66.85	750.0	720.6
68.95	756.6	—
70.15	762.0	720.5
79.74	794.1	719.7
90.82	830.2	714.2
94.99	840.8	718 *
100.00	858.4	—

* found by DTA.

Table 3. The system NaF—RbF. Temperatures obtained by thermal and differential thermal analysis.

Comp. mole % RbF	Liquidus curve °C	Solidus curve eutectic temperature °C
0	994.5	—
1.99	—	662 *
5.26	974.1	665
10.85	951.4	665
19.14	919.4	665.4
30.05	873.0	665.6
37.25	841.8	665.8
51.07	771 *	666 *
59.94	723 *	667 *
67.69	670 *	—
77.11	708 *	669 *
88.26	750 *	666 *
94.03	775 *	665 *
97.98	787 *	658 *
100.00	793 *	—

* found by DTA.

4a). On the LiF-side, however, a very distinct exothermic peak is observed for a sample containing only 2 mole % NaF (Fig. 4c).

From microscopic examination of a quenched sample containing 2.5 mole % LiF it was found that the first liquid appeared between 785°C and 830°C.

Table 4. Phase relations in some binary fluoride and chloride systems.

System	Phase relations	Difference in cation radius, Å	Reference
LiF—NaF	limited solubility on the NaF-side (4 mole %)	0.35	this work Smits <i>et al.</i> ⁷
LiCl—NaCl	continuous solid solutions		
NaF—KF	limited solubility on the KF-side (5 mole %)	0.38	this work different works ^{8,9}
NaCl—KCl	continuous solid solutions		
NaF—RbF	no solid solutions *	0.53	this work
NaCl—RbCl	limited solid solubility on the RbCl-side (6 mole %)		
			Short and Roy ⁶

* Possibly less than 1 mole %.

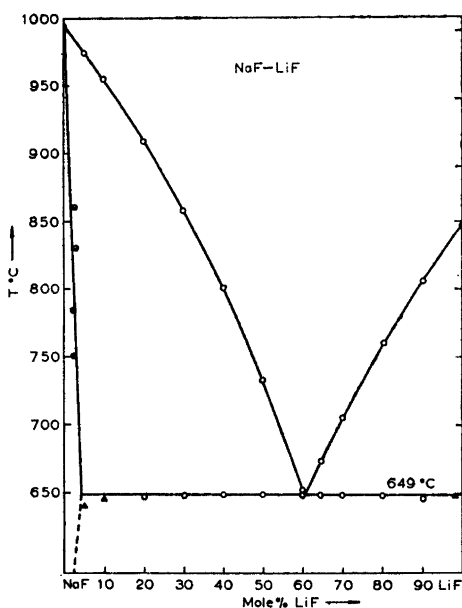


Fig. 1. The phase diagram NaF—LiF from the present work. Open circles: results from thermal analysis.

Half filled and filled circles: results from quenching experiments.

A half-filled circle means that liquid + one solid phase are present, a filled circle means that one or two solid phases are present. Triangles: results from differential thermal analysis.

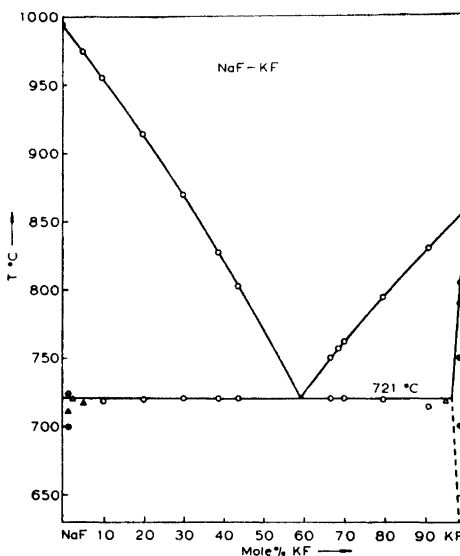


Fig. 2. The phase diagram NaF—KF from the present work. (Symbols see Fig. 1).

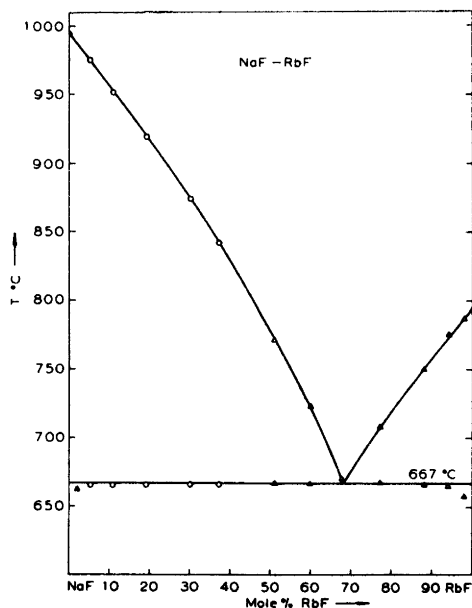


Fig. 3. The phase diagram NaF—RbF from the present work. (Symbols see Fig. 1).

On the basis of these experiments it is assumed that NaF can take up 4 ± 0.5 mole % LiF in the solid state at 649°C , while the solubility of NaF in LiF is less than 1 mole %.

Recently Short and Roy⁶ have concluded by measuring the interdiffusion in NaF—LiF mixtures that the crystalline solubility of LiF in NaF is 8 ± 1 mole % and of NaF in LiF is 1.5 ± 0.5 mole % at 625°C . These values are considerably higher than the results obtained in the present work.

The system NaF—KF. The eutectic point in the system is established at 40 mole % NaF and 721°C . This temperature is about 20 degrees higher than the eutectic temperature reported by Kurnakov.²

The cooling curves from the DTA examination of samples containing 2, 43.7, and 94.5 mole KF are given in Figs. 4d, e, and f. The three diagrams all contain exothermic peaks which correspond to the eutectic temperature in the system. No such peak could be observed for samples containing less than 5 mole % NaF.

From the microscopic examinations of quenched samples containing 2 mole % NaF, it was found that the first liquid appeared at $805 \pm 10^\circ\text{C}$ and not at the eutectic temperature.

These experiments show that solid potassium fluoride can contain 5 ± 0.5 mole % sodium fluoride at 721°C . No solid solubility of potassium fluoride in sodium fluoride could be detected for samples containing more than 1 mole % KF.

The system NaF—RbF. The eutectic point is established at 32.8 mole % NaF and 667°C . This temperature is about 20 degrees higher than the eutectic temperature reported by Dergunov.³

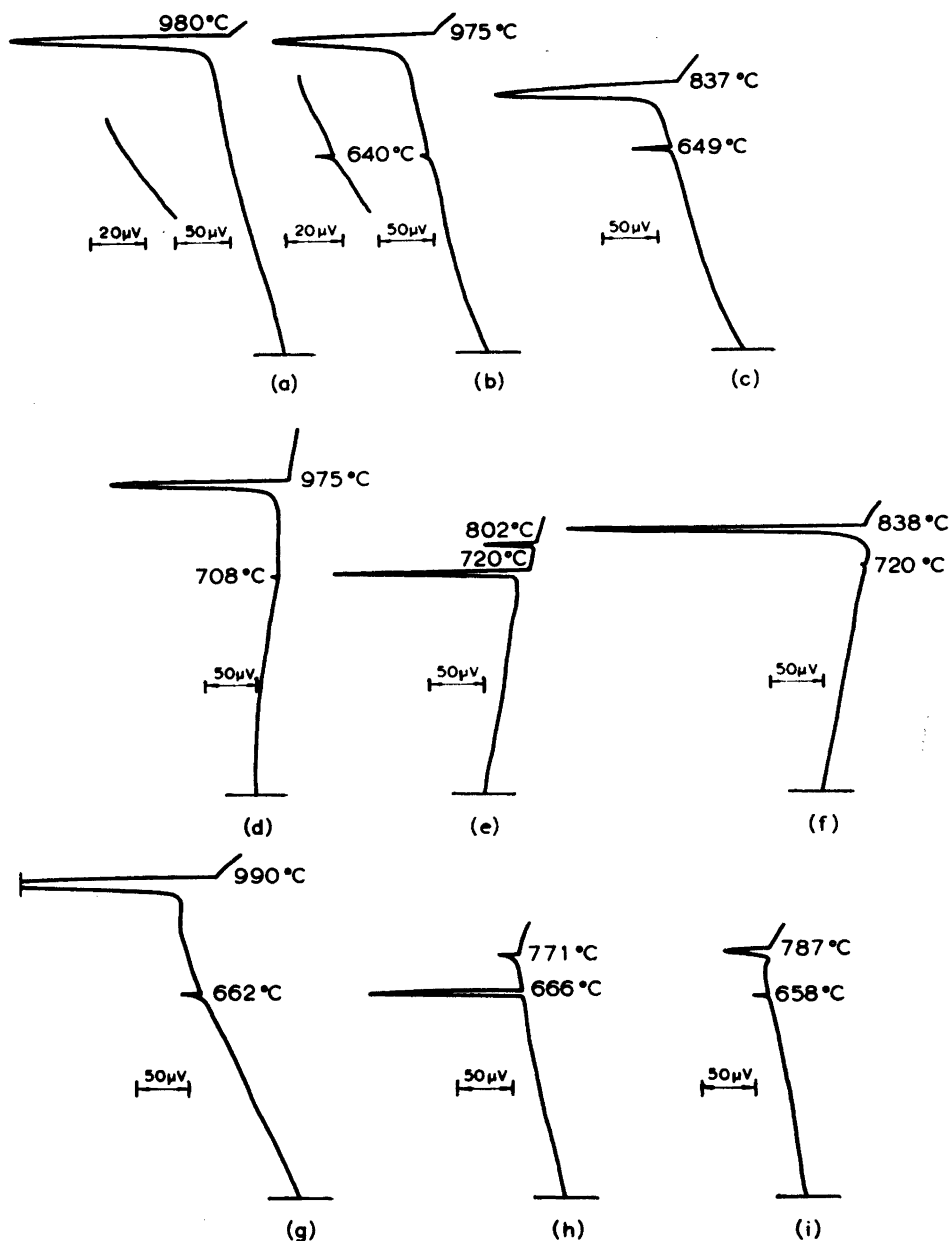


Fig. 4. Differential thermal analysis curves for some of the fluoride mixtures. System NaF—LiF: a) 3 mole % LiF; b) 5 mole % LiF; c) 98 mole % LiF. System NaF—KF: d) 2 mole % KF; e) 43.7 mole % KF; f) 94.5 mole % KF. System NaF—RbF: g) 2 mole % RbF; h) 51.1 mole % RbF; i) 98 mole % RbF.

The cooling curves from the DTA examination of samples containing 2, 51.1, and 98 mole % RbF are given in Figs. 4 g, h, and i. The three diagrams all contain exothermic peaks at temperatures which correspond to the eutectic temperature in the system. Since the eutectic peaks are very distinct, it may be assumed that the solid solubility on either side is less than 1 mole %.

Compared with the chloride, bromide and iodide systems, the fluorides ordinarily show very little tendency to form solid solutions (Table 4). Foreign cations do not easily fit into the fluoride lattice due to the unfavourable radius ratio, $r_{\text{cat}}/r_{\text{an}}$, and the low polarizability of the fluoride ion.

The NaF—RbF system differs from the two other fluoride systems since there is no detectable crystalline solubility in either of the compounds in the system. This behaviour can be explained by the fact that the difference in radius between the Rb⁺-ion and Na⁺-ion is more unfavourable than the difference between the K⁺-ion and the Na⁺-ion and the difference between the Na⁺-ion and the Li⁺-ion with respect to a solid solution formation.

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