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Equilibrium Studies in the Systems K_3AlF_6-Na_3AlF_6 and K_3AlF_6-Rb_3AlF_6

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The binary systems K_3AlF_6-Na_3AlF_6 and K_3AlF_6-Rb_3AlF_6 have been investigated and the phase diagrams constructed, using ordinary thermal analysis (TA), differential thermal analysis (DTA), low- and high-temperature X-ray diffraction studies. In the system K_3AlF_6-Na_3AlF_6 an intermediate compound with the composition $2K_3AlF_6.Na_3AlF_6$, corresponding to the mineral elpasolite, K_2NaAlF_6, which melts congruently at 954°C, was detected. The compound was found to be cubic, with $a = 8.095 \pm 0.02$ Å, and has no polymorphic transformations. In the system K_3AlF_6-Rb_3AlF_6, a continuous solid solution was detected.

There has been a great interest in the structure and behaviour of the alkali-metal hexafluoroaluminates in recent years. The results reported in the literature, however, are often in disagreement. The present work is a part of an extensive study on the hexafluoroaluminates of Li, Na, K, Rb, and Cs. In a previous paper,[1] the phase diagrams of the binary systems Li_3AlF_6-K_3AlF_6 and Li_3AlF_6-Rb_3AlF_6 were presented. In this work, the phase diagrams of the systems K_3AlF_6-Na_3AlF_6 and K_3AlF_6-Rb_3AlF_6 have been determined.

EXPERIMENTAL

(a) *Thermal analysis (TA).* The equipments and technique used for the determination of cooling curves were similar to those used by Grjotheim.[2] An ordinary vertical tube furnace, with Kanthal A wire as the heating element, was used. The samples were melted in a crucible made of pure graphite (from Skandinaviska Grafitindustri AB with a minimum carbon content of 99.79 %. The temperature was measured with a Pt-Pt 10 % Rh thermocouple (calibrated at the melting point of silver) connected to a precision potentiometer (W. G. Pye, Cambridge, England), with a mirror galvanometer (Multiflex-Galvanometer, type MGO, Berlin, Germany). The end of the alumina

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jacket containing the hot junction of the thermocouple was sealed off with alundum cement. The temperature could be measured with an accuracy of ± 0.1°C, and was recorded at half minute intervals.

The runs were carried out in a purified nitrogen atmosphere. Before cooling, the temperature of the furnace was kept 10°C above the expected crystallization temperature for about 15 min. The cooling rate was 1 – 1.5°C per minute. Supercooling of the melt was prevented by continuous stirring as well as seeding with small crystals of one of the cryolites. For each experiment, about 80 g of the sample were used.

(b) *Differential thermal analysis (DTA), low- and high-temperature X-ray measurements.* The procedure was the same as in the previous paper.[1]

(c) *Materials.* Na_3AlF_6: Handpicked natural cryolite from Ivigtut, Greenland, of the same type as used by Holm.[3] AlF_3: Prepared at the Slovak Academy of Sciences, Bratislava, Czechoslovakia, purified by sublimation. Analysis: AlF_3 99.2 – 99.5 %, Al_2O_3 0.5 – 0.8 % as reported by Matiasovsky and Malinovsky.[4] KF: Anhydrous KF, laboratory reagent (B.D.H., Poole, England). Dried at 400°C under vacuum for 3 h in a Pt-crucible. RbF: Rubidium fluoride for laboratory use (Koch-Light Laboratories, Colnbrook, Bucks, England, min. 99.8 %), as well as El. quality (Merck, Darmstadt, Germany) was used. The fluoride was melted in a Pt-crucible under pure nitrogen atmosphere, and pure crystals were selected from the sample. KF and RbF were always handled inside a dry box.

For the preparation of K_3AlF_6 and Rb_3AlF_6, stoichiometric amounts of the alkali fluoride and aluminium fluoride were melted together in a Pt-crucible in a purified nitrogen atmosphere. The composition of each of the cryolites was carefully adjusted by adding aluminium fluoride until no eutectic reaction could be observed by DTA.

RESULTS AND DISCUSSION

(a) *The system K_3AlF_6-Na_3AlF_6.* The binary system K_3AlF_6-Na_3AlF_6 has been studied by several authors,[5–13] but their results are not in agreement. Neither the solidus line nor the change in the polymorphic transformation temperature with composition has been clearly determined in any of these works.

Belyaev and Studentsov,[5] Baimakov and Bataschev,[6] as well as Lundina [7] reported that a continuous solid solution exists between Na_3AlF_6 and K_3AlF_6, and that the liquidus line has a minimum at 940°C and about 50 mol % K_3AlF_6. Bukhalova *et al.*[8] indicated the minimum to be at 927°C and about 26 mol % K_3AlF_6. Naray-Szabo and Sigmond [9] reported the existence of six intermediate compounds as follows: $5K_3AlF_6.2Na_3AlF_6$, $2K_3AlF_6.Na_3AlF_6$ (elpasolite), $5K_3AlF_6.3Na_3AlF_6$, $K_3AlF_6.Na_3AlF_6$, $3K_3AlF_6.5Na_3AlF_6$ and $K_3AlF_6.2Na_3AlF_6$. Only the compound $2K_3AlF_6.Na_3AlF_6$ was reported to be stable at room temperature. Edoyan *et al.*[10] confirmed the existence of the same compounds.

Bukhalova and Mal'tsev [11] reported the presence of the following compounds: $3K_3AlF_6.Na_3AlF_6$, formed in the solid phase at 796°C and decomposed at 715°C; $K_3AlF_6.Na_3AlF_6$, formed in the solid phase at 832°C and decomposed at 736°C; and $2K_3AlF_6.Na_3AlF_6$ which does not decompose when cooled to room temperature. Chin and Hollingshead [12] reported that with the addition of increasing amounts of K_3AlF_6, the primary freezing point of Na_3AlF_6 decreases to 945°C at 40 mol % K_3AlF_6 and then rises to 955°C at 60 – 70 mol % K_3AlF_6. They also confirmed the presence of the compound K_2NaAlF_6. Yoshioka and Koroda [13] determined the liquidus line and their results were in fair agreement with those of Chin and Hollingshead.[12]

Table 1. DTA and TA data for the system Na_3AlF_6-K_3AlF_6.

Mol % Na_3AlF_6	Mol % K_3AlF_6	Experimental, °C DTA T_1	DTA T_2	TA T_1
100.00	0.00	1010	560.0	–
97.50	2.50	999.0	545.0	–
95.90	4.10	995.0	542.0	995.6
91.71	8.29	983.0	–	–
87.46	12.54	–	–	974.0
83.11	16.89	963.5	498.0	964.0
81.35	18.65	956.8	–	–
78.68	21.32	953.0	–	952.2
74.16	25.84	945.0	482.0	945.6
71.41	28.59	941.0	–	–
69.55	30.45	–	–	938.0
66.74	33.26	940.0	–	–
64.85	35.15	940.0	420.0	940.4
62.40	37.60	941.7	–	–
60.05	39.95	941.2	–	941.5
57.13	42.87	943.0	–	–
55.16	44.84	943.7	390.0	944.0
52.17	47.83	947.6	–	–
50.16	49.84	947.0	–	947.2
47.11	52.89	950.6	354.0	–
45.06	54.94	950.3	350.0	–
39.84	60.16	951.0	338.0	–
34.52	65.48	954.0	–	–
33.33	66.67	954.0	–	–
29.08	70.92	951.0	–	–
23.52	76.48	956.4	340.0	–
17.84	82.16	966.0	–	–
12.02	87.98	974.9	–	–
6.08	93.92	983.0	–	–
3.65	96.35	987.0	–	–
0.00	100.00	995.0	310.0	–

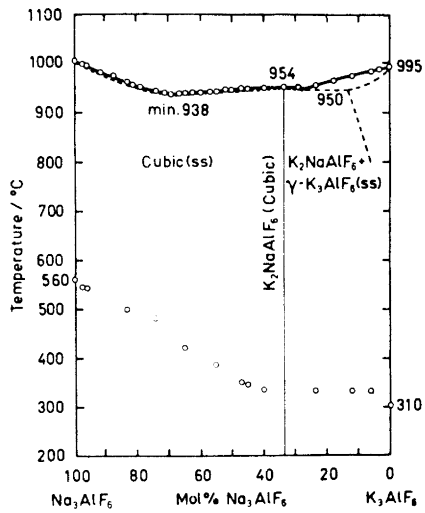

Fig. 1. The phase diagram of the system Na_3AlF_6-K_3AlF_6 according to the TA and DTA results (cooling curves).

The results obtained in the present work for the system K_3AlF_6-Na_3AlF_6 are shown in Table 1, and the corresponding phase diagram in Fig. 1. The results obtained by thermal analysis are in good agreement with those obtained by differential thermal analysis. The melting points and the solid transformation temperatures of the pure compounds K_3AlF_6 and Na_3AlF_6 were determined as 995, 310, 134°C (K_3AlF_6), and 1010 and 560°C (Na_3AlF_6).

Representative samples were examined by X-ray powder diffraction at different temperatures as follows:

Pure Na_3AlF_6 at room temp. 492, 605, 700°C
87.46 mol % Na_3AlF_6 at room temp. 437, 498, 590, 695, 812, 906°C
66.74 mol % Na_3AlF_6 at room temp. 430, 817, 884°C
55.16 mol % Na_3AlF_6 at room temp. 500, 599, 685°C
34.52 mol % Na_3AlF_6 at room temp. 592, 646, 690°C
23.52 mol % Na_3AlF_6 at room temp. 622, 752, 822°C
12.02 mol % Na_3AlF_6 at room temp. 594, 649, 693, 710, 770°C
Pure K_3AlF_6 at room temp. 510, 620, 710°C

The liquidus line is relatively flat throughout the whole diagram, especially in the middle region. No solidus line was detected, even by using low cooling rates (less than 0.5°C per minute in the case of the differential thermal analysis). An intermediate compound with the composition $2K_3AlF_6.Na_3AlF_6$, which melts congruently at 954°C, was the only compound detected. The X-ray data of this compound (Table 2) are in good agreement with those reported by Frondel [14] for the mineral elpasolite. The results indicate that the compound has a cubic structure with a lattice constant $a = 8.095 \pm 0.02$ Å at 20°C. No solid transformation of this compound was observed. From the obtained results

Table 2. X-Ray data for K_2NaAlF_6 (20°C); cubic: $a = 8.095 \pm 0.02$ Å.

h k l	Int.	$\sin^2 \theta_{obs} \times 10^4$	$\sin^2 \theta_{calc} \times 10^4$	d_{obs} This work	d_{obs} Frondel [14]
1 1 1	vw	272	272	4.667	4.673
2 0 0	vw	364	363	4.037	4.047
2 2 0	vs	718	726	2.873	2.862
2 2 2	vs	1085	1088	2.339	2.336
					2.244
4 0 0	vs	1440	1451	2.030	2.023
3 3 1	vw	1720	1723	1.857	1.852
4 2 2	m	2168	2177	1.654	1.652
					1.587
5 1 1	w	2448	2449	1.557	1.558
4 4 0	m	2892	2902	1.433	1.431
5 3 1	vw	3173	3175	1.368	1.368
6 2 0	w	3622	3628	1.280	1.280
6 2 2	vw	3978	3991	1.220	1.220
4 4 4	w	4339	4354	1.169	1.168
5 5 1	vw	4616	4626	1.134	1.133

it seems more convenient to describe the system as two separate systems, namely Na_3AlF_6-K_2NaAlF_6 and K_2NaAlF_6-K_3AlF_6.

In the first system, Na_3AlF_6-K_2NaAlF_6, it is observed that the polymorphic transformation temperature of pure Na_3AlF_6 (560°C) decreases with the addition of increasing amounts of the compound K_2NaAlF_6. Near the composition of pure K_2NaAlF_6, the transformation temperature was found to be about 340°C. Guinier X-ray patterns at room temperature showed the presence of a mechanical mixture of Na_3AlF_6 and K_2NaAlF_6 in this region. From the high-temperature X-ray diffraction experiments, a mechanical mixture was also found to exist in the area just below the transformation line. The area above the transformation line, however, was found to contain a solid solution of K_2NaAlF_6 and the cubic high-temperature modification of Na_3AlF_6. These results suggest that the solidus line is very close to the liquidus, enclosing an area where the liquid phase is present in equilibrium with the solid solution, with a minimum at about 938°C and 69.5 mol % Na_3AlF_6, as shown in the diagram.

The system K_2NaAlF_6-K_3AlF_6 on the other hand is a binary system with a eutectic point. The eutectic point was determined at 950°C and 27 mol % Na_3AlF_6. The solid transformation temperature of K_3AlF_6 (310°C) shows a small increase very near to pure K_3AlF_6 and is then almost constant at all other compositions. The transformation line was determined at 340°C. The area below this line and down to room temperature was found to contain a mechanical mixture of K_3AlF_6 and K_2NaAlF_6. Above this line, a mechanical mixture of the high temperature modification of K_3AlF_6 and K_2NaAlF_6 was determined. However, the high-temperature X-ray diffraction method is inefficient for detecting as little as 3 – 4 % of one compound in a mixture, and the change in the solid transformation temperature of K_3AlF_6 indicates that there is a narrow area of solid solution on the K_3AlF_6 side of the diagram.

(b) *The system K_3AlF_6-Rb_3AlF_6.* The only work published on the system K_3AlF_6-Rb_3AlF_6 was carried out by Mal'tsev and Bukhalova,[15] using visual observation and thermal analysis. They indicated the presence of a continuous solid solution of K_3AlF_6 and Rb_3AlF_6 which decomposes at low temperatures. The melting points of the pure compounds K_3AlF_6 and Rb_3AlF_6 were found to be 986 and 914°C, and the polymorphic transformation temperatures 310 and 340°C, respectively. A minimum was found at 900°C and 20 mol % Rb_3AlF_6 by visual observation, and at 906°C and the same composition by thermal analysis.

In the present work, the system K_3AlF_6-Rb_3AlF_6 was studied by DTA. The results are presented in Table 3 and the corresponding phase diagram is shown in Fig. 2. The melting points of the pure compounds K_3AlF_6 and Rb_3AlF_6 were found to be 995 and 924°C, respectively, and polymorphic transformations were found at 310 and 134°C for K_3AlF_6 and 356°C for Rb_3AlF_6. A continuous solid solution of K_3AlF_6 and Rb_3AlF_6 was detected. The solidus points were recorded as small breaks in the DTA cooling/heating curve when the cooling (or heating) rate was sufficiently low (T_2). The system seems to contain a very narrow field where liquid exists in equilibrium with solid solution. The temperature difference between the liquidus and the solidus line does not exceed 6°C at any composition.

Table 3. DTA data for the system K_3AlF_6-Rb_3AlF_6.

Mol %		Experimental, °C		
K_3AlF_6	Rb_3AlF_6	T_1	T_2	T_3
100.00	0.00	995.0	–	310.0
92.90	7.10	985.0	–	296.0
89.71	10.29	982.0	979.0	282.0
85.22	14.78	978.2	974.2	280.0
82.20	17.80	975.0	970.5	254.0
78.21	21.79	969.4	965.0	–
72.08	25.92	966.0	961.5	212.0
69.77	30.23	960.4	954.2	–
65.29	34.71	957.0	–	–
60.61	39.39	953.0	–	–
55.73	44.27	949.5	–	–
50.64	49.36	946.2	942.0	–
45.31	54.69	942.0	939.2	–
39.74	60.26	940.0	937.5	–
34.12	65.88	936.5	933.0	–
27.78	72.22	934.0	930.0	–
21.36	78.64	930.0	927.0	–
14.60	85.40	928.2	926.0	–
7.49	92.51	926.0	923.0	–
3.79	96.21	925.0	–	292.0
0.00	100.00	924.0	–	356.0

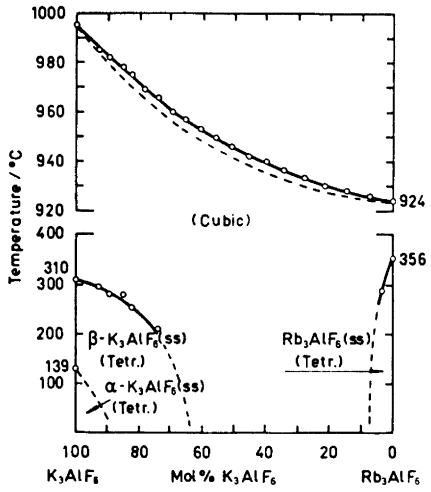

Fig. 2. The phase diagram of the system K_3AlF_6-Rb_3AlF_6 according to the DTA results (cooling curves).

Guinier X-ray studies were made of the following samples at room temperature: Pure Rb_3AlF_6, 3.79, 7.49, 14.6, 21.36, 34.12, 50.64, 55.73, 60.61, 65.29, 69.77, 74.08, 78.21, 82.20, 85.22, 89.71, 92.90 mol % K_3AlF_6, and pure K_3AlF_6. The results show that at room temperature, a tetragonal solid

solution is present in the region between pure Rb_3AlF_6 and 7.5 ± 2.5 mol % K_3AlF_6. In the region between 7.5 ± 2.5 and 62 ± 2.5 mol % K_3AlF_6, a cubic solid solution was detected, which indicates that the high-temperature modifications of K_3AlF_6 and Rb_3AlF_6 can be preserved even at room temperature in that region. The change in the lattice constant with composition in

Table 4. The lattice constant a, as a function of composition in the system K_3AlF_6-Rb_3AlF_6 at room temperature.

K_3AlF_6 mol %	a Å
21.36	8.692
34.12	8.665
50.60	8.602
60.61	8.555

this region is given in Table 4. Between 62 ± 2.5 mol % and 87 ± 2.5 mol %, and between 87 ± 2.5 mol % and pure K_3AlF_6, two regions of tetragonal [16] solid solutions, β-K_3AlF_6(ss) and α-K_3AlF_6(ss), were detected.

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