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The Systems K_3AlF_6-Li_3AlF_6 and Rb_3AlF_6-Li_3AlF_6

I. The Phase Diagrams

KAI GRJOTHEIM, JAN LÜTZOW HOLM, MILAN MALINOVSKY and SHAHEER AZIZ MIKHAIEL

Institute of Inorganic Chemistry, The Technical University of Norway, Trondheim, Norway

As a part of an extensive study of the phases and structural relations in alkali cryolite systems, the two binary systems $Li_3AlF_6-K_3AlF_6$ and $Li_3AlF_6-Rb_3AlF_6$ have been reinvestigated. The techniques used during the studies were differential thermal analysis (DTA), low and high temperature X-ray diffraction studies, and density measurements. One intermediate compound was found in each system, both melting incongruently, K_2LiAlF_6 at 780°C, and Rb_2LiAlF_6 at 700°C. K_2LiAlF_6 was found to be hexagonal with $a_0 = 5.593$ Å, $c_0 = 13.754$ Å, and with 3 formula units in the cell. This is in good agreement with the values published by Winkler on the high-temperature modification of K_2LiAlF_6. Rb_2LiAlF_6 was found to have an orthorhombic structure with $a_0 = 5.797$ Å, $b_0 = 11.629$ Å, $c_0 = 16.203$ Å, and 8 formula units in the cell.

Investigations of complex aluminium fluoride systems started at this Institute around 1950 with an extensive investigation of the $NaF-AlF_3$ system.[1] This work also included a discussion of cryolite, Na_3AlF_6, and the structure and stability of sodium fluoride-aluminium fluoride mixtures in the molten state.

Since then, much work at this Institute has been devoted to the examinations of the structure and stability of complex aluminium fluoride mixtures and cryolite-alumina mixtures in the solid as well as in the molten state.[2,3] Recently, this work has been extended to other alkali cryolite systems.[3,4] The phase transitions and the structure of the compounds K_3AlF_4, Rb_3AlF_6, and Cs_3AlF_6,[5] and of Li_3AlF_6[6,7] have been investigated, and the phase diagram of the system $Li_3AlF_6-Na_3AlF_6$ has been determined.[8]

In this paper, we present an investigation of the phase diagrams of the two binary systems, $Li_3AlF_6-K_3AlF_6$ and $Li_3AlF_6-Rb_3AlF_6$. Some works, mainly from the Russian school, have already been published on these systems. However, their results are not at all conclusive. The aim of the present work is therefore to clarify the phase relations in the two systems.

EXPERIMENTAL

(a) Differential thermal analysis (DTA)

The DTA instrument used in the present investigation consists of three major components, a sample holder, a controlled source of heat, and a device for temperature measurements. The sample holder is a nickel block with a thermocouple (Pt/Pt 10 % Rh) for recording the temperature, placed inside the block. The differential thermocouple consists of two long platinum wires welded together with one short Pt 10 % Rh wire. One junction of the thermocouple was immersed directly in the sample, while the other junction was immersed in the reference sample (alumina). Two thin-walled platinum crucibles were used to hold the sample and the reference material. The block was placed inside a vertical tube furnace with Kanthal A wire as heating element.

An automatic recorder was used for measuring and recording the differential temperature. The recorder was a Speedomax G, X – Y recorder (Leeds and Northrup Co., Philadelphia, Penn.) with a D.C. Microvolt Amplifier (range 50 – 2000 μV). The temperature was measured by a potentiometer (Otto Wolff, Berlin 5881, Germany) used together with a mirror galvanometer (Multiflexgalvanometer, type MGO, Germany). In this way, an accuracy of $\pm$ 1° in the temperature measurements was attained. In some runs, the DTA curves were recorded by a Varian G 2022 Dual Channel Recorder. Here, the accuracy obtained was the same $\pm$ 1°C, as without use of the extra potentiometer.

The samples were weighed out in stoichiometric compositions, ground and melted under nitrogen atmosphere. Before cooling, the charge was kept for 5 – 10 min at a temperature about 10° above the liquidus point of the system. Approximately 2 g of the sample were used in each experiment.

(b) X-Ray investigation

A high temperature X-ray camera made at this Institute, similar to that used by Smith,[9] was used for the high temperature measurements. The sample holder was made of Pt 10 % Rh alloy. The camera was connected to a goniometer (Philips PW 1050/25) in conjunction with the supplementary set (type Philips PW 1049) and Philips Electronic circuit panel.

Room temperature X-ray investigations of some mixtures were carried out, using a Guinier camera, Nonius type (Delft, Holland), and Cu$K\alpha$-radiation, with the Philips diffractometer (Goniometer PW 1050/25 and Electronic circuit panel), equipped with a scintillation counter.

(c) Density measurements

The density of the compound Rb_3LiAlF_6 was measured at 25°C by a vacuum pycnometric method, using Shell odourless Kerosene as a displacement liquid.

(d) Materials

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 Matiasovský and Malinovský.[10]

KF. Anhydrous KF, laboratory reagent (B.D.H., Poole, England). Dried at 400°C under vacuum for 3 h in a Pt-crucible.

LiF. Certified LiF, for laboratory use (Fisher Scientific Co., Chemical Manufacturing Division, Fair Lawn, New Jersey). Certificate of analysis: Cl 0.01 %, Ba 0.01 %, Pb 0.003 %. Dried at 300°C under vacuum for 2 h in a Pt-crucible.

RbF. Rubidium fluoride for laboratory use (Koch-Light Laboratories, Colnbrook, Bucks, England, as well as E. Merck AG, Darmstadt, Germany) was used. The fluoride was melted in a Pt-crucible under pure N_2 atm., and after cooling, pure crystals were selected. RbF was always handled inside a dry box.

For the preparation of Li_3AlF_6, K_3AlF_6 and Rb_3AlF_6, stoichiometric amounts of the alkali fluoride and AlF_3 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 $Li_3AlF_6 - K_3AlF_6$

The system $Li_3AlF_6 - K_3AlF_6$ has been investigated by several authors, but their results do not agree. Bukhalova and Mal'tsev [11,12] investigated the system, using visual observation and thermal analysis. They reported that two compounds are formed in the system: an incongruently melting compound with the composition $2\ K_3AlF_6.Li_3AlF_6$, and another which is formed by a solid state reaction at 506°C, with the composition $K_3AlF_6.Li_3AlF_6$. By the visual polythermal method, they reported the peritectic point at 762°C and 47 mol % Li_3AlF_6, and the eutectic at 638°C and 80 % Li_3AlF_6. On the basis of the thermographic investigations, they obtained the same peritectic point at 756°C and 47 mol %, and the eutectic at 631°C and 82 % Li_3AlF_6.

Edoyan *et al.*,[13] in their studies of systems containing Li_3AlF_6, Na_3AlF_6, and K_3AlF_6, determined the phase diagram of the system $K_3AlF_6 - Li_3AlF_6$ on the basis of cooling curves. They indicated the presence of 3 congruently melting compounds: $2K_3AlF_6.Li_3AlF_6$, $5K_3AlF_6.6Li_3AlF_6$, and $3K_3AlF_6.5Li_3AlF_6$. The three compounds were reported to melt at 820°, 740°, and 720°C,

Table 1. DTA data for the system $Li_3AlF_6 - K_3AlF_6$

Mol %		Experimental, °C			
Li_3AlF_6	K_3AlF_6	T_1	T_2	T_3	T_4[a]
100.00	0.00	780.0	–	–	–
93.50	6.50	756.2	651.0	–	–
86.46	13.54	717.0	650.0	–	–
78.84	21.16	677.0	652.2	–	–
70.54	29.46	685.4	649.0	–	–
66.12	33.88	710.2	650.0	–	–
61.50	38.50	734.0	650.0	–	–
51.56	48.44	762.0	648.4	–	–
46.22	53.78	775.0	650.0	–	–
44.01	55.99	780.4	648.2	–	–
40.62	59.38	788.0	779.0	650	–
38.30	61.70	802.0	781.0	640	–
37.12	62.88	812.0	781.2	640	–
34.73	65.27	832.2	782.4	–	–
28.52	71.48	871.0	783.0	–	–
21.98	78.02	908.0	781.0	–	–
15.06	84.94	945.0	779.0	–	–
7.75	92.25	972.0	762.0	–	–
0.00	100.00	995.0	–	–	327.0

[a] T_4: phase transition temperature of K_3AlF_6 (see Ref. 5).

respectively. Four eutectic points were found at 760°C and 29 mol % Li_3AlF_6, at 700°C and 50 mol % Li_3AlF_6, at 695°C and 58 mol % Li_3AlF_6, and 640°C and 81 mol % Li_3AlF_6.

The results obtained for the system $Li_3AlF_6 - K_3AlF_6$ in the present work are shown in Table 1, and the corresponding phase diagram is presented in Fig. 1. The system contains one incongruently melting compound with the composition $2K_3AlF_6.Li_3AlF_6$, corresponding to K_2LiAlF_6. A peritectic point was found at 780°C and 41.5 mol % Li_3AlF_6, and an eutectic one at 650°C and 75 mol % Li_3AlF_6. By the present DTA method, solid solutions of 2 % or more could easily be detected. Since eutectic reactions were obtained until this limit, solid solutions of 2 % or more were ruled out. The X-ray measurements at room temperature showed that both K_3AlF_6 and K_2LiAlF_6 were

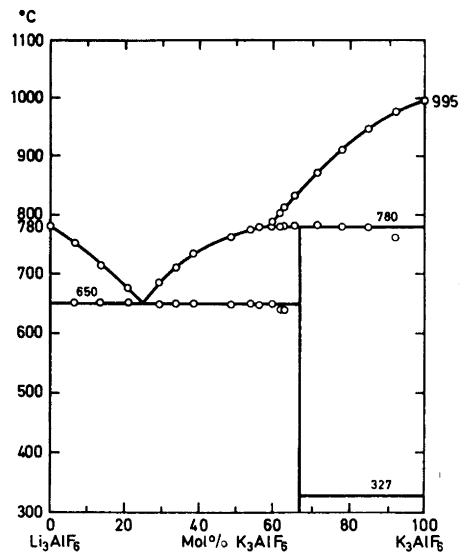

Fig. 1. The phase diagram of the system $Li_3AlF_6 - K_3AlF_6$ according to DTA (cooling curves).

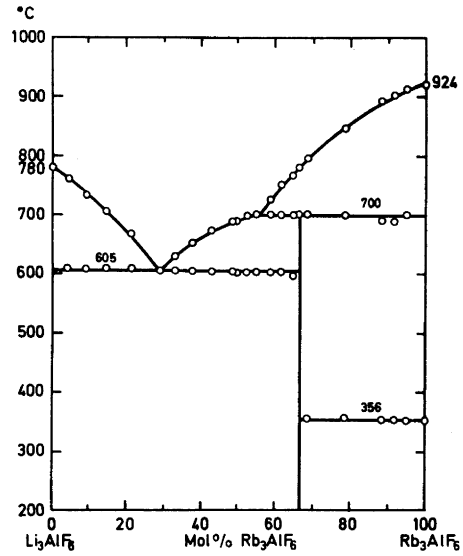

Fig. 2. The phase diagram of the system $Li_3AlF_6 - Rb_3AlF_6$ acccording to DTA (cooling curves).

always present in the region between pure K_3AlF_6 and 33.3 mol % Li_3AlF_6, and both K_2LiAlF_6 and Li_3AlF_6 in the region between 33.3 mol % Li_3AlF_6 and pure Li_3AlF_6. This indicates that no other compounds than K_2LiAlF_6 exist in the system at room temperature.

The compound K_2LiAlF_6 was examined by X-ray diffraction both at room temperature and at temperatures up to 650°C. X-Ray data for K_2LiAlF_6 are given in Table 2. The compound was found to have a hexagonal structure with the lattice parameters $a_0 = 5.593 \pm 0.002$ Å, and $c_0 = 13.754 \pm 0.009$ Å. The cell contains 3 formula units, and the X-ray density is 3.018 g/cm^3, compared to the experimental one of 3.00 g/cm^3.[14,15] The high temperature experiments up to 650°C indicated that no phase transitions occurred in this tem-

Table 2. X-Ray data for K_2LiAlF_6 (20°C), $\lambda_{CuK\alpha_1} = 1.5405$. Hexagonal: $a_0 = 5.593 \pm 0.002$ Å, $b_0 = 5.593 \pm 0.002$ Å, $c_0 = 13.754 \pm 0.009$ Å.

hkl	Int.	$\sin^2\theta_{obs} \times 10^4$	$\sin^2\theta_{calc} \times 10^4$	d_{obs}
101	s	285	284	4.563
102	m	379	378	3.957
103	m	538	535	3.321
110	s	758	759	2.798
{113}	m	{1042}	1040	2.386
{201}	m	{1042}	1043	2.386
006	m	1126	1127	2.295
202	s	1136	1137	2.285
203	s	1297	1293	2.139
204	s	1519	1512	1.976
211	m	1803	1801	1.814
108	w	2256	2256	1.622
300	m	2276	2276	1.615
303	w	2561	2558	1.522
220	s	3032	3035	1.399
{223}	w	{3320}	3316	1.337
{311}	w	{3320}	3319	1.337
313	w	3569	3569	1.289
314	vw	3790	3788	1.251

s = strong. m = medium. w = weak. vw = very weak.

perature range. Our results are in good agreement with the results obtained by Winkler [14,15] on the so-called "high-temperature" modification of K_2LiAlF_6. He reported two modifications of K_2LiAlF_6, one "low-temperature" modification, and another "high-temperature" modification made by annealing K_2LiAlF_6 at higher temperatures for 1 – 5 days at temperatures between 450 and 700°C. Winkler [14,15] found both modifications to have hexagonal symmetry. For the "low-temperature" modification, he gave $a_0 = 5.574 \pm 0.001$ Å, and $c_0 = 13.648 \pm 0.02$ Å, and for the "high-temperature" modification $a_0 = 5.615 \pm 0.001$ Å, and $c_0 = 13.574 \pm 0.01$ Å. He reported that a phase transition between the two modifications occurs at 470 ± 5°C.

As already mentioned, our high-temperature X-ray investigations up to 650°C indicated that no phase transitions occurred within the time of the experiments, which was 2 – 3 h.

(b) The system $Li_3AlF_6 - Rb_3AlF_6$

The only published work on the phase diagram of the system $Li_3AlF_6 - Rb_3AlF_6$ is the one by Bukhalova and Mal'tsev.[11] In their work, they used visual observation and thermal analysis by recording cooling curves. Their work indicates the existence of one incongruently melting compound with the composition $2Rb_3AlF_6.Li_3AlF_6$. By visual observation, they found the peritectic to be at 694°C and 44 mol % Li_3AlF_6, and the eutectic at 606°C and 73 mol % Li_3AlF_6. By the thermographic method, they obtained the

peritectic at 690°C and 44 mol % Li_3AlF_6, and the eutectic at 606°C and 73 mol % Li_3AlF_6.

The results of the present work obtained by the differential thermal analysis are presented in Table 3, and plotted in a phase diagram in Fig. 2. This system is very similar to the system $Li_3AlF_6 - K_3AlF_6$.

Table 3. DTA data for the system $Li_3AlF_6 - Rb_3AlF_6$.

Mol %		Experimental, °C				
Li_3AlF_6	Rb_3AlF_6	T_1	T_2	T_3	T_4[a]	T_5[b]
100.00	0.00	780.0	–	–	403.0	–
95.67	4.33	763.0	609.0	–	416.0	–
90.76	9.24	736.2	608.0	–	398.0	–
85.14	14.86	709.0	608.2	–	412.0	–
78.65	21.35	668.4	608.0	–	–	–
71.07	28.93	606.0	–	–	405.0	–
66.77	33.23	629.0	606.2	–	–	–
62.08	37.92	652.6	605.0	–	381.0	–
56.95	43.05	673.2	605.0	–	395.0	–
51.28	48.72	687.0	605.6	–	–	–
50.00	50.00	690.4	602.4	–	–	–
47.60	52.40	699.0	604.0	–	388.0	–
45.02	54.98	701.0	603.4	–	388.0	–
40.93	59.07	726.2	701.0	603.0	383.0	–
38.04	61.96	751.4	698.0	–	–	–
35.03	64.97	766.0	700.6	597.0	–	–
33.30	66.70	780.0	702.2	–	–	–
31.23	69.77	795.6	701.0	–	–	358.0
21.44	78.56	846.0	700.4	–	–	360.0
11.45	88.55	891.0	691.0	–	–	356.0
8.19	91.81	900.0	689.0	–	–	356.0
4.77	95.23	912.0	701.0	–	–	356.0
0.00	100.00	924.0	–	–	–	356.0

[a] T_4: phase transition temperature of Li_3AlF_6 on cooling (non-equilibrium data, see Refs. 6 and 7).
[b] T_5: phase transition temperature of Rb_3AlF_6 (see Ref. 6).

The melting point of pure Rb_3AlF_6 was found to be 924°C, and a polymorphic transformation was found to occur at 356°C. This is in good agreement with earlier values reported by Holm.[6] One incongruently melting compound, with the composition $2Rb_3AlF_6.Li_3AlF_6$, or Rb_2LiAlF_6, was detected. A peritectic point was found at 700°C and 44 mol % Li_3AlF_6, and a eutectic point at 605°C and 71 mol % Li_3AlF_6. This is in fair agreement with the values reported by Bukhalova and Mal'tsev.[11,12] X-Ray investigations of the samples in the system showed that only mixtures of Rb_3AlF_6 and Rb_2LiAlF_6 were present in the region 0 – 33.3 mol % Li_3AlF_6, while Rb_2LiAlF_6 and Li_3AlF_6 were the only compounds present in samples in the region 33.3 – 100 mol % Li_3AlF_6.

The compound Rb_2LiAlF_6 was examined by X-ray diffraction, both at room temperature and at temperatures up to 600°C. X-Ray data for Rb_2LiAlF_6 are given in Table 3. An attempt to relate the structure of Rb_2LiAlF_6 to the hexagonal cell of K_2LiAlF_6 was not successful. However, indexing Rb_2LiAlF_6 on the basis of an orthorhombic structure with $a_0 = 5.797 \pm 0.003$ Å, $b_0 = 11.629 \pm 0.009$ Å, and $c_0 = 16.203 \pm 0.013$ Å, gives a good agreement between experimental and calculated data, as shown in Table 4. The unit cell of Rb_2LiAlF_6 contains 8 formula units, and the calculated density is 3.877 g/cm³ as compared to the experimental one of 3.79 g/cm³.

Table 4. X-Ray data for Rb_2LiAlF_6 (20°C), $\lambda_{CuK\alpha_1} = 1.5405$. Orthorhombic: $a_0 = 5.797 \pm 0.003$ Å, $b_0 = 11.629 \pm 0.009$ Å, $c_0 = 16.203 \pm 0.013$ Å.

hkl	Int.	$\sin^2\theta_{obs} \times 10^4$	$\sin^2\theta_{calc} \times 10^4$	d_{obs}
111	m	243	243	4.941
022	w	264	266	4.750
120	w	354	352	4.094
113	s	422	424	3.749
033	s	600	598	3.145
015	m	610	609	3.119
040	vs	700	702	2.911
200	s	710	706	2.891
213	w	950	953	2.479
222	m	970	972	2.473
204	m	1076	1068	2.348
231	s	1123	1124	2.299
233	vs	1307	1305	2.131
240	m	1416	1408	2.050
{242} {037}	w	{1503} {1503}	1499 1502	1.987 1.987
046	vw	1515	1516	1.979
062	w	1670	1670	1.885
146	w	1688	1692	1.875
226	w	1703	1695	1.865
244	w	1780	1770	1.826
251	w	1825	1824	1.803
253	m	2009	2007	1.719
164	w	2114	2118	1.675
324	w	2129	2127	1.670
066	m	2395	2393	1.574
139	m	2402	2402	1.572
400	m	2830	2825	1.448
{159} {346}	w	{3112} {3112}	3104 3104	1.381 1.381
431	w	3238	3242	1.354
275	w	3419	3421	1.317
{440} {364}	w	{3532} {3532}	3527 3530	1.296 1.296
259	vw	3630	3634	1.278
{426} {339}	w	{3807} {3807}	3814 3815	1.248 1.248

vs= very strong. s= strong. m= medium. w= weak. vw= very weak.

In a forthcoming paper, a discussion of theoretical models for the structure of these melts will be given. The experimental results of the present work will be evaluated, together with the results for other cryolite systems. In anticipation of this broader discussion, it may be pointed out that the observed melting point depressions reported here are compatible with the existence of complex ions in cryolite melts.

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