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Thermochimica Acta 354 (2000) 161–164

thermochimica acta

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Investigation of the systems $KAlF_4$–KBe_2F_5 and K_3AlF_6–KBe_2F_5

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Received 8 October 1999; accepted 17 February 2000

Abstract

Phase relations in the systems $KAlF_4$–KBe_2F_5 and K_3AlF_6–KBe_2F_5 have been investigated by DTA and XRD methods. The $KAlF_4$–KBe_2F_5 is a simple eutectic system with the eutectic point at a composition of 80.0 mol% KBe_2F_5 at 335°C. For the later system, two incongruent compounds $2K_3AlF_6{\cdot}KBe_2F_5$ and $K_3AlF_6{\cdot}KBe_2F_5$ melting at 448 and 378°C, respectively were confirmed. They have been XRD indexed as both orthorhombic cells with cell parameters a=10.70±0.01, b=10.36±0.01, c=5.85±0.02 Å for the former and a=10.499±0.003, b=9.685±0.005, c=7.554±0.005 Å for the later. One eutectic point located at 85.0 mol% KBe_2F_5 at 336°C was also observed.

Keywords: $KAlF_4$; K_3AlF_6; KBe_2F_5; Phase diagram

1. Introduction

$KAlF_4$ and K_3AlF_6 are two congruent melting intermediate compounds in the system AlF_3–KF [1]. Pairing the two compounds up with KBe_2F_5, which formed two binary sub-systems: $KAlF_4$–KBe_2F_5 and K_3AlF_6–KBe_2F_5. Investigating these we have determined the characteristics of the two intermediate compounds of $KAlF_4$ and K_3AlF_6. No related systems have been studied in the literatures.

2. Experimental

2.1. Sample preparation

Anhydrous K_2CO_3, $Al(OH)_3$, BeO and 40% HF used for the present study were all AR grade. The former three reagents were dehydrate to a constant weight at 120°C. Relative humidity of environment was <30%. Samples for DTA were prepared by reacting mixtures of K_2CO_3 in solution with a specified amount of $Al(OH)_3$ and BeO. The reacted mixture was then acidified with excess aqueous HF. The acidified products were placed in platinum crucibles and dried at 100°C. All samples were annealed at temperatures above which the liquid phase did not occur. The total annealed time was 48 h.

Liquidus in the systems was repeatedly measured by visual polythermal methods.

2.2. Differential thermal analysis

The high temperature DTA equipment used was the CR-G type manufactured by Beijing Optical Instrument, Inc. It was calibrated using standard substances of known melting points. Both heating and cooling curves were calibrated. Baked Al_2O_3 was used as a reference. The heating rate was 15°C min^{-1}. Temperatures were determined by the heating curve and the cooling curve also was used to correct the liquidus

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0040-6031/00/$ – see front matter
PII: S0040-6031(00)00471-8

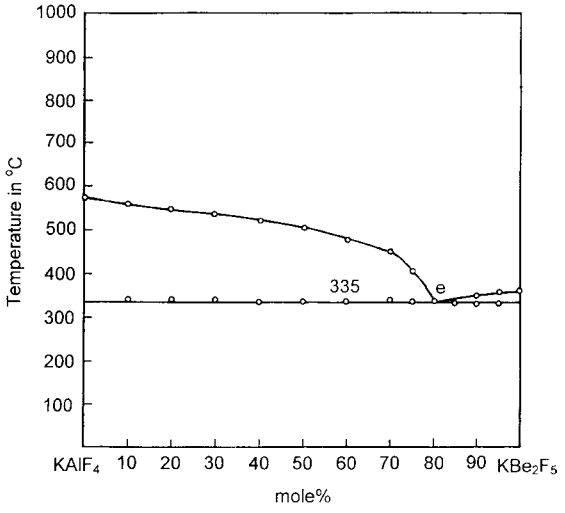

Fig. 1. Phase diagram of the sub-system $KAlF_4$–KBe_2F_5.

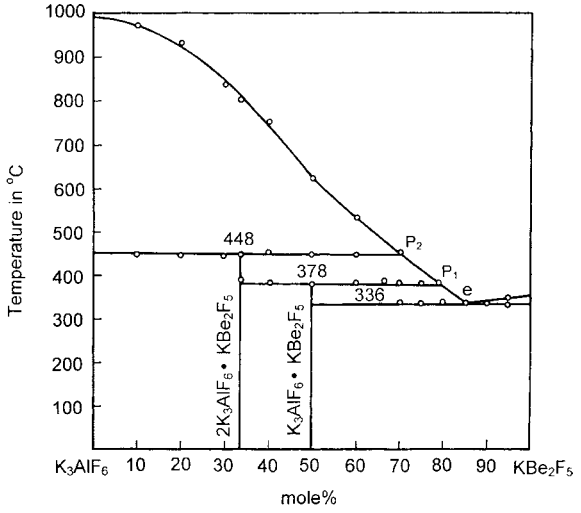

Fig. 2. Phase diagram of the sub-system K_3AlF_6–KBe_2F_5.

Table 1
DTA analysis of $KAlF_4$–KBe_2F_5

KBe_2F_5 (mol%)	Eutectic temperature (°C)	Liquidus temperature (°C)	KBe_2F_5 (mol%)	Eutectic temperature (°C)	Liquidus temperature (°C)
0		575	70	335	458
10	338	555	75	335	405
20	337	545	80	335	
30	334	538	85	336	
40	332	520	90	333	345
50	331	500	95	336	351
60	335	478	100		358

Table 2
DTA analysis of K_3AlF_6–KBe_2F_5

Kbe_2F_5 (mol%)	Eutectic temperature (°C)	Incongruent 1 temperature (°C)	Incongruent 2 temperature (°C)	Liquidus temperature (°C)
10		448		970
20		447		950
30		447		838
33.3		449		801
40		452	378	752
50		448	380	597
60		445	381	531
66.7	334		381	
70	336		371	457
75	338		379	
80	336			388
85	335			
90	338			
95	335			345

Table 3
Indexed data of $2K_3AlF_6{\cdot}KBe_2F_5$ orthorhombic cell[a]

d (Å) observed	d (Å) calculated	I/I_0	h	k	l
3.941	3.948	12	2	0	1
3.873	3.878	15	0	2	1
3.157	3.140	39	2	2	1
	2.938		3	2	0
	2.923		0	0	2
2.921	2.922	64	3	1	1
	2.900		2	3	0
2.850	2.864	48	1	3	1
2.632	2.626	36	3	2	1
2.490	2.490	27	2	1	2
	2.483		3	3	0
	2.375		4	2	0
	2.368		4	1	1
2.366	2.267	55	0	4	1
2.337	2.330	58	2	4	0
2.217	2.208	24	3	1	2
2.119	2.116	100	4	3	0
2.033	2.034	36	1	5	0
2.008	2.009	45	5	0	1
1.904	1.906	30	1	4	2
1.858	1.861	27	4	4	0
1.788	1.792	15	3	5	0
1.589	1.588	18	5	4	1
	1.462		0	0	4
1.461	1.460	15	6	2	2
	1.344		7	1	2
1.342	1.341	18	3	1	4
1.218	1.216	24	5	7	0
	1.215		3	8	0
	1.214		8	0	2

[a] a=10.70±0.01, b=10.36±0.01, c=5.85±0.02 Å.

Table 4
Indexed data of $K_3AlF_6{\cdot}KBe_2F_5$ orthorhombic cell[a]

d (Å) observed	d (Å) calculated	I/I_0	h	k	l
6.146	6.145	27	1	0	1
5.266	5.261	7	2	0	0
4.066	4.073	5	0	2	1
3.941	3.940	8	2	1	1
3.487	3.495	4	3	0	0
3.343	3.336	29	1	1	2
3.283	3.287	31	3	1	0
	3.087		1	3	0
3.066	3.066	100	2	0	2
2.746	2.750	4	2	3	0
2.653	2.254	29	3	2	1
2.399	2.401	5	4	1	1
	2.390		1	3	2
	2.307		4	2	0
2.298	2.306	13	0	4	1
2.272	2.270	10	2	0	3
	2.268		3	2	2
	2.264		3	3	1
2.254	2.252	13	1	4	1
2.184	2.185	16	1	2	3
2.045	2.043	17	3	0	3
	2.039		0	4	2
2.024	2.022	9	5	0	1
1.984	1.985	20	0	3	3
	1.980		5	1	1
	1.883		3	2	3
1.878	1.876	10	0	5	1
	1.853		0	1	4
1.850	1.848	7	1	5	1
	1.817		2	5	0
1.814	1.816	5	4	0	3
1.779	1.780	11	4	4	0
	1.777		2	0	4
1.646	1.645	5	6	2	0
1.538	1.539	9	6	3	0
	1.535		0	5	3

[a] a=10.499±0.003, b=9.685±0.005, c=7.554±0.005 Å.

temperature. The experiment were conducted in static dry air (relative humidity <30%).

2.3. Powder X-ray diffraction analysis

Intermediate compounds in the systems were analysed by X-ray diffractometry are XRD, Model Dmax 2400, Rigaku, Tokyo, Japan with Cu Kα radiation, and with a nickel filter (λ=1.5409 Å).

3. Results and discussion

3.1. System $KAlF_4$–KBe_2F_5

A phase diagram, based on the DTA analysis of this system is given in Fig. 1. The corresponding results are listed in Table 1. Samples with high KBe_2F_5 content ferrel glasses on cooling, and crystallisation could not be followed above 70 mol%. The data listed in Table 1 were obtained only on heating.

The system $KAlF_4$–KBe_2F_5 presented in Fig. 1 is a simple eutectic. The eutectic point occurred at a composition of 80.0 mol% KBe_2F_5 and at 335°C.

3.2. System K_3AlF_6–KBe_2F_5

A phase diagram for this system is shown in Fig. 2. Relative data by DTA and visual determination listed

in Table 2. Two intermediate compounds, $2K_3AlF_6 \cdot KBe_2F_5$ and $K_3AlF_6 \cdot KBe_2F_5$, can be detected in the diagram. One eutectic point is located at 85.0 mol% KBe_2F_5 at 336°C. Both compounds incongruent melted at 448 and 378°C, respectively. X-ray analysis and indexing on $2K_3AlF_6 \cdot KBe_2F_5$ and $K_3AlF_6 \cdot KBe_2F_5$; see in Tables 3 and 4, showed that they were both orthorhombic cells with the cell parameters a=10.70±0.01, b=10.36±0.01, c=5.85±0.02 Å and a=10.499±0.003, b=9.685±0.005, c=7.554±0.005 Å, respectively.

From the two pseudo-binary systems in which one component was the same as KBe_2F_5, quite different results were observed. In system $KAlF_4$–KBe_2F_5, a simple eutectic formed, as for system K_3AlF_6–KBe_2F_5, two incongruent compounds were observed, suggesting that there was stronger interactions between K_3AlF_6 and KBe_2F_5.

4. Conclusions

From the comparison of the phase diagrams, it appears that $KAlF_4$ behaves in a similar way to a molecular species in the molten state as KBe_2F_5 does. This can also be used to explain why simple ionic fluoride such as the alkaline and rare-earth metal fluorides are very difficult to dissolve in molten $KAlF_4$ even at temperature as high as 800°C, but complex compounds with molecular characteristics are easy to dissolve at low temperature.

Acknowledgements

The authors wish to acknowledge the support from Beijing Science Fund.

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