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Journal of Fluorine Chemistry 124 (2003) 1–3
JOURNAL OF FLUORINE CHEMISTRY
www.elsevier.com/locate/jfluchem

Phase diagram of KF–InF_3 system

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Received 23 July 2002; received in revised form 16 January 2003; accepted 6 June 2003

Abstract

The phase diagram of the KF–InF_3 system was investigated by DTA and XRD methods. In the system, two incongruent compounds, $2KF{\cdot}InF_3$ and $KInF_4$, were observed. The compound $2KF{\cdot}InF_3$ was XRD-indexed as orthorhombic, where $a = 8.870 \pm 0.003$, $b = 6.271 \pm 0.002$, $c = 4.553 \pm 0.001$ Å. Another compound $KInF_4$ polymorphously reacted at 784 °C. The room temperature phase was tetragonal, where $a = 7.160 \pm 0.004$ and $c = 5.068 \pm 0.007$ Å. The structure of higher temperature phase has not been determined yet. An eutectic point was observed at 785 °C at 19.0 mol% InF_3.

Keywords: KF; InF_3; Phase diagram

1. Introduction

The molten salt of eutectic composition of the KF–AlF_3 system is widely used as Nocolok flux in aluminum brazing technique [1–3]. Compared with KF–AlF_3 system, whether the resembling system KF–InF_3 in which indium is the similar element with aluminum in the periodic system, has the similar brazing properties was the tentative idea. For this consideration, the phase diagram of the KF–InF_3 system was finely researched in this paper.

2. Results and discussion

Phase diagram of the system KF–InF_3, based on the results of DTA (as shown in Table 1) is given in Fig. 1. Invariant points are listed in Table 2.

Two incongruent compounds, $2KF{\cdot}InF_3$ and $KInF_4$ were observed in this system as shown in Fig. 1. The former decomposed into $KInF_4$ and liquid phase P_1 at 808 °C. The latter has a polymorphic reaction at 784 °C, and decomposed into InF_3 and liquid phase P_2 at 826 °C. Eutectic point E melting at 785 °C with 19.0 mol% InF_3 was observed between KF and $2KF{\cdot}InF_3$.

The compounds $2KF{\cdot}InF_3$ and $KInF_4$ have been confirmed and indexed by XRD analysis. The XRD data of $2KF{\cdot}InF_3$ are listed in Table 3. The analytical results indicated that $2KF{\cdot}InF_3$ is orthorhombic, where $a = 8.870 \pm 0.003$, $b = 6.271 \pm 0.002$ and $c = 4.553 \pm 0.001$ Å. The $KInF_4$ phase at room temperature is tetragonal, where $a = 7.160 \pm 0.004$ and $c = 5.068 \pm 0.007$ Å (see Table 4).

In the XRD analysis, only the compositions of $2KF{\cdot}InF_3$ and $KInF_4$ could be indexed. Any other composition in the system expressed a mixture XRD patterns and could not be indexed. That meant, only the mentioned two compounds could exist in the system.

The temperature effects about 784–785 °C from DTA data acrossed all over the compositions in the system. The eutectic temperature between KF and $2KF{\cdot}InF_3$ should not pass over the composition of 33 mol% InF_3 obviously. Therefore, the effects in the composition range higher than 33 mol% InF_3 is caused by other reaction, the only deduction of which is a polymorphous reaction of the $KInF_4$ itself. The phase change of $KInF_4$ occurs at 784 °C and this temperature happened to be close to the eutectic temperature at 785 °C between KF and $2KF{\cdot}InF_3$. The higher temperature phase β-$KInF_4$ has not been XRD-indexed yet.

Grannec et al. firstly studied the KF–InF_3 system, samples of which was prepared by the reaction of KF with InF_3 in a sealed metal tube at 500–600 °C, and reported the existence of K_3InF_6, $K_5In_3F_{14}$, $KInF_4$ and KIn_2F_7 [4]. The results were quite different from ours, even the common recognition compound $KInF_4$ also be reported in different structures, for which Grannec reported as orthorhombic where $a = 9.930$, $b = 7.760$ and $c = 12.57$ Å.

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doi:10.1016/S0022-1139(03)00167-2

Table 1
DTA data of the system KF–InF_3

KF (mol%)	Liquid's temperature (°C)	Eutectic temperature (°C)	Incongruent 1 temperature (°C)	Polymorphic transition (°C)	Incongruent 1 temperature (°C)
100.0	858				
97.0	847				
93.0	830	784			
90.8	826	789			
87.4	826	789			
85.7	822	790			
82.4	809	789			
78.2	843	786			824
75.0	862	783			
71.0		787	806		834
66.3	905	781			
62.5	982	773	810		825
60.0					828
57.5					823
55.0					822
51.6			810	786	828
50.0				775	
47.5				785	817
45.0				793	
40.0					823
36.8					828
33.3				783	827
25.0					830
17.0					827

We can hardly comment and discuss the differences between the two results but we would rather believe the reliability of our data, because the start material InF_3 was made by high pure metal indium, instead of commercial chemical reagent.

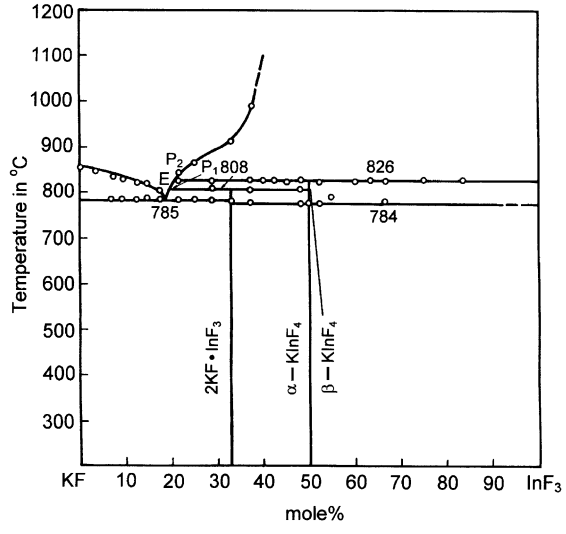

Fig. 1. Phase diagram of the system KF–InF_3.

Table 2
Invariant points in the system KF–InF_3

Invariant points	°C	InF_3 mol%
E	785	19.0
P_1	808	20.0
P_2	826	21.0

Table 3
Indexed data of $2KF{\cdot}InF_3$[a]

d (Å) (observed)	d (Å) (calculated)	I/I_0	h	k	l
5.136	5.122	57	1	1	0
4.436	4.436	30	2	0	0
3.405	3.410	3	1	1	1
3.135	3.140	100	0	2	0
2.673	2.673	18	3	1	0
	2.479		3	0	1
2.479	2.478	8	1	2	1
2.304	2.307	9	3	1	1
2.212	2.215	30	4	0	0
	2.205		1	0	2
2.034	2.034	9	1	3	0
1.807	1.810	35	4	2	0
	1.804		3	0	2
	1.803		1	2	2
	1.707		5	1	0
	1.706		3	3	0
1.704	1.703	13	2	2	2
1.564	1.564	14	3	2	2
1.496	1.496	12	1	0	3
1.475	1.475	9	0	1	3
	1.400		2	1	3
1.399	1.399	8	5	0	2
	1.351		3	0	3
1.350	1.350	4	1	2	3
	1.278		5	2	2
1.276	1.277	3	1	4	2
	1.240		3	2	3
	1.241		6	0	2
1.239	1.239	4	2	4	2
	1.228		4	1	3
1.227	1.277	3	0	3	3
	1.184		2	3	3
1.182	1.183	6	3	4	2

[a] Orthorhombic cell: $a = 8.870 \pm 0.003$, $b = 6.271 \pm 0.002$, $c = 4.553 \pm 0.001$ Å.

Table 4
Indexed data of $KInF_4$[a]

d (Å) (observed)	d (Å) (calculated)	I/I_0	h	k	l
4.149	4.150	12	1	0	1
2.928	2.926	100	2	0	1
2.537	2.533	30	0	0	2
	2.534		2	2	0
2.390	2.390	6	1	0	2
	2.388		3	0	0
2.162	2.160	6	3	0	1
1.988	1.988	10	2	1	2
	1.986		3	2	0
1.849	1.849	3	3	2	1
1.791	1.791	37	2	2	2
	1.789		4	0	0
	1.738		3	0	2
1.737	1.737	3	4	1	0
	1.602		1	1	3
	1.601		3	3	1
1.600	1.600	1	4	2	0
	1.528		2	0	3

Table 4 (*Continued*)

d (Å) (observed)	d (Å) (calculated)	I/I_0	h	k	l
1.527	1.527	24	4	2	1
1.462	1.462	5	4	0	2
1.433	1.432	2	4	1	2
	1.431		5	0	0
	1.379		3	0	3
1.378	1.378	3	5	0	1
1.287	1.287	2	3	2	3
	1.286		5	2	1
	1.267		0	0	4
1.266	1.266	4	4	4	0
	1.178		5	2	2
1.176	1.176	3	6	1	0
	1.162		4	2	3
1.161	1.161	6	6	0	1
	1.133		2	2	4
	1.133		4	4	2
1.132	1.132	4	6	1	0

[a] Tetragonal cell: $a = 7.160 \pm 0.004$, $c = 5.068 \pm 0.007$ Å.

3. Conclusion

1. The KF–InF_3 system is one of eutectic type. The eutectic point E is located in 19.0 mol% InF_3 at 785 °C.
2. Two intermediate compounds $2KF{\cdot}InF_3$ and $KInF_4$ were observed in the system. The former peritectically melts at 808 °C, the later has a crystalline transition at 784 °C and a peritectic decomposition at 826 °C.

4. Experimental

4.1. Preparation of InF_3

A certain amount of metal indium (>99.99%) was dissolved in hydrofluoric acid in a polyethylene beaker under the protection of a N_2 atmosphere, and heated on a water bath. For enhancing the dissolution, an oxidiser H_2O_2 was dropped-in during continuous stirring. After the reaction between In and HF ended, the solution was evaporated on a water bath. The obtained white crystal $InF_3{\cdot}xH_2O$ were put into a Pt crucible then heated at 200 °C for 2 h under a HF atmosphere. A white powdery product was finally obtained, and was identified as anhydrous InF_3 by XRD analysis.

4.2. Preparation of samples

Twenty-four samples were prepared by reacting of anhydrous InF_3 with KF and HF. The products were placed in he Pt crucibles, and dried at 200 °C, and then annealed for 48 h at 500 °C. During the annealing process, grinding and mixing of the samples were carried out repeatedly in order to obtain homogeneous samples.

4.3. Differential thermal analysis

The CR-G type high-temperature DTA equipment (Beijing Optical Instrument) was used and calibrated with the melting points of some standard substances on the heating and cooling curves. Calcined aluminum oxide was used as a reference substance. The heating rate was 15 °C/min. Liquid's temperature was determined from the cooling curve. Experiments were carried out under the dry air (relative humidity < 30%). The error in measuring temperature was ±3 °C.

4.4. X-ray powder diffraction analysis

The compounds observed in the system were determined by Rigaku Dmax 2400 X-ray diffractometer (Radiation Cu Kα-$\lambda = 1.5409$ Å, Filter Ni) at room temperature. Silicon powder was added as a cross-reference for fine-tuning the results of determination.

Acknowledgements

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

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