

Recognition on systems RbF–GaF₃ and CsF–GaF₃

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Abstract

The systems RbF–GaF₃ and CsF–GaF₃ were re-investigated by DTA and XRD method. In the system RbF–GaF₃, with eutectic E₁ at 750°C in the location of 8.5 mol% GaF₃ and E₂ at 749°C in the location of 43.0 mol% GaF₃, three compounds Rb₃GaF₆, RbGaF₄ and RbF·2GaF₃ were identified and indexed by XRD. The indexed result of α -Rb₃GaF₆ could not be successfully obtained, β -Rb₃GaF₆ is tetragonal, $a = 6.324 \pm 0.004$, $c = 8.860 \pm 0.003$ Å. RbGaF₄ is orthorhombic, $a = 9.821 \pm 0.006$, $b = 9.517 \pm 0.005$, $c = 8.060 \pm 0.006$ Å; RbF·2GaF₃ is also orthorhombic, $a = 9.459 \pm 0.005$, $b = 9.336 \pm 0.005$, $c = 7.685 \pm 0.005$ Å. In the system CsF–GaF₃, with eutectic E₁ at 664°C in the location of 7.5 mol% GaF₃ and E₂ at 675°C in the position of 44.0 mol% GaF₃, two compounds were confirmed. α -Cs₃GaF₆ is orthorhombic with $a = 10.62 \pm 0.02$, $b = 9.959 \pm 0.006$ and $c = 5.607 \pm 0.005$ Å; β -Cs₃GaF₆ is also orthorhombic, $a = 10.356 \pm 0.003$, $b = 8.280 \pm 0.003$, $c = 7.621 \pm 0.005$ Å; γ -Cs₃GaF₆ is tetragonal, $a = 6.833 \pm 0.003$, $c = 9.869 \pm 0.002$ Å; CsGaF₄ is orthorhombic, $a = 8.571 \pm 0.007$, $b = 7.575 \pm 0.007$ and $c = 6.981 \pm 0.006$ Å. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: RbF; CsF; GaF₃; Phase diagram; Aluminum brazing

1. Introduction

The systems RbF–GaF₃ and CsF–GaF₃ have been investigated by Chassaing [1]. Minimal eutectic were located at 43 mol% at 548°C and 45 mol% at 500°C of GaF₃ in respective systems were determined. A system of type similar to that of RbF–AlF₃ and CsF–AlF₃ [2,3], along with their lower temperature of eutectics suggested at these compositions as a flux used in Nocolok method [4] for brazing aluminum and its alloys. But we could not repeat the reported temperatures of Chassaing. So we decided to re-study these two systems.

2. Experimental

2.1. Preparation of GaF₃

A certain amount of Ga metal with purity > 99.99% was reacted with excessive hydrofluoric acid in a polyvinyl beaker protected with N₂ flow. The beaker was heated on a water-bath. H₂O₂ was gradually dropped into the blend under continuous stirring. As the reaction was completed the product was vaporized until dry on the water-bath. The white crystal hydrate GaF₃·xH₂O was obtained. The GaF₃·xH₂O was put into a platinum crucible which was heated at 200°C for 2 h under HF-flow protection. The white mass obtained was confirmed as anhydrous GaF₃ by X-ray diffraction analysis.

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2.2. Preparation of the samples

Samples were prepared from GaF_3 which was placed in a platinum crucible blending with a HF solution of RbF or CsF with known concentration and content. Twenty-three samples of RbF– GaF_3 and 18 samples of CsF– GaF_3 mixtures were prepared in this way and gradually heated until dry at 200°C , then annealed for 48 h at a higher temperature such that no melting of any phase could occur. During the annealing process, grinding and mixing of the samples were repeatedly carried out in order to obtain homogeneous and equilibrium samples.

2.3. Differential thermal analysis

The high-temperature DTA equipment used (of the CR-G type, Beijing Optical Instruments, Inc.) was employed and calibrated using standard substances with known melting points. Both heating and cooling curves were calibrated. Al_2O_3 was used as a reference. The heating rate was 15 min. Temperatures were determined by the heating curve, and the cooling curve also was used to correct the liquidus temperature. Experiments were conducted in dry air (relative humidity <30%) in the static state. The error in measuring temperature was $\pm 3^\circ\text{C}$.

2.4. X-ray powder diffraction analysis

The intermediate compounds in the system were determined by X-ray diffractometry (XRD, Model D_{max} 2400, Rigaku Co., Tokyo, Japan) under $\text{CuK}\alpha$ radiation, with a nickel filter and $\lambda = 1.5409$.

3. Results and discussion

3.1. System RbF– GaF_3

Phase diagram of the system RbF– GaF_3 , based on DTA data is shown in Fig. 1. The invariant data is presented in Table 1.

Fig. 1 reveals three intermediate compounds formed in the system RbF– GaF_3 :

1. Rb_3GaF_6 congruently melts at 860°C and transforms from α to β form at 388°C . The compound

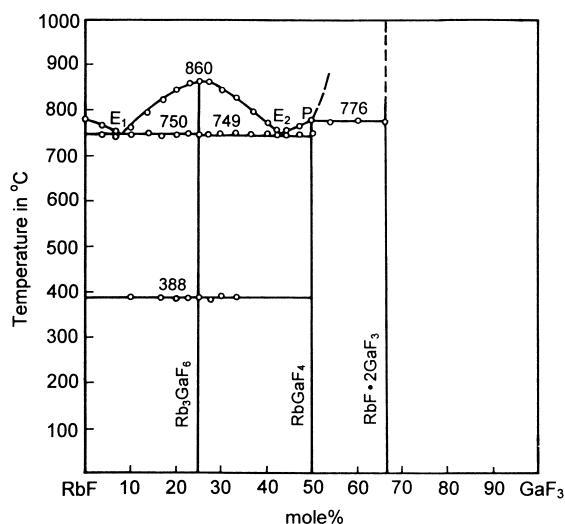


Fig. 1. Phase diagram of system RbF– GaF_3 .

reacts with RbF to form eutectic E_1 at 750°C in the location of 8.5 mol% GaF_3 .

2. RbGaF_4 peritectic melts at 776°C and reacts with Rb_3GaF_6 to form E_2 at 749°C and in the location of 43.0 mol% GaF_3 .
3. The existence of $\text{RbF} \cdot 2\text{GaF}_3$ is identified by X-ray diffraction powder analysis. Its formation temperature was at least over 900°C has not been determined yet.

All these compounds were identified and indexed by X-ray diffraction analysis. The diffraction data of α - Rb_3GaF_6 coincided with JCDPS(22–1275). Due to the data too complicated, the indexed result could not be successfully obtained. XRD data of β - Rb_3GaF_6 listed in Table 2 was indexed as tetragonal, the cell parameters being: $a = 6.324 \pm 0.004$, $c = 8.860 \pm 0.003$ Å. XRD data of RbGaF_4 are presented in Table 3. The compound is orthorhombic, with

Table 1
Invariant points of the system RbF– GaF_3

Invariant point	Temperature ($^\circ\text{C}$)	GaF_3 (mol%)
E_1	750	8.5
E_2	749	43.0
P	776	50.0
m.p. (Rb_3GaF_6)	860	25.0

Table 2
Indexed data of β -Rb₃GaF₆^a

Observed <i>d</i> (Å)	Calculated <i>d</i> (Å)	<i>I</i> / <i>I</i> ₀	<i>h</i>	<i>k</i>	<i>l</i>
5.151	5.151	3	1	0	1
	3.162		2	0	0
3.151	3.151	100	1	1	2
2.572	2.576	9	2	0	2
2.239	2.236	13	2	2	0
2.218	2.215	20	0	0	4
1.812	1.816	17	2	0	4
1.575	1.574	8	2	2	4
1.414	1.414	5	4	2	0
	1.412		3	3	2
1.403	1.403	5	1	1	6
1.187	1.188	3	3	1	6

^aTetragonal cell: $a = 6.324 \pm 0.004$; $c = 8.860 \pm 0.003$ Å.

Table 3
Indexed data of RbGaF₄^a

Observed <i>d</i> (Å)	Calculated <i>d</i> (Å)	<i>I</i> / <i>I</i> ₀	<i>h</i>	<i>k</i>	<i>l</i>
4.197	4.192	13	2	0	1
4.073	4.092	15	0	2	1
3.735	3.735	9	1	0	2
3.418	3.424	54	2	2	0
3.276	3.276	23	3	0	0
2.919	2.938	43	1	2	2
2.316	3.313	17	1	4	0
	2.279		4	1	1
	2.276		3	3	0
2.271	2.274	9	1	2	3
2.197	2.194	24	3	3	1
2.102	2.106	12	4	2	1
	2.097		4	0	2
2.026	2.029	16	3	1	3
	2.008		1	3	3
2.004	2.006	14	1	4	2
1.765	1.767	6	5	0	2
1.705	1.708	18	4	4	0
1.489	1.489	8	5	4	1
1.460	1.460	28	1	6	2
	1.458		2	2	5
1.297	1.297	7	4	2	5
	1.299		2	0	6
1.265	1.265	8	4	6	2
1.149	1.149	5	6	0	5

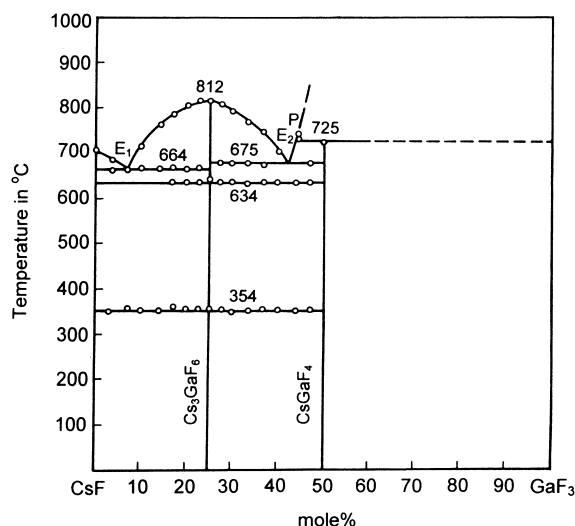
^aOrthorhombic cell: $a = 9.821 \pm 0.006$; $b = 9.517 \pm 0.005$; $c = 8.060 \pm 0.006$ Å.

$a = 9.821 \pm 0.006$, $b = 9.517 \pm 0.005$, $c = 8.060 \pm 0.006$ Å. Compound RbF·2GaF₃ was also indexed (data listed in Table 4) as orthorhombic too, with $a = 9.459 \pm 0.005$, $b = 9.336 \pm 0.005$, $c = 7.685 \pm 0.005$ Å.

Table 4
Indexed data of RbF·2GaF₃^a

Observed <i>d</i> (Å)	Calculated <i>d</i> (Å)	<i>I</i> / <i>I</i> ₀	<i>h</i>	<i>k</i>	<i>l</i>
5.961	5.980	8	1	0	1
	5.941		0	1	1
4.679	4.667	3	0	2	0
	3.326		1	1	2
3.318	3.324	5	2	2	0
	2.986		3	1	0
	2.985		2	0	2
2.966	2.966	12	0	2	2
	2.957		1	3	0
2.928	2.919	15	3	0	1
2.816	2.829	34	1	2	2
2.623	2.612	23	3	2	0
2.523	2.513	23	2	2	2
2.412	2.418	10	0	3	2
2.351	2.360	15	3	1	2
	2.342		1	3	2
2.231	2.233	5	0	4	1
2.132	2.130	7	3	3	1
2.026	2.030	4	2	2	3
	2.021		2	4	1
1.971	1.967	3	4	1	2
1.922	1.922	100	0	0	4
	1.920		3	3	2
1.890	1.892	3	5	0	0
1.840	1.840	3	2	4	2
	1.836		5	0	1
	1.826		2	3	3
1.823	1.823	3	3	4	1
	1.694		2	5	1
1.692	1.691	8	4	3	2
1.665	1.663	12	2	2	4
	1.623		4	4	1
1.621	1.622	5	2	4	3
1.552	1.555	4	6	1	0
1.478	1.478	11	2	6	0
	1.466		2	0	5
1.461	1.461	15	0	2	5
	1.460		6	0	2
1.420	1.420	3	4	2	4
1.406	1.407	6	6	3	0

^aOrthorhombic cell: $a = 9.459 \pm 0.005$; $b = 9.336 \pm 0.005$; $c = 7.685 \pm 0.005$ Å.

Fig. 2. Phase diagram for the system CsF–GaF₃.

3.2. System CsF–GaF₃

The phase diagram of the CsF–GaF₃ system, based on the results of DTA is displayed in Fig. 2. Invariant points can be seen in Table 5.

Fig. 2 reveals two intermediate compounds formed in the system.

1. Cs₃GaF₆ congruently melts at 812°C and transforms from α to β and γ form at 354°C and 634°C, respectively. Cs₃GaF₆ reacts with CsF to form eutectic E₁ at 664°C in the location of 7.5 mol% GaF₃.
2. Peritectic reaction of CsGaF₄ takes place at 725°C. The compound reacts with Cs₃GaF₆ to form eutectic E₂ at 675°C and in the position of 44.0 mol% GaF₃.

A technique of quenching in liquid N₂ flow was used to keep the structure for determining the sample by X-ray diffractometry.

Table 5
Invariant points of the system CsF–GaF₃

Invariant point	Temperature (°C)	GaF ₃ (mol%)
E ₁	664	7.5
E ₂	675	42.0
P	725	44.0
m.p. (Cs ₃ GaF ₆)	812	25.0

α -Cs₃GaF₆ was indexed as orthorhombic with $a = 10.62 \pm 0.02$, $b = 9.959 \pm 0.006$, and $c = 5.607 \pm 0.005$ Å; β -Cs₃GaF₆ is also orthorhombic with $a = 10.356 \pm 0.003$, $b = 8.280 \pm 0.003$, $c = 7.621 \pm 0.005$ Å; γ -Cs₃GaF₆ is tetragonal with $a = 6.833 \pm 0.003$, $c = 9.869 \pm 0.002$ Å. The indexed results of these compounds are listed in Tables 6–8.

CsGaF₄ was indexed (see Table 9) by X-ray diffraction as orthorhombic with $a = 8.571 \pm 0.007$, $b = 7.575 \pm 0.007$ and $c = 6.981 \pm 0.006$ Å.

Except for two compounds Rb₃GaF₆ (Cs₃GaF₆) and RbGaF₄ (CsGaF₄) being only commonly recognized, these re-investigated phase diagrams are quite different from that reported in Chassaing's research. The compounds Rb₂GaF₅ and Rb₂Ga₅F₁₇ in system RbF–GaF₃, Cs₅Ga₃F₁₄ and CsGa₂F₇ in the system CsF–GaF₃ reported by Chassaing, could not confirm their existence in this research. Another compound RbF·2GaF₃ was indexed in our research but no infor-

Table 6
Indexed data of α -Cs₃GaF₆^a

Observed d (Å)	Calculated d (Å)	hkl	h	k	l
4.993	4.985	36	0	2	0
	4.960		1	0	1
4.447	4.436	43	1	1	1
3.743	3.720	35	0	2	1
3.594	3.601	34	2	1	1
	3.336		3	1	0
3.312	3.323	84	0	3	0
	2.712		1	0	2
2.700	2.696	27	0	1	2
2.608	2.612	21	1	1	2
2.428	2.427	21	1	4	0
	2.421		3	3	0
2.342	2.342	33	4	2	0
	2.331		4	1	1
1.930	1.931	21	4	0	2
1.911	1.912	29	3	4	1
1.653	1.652	18	3	0	3
1.641	1.641	100	1	6	0
	1.481		1	4	3
	1.480		6	1	2
1.479	1.479	16	3	3	3
1.392	1.391	16	1	0	4
	1.335		2	7	1
1.333	1.333	15	7	0	2

^aOrthorhombic cell: $a = 10.62 \pm 0.02$; $b = 9.959 \pm 0.006$; $c = 5.607 \pm 0.005$ Å.

Table 7
Indexed data of β -Cs₃GaF₆^a

Observed <i>d</i> (Å)	Calculated <i>d</i> (Å)	<i>I</i> / <i>I</i> ₀	<i>h</i>	<i>k</i>	<i>l</i>
5.157	5.180	26	2	0	0
3.639	3.644	6	0	2	1
3.581	3.575	9	1	0	2
3.466	3.463	4	0	1	2
	3.451		3	0	0
3.411	3.410	6	1	2	1
3.300	3.288	100	1	1	2
3.140	3.145	15	3	0	1
3.083	3.066	5	2	0	2
2.693	2.704	11	1	2	2
2.595	2.597	4	0	3	1
	2.590		4	0	0
	2.453		4	0	1
2.442	2.446	4	3	1	2
	2.434		2	3	0
2.328	2.324	18	2	3	1
2.151	2.154	5	3	3	0
1.922	1.922	26	2	4	0
	1.905		0	0	4
1.902	1.902	18	4	2	2
1.856	1.857	4	0	1	4
	1.852		5	2	0
1.826	1.827	4	1	1	4
	1.819		5	0	2
1.817	1.818	4	0	4	2
	1.816		4	0	3
1.799	1.799	4	5	2	1
1.780	1.776	4	5	1	2
1.770	1.771	4	4	1	3
1.730	1.730	3	0	2	4
1.730	1.729	5	3	4	1
	1.726		6	0	0
1.649	1.649	6	6	1	1
	1.640		2	2	4
1.638	1.636	4	3	1	4
	1.636		1	5	0
1.478	1.478	4	7	0	0
1.473	1.471	7	6	2	2
1.358	1.358	4	0	6	1
1.246	1.247	16	1	1	6

^aOrthorhombic cell: $a = 10.356 \pm 0.003$; $b = 8.280 \pm 0.003$; $c = 7.621 \pm 0.005$ Å.

Table 8
Indexed data of γ -Cs₃GaF₆^a

Observed <i>d</i> (Å)	Calculated <i>d</i> (Å)	<i>I</i> / <i>I</i> ₀	<i>h</i>	<i>k</i>	<i>l</i>
3.288	3.287	47	0	0	3
3.054	3.070	11	2	1	0
2.966	2.966	15	1	0	3
2.919	2.930	12	2	1	1
2.740	2.724	7	1	1	3
2.321	2.321	10	1	0	4
1.920	1.924	100	2	1	4
1.898	1.897	12	1	0	5
	1.600		1	0	6
1.599	1.599	6	3	3	1
1.520	1.518	6	4	2	1

^aTetragonal cell: $a = 6.833 \pm 0.003$; $c = 9.869 \pm 0.002$ Å.

Table 9
Indexed data of CsGaF₄^a

Observed <i>d</i> (Å)	Calculated <i>d</i> (Å)	<i>I</i> / <i>I</i> ₀	<i>h</i>	<i>k</i>	<i>l</i>
3.645	3.647	26	2	0	1
3.336	3.330	15	0	2	1
3.306	3.290	100	2	1	1
2.829	3.837	23	2	2	0
2.704	2.704	22	2	0	2
2.527	2.526	20	0	3	0
2.328	2.328	27	0	0	3
1.907	1.908	25	3	2	2
1.646	1.646	8	4	2	2
1.461	1.461	16	3	1	4
	1.460		1	5	1

^aOrthorhombic cell: $a = 8.571 \pm 0.007$; $b = 7.575 \pm 0.007$; $c = 6.981 \pm 0.006$ Å.

Acknowledgements

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mation was indicated in the Chassaing's report. The difference in our study is that the original material GaF₃ was prepared from super-pure metal gallium and the samples used for DTA analysis were prepared by total solution synthesis. This, we believe, may be the best way for preparing the real homogeneous and equilibrium samples.