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A study on the phase diagram of AlF_3–CsF system

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Abstract

Phase relations of the AlF_3–CsF system have been investigated by the methods of DTA and XRD with quenching technique. Four compounds were identified: Cs_3AlF_6, $CsAlF_4$, $CsF\cdot 2AlF_3$ and $CsF\cdot 3AlF_3$. Cs_3AlF_6 melts congruently at 790°C. The first eutectic, E_1, between Cs_3AlF_6 and CsF is located in 10.0 mol% AlF_3 at 654°C. $CsF\cdot 2AlF_3$ and $CsF\cdot 3AlF_3$ melt incongruently at 508° and 653°C, respectively. The second eutectic, E_2, was observed in 42.0 mol% AlF_3 at 471°C. The compound $CsAlF_4$ formed in the solid eutectic when cooled below 443°C. $CsAlF_4$ has α and β forms, transformation of which takes place reversibly at 422°C. All phase structures in the system were confirmed by X-ray powder diffraction analysis. © 1997 Published by Elsevier Science B.V.

Keywords: Aluminum fluoride; Cesium fluoride; Crystal structure; Phase diagram; System

1. Introduction

The phase relations between AlF_3 and alkali fluorides have been thoroughly investigated, except for the AlF_3–CsF system [1–4]. The ionic radius of Cs^+ is the largest among all alkali metals. Hence, it is suggested that complex formation in the AlF_3–CsF system must have some special characteristics. On the other hand, although the molten eutectic of the AlF_3–CsF system has been applied to aluminum brazing [5], the complete phase diagram of the system has not been reported. Only some fragmentary materials could be found: Puschin [6] established the partial phase diagram of AlF_3–CsF system at an AlF_3 content < 31.5 mol%. This indicated that Cs_3AlF_6 melts congruently at 823°C. Dergunov [7] only visually determined the liquidus of this system in the region of $AlF_3 < 30.0$ mol% and indicated that the melting point of Cs_3AlF_6 is 808°C. Beutrup [8] determined the structure of $CsAlF_4$, but did not study the AlF_3–CsF system completely. We have examined the phase diagram in great details and determined the structures of intermediate compounds formed in the AlF_3–CsF system in our research.

2. Experimental

2.1. Preparation of fluorides

CsF (purity > 99.5%, Beijing Chem. Works) was dehydrated at 400°C for 3 h; $AlF_3\cdot 3.5H_2O$ (A.R., Tianjin Chem. Works) was heated in a N_2 plus HF atmosphere at 600°C for 2 h. The product was identified as anhydrous AlF_3 by XRD. All fluorides were kept in a desiccator.

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2.2. *Preparation of samples*

We prepared 25 samples by reacting mixtures of anhydrous AlF_3 with solutions of CsF in HF. The samples were placed in Pt crucibles and heated until dry at 200°C, then annealed for 48 h at a higher temperature such that no melting of any phase could occur, e.g. for AlF_3 of < 25 mol% at 600°C; between 25–66 mol% at 400°C and > 66 mol% at 470°C. 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*

CR–G-type high-temperature DTA equipment (Beijing Optical Instrument) was employed and calibrated by standard substances with known melting points (calibrating both, the heating and cooling curves). Al_2O_3 was used as a reference substance. The heating rate was 15°C/min. Liquidus temperature was determined from the cooling curve, and the other temperatures were determined by extrapolating initial temperatures of the peaks in the heating curve. Experiments were carried out in dry air (relative humidity $< 30\%$) in the static state. The error in measuring temperature was ±3°C.

2.4. *X-ray powder diffraction analysis*

The intermediate compounds in the system were determined by a Rigaku Dmax 2400 X-ray diffractometer (Radiation CuK_α – $\lambda = 1.5409$, Filter Ni). Quenching technique was used for determining the structures of high-temperature phases. Si powder was added as a cross reference for fine-tuning the results of determination.

2.5. *Measurement of infrared absorption spectra*

Far-infrared absorption spectra were recorded at room temperature with Nicolet Magna IR-750 II type spectrometer (700–50 cm^{-1}) on Nujol mulls; The sample was dispersed in Nujol mull and inserted between thin polyethylene films.

3. Results and discussion

Phase diagram of the AlF_3–CsF system, based on the results of DTA (as shown in Table 1) is displayed in Fig. 1. Invariant points can be seen in Table 2.

Fig. 1 reveals four intermediate compounds formed in the system:

1. Cs_3AlF_6 congruently melts at 790°C, and reacts with CsF to form eutectic E_1 at 654°C in the location of 10.0 mol% AlF_3;
2. Peritectic reaction of $CsF \cdot 3AlF_3$ takes place at 653°C, and decomposes into AlF_3 and P_2 liquid phase at which it contains 52.5 mol% of AlF_3; and
3. $CsF \cdot 2AlF_3$ incongruently decomposes into $CsF \cdot 3AlF_3$ and P_1 liquid phase at 508°C, and reacts with Cs_3AlF_6 to form another eutectic E_2 at 471°C, and 42.0 mol% AlF_3.

In the eutectic, compound $CsAlF_4$ formed in the solid phase while being cooled below 443°C. $CsAlF_4$ has α and β forms, transformation of which takes place reversibly at 422°C. The existence of Cs_3AlF_6, $CsAlF_4$, $CsF \cdot 2AlF_3$ and $CsF \cdot 3AlF_3$ as well as their structures have been confirmed by X-ray powder diffraction analysis.

The structure of Cs_3AlF_6 has not been reported so far. XRD data on Cs_3AlF_6 are presented in Table 3. Analytical results indicated that Cs_3AlF_6 is cubic, the cell parameter being $a = 9.212 \pm 0.004$ Å (Table 4).

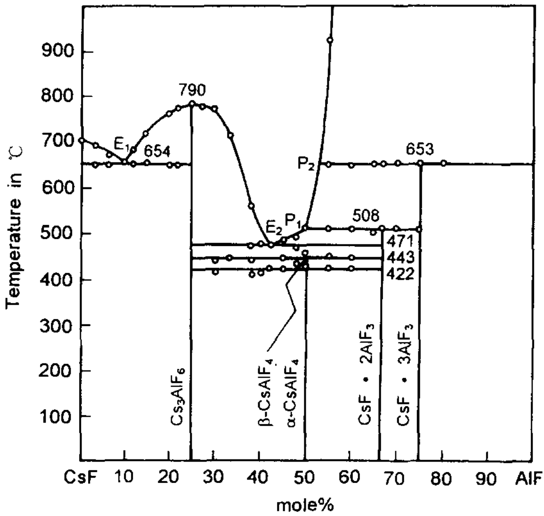

Fig. 1. The phase diagram of the AlF_3–CsF system.

Table 1
Results of DTA for the AlF_3–CsF system

AlF_3/ mol%	Liquidus temperature/ °C	E_1, temperature/ °C	E_2, temperature/ °C	Reaction in E_2, temperature/ °C	Incongr. 1, melt/ °C	Incongr. 2, melt/ °C	Polymorphic. 1, trans./ °C
0.0	706	—	—	—	—	—	—
3.0	684	650	—	—	—	—	—
6.0	670	650	—	—	—	—	—
10.0	—	662	—	—	—	—	—
12.0	675	647	—	—	—	—	—
15.0	722	652	—	—	—	—	—
20.0	758	650	—	—	—	—	—
22.0	770	646	—	—	—	—	—
25.0	790	—	—	—	—	—	—
27.0	776	—	—	—	—	—	—
30.0	772	—	—	430	—	—	413
33.0	717	—	—	450	—	—	—
38.0	559	—	472	447	—	—	408
40.0	—	—	476	—	—	—	408
42.0	—	—	470	—	—	—	428
45.0	486	—	—	438	—	—	428
48.0	488	—	465	438	—	—	—
50.0	507	—	—	451	—	—	435
55.0	923	—	—	444	650	508	428
60.0	—	—	—	442	650	512	428
65.0	—	—	—	—	656	495	—
66.7	—	—	—	—	650	513	—
70.0	—	—	—	—	655	514	—
75.0	—	—	—	—	656	507	—
80.0	—	—	—	—	652	—	—

Table 2
Invariants of the AlF_3–CsF system

Invariant point	Temperature/(°C)	mol% AlF_3
E_1	654	10.0
E_2	471	42.0
P_1	508	50.0
P_2	653	52.5
m.p. (Cs_3AlF_6)	790	25.0

Table 3
Cs_3AlF_6. Cubic, $a = 9.212 \pm 0.004$ Å

d_{obs}/Å	d_{calc}/Å	I/I_0	h	k	l
5.336	5.336	2	1	1	1
3.252	3.264	100	2	2	0
2.657	2.665	15	2	2	2
2.460	2.466	2	3	2	1
2.302	2.307	24	4	0	0
2.120	2.116	2	3	3	1
2.061	2.061	5	4	2	0
1.883	1.883	21	4	2	2
1.806	1.809	5	5	1	0
1.630	1.630	8	4	4	0
1.536	1.536	3	6	0	0
1.460	1.458	4	6	2	0

In this paper, the existence of the compounds $CsF{\cdot}2AlF_3$ and $CsF{\cdot}3AlF_3$ has been reported for the first time. XRD data for these compounds are presented in Tables 5 and 6, respectively. The compound $CsF{\cdot}2AlF_3$ is hexagonal, with $a = 9.455 \pm 0.003$ and $c = 3.703 \pm 0.003$ Å; The compound $CsF{\cdot}3AlF_3$ is orthorhombic, with $a = 10.86 \pm 0.01$, $b = 9.33 \pm 0.02$ and $c = 7.54 \pm 0.01$ Å.

For XRD data determination, the sample of $CsAlF_4$ was thoroughly ground and heated up to 450°C in an HF atmosphere, then slowly cooled to 350°C and annealed at this temperature for a period of one week, so as to obtain reliable α-$CsAlF_4$. A part of the α-$CsAlF_4$ was sealed in a small quartz tube and annealed

Table 4
$CsF{\cdot}2AlF_3$. Hexagonal, $a = 9.455 \pm 0.003$ and $c = 3.703 \pm 0.003$ Å

d_{obs}/Å	d_{calc}/Å	I/I_0	h	k	l
4.736	4.741	85	1	1	0
4.103	4.111	100	2	0	0
3.101	3.110	82	2	1	0
2.919	2.921	39	1	1	1
2.751	2.755	48	2	0	1
—	2.738	—	3	0	0
2.379	2.378	38	2	1	1
—	2.372	—	2	2	0
2.277	2.279	95	3	1	0
1.997	1.996	9	2	2	1
1.940	1.940	26	3	1	1
1.853	1.854	8	0	0	2
—	1.796	—	4	0	1
1.792	1.792	6	4	1	0
1.726	1.726	5	1	1	2
1.688	1.687	5	2	0	2
1.679	1.679	11	3	2	1
1.613	1.614	14	4	1	1
1.591	1.591	9	2	1	2
1.580	1.581	17	3	3	0
1.475	1.474	5	5	1	0
1.454	1.454	7	3	3	1
1.438	1.438	13	3	1	2
1.431	1.432	8	4	2	1
1.370	1.370	14	5	1	1
—	1.369	—	6	0	0
1.240	1.239	8	5	2	1
1.173	1.173	6	7	0	0
1.139	1.139	5	6	2	0
1.119	1.119	5	7	0	1

Table 5
$CsF{\cdot}3AlF_3$. Orthorhombic, $a = 10.86 \pm 0.01$, $b = 9.33 \pm 0.02$ and $c = 7.54 \pm 0.01$ Å

d_{obs}/Å	d_{calc}/Å	I/I_0	h	k	l
7.531	7.493	9	0	0	1
4.235	4.247	12	1	2	0
3.973	3.966	17	2	1	1
3.770	3.751	100	0	0	2
3.696	3.705	13	1	2	1
3.515	3.517	14	2	2	0
3.393	3.361	40	3	1	0
3.243	3.252	34	3	0	1
2.516	2.526	27	2	3	1
	2.506	—	3	1	2
2.449	2.460	44	4	1	1
	2.336	—	4	2	0
2.330	2.325	31	1	3	2
2.114	2.111	12	5	1	0
2.056	2.056	50	3	0	3
	1.760	—	4	4	0
1.756	1.757	13	6	0	1
	1.639	—	3	1	4
1.635	1.638	9	5	0	3
	1.600	—	6	1	2
1.599	1.601	9	0	3	4
1.543	1.545	11	5	2	3
	1.543	—	0	6	0
	1.542	—	4	0	4
1.514	1.515	12	7	0	1
	1.498	—	4	5	1
	1.497	—	1	6	1
1.496	1.496	10	7	1	1
	1.418	—	5	0	4
1.416	1.415	18	4	5	2
	1.414	—	1	2	5
	1.414	—	1	6	2
	1.413	—	7	1	2
	1.326	—	3	2	5
1.326	1.326	11	3	6	2
	1.288	—	5	3	4
	1.287	—	6	1	4
1.287	1.286	11	7	4	0
	1.227	—	5	5	3
1.226	1.225	6	2	4	5
	1.224	—	3	7	1

at 440 ± 5°C for 5 h, followed by quenching in an ice-water bath; thus, β-$CsAlF_4$ sample was obtained. The XRD data for both these are listed in Tables 6 and 7. α-$CsAlF_4$ is hexagonal with $a = 9.494 \pm 0.002$ and $c = 3.703 \pm 0.001$ Å; β-$CsAlF_4$ is orthorhombic, the cell parameters being $a = 10.081 \pm 0.006$, $b = 6.730 \pm 0.004$ and $c = 3.937 \pm 0.003$ Å.

The existence of the two forms of $CsAlF_4$ have been confirmed by the results from XRD. The DTA data further identified that the polymorphic reaction $\alpha \rightleftharpoons \beta$-$CsAlF_4$ at 422°C is reversible. This is because of DTA peak of $\alpha \rightleftharpoons \beta$ at 422°C always appearing on the heating and re-heating curves. The conclusion did not coincide with the results reported by Beutrup et al. [7]. They prepared three types of $CsAlF_4$ from dehydration of $Cs[AlF_4(H_2O)]$ and also determined the crystal structures of β-$CsAlF_4$ and γ-$CsAlF_4$. The report considered that β-$CsAlF_4$ is tetragonal ($a = 11.8101$, $c = 13.3741$ Å) and isomorphous with β-$RbAlF_4$. However, the transformation $\beta \rightarrow \gamma$ is irreversible.

In order to compare the structural characteristics of α-$CsAlF_4$, α-$RbAlF_4$ and $KAlF_4$, far-infrared spectra measurements were carried out. The results are shown

Table 6
α-$CsAlF_4$. Hexagonal, $a = 9.493 \pm 0.002$ and $c = 3.703 \pm 0.001$ Å

d_{obs}/Å	d_{calc}/Å	I/I_0	h	k	l
4.741	4.741	68	1	1	0
4.112	4.111	67	2	0	0
3.373	3.373	20	1	0	1
3.108	3.108	95	2	1	0
2.928	2.928	64	1	1	1
2.753	2.753	72	2	0	1
	2.744	—	3	0	0
	2.384	—	2	1	1
2.378	2.372	56	2	2	0
2.279	2.279	100	3	1	0
1.996	2.000	7	2	2	1
1.943	1.943	35	3	1	1
1.850	1.854	10	0	0	2
1.688	1.687	1	2	0	2
1.679	1.682	9	3	2	1
1.646	1.646	15	5	0	0
1.617	1.614	15	4	1	1
1.594	1.591	10	2	1	2
1.581	1.584	17	3	3	0
1.502	1.504	1	5	0	1
1.478	1.478	1	5	1	0
1.456	1.455	4	3	3	1
1.440	1.438	17	3	1	2

Table 7
β-$CsAlF_4$. Orthorhombic, $a = 10.081 \pm 0.006$, $b = 6.730 \pm 0.004$ and $c = 3.937 \pm 0.003$ Å

d_{obs}/Å	d_{calc}/Å	I/I_0	h	k	l
4.040	4.037	73	2	1	0
	3.367	—	0	2	0
3.361	3.361	100	3	0	0
3.097	3.108	77	2	0	1
2.996	3.005	70	3	1	0
2.241	2.241	50	0	3	0
1.955	1.947	18	0	3	1
1.916	1.912	7	1	3	1
1.864	1.864	20	3	3	0
1.833	1.833	9	2	0	2
1.735	1.735	2	5	1	1
1.729	1.729	8	5	2	0
1.702	1.700	9	0	2	2
	1.699	—	3	0	2

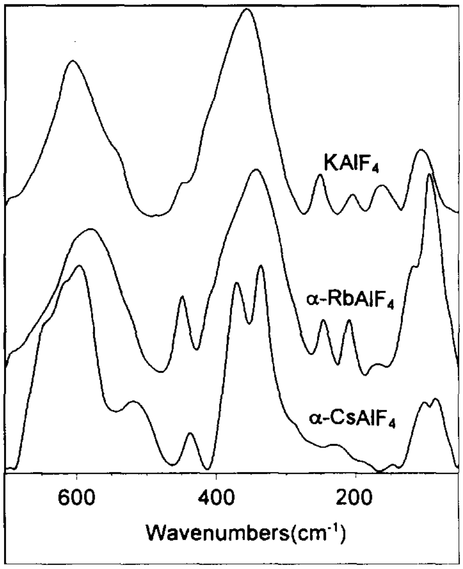

Fig. 2. Far-IR spectra of $MAlF_4$ (M = K, Rb, Cs).

in Fig. 2. α-$RbAlF_4$ is isostructural to $KAlF_4$. This agrees with the results reported by Soga et al. [9]. They measured the infrared absorption spectra of α-$RbAlF_4$ and $KAlF_4$. Both the intermolecular vibrations such as the Al–F bond stretching and the F–Al–F bending vibrations and the lattice vibrations due to the interaction between the inner complex and the outer ions have been observed in the frequency regions of 800–160 cm^{-1} and below 160 cm^{-1}, respectively. A normal coordinate analysis of the crystal as a whole has been carried out on the basis of a simple valence force field by these authors. IR spectral forms of both α-$RbAlF_4$ and $KAlF_4$ are about the same. IR bands of α-$RbAlF_4$ moved toward low wave numbers only because the ionic radius of Rb^+ is different from that of K^+. IR spectra of α-$RbAlF_4$ and $KAlF_4$ determined by us agree exactly with those obtained by Soga. However, IR spectrum of α-$CsAlF_4$ is quite different from that of α-$RbAlF_4$ and $KAlF_4$. Hence the conclusion that α-$CsAlF_4$ is not isostructural to α-$RbAlF_4$ and $KAlF_4$, i.e. the former is not tetragonal.

We can hardly confirm whether the $CsAlF_4$, synthesized by Beutrup, and by us are exactly the same. This needs further investigation.

The phase diagram of the AlF_3–MF system (M = Li, Na, K, Rb, Cs) have been thoroughly investigated. A summary is given in Table 8.

Table 8 reveals that the compound M_3AlF_6 (M = Li, Na, K, Rb, Cs) exists in all components of the AlF_3–MF system. The crystal symmetry of M_3AlF_6 (M = Na, K, Rb, Cs) increases as the ionic radius of M^+ increases (e.g. Na_3AlF_6 at room temperature is monoclinic) [10]; α-K_3AlF_6 is tetragonal

Table 8
Data related with the AlF_3–MF system (M = Li, Na, K, Rb, Cs)

AlF_3–MF	MF/ m.p. (°C)	E_1/ °C	M_3AlF_6/ m.p. (°C)	E_2 (°C)	3AlF–5MF	$MAlF_4$	$3AlF_3$–MF	$2AlF_3$–F
AlF_3·LiF[1]	848	710	785	709	No	No	No	No
AlF_3·NaF[2]	995	888	1010	695 α, Mono.	734 Incongr.	Metastable	No	No
AlF_3·KF[3]	862	820	1000	560 α, Tetrag.	No	575 Incongr.	No	No
AlF_3·RbF[4]	781	729	878	486 α, cubic	No	473 formed in eutectic	745 Incongr.	No
AlF_3·CsF	706	654	790	471 α, cubic	No	443 formed in eutectic	653 Incongr.	508 Incongr.

[3]. (The data included by JCPDS [11] mentions the cubic form, $a = 8.49$ Å. But Jenssen [3] reported that K_3AlF_6 is tetragonal, $a = 5.94$ and $c = 8.46$. We repeatedly calculated the data of [11], the result showed that K_3AlF_6 is tetragonal, $a = 5.98$ and $c = 8.60$ Å, thus confirming the result cited by Jenssen. The calculation of [11] is incorrect.) In fact, α-Rb_3AlF_6 is in the cubic form [4], $a = 7.612$ Å; α-Cs_3AlF_6 is also cubic, $a = 9.212$ Å. In addition, the melting points of all compounds of peritectic temperatures in the system decrease as the ionic radii of M^+ increase. A contradiction is observed in the AlF_3–LiF system, e.g. Li_3AlF_6 (at room temperature) is orthorhombic [3] with a melting point of 785°C. This fact coincides with the unusual characteristics of Li^+ in the periodic table. The regularity mentioned above is also reflected on E_1 and E_2 by both sides near M_3AlF_6.

Although Garton [12] synthesized $LiAlF_4$ and determined its structure, $LiAlF_4$ did not exist in the high-temperature region in the phase diagram of LiF–AlF_3. The debate on whether $NaAlF_4$ exists in the phase diagram at lower temperatures has lasted more than 60 years. However, the metastable hypothesis by Holms [2] seems to be more reasonable. The existence of $MAlF_4$ in the MF–AlF_3 system is increasingly evident as the ionic radius of M^+ increases, but the decomposing temperature of the incongruent compound dropped down.

$3AlF_3$·MF could be observed in both the AlF_3–RbF and AlF_3–CsF systems, whereas $2AlF_3$·MF was only found in the AlF_3–CsF system. This only indicates that the larger M^+ ion is advantageous for the formation of complex ions in the systems.

$3AlF_3$·5NaF ($Na_5Al_3F_{14}$), formed in the AlF_3–NaF system, is the only exception. A compound similar to $3AlF_3$·5NaF did not exist in other systems. We have closely examined the XRD spectra of samples between Rb_3AlF_6 and $RbAlF_4$ and also between Cs_3AlF_6 and $CsAlF_4$. No evidence was found about the formation of any intermediate phases.

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