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Pseudo-binary systems $CsAlF_4$–$KAlF_4$ and Cs_3AlF_6–K_3AlF_6

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Abstract

Phase relations in the system $CsAlF_4$–$KAlF_4$ and Cs_3AlF_6–K_3AlF_6 were investigated by DTA and XRD methods. In the system $CsAlF_4$–$KAlF_4$, two intermediate compounds $3CsAlF_4 \cdot KAlF_4$ and $CsAlF_4 \cdot KAlF_4$ were confirmed. The first one was indexed as orthorhombic with $a = 9.079 \pm 0.003$, $b = 7.958 \pm 0.002$, $c = 7.648 \pm 0.004$ Å. The second one α-$CsAlF_4 \cdot KAlF_4$ is also orthorhombic, $a = 10.982 \pm 0.005$, $b = 10.093 \pm 0.006$, $c = 6.160 \pm 0.002$ Å. Among the two compounds and $KAlF_4$, two eutectic temperatures e_1 and e_2 are formed. The first eutectic temperature e_1 is located in 42 mol % $KAlF_4$ at 525°C, and e_2 in 70 mol % $KAlF_4$ at 510°C. The system Cs_3AlF_6–K_3AlF_6 is a successive solid solution system with the lowest melting point, the composition of which is 75 mol % Cs_3AlF_6 at 775°C. In the solid solution, compound $2Cs_3AlF_4 \cdot K_3AlF_6$ was formed at 656°C, and was indexed as a cubic cell with $a = 8.891$ Å. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: $CsAlF_4$; $KAlF_4$; Cs_3AlF_6; K_3AlF_6; Phase diagram

1. Introduction

The systems $CsAlF_4$–$KAlF_4$ and Cs_3AlF_6–K_3AlF_6 are two polythermal sections in the ternary system AlF_3–CsF–KF, in which the three-side binary systems AlF_3–KF [1], AlF_3–RbF [2] and AlF_3–CsF [3] have been well investigated. However, no one has published about the inner sections. Given that the chemical formula of the components is similar, we were firstly interested in the research of the mentioned systems.

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 N_2 plus HF atmospheres at 600°C for 2 h, the product was identified as anhydrous AlF_3 by XRD. All fluorides were kept in a desiccator.

2.2. Preparation of samples

Samples were prepared by reacting mixtures of anhydrous AlF_3 with a solution of CsF in HF. Products were placed in Pt crucibles and heated until dry at 200°C, then annealed for 48 h at a higher temperature at which no melting of any phase would 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. Method for determination

A CR-G type high-temperature DTA equipment (Beijing Optical Instrument) was employed and

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Table 1
DTA data of the section $CsAlF_4$–$KAlF_4$

$KAlF_4$ (mol %)	Temperatures (°C)			
	Polymorphic transition	Eutectic 1	Eutectic 2	Liquidus
0				507
6				487
10				452
13				480
16				523
20				530
25				585
30	480	527		590
33.3				589
35	484	524		575
40	485	517		545
42				535
45	485	522		540
50		526	510	560
55	483		513	553
60			514	536
65	479		512	523
70				520
75	495		511	521
80	478		511	550
85	475		507	556
90	490		513	563
100				575

calibrated by standard substances with known melting point (calibrating both, the heating and cooling curves). Al_2O_3 was used as a reference substance. The heating rate was 15°/min. Liquidus temperature was determined from the cooling curve, and the other temperatures were determined by extended extrapolating initial temperature 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 the temperature was ±3°C.

In addition, visual polythermal method was also used to determine some liquidus temperatures.

2.4. *X-ray powder diffraction analysis*

The intermediate compounds in the sections were determined by Rigaku Dmax 2400 X-ray diffractometer (Radiation Cu Kα, $\lambda = 1.5409$ Å, filter Ni). Si powder was added as a cross reference for fine-tuning the results during determination.

3. Results and discussion

Phase diagrams of $CsAlF_4$–$KAlF_4$ and Cs_3AlF_6–K_3AlF_6 based on the results of DTA data listed in Tables 1 and 2 are given in Figs. 1 and 2.

Fig. 1 reveals two intermediate compounds $3CsAlF_4 \cdot KAlF_4$ and $CsAlF_4 \cdot KAlF_4$ congruently melting at 585°C and 560°C, respectively.

$CsAlF_4$ formed in the solid state just below the eutectic temperature between Cs_3AlF_6 and $CsF \cdot 2AlF_3$ at 443°C [4], so we can hardly consider that the vertical axis of $CsAlF_4$ in Fig. 1 is a dependent component. The phase relations between $CsAlF_4$ and $3CsAlF_4 \cdot KAlF_4$ were too complicated to draw up the exact picture. We could only leave the liquidus on the diagram. The lowest point (m) on liquidus is located in 90 mol % $CsAlF_4$ at 450°C, and also the two eutectic temperatures e_1 and e_2 were found in 58 mol % $CsAlF_4$ at 525°C and 30 mol % $CsAlF_4$ at 510°C, respectively.

The compounds $3CsAlF_4 \cdot KAlF_4$ and $CsAlF_4 \cdot KAlF_4$ have not been reported so far. Their XRD

Table 2
DTA data of the system Cs_3AlF_6–K_3AlF_6

K_3AlF_6 (mol %)	Temperatures (°C)		
	Solid reaction	Solidus	Liquidus
0			790
3.0	668		775
6.0	663	770	780
10	645	770	775
15	660		775
20	610	770	778
25	650		775
30	645	779	784
33.3	660	790	795
40	665	790	807
45	665	790	810
50	654	793	832
60	658	795	850
70	658	850	877
75	670		902
80	669	890	920
90		943	960
100			995

and indexed data are presented in Tables 3 and 4. $3CsAlF_4{\cdot}KAlF_4$ is orthorhombic with $a = 9.079 \pm 0.003$, $b = 7.958 \pm 0.002$, $c = 7.648 \pm 0.004$ Å. The transformation of $CsAlF_4{\cdot}KAlF_4$ takes place at 485°C. α-$CsAlF_4{\cdot}KAlF_4$ is also orthorhombic, $a = 10.982 \pm 0.005$, $b = 10.093 \pm 0.006$, $c = 6.160 \pm 0.002$ Å.

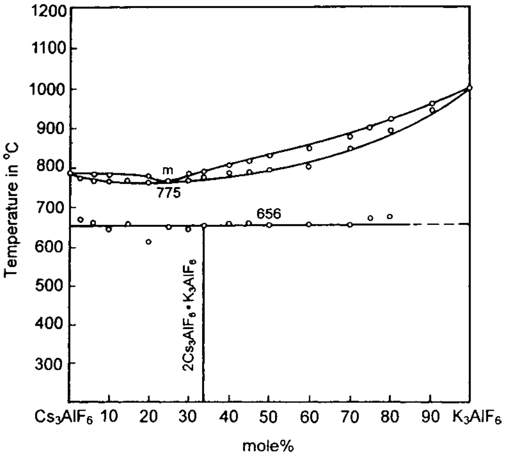

Fig. 1. Diagram of the pseudo-binary system Cs_3AlF_6–K_3AlF_6.

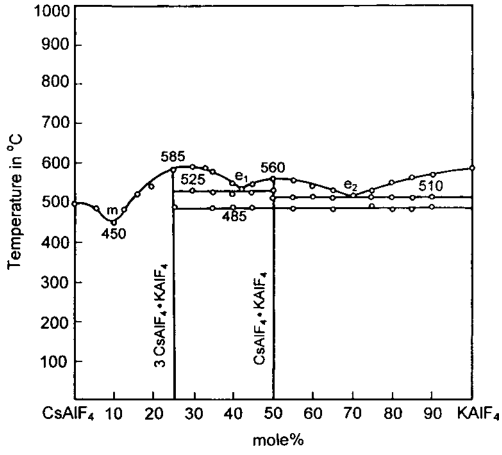

Fig. 2. Diagram of the section $CsAlF_4$–$KAlF_4$.

Fig. 2 gives a result that the pseudo-binary system Cs_3AlF_6–K_3AlF_6 is a successive solid solution system with a lowest melting point 'm', at which the composition is 75 mol % Cs_3AlF_6 at 775°C. The intermediate compound $2Cs_3AlF_4{\cdot}K_3AlF_6$ formed at 656°C when the solid solution was cooled. XRD and indexed data for $2Cs_3AlF_4{\cdot}K_3AlF_6$ is presented in Table 5. The compound is in cubic, $a = 8.891$ Å.Each system in $CsAlF_4$–$KAlF_4$ and Cs_3AlF_6–K_3AlF_6 has the same component formula; however, different types of phase diagram were observed. In the system $CsAlF_4$–$KAlF_4$, the two components are not isostructural. $KAlF_4$ has only one type of structure — tetragonal, however, $CsAlF_4$ has two types, and the polymorphic transition is as follows [3]:

$$\alpha\text{-}CsAlF_4 \text{ (hexagonal)} \overset{422^\circ C}{\rightleftarrows} \beta\text{-}CsAlF_4 \text{ (orthorhombic)}$$

The ionic structures of Cs^+ and K^+ are quite similar, and the difference between their ionic radii is not so large. The formation of two intermediate compounds $3CsAlF_4{\cdot}KAlF_4$ and $CsAlF_4{\cdot}KAlF_4$ could only be explained as due to their being non-isostructural.

In the system Cs_3AlF_6–K_3AlF_6 continous solid solution with lower melting temperature was observed. Cs_3AlF_6 has only cubic structure (Amorasit [4] reported tetragonal formation below 290°C), and

Table 3
Indexed data[a] of $3CsAlF_4 \cdot KAlF_4$

d (Å) obs.	*d* (Å) calc.	I/I_0	*h*	*k*	*l*
5.832	5.840	23	1	0	1
3.651	3.645	77	1	2	0
3.545	3.531	100	0	2	1
3.211	3.217	51	1	1	2
3.027	3.025	70	3	0	0
2.917	2.920	25	2	0	2
2.377	2.373	80	3	0	2
2.301	2.300	28	3	2	1
2.198	2.194	23	2	3	1
2.095	2.097	33	4	1	1
	2.090		1	2	3
2.040	2.039	23	3	2	2
1.971	1.971	22	4	2	0
	1.943		1	4	0
1.942	1.940	62	2	2	3
	1.895		4	1	2
1.892	1.894	19	3	1	3
1.804	1.803	17	1	3	3
	1.773		2	4	1
	1.770		5	1	0
1.769	1.769	75	3	3	2
	1.767		5	0	1
	1.765		0	4	2
1.650	1.652	20	5	2	0
	1.539		1	3	4
1.526	1.524	22	3	4	2
1.438	1.438	22	4	1	4
1.350	1.350	25	0	5	3
1.335	1.335	19	1	5	3
1.307	1.307	23	0	6	1
	1.285		4	5	1
1.283	1.283	14	6	1	3
1.243	1.243	13	6	3	2
1.205	1.204	12	6	4	0
	1.203		1	2	6

[a] Orthorhombic cell: $a = 9.079 \pm 0.003$, $b = 7.958 \pm 0.002$, $c = 7.648 \pm 0.004$ Å.

for K_3AlF_6, three crystal structures were reported [5]. The polymorphic transition is as follows:

$$\begin{aligned} &\alpha\text{-}K_3AlF_6 \text{ (tetragonal)} \\ &\overset{131^\circ C}{\rightleftarrows} \beta\text{-}K_3AlF_6 \text{ (orthorhombic)} \\ &\overset{318^\circ C}{\rightleftarrows} \gamma\text{-}K_3AlF_6 \text{ (cubic)} \end{aligned}$$

At higher temperatures, the two components have isostructural cubic cell structures. They form a continuous solid solution, and as the temperature is decreased, K_3AlF_6 changes its structure into orthorhombic and tetragonal, and the intermediate compound $2Cs_3AlF_4 \cdot K_3AlF_6$ is thus formed.

Table 4
Indexed data[a] of $CsAlF_4 \cdot KAlF_4$

d (Å) obs.	*d* (Å) calc.	I/I_0	*h*	*k*	*l*
6.146	6.145	15	0	0	1
5.467	5.496	12	2	0	0
3.907	3.910	24	0	2	1
3.726	3.720	31	2	2	0
3.455	3.450	23	3	1	0
3.166	3.184	28	2	2	1
3.134	3.151	42	3	0	1
3.078	3.076	100	0	0	2
3.011	3.005	20	3	1	1
2.564	2.561	23	1	2	2
2.457	2.460	20	1	4	0
2.373	2.372	37	2	2	2
	2.303		3	3	1
2.295	2.296	14	3	1	2
	2.294		2	4	0
2.194	2.197	13	5	0	0
1.778	1.779	15	4	4	1
1.659	1.658	15	6	2	1
	1.657		5	4	0
1.540	1.540	15	0	0	4

[a] Orthorhombic cell: $a = 10.982 \pm 0.005$, $b = 10.093 \pm 0.006$, $c = 6.160 \pm 0.002$ Å.

From the above-mentioned discussion, it appears that the different crystal structure is a necessary factor

Table 5
Indexed data[a] of $2Cs_3AlF_6 \cdot K_3AlF_6$

d (Å) obs.	*d* (Å) calc.	I/I_0	*h*	*k*	*l*
4.462	4.458	19	2	0	0
3.151	3.140	100	2	2	0
2.570	2.569	45	2	2	2
2.224	2.225	43	4	0	0
2.041	2.038	4	3	3	1
1.989	1.988	21	4	2	0
1.816	1.816	40	4	2	2
1.572	1.572	21	4	4	0
1.482	1.482	9	6	0	0
1.406	1.405	19	6	2	0
1.340	1.340	8	6	2	2
1.283	1.283	6	4	4	4
1.233	1.233	3	6	4	0
1.188	1.188	16	6	4	2
1.111	1.111	2	8	0	0

[a] Cubic cell: $a = 8.891 \pm 0.001$ Å.

for the formation of the intermediate compounds in a molten salt system, even though the components have the same chemical formula, same anion, similar ionic structure and almost identical chemical properties.

Acknowledgements

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