Phase Equilibrium in the System BaF₂—AlF₃

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The system $BaF_2 - AlF_3$ has been studied by differential thermal analysis and by the X-ray diffraction of quenched samples. In this study, four compounds have been found, two of which undergo phase transitions at approximately 770°C.

Ravez [2,3] has reported compounds in this system at Ba/Al ratios of 1 : 2, 1 : 1, 3 : 2, 5 : 2, and 9 : 2, corresponding to the formulas $BaAl_2F_8$, $BaAlF_5$, $Ba_3Al_2F_{12}$, $Ba_5Al_2F_{16}$, and $Ba_9Al_2F_{24}$.

In the present work, only the compounds at Ba/Al ratios of 1 : 1, and 3 : 2, *i.e.* $BaAlF_5$ and $Ba_3Al_2F_{12}$, have been confirmed from Ravez's [2,3] work, and new compounds at ratios of 2 : 3 and 3 : 1, *i.e.* $Ba_2Al_3F_{13}$ and Ba_3AlF_9, have been found.

The X-ray data of the compounds are given as well as the experimental densities.

Systems containing AlF_3 are of importance in the technical electrolysis of aluminium. Although BaF_2 is not normally added to the electrolyte, its potential as a possible addition is discussed by Grjotheim *et al.*[1]

Ravez [2,3] has reported compounds in this system at Ba/Al ratios of 1 : 2, 1 : 1, 3 : 2, 5 : 2, and 9 : 2 corresponding to the formulas $BaAl_2F_8$, $BaAlF_5$, $Ba_3Al_2F_{12}$, $Ba_5Al_2F_{16}$ and $Ba_9Al_2F_{24}$. He, however, neither describes his experimental procedure in detail, nor gives a phase diagram. In order that the phases and their fields of stability could be accurately known, this work was undertaken.

EXPERIMENTAL

The BaF_2 employed was "Selectipur" grade, obtained from Merck, Darmstadt, Germany. The AlF_3 was obtained by vacuum sublimation of anhydrous AlF_3 (A.D. Mackay, Inc., USA). The samples for the DTA experiments were weighed out in the proper proportions, mixed thoroughly, and then encapsulated in sealed platinum tubes. They were then melted to insure homogeneity before use.

The DTA experiments were carried out in a platinum wound vertical tube furnace employing a ceramic block. The samples and the reference material were held in platinum crucibles, which fit into the ceramic block. Pure Al_2O_3 from Merck was used as reference material. In order to avoid oxidation of the samples, an atmosphere of flowing purified nitrogen was used in the furnace. The differential thermocouple (Pt/Pt − 10Rh) was

placed in the center of the sample and reference material. The control thermocouple (Pt/Pt − 10Rh) was placed in the center of the ceramic block approximately 3 − 4 mm away from both Pt crucibles.

The rates of heating and cooling were approximately 1 − 2°C/min, in the temperature range between 875 and 975°C for samples with more than 65 mol % BaF_2. These rates were employed, so as to obtain all heat changes in this temperature range, since the melting temperatures for the compounds in this system are close. The DTA curves were recorded by a Varian G-2000 recorder and by the use of a DC Microvolt Amplifier (range 50 − 2000 μV, Leeds and Northrup, USA).

Quenching experiments were carried out in a Kanthal-would vertical tube furnace and the quenching medium used was kerosene. Samples to be quenched were sealed in Pt-tubes and then suspended in the furnace by means of a thin Pt-wire. After the samples had been melted and then equilibrated at the desired temperature, for times ranging from 24 to 60 h, they were quenched by cutting the Pt-wire. Annealing temperatures ranged from 700 to 900°C and were controlled by means of a Siemens NZV controller. The temperatures were measured by a Pt/Pt − 10Rh thermocouple placed adjacent to the sample. The temperature variation was less than ± 3°C.

The X-ray investigations were carried out with a Philips Widerange goniometer PW 1050, connected to a Philips PR 2262 recorder (Philips, Eindhoven, Holland). Nickel filtered CuKα, $\lambda = 1.5418$ Å, was used.

The densities of the powdered samples were determined with the use of the vacuum pycnometric method using odorless kerosene as displacement liquid.

RESULTS AND DISCUSSION

The investigated part of the phase diagram is shown in Fig. 1. It can be seen that the compounds Ba_3AlF_9, $BaAlF_5$, and $Ba_2Al_3F_{13}$ melt incongruently at temperatures of $912 \pm 3°C$, $895 \pm 3°C$, and $871 \pm 3°C$, respectively. The compound $Ba_3Al_2F_{12}$ was found to melt congruently at a temperature of $966 \pm 3°C$. This agrees well with the data of Ravez [2,3] who found a melting
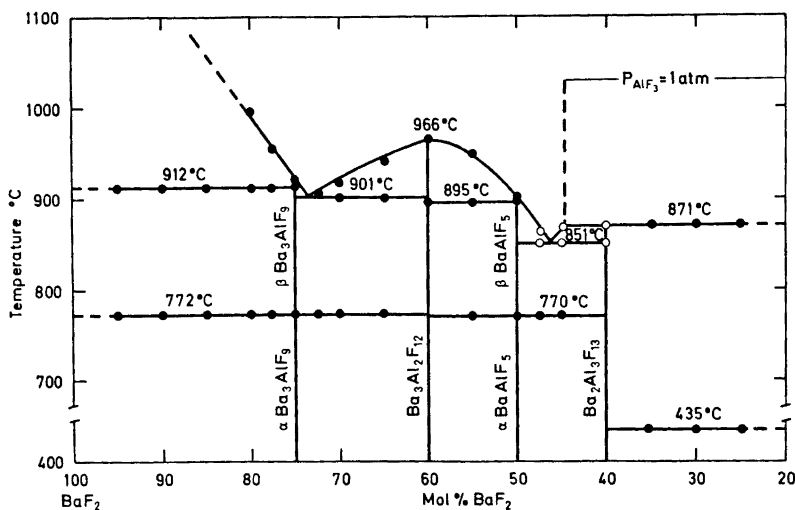

Fig. 1. The phase diagram of the investigated part of the system $AlF_3 − BaF_2$. ● Cooling curves. ○ Heating curves.

point of 970°C. The melting point of $BaAlF_5$ also agrees favorably with the value of 904°C which was determined by Ravez.[2,3]

The phase transformation of the 1 : 1 compound, which Ravez [2,3] found to be at 760 ± 8°C, was found to be at a slightly higher temperature of 770 ± 3°C. The phase transformation of the compound $Ba_3Al_2F_{12}$, which Ravez [2,3] said occurred at 885 ± 10°C, could not be found. A phase transformation of the compound Ba_3AlF_9 was found to occur at approximately 772 ± 3°C. While cooling during the course of the DTA experiments, the transformations of $BaAlF_5$ and Ba_3AlF_9 occurred at lower temperatures due to supercooling.

The two eutectic points in this system were found to occur at 73.2 mol % BaF_2 and 901 ± 3°C, and at 46.2 mol % BaF_2 and 851 ± 3°C.
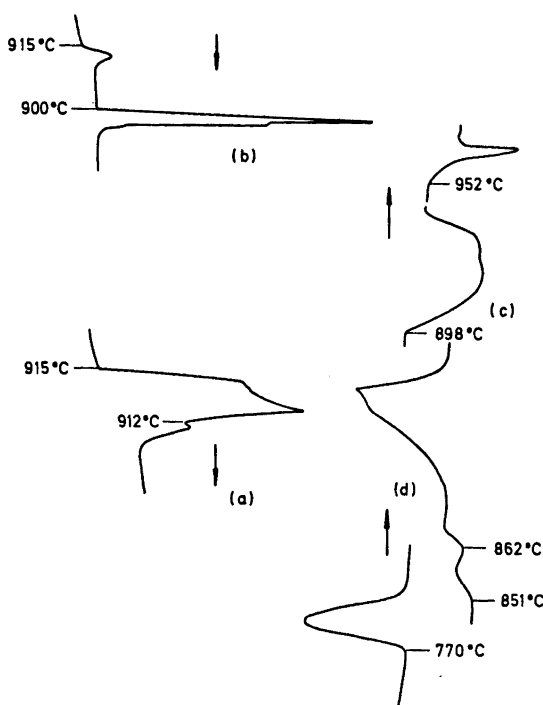

Fig. 2. DTA heating and cooling curves for AlF_3—BaF_2 mixtures: (a) 75 mol % BaF_2 (cooling curve); (b) 70 mol % BaF_2 (cooling curve); (c) 55 mol % BaF_2 (heating curve); (d) 47.5 mol % BaF_2 (heating curve).

Fig. 2 gives four heating and cooling curves for some BaF_2—AlF_3 mixtures. From these curves, it is clear that $BaAlF_5$ and Ba_3AlF_9 melt incongruently.

Ravez [2,3] has stated that the compound $BaAl_2F_8$ also exists. The existence of this compound could not be confirmed in this work. Mixtures up to and including 35 mol % BaF_2 gave DTA peaks at 435 ± 3°C corresponding to the phase transformation of pure AlF_3. The absence of $BaAl_2F_8$ was also confirmed

by the X-ray diffraction of quenched samples. In the powder patterns of samples with 35 mol % BaF_2, peaks corresponding to free AlF_3 were found. This fact that free AlF_3 was present in the mixture of 35 mol % BaF_2 proves that $BaAl_2F_8$ (with 33.3 mol % BaF_2) does not form under the conditions of the present investigation.

At compositions between 40 and 50 mol % BaF_2, the AlF_3 peak was not found in the DTA experiments, thus indicating that a new compound has been formed. Although there are several possible compounds between 40 and 50 mol % BaF_2, the new compound was believed to be $Ba_2Al_3F_{13}$, because this composition gives a simple Ba : Al ratio. The existence of a new compound was also verified by X-ray diffraction of quenched samples. In the powder patterns of samples with less than 40 mol % BaF_2, peaks corresponding to free AlF_3 were present. However, when 40 mol % BaF_2 was reached, these reflections disappeared. It should be mentioned that when a sample of 50 mol % BaF_2 or less is heated to 900°C for a time and then cooled slowly to room temperature, the resulting powder patterns contain peaks belonging to $BaAlF_5$, $Ba_2Al_3F_{13}$, and AlF_3. Thus the samples tend to equilibrate with the $BaAlF_5$ compound, and the existence of the $Ba_2Al_3F_{13}$ compound can only be proved by long equilibrating times and quenching.

The compounds $Ba_9Al_2F_{24}$ and $Ba_5Al_2F_{16}$, which Ravez [2,3] claims to have found, could neither be detected in our study. The X-ray powder patterns given by Ravez [3] for these two compounds are not similar to anything obtained in the present study. Detailed X-ray studies of quenched samples, containing 80 and 85 mol % BaF_2, show almost identical powder patterns with only slight intensity changes. The patterns also contain reflections due to free BaF_2. From these two facts, it is clear that a compound $Ba_9Al_2F_{24}$, at 81.8 mol % BaF_2, cannot exist. In a like manner, the powder patterns of samples containing 72.5 and 70.0 mol % BaF_2 are indistinguishable, thus indicating that the compound $Ba_5Al_2F_{16}$ at 71.4 mol % BaF_2 is non-existent.

Samples used in these studies were equilibrated at the desired temperatures for 2 to 3 days to insure equilibrium. Ravez [2,3] used shorter equilibrating times than in the present study, so that the absence of these compounds in our work is not thought to be a kinetic phenomenon. It should be realized, however, that different impurities could change the kinetics of the reactions and allow other phases to appear. It is possible also, that Ravez [2,3] has not known the purity of his starting materials. Humidity, for instance, may perhaps react to give oxide or hydroxide ion containing compounds, and it is possible that oxygen in the atmosphere may promote or stabilize new fluoride phases. Also, the complexity of the powder patterns is such that only by careful examination, can the phases present be identified.

The experimental X-ray powder patterns for the four compounds and the two high-temperature forms, $\beta BaAlF_5$ and βBa_3AlF_9, are given in Tables 1 − 6. The calculated X-ray powder pattern of the compound $\alpha BaAlF_5$ in Table 2 has been obtained from single crystal data due to Holter.[4] The experimental X-ray pattern, agrees well with the data of Holter,[4] who found by single crystal Weissenberg methods the compound $\alpha BaAlF_5$ to have orthorhombic symmetry with lattice parameters, $a = 5.156$ Å, $b = 7.575$ Å, and $c = 19.64$ Å.

Table 1. 40 mol % BaF_2, $Ba_2Al_3F_{13}$.

$d(Å)_{obs}$	I/I_0	$d(Å)_{obs}$	I/I_0
4.854	20	2.426	30
4.299	5	2.378	20
4.243	5	2.334	40
4.049	30	2.222	3
3.938	10	2.212	30
3.888	20	2.203	40
3.563	100	2.196	60
3.512	40	2.152	20
3.441	60	2.117	20
3.222	20	2.104	30
3.192	30	2.072	30
2.962	20	1.969	10
2.899	20	1.957	10
2.858	10	1.878	40
2.623	30	1.840	20

Table 2. 50 mol % BaF_2, $\alpha BaAlF_5$.

This work $d_{obs}(Å)$	Holter $d_{calc}(Å)$	h	k	l	I/I_0
4.956	4.953	0	1	3	21
4.267	4.262	1	1	0	10
4.122	4.120	0	1	4	14
3.553	3.556	1	0	4	100
3.273	3.273	0	0	6	17
3.009	3.005	0	1	6	15
2.919	2.915	1	2	2	12
2.633	2.631	0	1	7	13
2.584	2.578	2	0	0	25
2.505	2.504	0	3	1	3
2.478	2.477	0	2	6	7
2.458	2.455	0	0	8	8
2.403	2.399	2	0	3	5
2.335	2.335	0	1	8	28
2.284	2.287	2	1	3	29
	2.283	2	0	4	
2.254	2.253	1	3	1	20
2.230	2.232	1	2	6	16
2.216	2.217	1	0	8	35
2.176	2.182	0	0	9	17
2.122	2.124	0	3	5	15
2.092	2.097	0	1	9	16
2.060	2.060	0	2	8	21
2.054	2.059	1	3	4	18
2.029	2.027	2	2	3	5
1.998	1.999	0	3	6	4
1.940	1.942	1	1	9	4
1.892	1.891	0	2	9	11

Table 3. 50 mol % BaF_2, $\beta BaAlF_5$.

$d(Å)_{obs}$	I/I_0	$d(Å)_{obs}$	I/I_0
4.868	4	2.631	10
4.285	10	2.432	20
4.075	10	2.382	10
3.933	80	2.310	40
3.576	100	2.238	5
3.455	60	2.204	10
3.220	40	2.160	20
2.975	20	2.103	20
2.933	2	2.076	30
2.906	4	1.973	10
2.863	20	1.958	20

Table 4. 60 mol % BaF_2, $Ba_3Al_2F_{12}$.

$d(Å)_{obs}$	I/I_0	$d(Å)_{obs}$	I/I_0
4.927	10	2.895	11
4.787	7	2.800	8
4.559	11	2.620	8
4.360	20	2.568	6
4.229	7	2.465	8
4.090	7	2.390	39
3.620	22	2.329	20
3.550	80	2.297	14
3.498	100	2.256	42
3.429	60	2.228	13
3.327	45	2.193	37
3.283	55	2.144	16
3.249	59	2.119	63
3.222	42	2.098	29
3.136	61	2.065	11
3.046	47	2.045	25
2.984	29	2.015	18
		1.996	17

Ravez [2,3] also gives the lattice parameters of the compound $\beta Ba_3Al_2F_{12}$, which he has determined from single crystal data. He found values of $a = 15.55$ Å, $b = 13.03$ Å, and $c = 7.17$ Å. Although this compound was not found in this investigation, the d values which were observed by Ravez [3] are given in Table 7.

In Table 8 are given the experimental densities of the compounds. The densities of the high temperature modifications are not given, as the amount of sample was not sufficient for measurement. The density of the 1 : 1 compound as found by Holter [4] was 4.52 g/cm³. The value found for the same compound in this study, 4.53 g/cm³, compares well with this value.

Table 5. 75 mol % BaF_2, αBa_3AlF_9.

$d(Å)_{obs}$	I/I_0	$d(Å)_{obs}$	I/I_0
4.075	30	2.428	3
3.729	20	2.414	3
3.616	100	2.376	3
3.577	50	2.237	10
3.479	10	2.223	8
3.333	10	2.188	20
3.263	10	2.174	30
3.096	2	2.116	30
3.052	5	2.060	40
2.981	10	1.988	30
2.956	10	1.948	20
2.847	5	1.872	40
2.781	30	1.790	3
2.556	5	1.740	4
2.483	5	1.728	4
		1.711	4

Table 6. 75 mol % BaF_2, βBa_3AlF_9.

$d(Å)_{obs}$	I/I_0	$d(Å)_{obs}$	I/I_0
5.180	5	3.043	30
3.967	5	2.931	20
3.919	4	2.905	3
3.757	3	2.850	5
3.580	50	2.757	10
3.512	50	2.713	2
3.461	45	2.579	2
3.345	100	2.545	4
3.303	5	2.374	5
3.266	15	2.316	10
3.241	10	2.302	20
3.195	10	2.277	2
		2.234	20

Table 7. 60 mol % BaF_2, $\beta Ba_3Al_2F_{12}$.

Ravez [3] $d(Å)_{obs}$	I/I_0	$d(Å)_{obs}$	I/I_0
3.99	36	2.168	58
3.53	100	2.089	29
3.44	70	2.025	38
3.26	52	1.996	8
3.17	29	1.931	3
2.99	16	1.895	3
2.86	10	1.865	55
2.77	17	1.832	14
2.41	12	1.781	14
2.301	16	1.752	5
2.319	26	1.712	16
2.218	35	1.652	7
		1.635	14

Table 8. Experimental densities of the compounds in the system $BaF_2 - AlF_3$.

Compound	Density (g/cm³)
$Ba_2Al_3F_{13}$	4.63 ± 0.03
$\alpha BaAlF_5$	4.53 ± 0.03
$\beta BaAlF_5$	—
$Ba_3Al_2F_{12}$	4.31 ± 0.03
αBa_3AlF_9	4.83 ± 0.03
βBa_3AlF_9	—

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