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Short Communication

Stability and Structure of Sodium Tetrafluoroaluminate, $NaAlF_4$

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The binary system $NaF–AlF_3$ contains two compounds, one congruently melting compound corresponding to the mineral cryolite, Na_3AlF_6, and one incongruently melting compound corresponding to the mineral chiolite, $Na_5Al_3F_{14}$. There has been some doubt about the existence and stability of a third compound in the system, sodium tetrafluoroaluminate, $NaAlF_4$. About 40 years ago Howard[1] demonstrated the existence of $NaAlF_4$ by quenching the vapour above a molten mixture of NaF and AlF_3. The existence of $NaAlF_4$ has later been verified by several authors. These investigations have been summarized among others by Holm and co-workers.[2–4] In the paper by Bjørseth *et al.*[4] published in 1986, the disproportionation of solid $NaAlF_4$ was studied by X-ray diffraction analysis and differential scanning calorimetry in the temperature range 400–900 K. Both techniques showed that solid $NaAlF_4$ is a metastable phase at room temperature, and that at higher temperatures it decomposes to chiolite, $Na_5Al_3F_{14}$, and aluminium fluoride, AlF_3. The disproprotionation takes place at a considerable rate between 700 K and 900 K. The stability of solid $NaAlF_4$ in water was tested and found to be far less than for the thermodynamically stable compounds $Na_5Al_3F_{14}$ and AlF_3.

Different attempts have been made to determine the structure of $NaAlF_4$; by Howard[1] in 1954, Mashovets[5] in 1957 and Garton and Wanklyn[6] in 1965. However, owing to coincidence and presence of reflections from both $Na_5Al_3F_{14}$ and AlF_3 and the instability of the compound, none of these examinations can be considered as accurate or reliable today. Mashovets,[5] for instance, deduced a unit cell with $a=3.48$ Å, $c=6.29$ Å and space group $P4/mmm$ (isomorphous with Rb, Tl and K compounds). Garton and Wanklyn[6] pointed out correctly that the true unit cell must be larger to account for the additional low-angle lines in their X-ray diagram. They suggested on the basis of their results a unit cell of dimensions $a=14.00$ Å and $c=12.00$ Å. Their X-ray data are often referred to in the literature today (PDF card 19-1243).

Experimental

The preparation of solid $NaAlF_4$ from its vapour under controlled conditions was performed by vaporization at 800 °C of a melt of bulk composition corresponding to 5 NaF : 3 AlF_3. A sample of the mineral chiolite, $Na_5Al_3F_{14}$ (hand-picked mineral, clear crystals of the highest purity available from Ivigtut, Greenland),† was used as a starting material.

The experimetal set up and the procedure was the same as described in the paper by Bjørseth *et al.*[4] During the experiment dry nitrogen gas was flushed through the furnace, and the condensation product from the vapour was collected on an alumina filter at room temperature.

X-Ray investigation of a freshly collected $NaAlF_4$ sample consisting of very fine crystals was carried out by use of a Phillips PW 1730/10 instrument using Cu Kα radiation ($\lambda=1.5418$ Å).

The density of $NaAlF_4$ had been determined earlier on a sample of $NaAlF_4$ of the same quality by a method described by Biltz.[7] Shell Odourless kerosene was used as a liquid during the experiment.

Results and discussion

Formation of gaseous $NaAlF_4$. in Fig. 1 are plotted the free energy taken from Ref. 8 for $NaAlF_4(g)$ in the temperature range 1200–1400 K together with the data

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† A gift to one of the authors (J.L.H.) from Kryolitselskabet Øresund, Denmark in 1960.

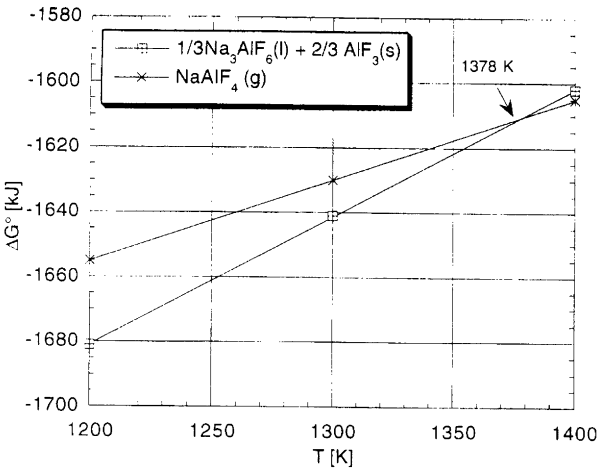

Fig. 1. Free energy data according to Ref. 8 for $NaAlF_4(g)$ and the equilibrium mixture $1/3\ Na_3AlF_6(l) + 2/3\ AlF_3(s)$ in the temperature range 1200–1400 K.

for $Na_3AlF_6(l) + AlF_3(s)$ according to the equilibrium

$$1/3\ Na_3AlF_6(l) + 2/3\ AlF_3(s) = NaAlF_4(g)$$

According to these data, the equilibrium pressure of gaseous $NaAlF_4$ will reach 1 atm at 1378 K or 1105 °C.

Structure of solid $NaAlF_4$. The results from the X-ray investigation of $NaAlF_4$ are presented in Fig. 2. The powder patterns are compared with the diagram based on the results of Garton and Wanklyn results from 1965.[6] Their diagram clearly contains lines from both $Na_5Al_3F_{14}$ and AlF_3.

In Table 1 are given the experimental d-values as well as the calculated values based on a tetragonal cell of dimensions $a = 7.449 \pm 0.002$ Å and $c = 10.523 \pm 0.008$ Å. As can be seen, this cell accounts satifactorily for all observed reflections. The volume of the cell is 583.92 Å^3 and contains eight formula units. The theoretical density is, according to the cell dimensions given above, 2.866g cm^{-3}, in excellent agreement with the experimentally determined value 2.86 g cm^{-3}. The ratio $c/a \approx \sqrt{2}$, and therefore the cell is closely related to a pseudocubic sub-cell with $a \approx c/2$ or 5.26 Å.

The cell parameters obtained for $NaAlF_4$ are compared with the cell parameters for chiolite, $Na_5Al_3F_{14}$, in Table 2. The structures of the two compounds [$Na_5Al_3F_{14}$ with two units in the cell ($Na_{10}Al_6F_{28}$) and $NaAlF_4$ with eight units in the cell ($Na_8Al_8F_{32}$)] are comparable in size. The differences in the cell parameters a and c can be explained by the fact that that in the chiolite structure one third of the AlF_6 octahedra share four corners and two thirds only two corners with others, while in the $MAlF_4$ structures all octahedra share four corners.[10]

In Fig. 3 are plotted the densities of the five compounds belonging to the NaF–AlF_3 system (NaF, Na_3AlF_6, $Na_5Al_3F_{14}$, $NaAlF_4$ and AlF_3) as a function of composition. As can be seen, the density of $NaAlF_4$ does not fit in with the other four compounds. This is due to the

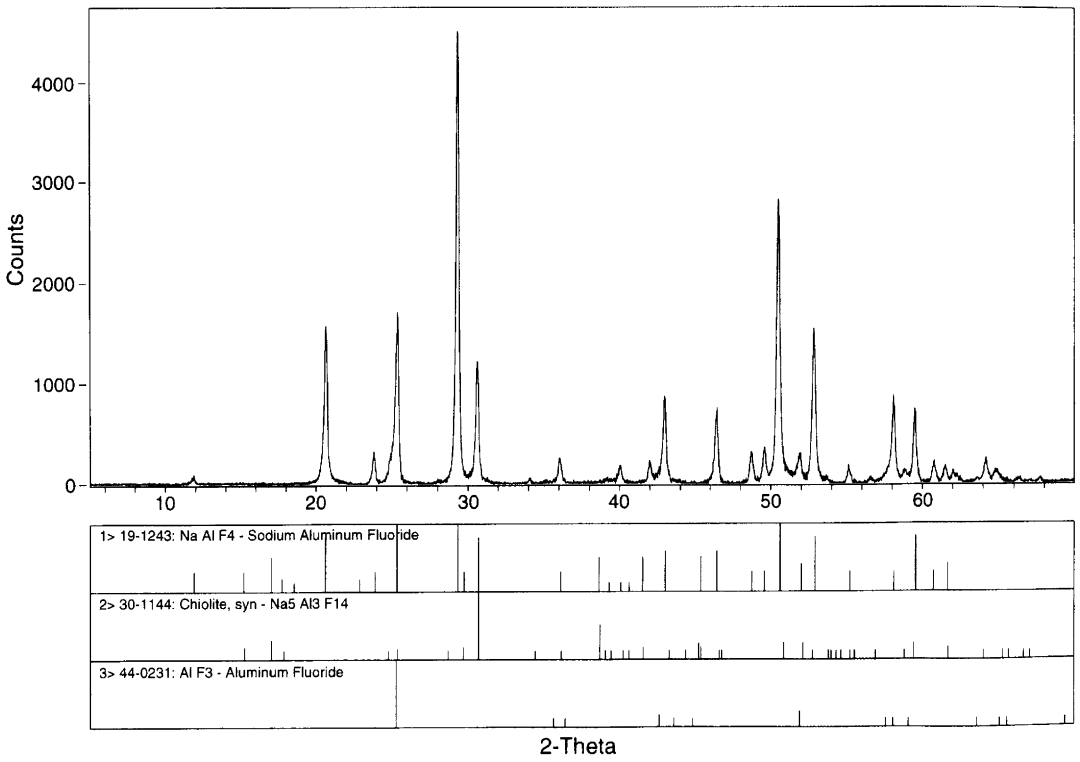

Fig. 2. Powder patterns of $NaAlF_4$ compared with literature values of powder patterns from $NaAlF_4$ (PDF: 19-1243), $Na_5Al_3F_{14}$ (PDF: 30-1144) and AlF_3 (PDF: 44-0231).

Table 1. Results from X-ray examination of $NaAlF_4$ (20 °C).

h k l	$d_{calculated}$	$d_{measured}$	I/I_0
1 0 0	7.4492	7.450	2
1 0 2	4.2975	4.298	35
2 0 0	3.7246	3.722	7
1 1 2	3.7225		
2 0 1	3.5111	3.511	38
2 0 2	3.0400	3.043	100
1 1 3	2.9195	2.919	27
2 2 0	2.6337	2.630	1
0 0 4	2.6308		
2 2 1	2.5549	2.555	1
2 0 3	2.5535		
3 0 0	2.4831	2.488	5
1 0 4	2.4808		
3 1 1	2.2987	2.300	1
3 0 2	2.2456	2.250	3
3 1 2	2.1500	2.147	4
2 0 4	2.1488		
2 2 3	2.1061	2.104	19
3 1 3	1.9556	1.956	16
1 1 5	1.9543		
4 0 0	1.8623	1.866	7
2 2 4	1.8612		
4 0 1	1.8338	1.836	7
2 0 5	1.8323		
4 1 0	1.8066	1.806	62
3 0 4	1.8057		
3 3 0	1.7558		
4 0 2	1.7556	1.759	5
3 1 4	1.7549		
3 3 1	1.7319	1.732	33
1 0 6	1.7071	1.706	1
4 2 0	1.6657		
3 3 2	1.6655	1.665	4
1 1 6	1.6640		
3 2 4	1.6248	1.625	1
4 2 2	1.5880	1.587	19
2 0 6	1.5867		
3 3 3	1.5701	1.570	2
3 1 5	1.5694	1.567	3
2 1 6	1.5519	1.553	16
4 0 4	1.5200	1.522	5
4 2 3	1.5047	1.506	4
5 0 0	1.4898	1.489	2
4 3 0	1.4898		
1 1 7	1.4455	1.450	5
5 0 2	1.4335	1.437	3
3 0 6	1.4325		
5 1 2	1.4077	1.407	1
3 1 6	1.4067		
2 0 7	1.3940	1.396	1
4 4 0	1.3168	1.315	8
0 0 8	1.3154		
5 0 4	1.2964	1.299	3
4 3 4	1.2964		
1 0 8	1.2953		
5 3 0	1.2775	1.278	10
4 4 2	1.2774		

[a]The experimental values are compared with *d*-values assuming a tetragonal cell with $a = 7.449 \pm 0.002$ Å and $c = 10.523 \pm 0.008$ Å.

Table 2. Unit-cell dimensions of $NaAlF_4$ and $Na_5Al_3F_{14}$ (space group $P4/mnc$).

Compound	*a*/Å	*c*/Å	*Z*	Ref.
$Na_5Al_3F_{14}$	7.0142	10.400	2	9
$NaAlF_4$	7.4492	10.523	8	This work

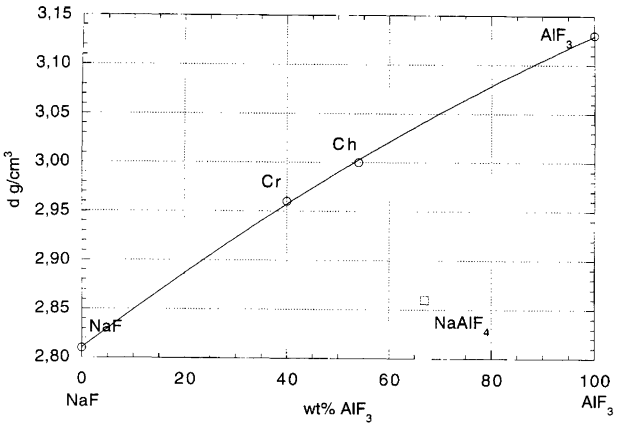

Fig. 3. Densities of five compounds in the NaF–AlF_3 system plotted as a function of composition. The densities of NaF, Na_3AlF_6, $Na_5Al_3F_{14}$ and AlF_3 are as given on their respective PDF cards.

unfavourable and open structure of $NaAlF_4$, as this solid compound is formed by quenching directly from the vapour.

The decomposition reaction

$$NaAlF_4(s) \rightarrow 1/5\ Na_5Al_3F_{14}(s) + 2/5\ AlF_3(s)$$

will, according to the new data, be accompanied by a reduction in volume of ca. 6%.

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