

# On the Physical and Thermodynamic Stability of Solid Sodium Tetrafluoroaluminate

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Bjørseth, O., Herstad, O. and Holm, J. L., 1986. On the Physical and Thermodynamic Stability of Solid Sodium Tetrafluoroaluminate. – Acta Chem. Scand. A 40: 566–571.

The disproportionation of solid tetrafluoroaluminate,  $\text{NaAlF}_4$ , was studied by X-ray diffraction analysis and differential scanning calorimetry in the temperature range 400–900 K. Both techniques showed that solid  $\text{NaAlF}_4$  is a metastable phase at room temperature; that at higher temperatures, it decomposes to chiolite,  $\text{Na}_5\text{Al}_3\text{F}_{14}$  and aluminium fluoride,  $\text{AlF}_3$ . The disproportionation takes place at a considerable rate between 700 K and 900 K. The stability of solid  $\text{NaAlF}_4$  in water was tested and found to be far less than for the thermodynamically stable compounds  $\text{Na}_5\text{Al}_3\text{F}_{14}$  and  $\text{AlF}_3$ .

The fluoride emission from the cryolite bath in alumina reduction cells has been the subject of numerous investigations.<sup>1–3</sup> Noticeable losses of electrolyte and possible health hazard to the workers in the aluminium plants have been the primary reasons for these investigations. About 30 years ago, Howard<sup>4</sup> demonstrated the existence of  $\text{NaAlF}_4$  particulates formed by rapid cooling of the vapour above a molten mixture of  $\text{NaF}$  and  $\text{AlF}_3$ . He claimed that the solid compound was unstable above 470°C and that the dissociation occurred according to the reaction scheme:  $5 \text{NaAlF}_4(\text{s}) = \text{Na}_5\text{Al}_3\text{F}_{14}(\text{s}) + 2 \text{AlF}_3(\text{s})$ . Also, Ginsberg and Wefers<sup>5</sup> concluded in a later work that the solid compound  $\text{NaAlF}_4$  is stable only in a very narrow temperature range, 680–710°C. They were, however, not able to prove the stability of the compound either by phase studies by high temperature X-ray diffraction or other methods.

Holm<sup>6</sup> demonstrated that by quenching of  $\text{NaAlF}_4$  vapour, he could obtain a metastable compound which disproportionated upon heating to chiolite,  $\text{Na}_5\text{Al}_3\text{F}_{14}(\text{s})$ , and aluminum fluoride,  $\text{AlF}_3(\text{s})$ , in agreement with Howard's result. In addition, he found that the compound had disproportionated after storage for 2–3 years in a desiccator at room temperature. Thus, it seems

reasonable to believe that solid  $\text{NaAlF}_4$  is a metastable compound at all temperatures.

Bjørseth,<sup>7</sup> and Gylseth *et al.*<sup>8</sup> have reported on the occurrence of  $\text{NaAlF}_4$  fibers in reacted alumina after dry scrubbing and in the work environment in the primary aluminium industry. Fibers collected on membrane filters could be stored at room temperature for months without any changes detectable by examination in an electron

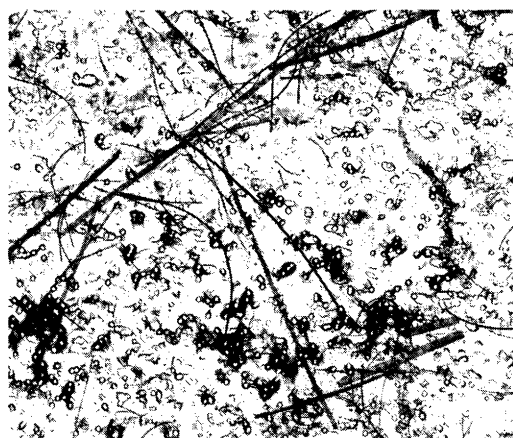


Fig. 1.  $\text{NaAlF}_4$  fibers grown at flow rate 9 dm<sup>3</sup>/h (810 °C). TEM 3100×.



Fig. 2.  $\text{NaAlF}_4$  fibers grown at flow rate  $12 \text{ dm}^3/\text{h}$  ( $810^\circ\text{C}$ ). TEM  $3100\times$ .



Fig. 3.  $\text{NaAlF}_4$  fibers grown at flow rate  $15 \text{ dm}^3/\text{h}$  ( $810^\circ\text{C}$ ). TEM  $3100\times$ .

microscope. In this study, we report on the growth of  $\text{NaAlF}_4$  fibers by precipitation of  $\text{NaAlF}_4$  vapour as a function of cooling rate. The disproportionation of the  $\text{NaAlF}_4$  fibers during heating to  $600^\circ\text{C}$  has been studied by high temperature X-ray diffraction and by differential scanning calorimetry. The water stability of solid  $\text{NaAlF}_4$  and its thermal dissociation products,  $\text{Na}_3\text{Al}_3\text{F}_{14}$  and  $\text{AlF}_3$ , has also been tested.

### Experimental

The preparation of solid  $\text{NaAlF}_4$  from its vapour under controlled conditions was performed by vaporization of a melt of bulk composition  $\text{Na:F:AlF}_3 = 1:1:1$ . The molten fluoride mixture was loaded in a platinum boat which was placed in the middle of a constant temperature zone ( $\pm 1^\circ\text{C}$  over  $10 \text{ cm}$ ) in an electrically heated tube furnace. The reaction chamber consisted of an alumina tube (Alsint®)  $20 \text{ mm}$  i.d. and  $720 \text{ mm}$  long. To alter the cooling rate of the vapour, dry nitrogen gas was flushed through the furnace volume at different flow rates. The precipitates formed in the flush gas were collected on Nuclepore filters (pore dia.  $0.2 \mu\text{m}$ ) connected to the outlet of the reaction tube. The flush gas was sucked through the filter by means of a DuPont 2500 constant flow sampler. Inspection of the collected precipitates was done by transmission electron microscopy (TEM). Specimens for TEM were prepared by carbon evaporation of filters

covered with a thin layer of particulates, and the polycarbonate filter was removed by dissolution in chloroform. The fluoride precipitate seemed not to be affected by chloroform.

The thermal decomposition products from solid  $\text{NaAlF}_4$  were studied by high temperature X-ray diffraction using a Guinier camera from Enraf Nonius, Delft, Holland, in conjunction with a Guinier SIMON programmable control and power unit. The diffraction pattern was recorded as a function of temperature on photographic film.

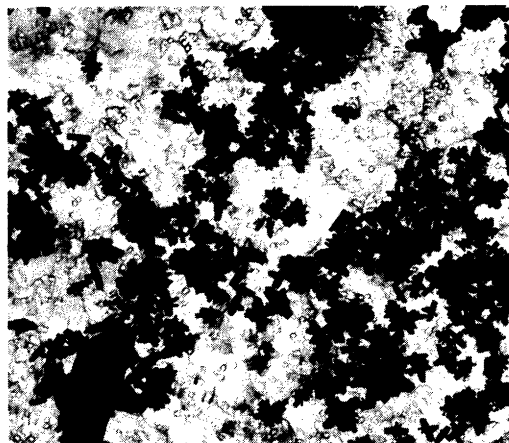


Fig. 4.  $\text{NaAlF}_4$  particles (clusters) grown at flow rate  $60 \text{ dm}^3/\text{h}$  ( $810^\circ\text{C}$ ). TEM  $3100\times$ .



Fig. 5.  $\text{NaAlF}_4$  particles (same sample as in Fig. 4) photographed in SEM 9000 $\times$ .

The enthalpy of reaction for the disproportionation of solid  $\text{NaAlF}_4$  was measured using a Perkin Elmer DSC-2 differential scanning calorimeter. In the calibration of the instrument, the following metals were used: indium, tin and zinc standards from the National Bureau of Standards

(USA). Samples for the calorimetric measurements consisted of 30–40 mg  $\text{NaAlF}_4$  fibers compressed into tablets and contained in a platinum crucible with a well-fitted lid.

The water stability of  $\text{NaAlF}_4(\text{s})$  and its thermal decomposition products,  $\text{Na}_5\text{Al}_3\text{F}_{14}(\text{s})$  and  $\text{AlF}_3(\text{s})$ , was tested by spreading the different compounds on Nuclepore filters, which then were stored in distilled water at room temperature. After some hours, parts of the filters were taken out of the water, dried and prepared for inspection by electron microscopy.

**Results and discussion**

In order to produce a vapour pressure of gaseous  $\text{NaAlF}_4$  over a melt of composition  $\text{NaF}:\text{AlF}_3 = 1:1$ , comparable to that over a commercial alumina reduction cell, the fluoride was evaporated at 780–810 $^\circ\text{C}$ , giving a vapour pressure of 0.27–0.33 kPa (see Ref. 3). By altering the flow rate of the flush gas from 9 to 60  $\text{dm}^3/\text{h}$ , the linear velocity through the reaction chamber was varied between 3–20 cm/sec. Typical particulates collected under these conditions are shown in the Figs. 1–5. As seen from Fig. 1, low flow rate resulted in long fibers of variable size. The probable rea-

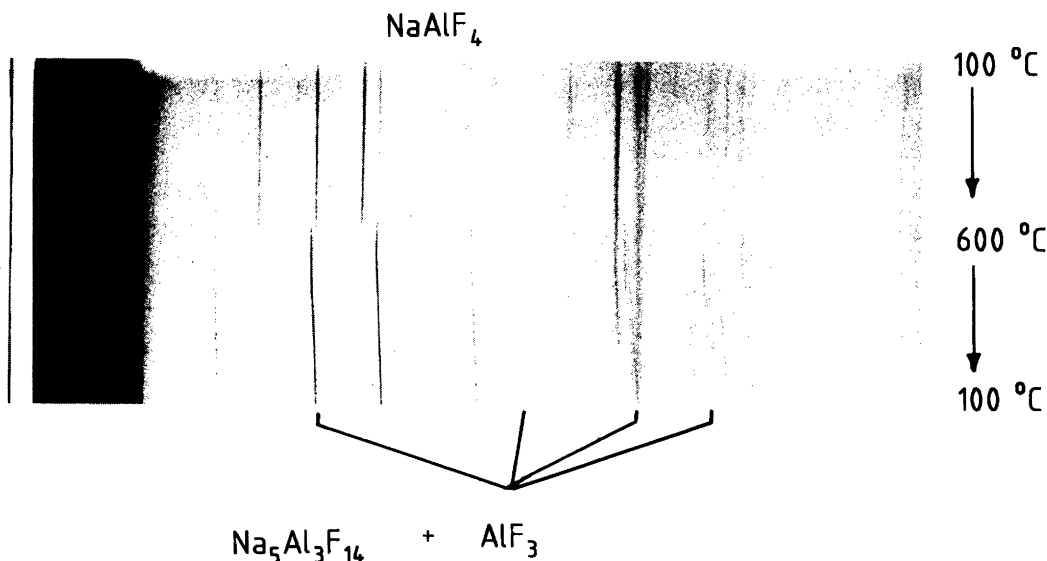


Fig. 6. Prints showing X-ray diffraction recording of the disproportionation of solid  $\text{NaAlF}_4$  in the temperature range 100 $^\circ\text{C}$ –600 $^\circ\text{C}$ , and down to 100 $^\circ\text{C}$ . Film displacement 5 mm/h, total exposure time 10 h. Top: Start of exposure showing only  $\text{NaAlF}_4$  present. Middle: Diffraction pattern at 600 $^\circ\text{C}$ .  $\text{NaAlF}_4$  not visible. Bottom: Diffraction pattern of disproportionated sample showing  $\text{Na}_5\text{Al}_3\text{F}_{14}$  and  $\text{AlF}_3$ .

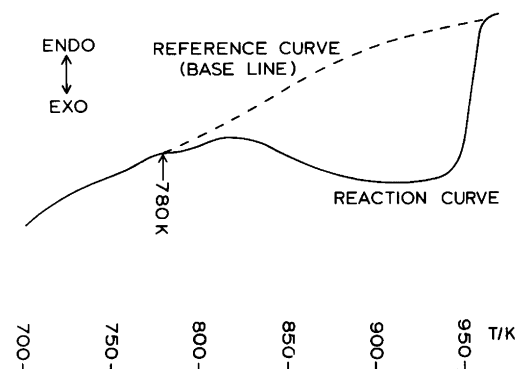


Fig. 7. Recording of the heat signal from the differential scanning calorimeter. The area between the solid and dotted lines gives together with a calibration factor the size of the heat signal.

son for this is that the growth of the fibers starts at different cold-points on the reactor wall, and they break away from the wall after reaching considerable size. Attempts to grow fibers at even lower flow rates resulted in none or very few fibers collecting on the Nuclepore filter. Instead, large crystals grew on the colder parts of the reactor walls. In the flow rate range 4–8 cm/sec (short residence times) needle-shaped particles of relatively equal size, 3–5  $\mu\text{m}$  long and 0.5–1  $\mu\text{m}$  diameter were obtained, as shown in Figs. 2 and 3.

Particulates formed at flow rates higher than approximately 10 cm/sec were no longer single rods, but pincushion-like crystals of more irregular shapes as shown in Figs. 4 and 5. This phenomenon was not studied in more detail since our original objective was to grow as large fibers as possible in the simple experimental setup we had at hand. The formation of these multipin clusters seems to be due to frequent changes in the direction of crystal growth during the time the particles reside in the temperature gradient together with NaAlF<sub>4</sub> vapour. At high flow rates this can be caused by turbulent gas flow, resulting in more frequent collisions between particles, and also frequent collisions between particles and the reactor wall.

An X-ray diffraction recording obtained for the disproportionation reaction of NaAlF<sub>4</sub> during the temperature cycle from 100–600 and down to 100°C is shown in Fig. 6. Both the heating and

cooling rates were set at 100°C/h; the displacement of the photographic film was 5 mm/h. The diffractogram showed that NaAlF<sub>4</sub> disappeared gradually on heating above 500°C, while Na<sub>5</sub>Al<sub>3</sub>F<sub>14</sub>(s) and AlF<sub>3</sub>(s) grew. There was no indication of any back reaction during the cooling period. The phase transition of AlF<sub>3</sub>(s) at approx. 450°C as reported in the literature<sup>9</sup> was observed and served as a temperature calibration of the X-ray equipment.

Differential scanning calorimetry measurements showed a pronounced exothermic heat effect appearing from about 510 to 690°C at scan rate 20°C/min, as shown in Fig. 7. A lower scan rate gave a similar result, but the profile of the heat signal became less regular. Since the reaction takes place over a wide temperature range (~180°C), one has to establish a base line (reference line) for an unreacting sample with an equal mass and heat capacity. This was obtained by running a second experiment using the disproportionated sample from the former experiment. The dotted line (base line) in Fig. 7 was established in this way. The calorimetric measurements for the disproportionation reaction,  $5 \text{ NaAlF}_4(\text{s}) \rightarrow \text{Na}_5\text{Al}_3\text{F}_{14} + 2 \text{ AlF}_3(\text{s})$ , gave the enthalpy value at the average temperature (900 K) of  $\Delta H_{900}^\circ = -66.9 \pm 7 \text{ kJ mol}^{-1}$ .

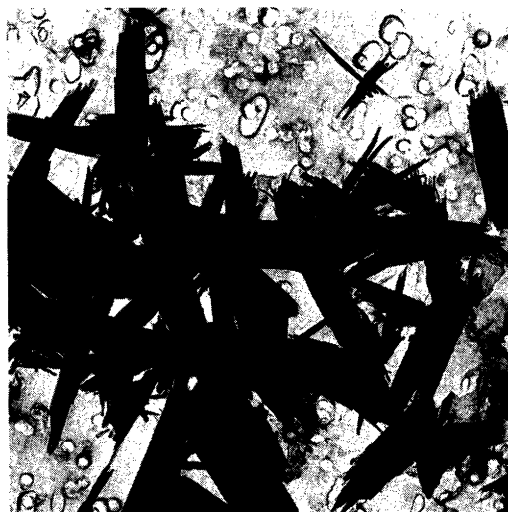


Fig. 8. NaAlF<sub>4</sub> fibers contained in distilled water for 11 h at 20°C. TEM 8400 $\times$ .

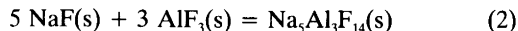
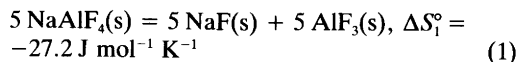


Fig. 9. NaAlF<sub>4</sub> fibers contained in distilled water for 24 h at 20°C. TEM 8400×.

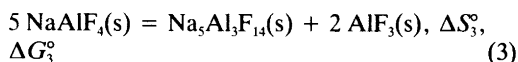
### Thermodynamic calculations

Our experimental results show that solid NaAlF<sub>4</sub> is a metastable compound, at least in the temperature range 700–900 K. Outside this range, the stability must be determined on the basis of the Gibbs energy of reaction. Thus, in addition to our measured enthalpy value, we took enthalpy and Gibbs energy data for chiolite from Sterten *et al.*,<sup>10</sup> who also listed and discussed the latest available data from the literature. Needed thermodynamic data on AlF<sub>3</sub>(s) and NaF(s) were taken from the JANAF tables.<sup>11</sup> Entropy data on solid NaAlF<sub>4</sub> was not available and had to be estimated. Entropy changes for the analogous reactions NaCl(s) + AlCl<sub>3</sub>(s) = NaAlCl<sub>4</sub>(s) and LiF(s) + BeF<sub>2</sub>(s) = LiBeF<sub>3</sub>(s), have been estimated by JANAF<sup>11</sup> to be 5.4 J mol<sup>-1</sup> K<sup>-1</sup> (1.3 cal mol<sup>-1</sup> K<sup>-1</sup>) and 2.1 J mol<sup>-1</sup> K<sup>-1</sup> (0.5 cal mol<sup>-1</sup> K<sup>-1</sup>), respectively. By choosing 5.4 J mol<sup>-1</sup> K<sup>-1</sup> as the most probable entropy change for formation of NaAlF<sub>4</sub> from the fluorides we found the entropy change for the reaction shown in eqn. (1).

Due to some scatter among the literature data discussed by Sterten *et al.*,<sup>10</sup> we have 4 different entropy values for the formation of chiolite from the sodium and aluminium fluorides at 900 K according to eqn. (2):  $\Delta S_3^\circ = 29.6 \text{ J mol}^{-1} \text{ K}^{-1}$  (Dewing<sup>13</sup>);  $87.9 \text{ J mol}^{-1} \text{ K}^{-1}$  (Grjotheim *et al.*<sup>12</sup>);  $88.7 \text{ J mol}^{-1} \text{ K}^{-1}$  (Cantor *et al.*<sup>14</sup>); and  $104.8 \text{ J mol}^{-1} \text{ K}^{-1}$  (Sterten *et al.*<sup>10</sup>).



Applying the above entropy data together with our calorimetrically measured enthalpy value,  $-66.9 \text{ kJ}$ , for the disproportionation reaction of eqn. (3), we could calculate both the changes in entropy and in Gibbs energy of reaction at 900 K:  $\Delta S_3^\circ = 2.2 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $\Delta G_3^\circ = -68.9 \text{ kJ mol}^{-1}$  (Ref. 13);  $\Delta S_3^\circ = 60.7 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $\Delta G_3^\circ = -121.6 \text{ kJ mol}^{-1}$  (Ref. 12);  $\Delta S_3^\circ = 61.5 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $\Delta G_3^\circ = -122.3 \text{ kJ mol}^{-1}$  (Ref. 14); and  $\Delta S_3^\circ = 77.6 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $\Delta G_3^\circ = -136.7 \text{ kJ mol}^{-1}$  (Ref. 10). The calculations showed, with a wide margin of safety, that solid NaAlF<sub>4</sub> is thermodynamically unstable at all temperatures below the eutectic temperature (968 K) of the system Na<sub>5</sub>Al<sub>3</sub>F<sub>14</sub>/AlF<sub>3</sub>.



The Gibbs energy data on chiolite based on the different experimental results are in fair agreement. However, it should be pointed out that Dewing's result<sup>13</sup> gives noticeable deviations in the enthalpy and entropy terms due to a different temperature dependence. It is believed that the enthalpy of reaction is more accurately determined from vapour pressure measurements than



Fig. 10. NaAlF<sub>4</sub> fibers contained in distilled water for 97 h at 20°C. TEM 8400×.

from emf measurements as applied by Dewing<sup>13</sup> and Sterten *et al.*<sup>10</sup> Thus, we chose enthalpy and entropy data from Grjotheim *et al.*<sup>12</sup> and Cantor *et al.*<sup>14</sup> for our calculation.

Applying their data<sup>12,14</sup> as recalculated by Sterten *et al.*<sup>10</sup> for the enthalpy of formation of chiolite together with our calorimetric result for the disproportionation reaction (3), we obtained for the enthalpy of formation of solid NaAlF<sub>4</sub> at 900 K:  $\Delta H_f^\circ = -2083.2 \pm 3 \text{ kJ mol}^{-1}$ . This enthalpy value together with the enthalpy data for NaF and AlF<sub>3</sub> gives  $-6.9 \text{ kJ mol}^{-1}$  at 900 K for the formation of solid NaAlF<sub>4</sub> from the fluorides. The result is in good agreement with the enthalpy data based on calculations of lattice energies by Holm.<sup>15</sup>

*Solubility in water of NaAlF<sub>4</sub> fiber and its disproportionation products.* To test whether NaAlF<sub>4</sub> or its disproportionation products can exist as solids in biological tissue, their stability in water was studied. The progression of the dissolution of NaAlF<sub>4</sub> fiber is well demonstrated in Figs. 8, 9 and 10. It is seen that an originally single fiber splits into a bundle of thin fibers, which finally dissolve completely in water. Particles of Na<sub>5</sub>Al<sub>3</sub>F<sub>14</sub> and AlF<sub>3</sub>, formed on heating of NaAlF<sub>4</sub>(s) to 600°C, were not noticeably corroded after storage in water for 60 h, as shown in Fig. 11. The thermodynamic instability of solid NaAlF<sub>4</sub> results in faster dissolution in water than for the stable compounds Na<sub>5</sub>Al<sub>3</sub>F<sub>14</sub> and AlF<sub>3</sub>.

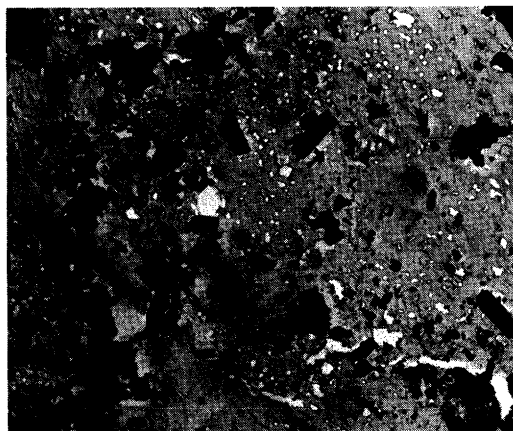


Fig. 11. Na<sub>5</sub>Al<sub>3</sub>F<sub>14</sub> and AlF<sub>3</sub>, formed by disproportionation of NaAlF<sub>4</sub> at 600°C, contained in distilled water for 60 h at 20°C. TEM 3100×.

*Acknowledgement.* This study has been supported by the Norwegian Council for Industrial and Technical Research.

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Received March 24, 1986.