ESRF	<b>Experiment title:</b> High Resolution Study of Sodium Aluminium Fluorides by Powder Diffraction	Experiment number: 01-01-285
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## **Report:**

High-resolution powder diffraction data have been collected for some compounds or minerals belonging to the binary system NaF - AlF<sub>3</sub>, which plays a central role in the melt electrolysis of aluminium. A major purpose of the work was to establish the crystal system and space group and to refine the structure of NaAlF<sub>4</sub>, which is a metastable member of this system and the subject of several previous attempts at crystallographic characterization with different results. Further, to reexamine chiolite, Na<sub>5</sub>Al<sub>3</sub>F<sub>14</sub>, from a sample prepared in a non-aqueous environment, in order to avoid possible partial substitution of fluorine by hydroxyl. This replacement is likely to occur in the synthetic method used for the sample that is the source of the data compiled in the ICDD data file (PDF # 30-1144).

Powder samples were contained in 0.7 mm Borosilicate capillaries, the experimental set-up included an analyzer crystal; data were collected with a NaI(Tl) point detector and  $\lambda = 0.49952$  Å.

Data for these compounds were collected: A freshly prepared sample of  $NaAlF_4$ , a sample of high purity of the natural mineral chiolite from Greenland, and two samples of synthetic chiolite, taken from two different regions of the ampule that was used during the synthetic preparation.

*NaAlF*<sub>4</sub>: The data were of very good quality and indicate that the space group is not tetragonal as was currently assumed, but is of lower symmetry. In view of this apparent discrepancy with previous

observations it is necessary to examine possible preferred orientation in the sample by diffraction using an area detector.

*Chiolite:* The diffractograms of the synthetic samples showed some unexpected features, which we first believed were caused by impurities formed during the preparation at high temperature. We found later that one of the starting reagents that had been acquired as high-purity grade for the synthesis, was actually contaminated. The synthetic preparation of chiolite has since been repeated from pure reagents and the product gives diffraction maxima in the expected angular positions.

Data for the natural mineral were of good quality.