

Marked exothermic reactions appeared in the thermal curves of many of the poorly-crystallized goethites (Fig. 1C), but were absent in others (Fig. 1D). X-ray analyses of the heated products chilled at the maximum endothermic decomposition temperatures produced γ - Fe_2O_3 patterns where an exothermic reaction had appeared in the goethite curve and α - Fe_2O_3 patterns where the exothermic peak was absent. The appearance of a variable exothermic peak due to the phase change of γ - to α - Fe_2O_3 is usually associated with lepidocrocite, and, as yet, no satisfactory explanation can be offered for its erratic appearance in the thermal curves of these poorly-crystallized goethite samples.

A full report on the present thermal studies is soon to be published by the New Mexico Bureau of Mines and Mineral Resources which aided in the research, but this brief note is submitted to bring out a few of the difficulties encountered with the hydrous ferric oxides. If a curve of the type shown in Figs. 1B, 1C, or 1D is obtained with an unknown, there is uncertainty as to whether the oxide in question is lepidocrocite or poorly-crystallized goethite. A thermal curve with double-peaks (Figs. 1E, 1F) may represent (1) a mixture of goethite and lepidocrocite or (2) a mixture of well-crystallized and poorly-crystallized goethite.

For reliable identification of mineral species of hydrous ferric oxide present in natural aggregates, it is still necessary to resort either to x-ray analysis or to the use of immersion media of high refractive index (H. E. Merwin and E. S. Larsen, 1912).

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SYNTHESIS OF ALUMINUM NITRIDE MONOCRYSTALS

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SYNTHESIS AND GENERAL DESCRIPTION

This note is intended to describe an interesting synthesis of aluminum nitride crystals and some of their properties. The aluminum nitride crystals were obtained incidentally during an attempt to impregnate a sintered carbide compact with alumina. Specifically, a cylindrical WC-TiC-Co compact (5/8 in. diameter \times 5/8 in.) was embedded in

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minus-100 mesh, high-purity (99%) alumina (Alcoa, A-14) in a horizontally positioned graphite crucible. The crucible was heated to 2000° C. in a carbon-tube resistance furnace, with a protective atmosphere of helium. Soon after the desired temperature had been reached, the furnace tube, which had been in use for many hours, began to burn out, and the temperature increased sharply to 2100–2200° C. Burning out of the tube allowed an influx of air, which in turn permitted the observed crystallization of aluminum nitride. The latter was formed inside the crucible lid and occurred as pale-blue, prismatic (six-sided) needles,

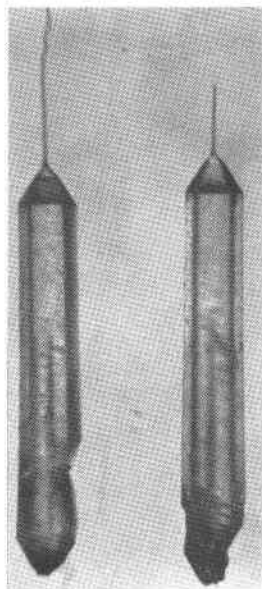


FIG. 1. Aluminum nitride crystals, showing axial "voids" and "antennae" (207 \times).

approximately 0.03 mm. in diameter and 0.2–0.3 mm. in length. The aluminum nitride crystals, identified as such by *x*-ray analysis, are shown in Fig. 1. They are clearly doubly terminated, the darker base probably being due to adhering graphitic material. The axial "voids" (negative skeletal structure) and "antennae" (positive skeletal structure) are probably indicative of a rapid rate of growth. An aluminum nitride of this color and habit has been reported by Matignon (1), while Ott (2) described pale-green crystals.

PROPERTIES

X-ray.—Rotation exposures taken about the *c* (length) axis with Cu radiation showed a pattern typical of the wurtzite-type (B4) structure.

Table 1 compares the hexagonal unit cell dimensions obtained with those previously recorded in the literature.

Departure of the axial ratio from the ideal value of 1.633 has recently been confirmed by Jeffrey and Parry (4), who have determined the u parameter as 0.385 (ideal=0.375). According to the latter authors, this implies that each atom is displaced by 0.05 Å along the c axis from the center towards the base of its coordination tetrahedron.

Hardness.—An attempt was made to obtain Knoop hardness data on the aluminum nitride crystals. Difficulty was experienced in mounting, but a few microindentations were finally placed parallel to the c axis on the prism face. A K_{100} value in the low apatite range (Mohs number = 5) was indicated. However, these indentations were not considered reliable, owing to the extreme brittleness and small size of the crystals.

Additional data were sought by a microscratch technique. A crystal was mounted upright in balsam, and a lightly weighted slide dragged across the point of the crystal by means of a micromanipulator. The

TABLE 1. AlN UNIT CELL DIMENSIONS

	Ott ²	Stackelberg and Spiess ³	Present
a_0	3.11 ₃ Å	3.104±0.005	3.10 ±0.01
c_0	4.98 ₁ Å	4.965±0.008	4.96 ₅ ±0.010
c_0/a_0	1.60 ₀ Å	1.600	1.60 ₂

process was observed under a binocular microscope to determine whether or not a scratch was made on the slide. It was found that the crystal was barely able to scratch the glass slide. Since the latter has a Mohs number of 5–5.5, it is probably not in error to quote the hardness of aluminum nitride as in the apatite range. The relative softness of aluminum nitride is in keeping with the fact that no hard material has yet been discovered with a wurtzite-type structure.

Optical.—The aluminum nitride crystals were determined to be uniaxial positive, i.e., length slow, since the elongation is parallel to c . By mounting in thallos chloride, the refractive indices were found to be somewhat lower than 2.247, and a similar comparison with stannic iodide showed them to be above 2.106. A direct birefringence measurement gave an average value of 0.07. These data permitted an estimation of the indices as 2.13±0.02 (omega) and 2.20±0.02 (epsilon). Refinement of these values by comparison with various sulfur-selenium mixtures proved unsuccessful.

Chemical.—By means of a small platinum loop affixed to a hot-wire

glass-cutting apparatus, the reaction of aluminum nitride crystals with various hot and cold solutions and with molten salts was observed under the binocular microscope.

The crystals were not affected by the following reagents under both hot and cold conditions: 1-3 HCl, conc. HCl, conc. HNO₃, 50% HF, and 1-3 NaOH. The crystals did not react with molten NaOH or KOH, although the darker adhering material (probably graphite; see Fig. 1) was rapidly destroyed. The aluminum nitride crystals dissolved *slowly* in molten borax; Al(OH)₃ was precipitated by NH₄OH from the acidified borax fusion.

The aluminum nitride product described by Matignon (1) was shown by chemical analysis to consist of approximately 1/6 silicon carbide. He stated that the silicon carbide was present either as a concurrent phase or in the form of a solid solution. The crystals studied in the present investigation were too small for chemical analysis. It is felt, however, owing to the relatively low refractive indices (compared to SiC), the relatively low hardness value, and the incompatibility of the structures (no wurtzite form of SiC is known), that there is probably no silicon carbide present.

Density.—An approximate density value was known from the literature (1, 2). Accordingly, a suitable heavy-liquid mixture was prepared and sealed in a glass capsule along with several selected aluminum nitride crystals. The capsule was then mounted in a water bath, the temperature of which could be varied. The temperature at which the crystals remained suspended within the capsule was determined, and an experimental density value of 3.24₇ g./cc. at 20° C. was calculated. Ott (2) reported 3.25, while Matignon (1) gave the value at 15° C. as 3.106. The theoretical density calculated from the unit cell dimensions determined herein is 3.30 g./cc. The relatively low experimental value can be accounted for by the negative skeletal structure visible along the needle axes of the crystals (Fig. 1).

Goniometric.—Several crystals were examined and measurements taken on a two-circle optical goniometer. First order prism faces and first order unit bipyramid faces were observed. Occasionally, reflections could be obtained from a basal pinacoid. Ten measurements of the prism-pyramid interfacial angle ranged from 28°17' to 28°26', averaging 28°21'. The calculated value is 28°24'.

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MINERALOGY OF THE MIDDLE DEVONIAN TIOGA K-BENTONITE

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A thin bed of "meta-bentonite" overlies the Onondaga limestones and cherts of southern New York, central and western Pennsylvania, southeastern Ohio, and West Virginia (Ebright, Fittke, and Ingham—1949), (Flowers—1952), (Fettke—1952).

These bentonite samples¹ have a relatively uniform clay mineral content and are similar in composition to the Ordovician K-bentonites (Weaver—1953). Table 1 contains some 00 l values for the untreated and glycolated less than one micron fractions of the Devonian material and a typical Ordovician sample.

These data indicate that the Devonian K-bentonites consist of randomly interstratified layers of illite and montmorillonite in the approximate ratio of 4:1 to 3:1. X-ray patterns of samples which contain euhedral flakes of "bleached biotite" indicate the presence of chlorite and muscovite. Figure 1 contains x-ray spectrometer patterns of the Albany sample.

The differential thermal curves are also similar to those of the Ordovician K-bentonites (Fig. 1). The molecular water is removed at 100 to 125° C. The hydroxyl water is usually removed in two fractions: 550-600° C. and 675-700° C. The 550-600° C. hydroxyl-endotherm is usually considerably smaller than the 675-700° C. endotherm. The high temperature endotherm occurs at 925° C. and the following exotherm near 1000° C.

Except for more Al_2O_3 and less Fe_2O_3 and MgO , chemical analysis and mineral formula of the West Virginia sample is similar to that of the

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¹ Outcrop samples from Syracuse, New York, were furnished by Dr. N. E. Chute, Syracuse University, and from Albany, New York, by Mr. B. Nelson, University of Illinois. Dr. R. E. Baylor supplied a sample from Chester Co., Pennsylvania, and Mr. W. S. Lytle furnished a sample from Cameron Co., Pennsylvania, and another from Erie Co.