A New Alumina Hydrate, "Tohdite" ($5Al_2O_3 \cdot H_2O$)

By Goro YAMAGUCHI, Hiroaki YANAGIDA and Shuitiro ONO

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A new crystal of alumina hydrate has been found by the present authors during an investigation into the hydrothermal reactions of the system aluminum oxide-water.[1] This crystal has been studied by various methods, such as X-ray diffraction, electron diffraction, differential thermal analysis, infrared absorption and polarizing microscopy, and has been proved to be a new alumina hydrate. The formula obtained is $5Al_2O_3 \cdot H_2O$. The species Tohdite is named for the Tokyo Daigaku (The University of Tokyo), where the present investigation was carried out.

Method of Preparation

An appropriate amount of aluminum hydroxide, boehmite AlOOH or gibbsite $Al(OH)_3$, was weighed in a silver capsule of the Morey-type autoclave, and a dilute aqueous solution of aluminum fluoride was added to fill about 80% of the reaction vessel. The autoclave was heated at 450～500°C in an electric furnace for 20～100 hr. The reaction was completed under these experimental conditions. Corundum was found to be useful as the seed crystals, and the new formed hydrate to be useful for the same purpose in the subsequent runs. Aluminum fluoride or titanium (IV) sulfate was effective as the mineralizer.

Properties

Crystallographic Forms and Optical Properties.—The new hydrate, Tohdite, occurs as thin hexagonal plates up to a few microns in thickness when aluminum fluoride is used as the mineralizer (Fig. 1). The crystal form is changed into needles when titanium sulfate is

1) G. Yamaguchi, H. Yanagida, S. Ono, S. Koyanagi and S. Wada, Presented at the 16th Annual Meeting of the Chemical Society of Japan, Paper No 1F08 (Tokyo, April, 1963).

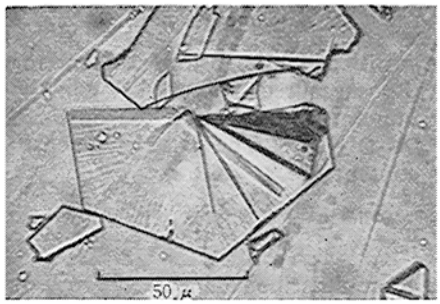

Fig. 1 The new alumina hydrate crystals.

added. Tohdite is uniaxial negative with $\omega=1.738\sim1.748$, $\omega-\varepsilon<0.01$, the c-axis being perpendicular to the plate.

Density.—The density was determined to be 3.72 ± 0.02 g./cm^3.

Thermal Analysis. — Differential thermal analysis was performed up to 1000°C. An endothermic peak was observed between 800 and 900°C, corresponding to the dehydration of Tohdite. The dehydrated form was identified with κ-alumina by X-ray diffraction. The water content, as determined from the weight loss, was about 3.6%. The value calculated for $5Al_2O_3\cdot H_2O$ is 3.42%.

Infrared Absorption Spectra.—The existence of crystalline water was confirmed by the infrared absorption spectra. The absorption band found at 3240 cm^{-1} can be assigned to the stretching frequency for OH groups.

X-Ray Investigations. — The X-ray powder pattern shown in Fig. 2 was recorded on a diffractometer using filtered CuK_α radiation. On the basis of the resemblance of the pattern to that of κ-alumina, this pattern was unmistakably indexed on the hexagonal unit cell with

$$a=5.576\text{Å} \text{ and } c=8.768\text{Å}.$$

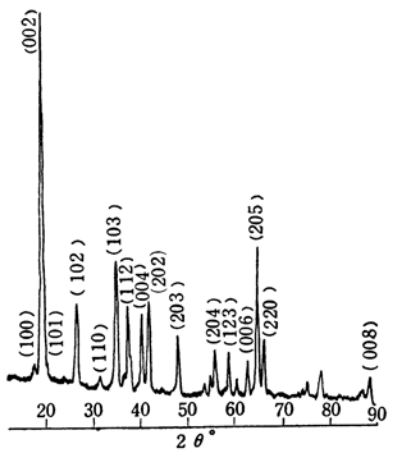

Fig. 2. X-ray powder diffraction pattern of the new hydrate using CuK_α radiation.

Table I. X-ray diffraction data

hkl	d-observed	d-calculated
100	4.85	4.8286
002	4.38	4.3840
101	4.23	4.2296
102	3.246	3.2458
110	2.788	2.7878
103	2.500	2.5003
200	2.416	2.4143
112	2.352	2.3524
201	2.329	2.3277
004	2.192	2.1920
202	2.1146	2.1148
203	1.8614	1.8614
122	1.6854	1.6849
105	1.6482	1.6482
204	1.6232	1.6229
123	1.5479	1.5480
302	1.5105	1.5105
006	1.4609	1.4613
205	1.4190	1.4188
220	1.3939	1.3939
222	1.3283	1.3278
132	1.2809	1.2808
125	1.2650	1.2645
206	1.2499	1.2502
133	1.2173	1.2175
107	1.2124	1.2124
401	1.1966	1.1959
402	1.1639	1.1638
403	1.1158	1.1158
207	1.1121	1.1118
008	1.0960	1.0960

The diffraction data are listed in Table I.

Electron Diffraction. — The $\{hk0\}$ spots of the (0001) orientation can be seen in Fig. 3. The incident beam is perpendicular to the hexagonal plate of the crystal. The inner spots gave a d-spacing of 4.8Å, corresponding to the (100) in Table I. The other diffraction pattern in Fig. 4 represents the periodicity along the c-axis. The beam is perpendicular to the direction of the elongated needle-like crystal, and the observed d-spacing was 4.4Å, corresponding to the (002) in

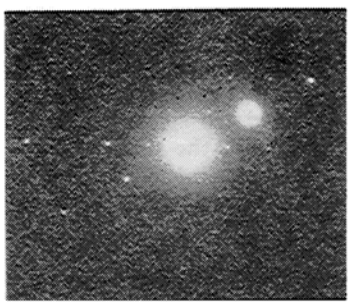

Fig. 3. N-pattern of the new hydrate (electron beam ∥ c-axis).

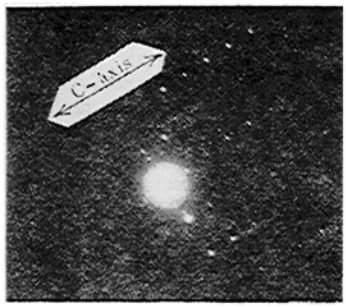

Fig. 4. N-pattern of the new hydrate (electron beam $\perp$ c-axis).

Table I. These results may justify the hexagonal unit cell derived from the powder pattern.

Conclusion

The unit cell dimensions, taken together with the measured values of density and water content, indicate that the unit cell contains $5Al_2O_3 \cdot H_2O$. The calculated density and water content are as follows:

Density	3.71 g./cm^3
Water content	3.42%

The afore-described data seem to establish the existence of a new alumina hydrate, $5Al_2O_3 \cdot H_2O$.

Department of Industrial Chemistry
Faculty of Engineering
The University of Tokyo
Hongo, Tokyo