The Crystal Structure of Tohdite

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The synthetic procedure and some crystallographic data of a new alumina hydrate, Tohdite $5Al_2O_3 \cdot H_2O$, were reported in a previous paper.[1] The crystallographic data are summarized in Table I. In the present work we will attempt to determine the crystal structure of Tohdite from the X-ray powder diffraction data.

Experimental

Crystals of Tohdite can be prepared by the hydrothermal treatment of boehmite with a small amount of some mineralizer. They occur in a variety of forms, such as hexagonal plates and needles. They are not, however, suitable for the

1) G. Yamaguchi, H. Yanagida and S. Ono, This Bulletin, 37, 752 (1964).

TABLE I.

Crystal system	hexagonal (or trigonal)
Unit cell dimensions	$a=5.576$ Å, $c=8.768$ Å
Formula unit per unit cell	$5Al_2O_3 \cdot H_2O$
Measured density	3.72 ± 0.02 g./cm^3
Calculated density	3.71 g./cm^3
Refractive index	$\omega=1.738 \sim 1.748$, $\omega-\varepsilon<0.01$
Systematic extinctions in powder diagram	(hhl) for $l=2n+1$

TABLE II. X-RAY DATA FOR TOHDITE

hkl	d_o	d_c	I_o	I_c
100	4.85	4.8286	10	9
002	4.38	4.3840	23	19
101	4.23	4.2296	11	17
102	3.246	3.2458	60	59
110	2.788	2.7878	12	10
103	2.500	2.5003	54	42
200	2.416	2.4143	12	18
112	2.352	2.3524	77	96
201	2.329	2.3277	38	47
004	2.192	2.1920	4	2
202	2.1146	2.1148	100	84
104		1.9960	*	2
203	1.8614	1.8614	48	73
120		1.8250	*	1
121		1.7867	*	2
114		1.7237	*	1
122	1.6854	1.6849	13	16
105	1.6482	1.6482	4	4
204	1.6232	1.6229	26	33
300		1.6095	*	2
301		1.5831	*	0
123	1.5479	1.5480	34	19
302	1.5105	1.5105	20	22
006	1.4609	1.4613	4	3
205	1.4190	1.4188	68	54
303		1.4099	*	0
124		1.4026	*	1
106		1.3987	*	1
220	1.3939	1.3939	85	74
130		1.3392	*	0
222	1.3283	1.3278	5	5
131		1.3239		
304		1.2974	*	2
116		1.2943	*	4
132	1.2809	1.2808	6	6
125		1.2645	3	3
206	1.2499	1.2502	7	13
133	1.2173	1.2175		
107		1.2124	21	15
400		1.2072		
401	1.1966	1.1959	5	5
305		1.1858	*	0
402	1.1639	1.1638	6	9
134		1.1455	*	0
126		1.1407	*	1
403	1.1158	1.1158	9	11
207	1.1121	1.1118		
230		1.1078	*	0
231		1.0990	4	5
008	1.0960	1.0960		

(Values marked * were not observed.)

measurement of the relative X-ray diffraction intensities, since the specimens always show preferred orientations. A new method for preparation has been found as follows. Eta-alumina was obtained from a dehydration, at 800°C in air, of bayerite $Al(OH)_3$ which had been prepared by neutralizing an aluminum chloride aqueous solution with ammonia. The eta-alumina was inverted to a microcrystalline tohdite when treated hydrothermally under a water vapor pressure of about 200 atm. at 460°C. Tohdite prepared by this method was used for the intensity measurement, since it showed no preferred orientation.

The X-ray diffraction data for Tohdite in Table II were recorded on a diffractometer using Cu$K\alpha$-radiation. A set of I_o experimental intensities relative to 202 was obtained by measuring the areas under the diffraction peaks.

Structure Analysis

In the following discussion, we will disregard the contribution of the two hydrogen atoms of the formula $5Al_2O_3 \cdot H_2O$ to the diffraction intensities and will instead pay attention to the arrangement of the 10 aluminum atoms and 16 oxygen atoms in the unit cell.

The unit cell of Tohdite is clearly related to those of kappa- and beta-alumina. (Kappa-alumina is the dehydrated product of Tohdite.) The lattice constants of Tohdite and these aluminas based on orthohexagonal lattices[2] are compared in Table III.

TABLE III. ORTHOHEXAGONAL LATTICE CONSTANTS OF TOHDITE AND KAPPA- AND BETA-ALUMINA (IN Å)

Kappa-alumina	$a=16.80$	$b=9.71$	$c=17.85$
Beta-alumina	$a=5.56$ $3a=16.70$	$b=9.65$	$c=22.55$
Tohdite	$a=5.58$ $3a=16.73$	$b=9.66$	$c=8.77$ $2c=17.54$

The crystal structures of kappa- and beta-alumina were studied by Saalfeld[2] and Beevers[3] respectively. The similarity between the unit cell of Tohdite and those of the above-mentioned aluminas indicates that in the Tohdite structure the layers of oxygen and aluminum atoms lie alternatively in sheets perpendicular to the c-axis and that the unit cell of Tohdite is formed by the close stacking of 4 oxygen layers, each layer containing 4 oxygen atoms. The high density and refractive index of Tohdite also imply a close-packed arrangement of oxygen atoms.

For the arrangement of aluminum atoms, it is well known that there are two types of aluminum positions, that is, octahedral sites

2) H. Saalfeld, *N. Jb. Abh.*, **95**, 1 (1960).
3) C. A. Beevers and M. A. S. Ross, *Z. Krist.*, **97**, 59 (1937).

and tetrahedral sites. In this case, since the 10 aluminum atoms in the unit cell are distributed over 4 aluminum layers, it can easily be assumed that two aluminum layers contain 2 aluminum atoms each, while the other two layers contain 3 atoms each.

With the above-mentioned extinctions the following space groups are possible; P31c, $P\bar{3}1c$, $P6_3mc$, $P\bar{6}2c$ and $P6_3/mmc$. The latter two of them, however, must be rejected, because the arrangement of the reflection planes and axial glide planes characteristic of these groups causes an unreasonable arrangement of aluminum atoms. $P\bar{3}1c$ characterized by centers of symmetry and axial glide planes is also improbable for a similar reason. Therefore, Tohdite must belong to the P31c or $P6_3mc$ group. Since there is no evidence of trigonal symmetry, the more highly symmetrical space group, $P6_3mc$, may be assumed for Tohdite.

First the sequence of the oxygen layers can be determined as:

$$\dot{A}BAC\dot{A}BAC\dot{A}, \text{ etc.}$$

(following theusual nomenclature),

since the unit cell contains a screw hexads, 6_3, in the [001]-direction. The vertical dashes denote the boundaries of the unit cells in the [001]-direction. Second, the arrangement of aluminum atoms must be taken into consideration. Since there are two types of aluminum positions, as has been mentioned above, we were able to assume several trial arrangements. These arrangements were examined and rejected bacause of the poor agreement of the calculated with the observed intensities. The best result was obtained by placing aluminum atoms at (1/6 1/3 3/8), (2/3 1/3 1/8) (octahedral sites) and (1/3 2/3 μ) (tetrahedral sites). μ is approximately 0.068.

Results

The atomic parameters are given in Table IV. A set of relative intensities for these atomic positions, I_c, was calculated by means of the following equation:

$$I_c = KnD \frac{1+\cos^2 2\theta}{\sin^2\theta \cdot \cos\theta} |F|^2$$

where θ is the Bragg angle; F, a structure factor; n, the multiplicity; D, a temperature factor for $B=1.62$ Å^2, and K, a scale factor. They give the agreement factor

$$\frac{\sum_{hkl}(I_o \sim I_c)}{\sum_{hkl} I_o}$$

of 0.26, where the unobserved reflections marked * were excluded.

Futher refinements on the basis of the data of the powder diagram are hardly possible. It, therefore, remains conceivable that the atoms may be slightly displaced from these special positions of $P6_3mc$ and that a less symmetrical space group should be taken for this crystal. However, it is sure that the structure given covers the principal features of the Tohdite lattice.

Table IV. Position parameters

Atom	x/a	y/a	z/c	Number of equivalent positions
O(1)	0	0	0	2
O(2)	1/2	0	0	6
O(3)	1/3	1/6	1/4	6
O(4)	1/3	2/3	1/4	2
Al(1)	1/6	1/3	3/8	6
Al(2)	2/3	1/3	1/8	2
Al(3)	1/3	2/3	0.068	2

Figure 1 shows a unit cell of Tohdite. In this structure four-fifths of the aluminum atoms are in octahedral sites, and the rest, in tetrahedral sites. Interatomic distances calculated from the atomic positions in Table IV are given in Table V. There are two different atomic distances for tetrahedral bonds, since the aluminum atoms in tetrahedral sites are not placed at the centers of the tetrahedra.

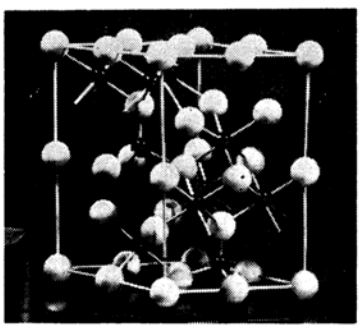

Fig. 1. The unit cell of the Tohdite structure. Oxygen atoms are shown as large and aluminum atoms as small spheres.

Table V. Interatomic distances (in Å)

O-O (I)	within a layer	2.79
O-O (II)	between layers	2.72
Al-O (I)	octahedral bond	1.95
Al-O (II)	tetrahedral bond	1.72 1.60

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