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Refinement of the Structure of Tohdite $5Al_2O_3\cdot H_2O$

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The structure of tohdite, $5Al_2O_3\cdot H_2O$, was determined by Yamaguchi Yanagida, and Ono (1964). Least-squares refinements based on their structure have been carried out using X-ray powder data. The final R factor of the reflection intensity reduced to 0.08 from the initial value of 0.26.

In previous papers the present authors reported on a new phase of alumina hydrate, tohdite $5Al_2O_3\cdot H_2O$,[1] the conditions of its formation,[2] and its crystal structure as determined from the X-ray powder diffraction data.[3] After these articles, the authors learned of Torkar's study,[4] in which he described a mineral denoted "Al_2O_3-Form K1," but did not determine its chemical formula or atomic arrangement. The mineral described by Torkar seemed identical with tohdite.[5]

The structure of tohdite as determined by Yamaguchi, Yanagida, and Ono is as follows:

Cell dimensions: $a=5.576$ Å, $c=8.768$ Å

Space group : $P6_3mc$

O(1)	0 0 0	Al(1)	1/6 1/3 3/8
O(2)	1/2 0 0	Al(2)	2/3 1/3 1/8
O(3)	1/3 1/6 1/4	Al(3)	1/3 2/3 1/16
O(4)	1/3 2/3 1/4		

Overall temperature factor: 1.62 Å^2

These parameters were obtained on the following assumptions: the unit cell is composed of the ideal stacking of oxygen layers, every O–O distance being equal, and aluminium atoms are placed exactly at the centers of the oxygen polyhedra.

The intensities were calculated for fifty reflections (up to $\sin\theta/\lambda=0.456$ Å^{-1}), and the reliability factor, $R_I=\sum(I_o-I_c)/\sum I_o$, of 0.26 was obtained by omitting unobserved reflections. In the present paper the least-squares refinements of the structure of tohdite by means of the powder data will be reported.

Experimental

A polycrystalline sample of tohdite was prepared from Eta-Alumina by hydrothermal treatment.[3] In this powder sample the effect of the preferred orientation on the integrated intensities was confirmed to be negligible.[3] The X-ray diffraction diagrams were obtained by means of a Rigaku Denki diffractometer equipped with a Geiger counter using Cu$K\alpha$ radiation. The intensities relative to the intensity of the 202 reflection were obtained by measuring the areas of the peaks. The intensities of 51 peaks could be measured up to $\sin\theta/\lambda=0.621$ Å^{-1}. In addition, 35 reflections with negligible intensities were expected.

Structure Refinement

First, the lattice dimensions were refined from a least-squares fit of 32 reflections as follows:

$$a=5.575\pm0.001\text{ Å},\quad c=8.761\pm0.001\text{ Å}.$$

Next, a least-squares analysis program was written for a HITAC 5020E computer in which the atomic parameters were varied so as to minimize $R_I'=\sum(I_o-I_c)^2$, where:

$\sum$=the summation of all peaks which can be separated in the diagram;

I_o=integrated intensity;

The calculated intensity, I_c, is presented as: $I_c=K\cdot Lp\cdot\sum_i m_i|F_i|^2$, where:

K=scale factor

Lp=Lorentz and polarization factor

m=multiplicity

F=structure factor.

In the calculation of the structure factors, only an overall isotropic temperature factor was used because the individual temperature factor for each atom did not give any physically significant results.

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

[2] G. Yamaguchi, H. Yanagida and S. Ono, *J. Ceram. Assoc. Japan*, **74**, 84 (1966).

[3] G. Yamaguchi, H. Yanagida and S. Ono, This Bulletin, **37**, 1555 (1964).

[4] K. Torkar and H. Krischner, *Ber. Deut. Keram. Ges.*, **39**, 131 (1962).

[5] K. Torkar and H. Krischner, This Bulletin, **39**, 1356 (1966).

As was mentioned in a previous paper,[3] the possible space groups are $P6_3mc$ and $P31c$. Therefore, refinement was undertaken in both these cases.

In $P6_3mc$ 11 parameters could be varied: that is, the x and z coordinates of Al(1), O(2) and O(3), the z coordinate of Al(2), Al(3), and O(4), the overall isotropic temperature factor, and the scale factor. The calculation was performed starting from the previous parameters[3] and by omitting hydrogen atoms. After several least-squares cycles, the reliability factor, R_I, could be reduced to 0.08 for 115 reflections. The final atomic coordinates, their standard deviations, and the overall isotropic temperature factor are listed in Table 1. The values of I_o and I_c calculated from the final parameters are given in Table 2.

TABLE 1. ATOMIC COORDINATES WITH THEIR STANDARD DEVIATIONS ($\times 10^4$)

	x	y	z
Al(1)	0.1647(9)	$2x$	0.3708(19)
Al(2)	2/3	1/3	0.1533(27)
Al(3)	1/3	2/3	0.0611(29)
O(1)	0	0	0
O(2)	0.5098(10)	$2x$	0.0143(19)
O(3)	0.8291(23)	$2x$	0.2666(20)
O(4)	1/3	2/3	0.2638(28)

Overall temperature factor 0.46(0.03)Å^2

Refinement was also attempted according to $P31c$, in which the Al(1), O(2), and O(3) atoms can shift out of the mirror plane, while the Al(2), Al(3), O(1), and O(4) atoms have to remain in the same position as in $P6_3mc$. This refinement was unsatisfactory, probably because the calculation was performed using the intensity values obtained by summarizing the hkl and $hk\bar{l}$ reflections; this was done since it is impossible to distinguish the hkl and the $hk\bar{l}$ reflections of $P31c$ in the powder diagram, although these reflections have different structure factors.

It, therefore, still remains conceivable that the atoms are slightly displaced from these special positions of $P6_3mc$ and that $P31c$ should be taken for this crystal.

Discussion

This refinement shows that the packing deviates from the postulated ideal model of the previous work. The oxygen atoms are closely packed in layers perpendicular to the c axis and are situated at z=0, 1/4, 1/2, and 3/4 but the individual atoms have different z parameters. Consequently, the oxygen layers are deformed; the first layer (at $z \approx 0$, O(1): z=0, O(2): z=0.014) and the third layer, which is symmetrically equivalent to the first layer,

TABLE 2.

hkl	I_o	I_c
1 0 0	10	10
0 0 2	23	23
1 0 1	11	11
1 0 2	60	61
1 1 0	12	10
1 0 3	54	55
2 0 0	12	12
1 1 2	77	79
2 0 1	38	42
0 0 4	4	8
2 0 2	100	96
1 0 4	0	1
2 0 3	48	46
1 2 0	0	1
1 2 1	0	1
1 1 4	0	1
1 2 2	13	16
1 0 5	4	4
2 0 4	26	28
3 0 0	0	2
3 0 1	0	0
1 2 3	34	36
3 0 2	20	20
0 0 6	4	4
2 0 5	76	74
3 0 3	0	0
1 2 4	0	0
1 0 6	0	0
2 2 0	73	73
1 3 0	0	0
2 2 2 1 3 1	5	4 1 } 5
3 0 4	0	0
1 1 6	0	1
1 3 2	6	6
1 2 5	3	4
2 0 6	7	4
1 3 3 1 0 7 4 0 0	21	11 8 } 21 2
4 0 1	5	6
3 0 5	0	0
2 2 4	1	2
4 0 2	6	6
1 3 4	0	0
1 2 6	0	0
4 0 3 2 0 7	9	5 2 } 7
2 3 0	0	0
2 3 1 0 0 8	4	1 3 } 4
3 0 6	0	1
3 2 2 1 0 8	6	4 2 } 6
3 1 5	1	2
4 0 4 4 1 0	5	5 1 } 6
4 1 1	0	0
3 2 3 2 1 7	11	5 8 } 13
4 1 2 1 1 8	12	11 3 } 14
2 2 6	8	6
2 0 8 4 0 5	23	0 21 } 21
4 1 3	0	0
2 3 4	0	0
1 3 6	0	0
0 3 7	0	0
5 0 0	0	0
5 0 1	0	0
1 0 9	0	0
1 4 4	0	0
5 0 2 2 1 8 3 2 5	6	1 2 } 4 1
4 0 6 3 3 0	7	2 0 } 2
5 0 3 3 1 7 4 2 0	15	5 8 } 15 2
3 3 2 4 2 1 3 0 8 2 0 9	20	5 7 3 } 19 4
4 1 5	0	0
4 2 2	6	6
3 2 6	0	0
5 0 4	0	0
0 0 10	3	3
4 2 3 4 0 7 5 1 0	9	7 2 } 9 0
1 5 1 1 0 10 2 2 8 2 1 9	18	0 1 15 } 16 0
3 3 4	0	0
4 1 6	0	1
5 1 2 3 1 8 5 0 5	7	2 3 } 6 1
4 2 4	8	9
1 1 10	0	2
3 0 9	0	0
5 1 3 3 2 7	22	8 11 } 19
2 0 10	14	15
4 0 8 4 2 5 5 1 4 4 1 7	51	0 54 } 54 0 0
5 0 6	0	0
6 0 0	29	29
6 0 1	0	0

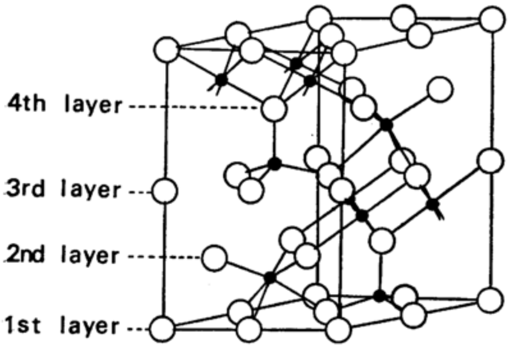

Fig. 1. The unit cell of the tohdite structure. Oxygen atoms are shown as large and aluminum atoms as small spheres.

are more deformed than the second layer (at $z\approx 1/4$, O(3): $z=0.267$, O(4): $z=0.264$) and the fourth. The distance between the first and second layers (0.26 Å) is larger than that between the second and the third layer (0.24 Å).

The interatomic distances were calculated from the coordinates of Table 1. The calculated standard deviations of the Al–O and O–O distances are from 0.01 to 0.03 Å.

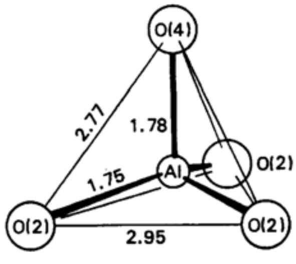

Fig. 2. Interatomic distances (Å) in $Al(3)O_4$.

The Al(3)–O distances are within the range of 1.78—1.75 Å, indicating that the $Al(3)O_4$ tetrahedra are slightly distorted (Fig. 2). In the $Al(2)O_6$ octahedra, aluminium atoms are placed at $z=0.153$, deviating from the $z=0.125$ of the ideal model, and are closer to the oxygen atoms of the upper face (in the second layer), 1.86 Å, than to the oxygen atoms of the lower face (in the first layer), 1.94 Å. The $Al(1)O_6$ octahedra are more distorted than the $Al(2)O_6$ octahedra. The Al–O and the O–O distances in these AlO_6 octahedra are shown in Fig. 3 and Fig. 4. For comparison, the interatomic distances in AlO_6 octahedra for α-Al_2O_3[6] are also given; the Al–O distances are 1.86 and 1.97 Å, and to O–O 2.52, 2.87, 2.62, and 2.73 Å.

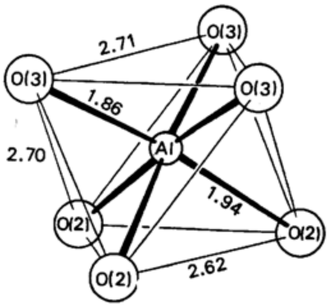

Fig. 3. Interatomic distances (Å) in $Al(2)O_6$.

This refinement supports the expected nature of the distortion caused by local ionic attraction and repulsion.

All the calculations were performed with a HITAC 5020E computer of the Computation Center of Tokyo University, using programs written by the authors.

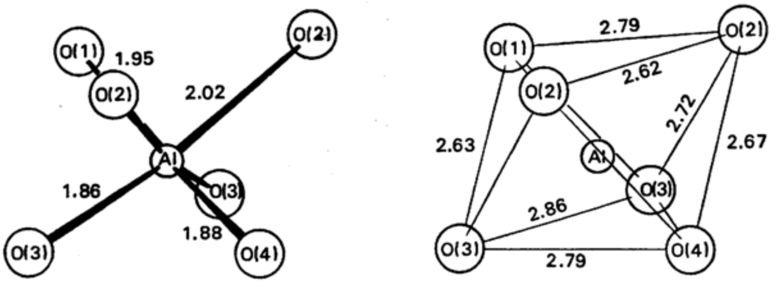

Fig. 4. Interatomic distances (Å) in $Al(1)O_6$.

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[6] R. E. Newnham and Y. M. de Haan, *Z. Krist.*, **117**, 235 (1962).