The Crystal Structure of κ'-Al_2O_3, the New Intermediate Phase

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A structure model of κ'-Al_2O_3 has been obtained by means of X-ray powder diffraction data. An hexagonal unit cell with $a=5.544$ and $c=9.024$ Å and containing $5\frac{1}{3}$ Al_2O_3 was assumed. The oxygen arrangement is the same close packed structure as that of tohdite, and $10\frac{2}{3}$ aluminium atoms are statistically distributed over several octahedral and tetrahedral positions. The R factor for the reflection intensity is 0.13 for 115 reflections.

The first investigation of the dehydration of tohdite $5Al_2O_3 \cdot H_2O$ was performed by Krischner in 1966 using the electron diffraction method.[1] In 1970, a more detailed investigation[2] was performed by the present authors using electron diffraction, X-ray powder diffraction, thermogravimetric measurement, differential thermal analysis, and the measurement of the density; the following transformation series were thus established:

$$\text{tohdite} \xrightarrow{\text{dehyd.}} \kappa'\text{-}Al_2O_3 \rightarrow \kappa\text{-}Al_2O_3 \rightarrow \alpha\text{-}Al_2O_3$$

The κ'-Al_2O_3 was found to be a new unstable intermediate phase and was easily produced by heating tohdite(F)[2] in a high vacuum at just the dehydration temperature. It seems necessary, for a further discussion of the transformation series, to elucidate the atomic arrangement of this unstable phase. The present work has been performed in order to elucidate the atomic arrangement and to confirm the conclusion of the previous discussion. For this purpose, the structure analysis was made by the X-ray powder diffraction method.

Experimental Procedure

The specimen of κ'-Al_2O_3 (from tohdite) used in this work was prepared as follows. Tohdite obtained by treating gibbsite hydrothermally with AlF_3 was heated in a high vacuum (10^{-4} mmHg) up to the temperature of complete dehydration (750°C) and then cooled rapidly to room temperature. This was performed in a high-vacuum TGA instrument[2] in order to check the dehydration percentage. The κ'-Al_2O_3 (from tohdite) was obtained as hexagonal plates with a micron-order size and containing about 0.3% of fluorine as an impurity; this specimen was denoted as κ'-Al_2O_3 (from tohdite(F)) in the previous paper.[2] In the present X-ray intensity calculation, the small amount of fluorine was neglected.

The X-ray powder diffraction diagram was obtained by means of Ni-filtered Cu$K\alpha$ radiation using a Rigaku Denki diffractometer equipped with a scintillation counter and a pulse-height discriminator. The diffraction intensities relative to the (202) intensity were obtained by measuring the peak areas. 41 peaks were measured up to $\sin\theta/\lambda=0.621$ Å^{-1}. No correction was made for the preferred orientation effect on the intensity.

Structure Determination

In the previous paper,[2] κ'-Al_2O_3(from tohdite) was assumed to have a hexagonal unit cell of almost the same size as that of tohdite $5Al_2O_3 \cdot H_2O$. The cell dimensions calculated from the powder diffraction data are $a=5.544\pm0.001$ and $c=9.024\pm0.001$ Å. Density measurement showed that this unit cell contains about $5\frac{1}{3}$ of Al_2O_3, namely, 16 oxygen atoms and $10\frac{2}{3}$ aluminium atoms.

On the basis of this unit cell, the X-ray powder diffraction pattern can be indexed. The systematic absences among the observed reflections of κ'-Al_2O_3 (from tohdite) are the same as those of tohdite: *hhl* with $l=2n+1$. The possible space groups are $P\bar{3}1c$, $P31c$, $P6_3mc$, $P\bar{6}2c$, and $P6_3/mmc$.

It was found that the intensity distribution of the reflections of κ'-Al_2O_3 (from tohdite) resembles that of the corresponding reflections of tohdite (especially that of the reflections at $2\theta>40°$) (Fig. 1). Therefore, we considered κ'-Al_2O_3 (from tohdite) to have a structure similar to that of tohdite. We attempted to derive a structure model of κ'-Al_2O_3 (from tohdite) from the structure of tohdite as determined from the X-ray powder diffraction data.[3,4] The space group of κ'-Al_2O_3 (from tohdite) was assumed to be the same as that of tohdite, $P6_3mc$.

The structure factors are obtained from the X-ray powder diffraction intensities. The intensities of the overlapping peaks were separated into the ratio of the calculated intensities of the corresponding reflections of tohdite. A three-dimensional Fourier synthesis was made using these structure factors and the phases of the corresponding reflections of tohdite.

After a several-cycle refinement of Fourier synthesis, the outline of the structure of κ'-Al_2O_3 (from tohdite) was obtained as follows: The arrangement of oxygen atoms was revealed to be the same as that of tohdite, ABAC closed packing. As for the positions of the aluminium atoms, it was found that the aluminium atoms are distributed over several octahedral and tetrahedral positions, including aluminium positions in tohdite, and that some of their occupancies are less than 1. These occupancy factors were refined by the least-squares method. The least-squares analysis program was written for the HITAC 5020E computer, in which the occupancy factors of aluminium atoms were varied so as to minimize $R_I'=\Sigma(I_o-I_c)^2$, where:

I_o=integrated intensity

$I_c=K \cdot I_p \cdot \sum_i m_i \cdot |F_c|^2$, where:

$\sum_i$=the sum over overlapping peaks

1) H. Krischner, *Ber. Deut. Keram. Ges.*, **39**, 1366 (1966).

2) M. Okumiya, G. Yamaguchi, O. Yamada, and S. Ono, *ibid.*, **44**, 418 (1971).

3) G. Yamaguchi, H. Yanagida, and S. Ono, *ibid.*, **37**, 752 (1964).

4) G. Yamaguchi, M. Okumiya, and S. Ono, *ibid.*, **42**, 2247 (1969).

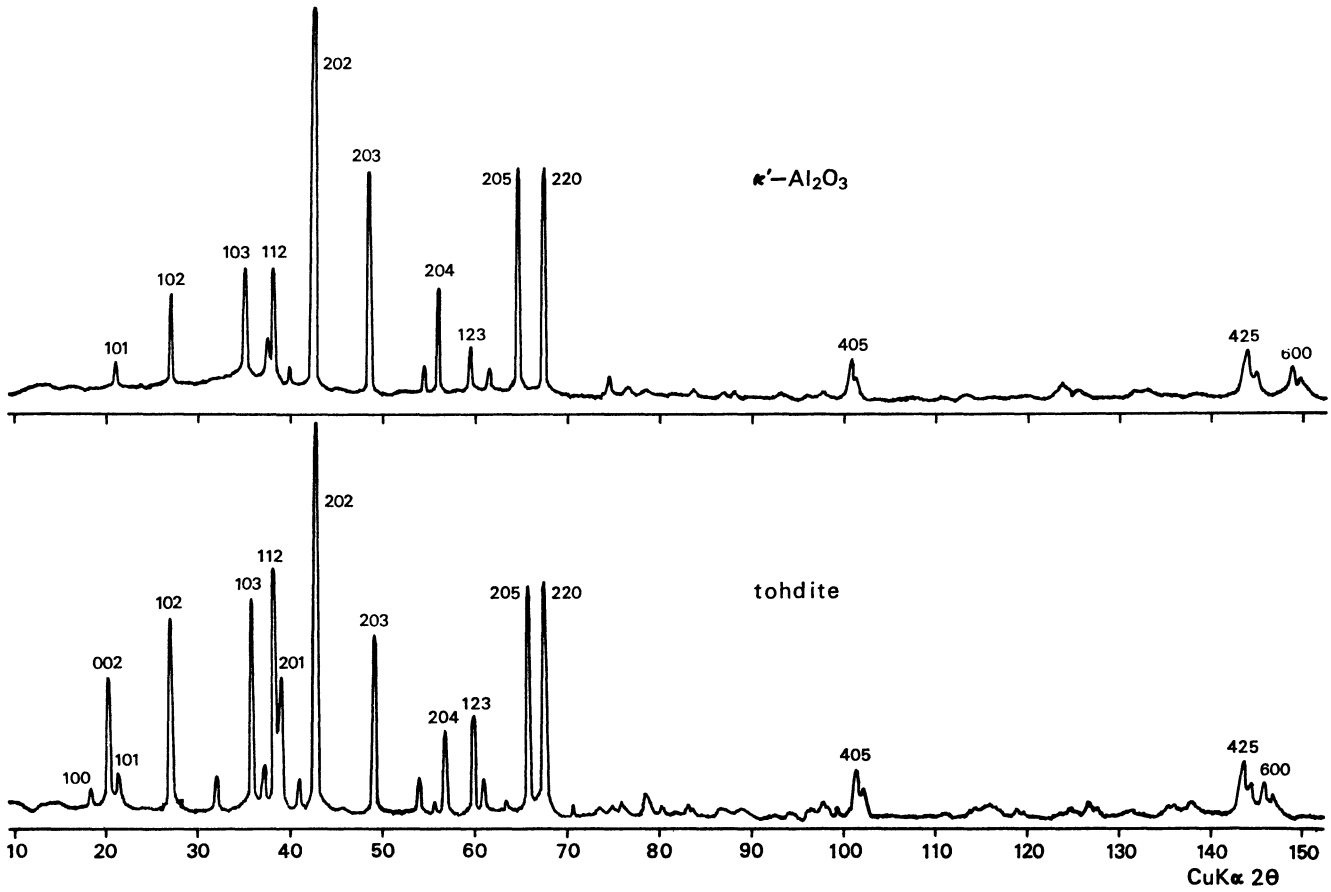

Fig. 1. X-Ray powder diffraction pattern of κ'-Al_2O_3 and tohdite.

K=scale factor
m_i=multiplicity
L_p=Lorentz and polarization factor

The structure factor, F_c, is presented as: $F_c=\sum_j p_j \cdot f_j \cdot \exp 2\pi i(hx_j+ky_j+lz_j)$, where:

p_j=occupancy factor

In the calculation of the structure factor, an overall isotropic temperature factor was used. Six occupancy factors were varied independently, while the restrictive condition, $\Sigma p=10\frac{2}{3}$, was neglected. The occupancy factors of oxygen atoms were fixed as 1.0. The final occupancy factors and their standard deviations, as estimated from the diagonal element of the inverse to the least-squares matrix, are listed in Table 1, together with the atomic coordinates.

Table 1. Atomic coordinates and occupancy factors with their standard deviations ($\times 10^2$)

Position	x	y	z	p	Number of equivalent positions
O(1)	0	0	0	1.0	2
O(2)	0.500	$-x$	0.006	1.0	6
O(3)	0.832	$-x$	0.256	1.0	6
O(4)	1/3	2/3	0.254	1.0	2
Al(1)	1/3	2/3	0.056	0.51(2)	2
Al(2)	0.833	$-x$	0.061	0.08(1)	6
Al(3)	2/3	1/3	0.148	0.98(5)	2
Al(4)	0.156	$-x$	0.118	0.34(1)	6
Al(5)	0.169	$-x$	0.363	0.67(3)	6
Al(6)	0.884	$-x$	0.448	0.12(2)	6

Overall isotropic temperature factor 0.72 (0.05)Å^2

The calculated intensities for the parameter of Table 1 are listed in Table 2. The $R_I=\Sigma|I_o-I_c|/\Sigma I_o$ factor is 0.13.

Discussion

The results of this structure calculation confirmed the previous conclusions that the oxygen sub-lattice is preserved during the transformation from tohdite to κ'-Al_2O_3 (from tohdite) and that aluminium atoms are randomly distributed over the octahedral and tetrahedral positions. The distribution of the aluminium atoms of Table 1 is illustrated in Fig. 2. The total number of aluminium atoms in the unit cell is calculated as 10.2 ($\sigma=0.3$). This is in fairly good agreement with the ideal, $\Sigma p_j=10\frac{2}{3}$.

Between the second and the third layers of oxygen atoms, aluminium atoms are distributed over the octahedral positions, Al(5), and the tetrahedral positions, Al(6). The obtained occupancy factor for the Al(5) positions of 0.67 is considered to be 2/3; this means that three Al(5) positions are occupied randomly by two aluminium atoms, while in the structure of tohdite the corresponding positions are fully occupied by three aluminium atoms. The Al(6) positions are partly occupied, with an occupancy factor of 0.12, while the

TABLE 2. X-RAY POWDER PATTERN DATA FOR κ'-Al_2O_3 (from tohdite)

h	k	l	d_{obs}	d_{cal}	I_o	I_c	h	k	l	d_{obs}	d_{cal}	I_o	I_c
1	0	0		4.801	0	0	2	1	7	(1.051)	1.051		5
0	0	2		4.512	0	0	4	1	0		1.048	5	0 7
1	0	1	4.233	4.239	7	7	1	1	8		1.045		2
1	0	2	3.284	3.288	24	24	4	1	1		1.041	0	0
1	1	0		2.772	0	2	3	2	3		1.034	2	4
1	0	3	2.546	2.549	37	36	2	0	8		1.021		0
2	0	0	2.399	2.401	12	12	4	1	2	1.021	1.021	4	4 5
1	1	2	2.360	2.362	32	33	2	2	6		1.020		1
2	0	1		2.320	0	3	3	0	7		1.004	0	0
0	0	4	2.255	2.256	6	5	4	0	5	0.999	0.999	17	16
2	0	2	2.118	2.119	100	101	1	3	6		0.997	0	0
1	0	4		2.042	0	0	2	3	4		0.990	0	0
2	0	3	1.876	1.876	61	58	4	1	3		0.989	0	1
1	2	0		1.815	0	1	1	0	9		0.981	0	0
1	2	1		1.779	0	0	5	0	0		0.960	0	0
1	1	4		1.750	0	1	2	1	8		0.958	1	1
1	2	2	1.683	1.684	8	9	5	0	1		0.955	0	0
1	0	5		1.689	0	1	1	4	4		0.950	0	0
2	0	4	1.643	1.644	28	33	3	2	5		0.940	0	0
3	0	0		1.600	0	0	5	0	2		0.939	0	1
3	0	1		1.576	0	1	4	0	6		0.938	3	2
1	2	3	1.553	1.554	14	14	3	1	7		0.926		3
3	0	2	1.507	1.508	7	8	2	0	9		0.925	9	3 8
0	0	6		1.504	0	0	3	3	0		0.924		0
2	0	5	1.442	1.443	76	73	3	0	8		0.922		2
1	0	6		1.435	0	0	5	0	3		0.915	2	1
1	2	4		1.414	0	0	4	2	0		0.907		1
3	0	3		1.413	0	0	4	1	5		0.906		0
2	2	0	1.386	1.386	72	75	3	3	2		0.905	8	1 6
1	3	0		1.332	0	0	4	2	1		0.903		2
2	2	2		1.325	0	0	0	0	10		0.902		1
1	1	6		1.322	0	1	4	2	2	(0.889)	0.890		7
1	3	1		1.317	0	1	3	2	6		0.889	6	0 7
3	0	4		1.305	0	0	1	0	10		0.887		0
1	2	5		1.280	0	1	5	0	4		0.884	0	0
1	3	2		1.227	0	2	4	0	7		0.878	0	0
2	0	6	1.274	1.275	11	8	2	1	9		0.878	0	0
1	0	7	1.245	1.245	6	4	2	2	8	0.875	0.875	14	17
1	3	3	1.218	1.218	7	8	4	2	3	0.869	0.869	9	9
4	0	0	1.200	1.200	2	2	5	1	0		0.862	0	0
3	0	5		1.197	0	0	3	1	8		0.861	0	1
4	0	1		1.190	1	2	4	1	6		0.860		1
2	2	4		1.181	0	3	5	1	1		0.858	3	0 2
4	0	2	1.160	1.160	4	5	1	1	10		0.858		1
1	2	6		1.158	0	1	3	3	4		0.855	0	0
1	3	4		1.147	0	0	3	0	9		0.850	0	0
2	0	7		1.136	0	0	5	0	5		0.848	0	0
0	0	8	1.128	1.128	5	4	5	1	2		0.847	0	1
4	0	3	1.115	1.115	5	7	2	0	10	0.845	0.845	16	9 19
2	3	0		1.101	0	0	4	2	4	0.842	0.842		10
1	0	8		1.098		1	3	2	7		0.837	6	4
3	0	6		1.096	1	0 1	5	1	3		0.829	3	3
2	3	1		1.093		0	4	0	8		0.822	0	0
3	1	5		1.072	0	1	4	1	7		0.813	0	0
3	2	2		1.070	0	1	4	2	5	0.811	0.811	40	38
4	0	4	1.060	1.060	4	6	5	0	6		0.809	0	1
							5	1	4		0.805	0	0
							6	0	0	0.800	0.800	27	26
							6	0	1		0.797	0	0

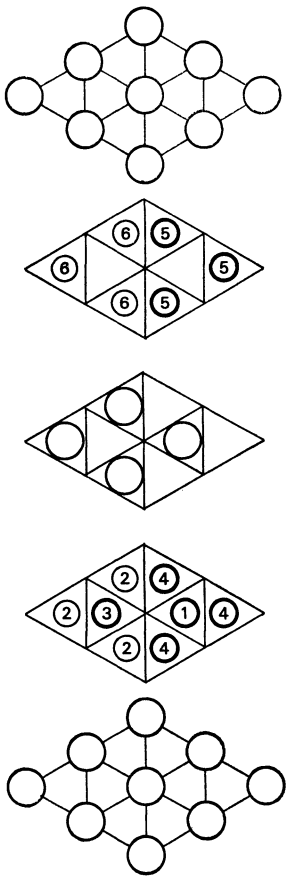

Fig. 2.

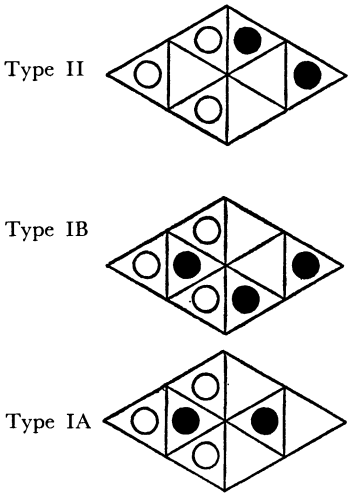

Fig. 3. Arrangement of aluminium atoms in the 1st (type IA, IB) and the 2nd (type II) aluminium layers of κ'-Al_2O_3 (from tohdite).

corresponding positions of tohdite are vacant. This type of cation arrangement is denoted as Type II; one of the three possible arrangements is illustrated in Fig. 3.

Between the first and the second oxygen layers aluminium atoms are distributed over octahedral, Al(3) and Al(4), and tetrahedral, Al(1) and Al(2), positions. The obtained occupancy factors, 0.98 for Al(3), 0.34 for Al(4), and 0.51 for Al(1), are considered to be 1, 1/3, and 1/2 respectively. The distribution of aluminium atoms between these oxygen layers could be explained as the average of two types of cation arrangement: Type IA: the Al(3) and Al(1) positions are fully occupied, and Al(2) is partly (12%) occupied. If we overlook the atoms in Al(2), this type is found in tohdite between the corresponding oxygen layers. Type IB: Al(3) is fully occupied, the three Al(4) positions are occupied by two aluminium atoms, and the Al(2) positions are partly (8%) occupied.

There are two types of combinations of adjacent aluminium layers, *i.e.*, IA-II and IB-II. In the former type, there is no face-shared contact between oxygen polyhedra around aluminium atoms. In the latter type, some of the oxygen octahedra have to share contact faces along the *c*-axis.

Considering that the occupancy factors for Al(6) and Al(2) are rather small and that the unstable κ'-Al_2O_3 (from tohdite) might not be described as a definite unit cell, but as a statistical structure average, it is possible that other octahedral and tetrahedral positions (Fig. 4) are also occupied by aluminium atoms with small occupancy factors. However, no other highly occupied aluminium positions should exist except those listed in Table 1, since the structure proposal of Table 1 is satisfactory enough to explain the X-ray powder pattern of κ'-Al_2O_3 (from tohdite).

2nd aluminium layer
Al(9) z≈3/8, octahedral
Al(10)z≈7/16, tetrahedral
Al(11)z≈5/16, tetrahedral
Al(12)z≈5/16, tetrahedral

1st aluminium layer
Al(7)z≈3/16, tetrahedral
Al(8)z≈3/16, tetrahedral

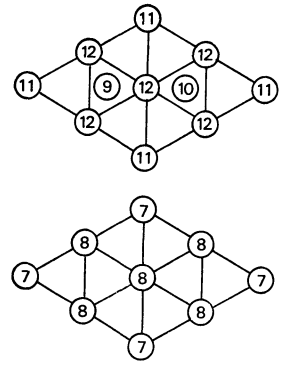

Fig. 4. Tetrahedral and octahedral positions of aluminium atoms which might be occupied with small occupancy.

According to the above-mentioned structure, κ'-Al_2O_3 (from tohdite) may be described as a partly cation-redistributed structure of tohdite and as an unstable intermediate phase in the transformation from tohdite to κ'-Al_2O_3 (from tohdite).

All the calculations were performed with HITAC 5020E computer of the Computation Center of the University of Tokyo. The calculation of the Fourier synthesis was done by the use of Universal Crystallographic Computation Program System 5020 UNICS.