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A New Method of Preparing θ-Alumina and the Interpretation of Its X-Ray-powder Diffraction Pattern and Electron Diffraction Pattern

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Highly crystallized θ-alumina was obtained by a two-step treatment, by hydrothermal and thermal treatment, of η-alumina. Its X-ray-powder diffraction pattern was interpreted based on the structure of β-gallia, and least-squares refinements were carried out. The electron diffraction pattern of θ-alumina from boehmite was also interpreted, and the directional relations between the phases were established.

The preparation of θ-alumina has been studied since θ-alumina was recognized as a transient alumina by Stumph *et al.*[1–3] As to the structure of θ-alumina, an attempt has been made to index the X-ray-powder diffraction peaks using a hexagonal cell, but the proper indices have not yet been given.[4]

On the other hand, β-gallia, the high-temperature form of gallias, was revealed to have an isostructure with θ-alumina.[5–7] The single crystal of β-gallia was prepared, and its structure analysis was carried out by X-ray diffraction.[8–10] The X-ray powder diffraction pattern of θ-alumina has, however, not been interpreted so precisely that the identification of pure θ-alumina is unperfect, this makes the studies of the alumina polymorphs unsure.

In the present study, a new method of preparation will be described, the X-ray-powder diffraction and the electron diffraction pattern will be interpreted, and a least-squares refinement of the structure will be reported.

Experimental

Preparation of θ-Alumina from η-Alumina (The New Method). The method of preparing the η-alumina used as the starting material of θ-alumina was as follows.[11] Alumina gel was prepared by the procedure

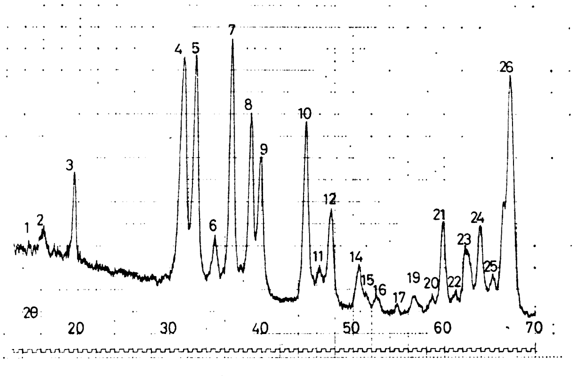

Fig. 1. X-Ray powder diffraction pattern of θ-alumina prepared by the new method.

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TABLE 1. PEAK NUMBER, INTENSITIES, *etc.*

Peak No.	*hkl*	*I* (obsd)	*I* (calcd)		*d* (obsd)	*d* (calcd)	sp. *HKL*	Mul.
1	200	1	1		5.7	5.7324		
2	001	9	9		5.45	5.4606		
3	$20\bar{1}$	17	15		4.535	4.5345		
4	400	80	81	29	2.837	2.8662		
	$40\bar{1}$			48		2.8330		
	100			4		2.8169		
5	$20\bar{2}$	64	67	26	2.730	2.7327		
	002			41		2.7303		
6	$11\bar{1}$	14	12		2.566	2.5658		
7	111	62	60		2.444	2.4454	311	4
8	401	46	44	33	2.315	2.3191		
	310			11		2.3132	222	4
9	$40\bar{2}$	37	41	4	2.257	2.2673	222	2
	$\underline{202}$			5		2.2631	222	2
	$31\bar{1}$			32		2.2506		
10	$\underline{311}$	45	40	8	2.019	2.0268		
	$11\bar{2}$			32		2.0210	400	4
11	$60\bar{1}$	8	8		1.9544	1.9558		
12	$\underline{600}$	30	32	14	1.9094	1.9108	400	2
	$31\bar{2}$			12		1.9068		
	112			6		1.9052		
13	$20\bar{3}$	0	0			1.8690		
14	$\underline{003}$	14	15	0	1.7998	1.8202	331	2
	$51\bar{1}$			0		1.8142	331	4
	510			15		1.8001		
15	602	5	3	1	1.7765	1.7788		
	402			2		1.7755		
16	$40\bar{3}$	4	4		1.7376	1.7376		
17	601	2	1		1.6807	1.6821		
18	$51\bar{2}$	0	0	0		1.6527		
	312			0		1.6506		
19	203	5	4	2	1.6216	1.6259		
	511			2		1.6212		
20	$11\bar{3}$	2	4		1.5715	1.5716		
21	313	23	23		1.5426	1.5436	511	4
22	603	5	5		1.5120	1.5115	333	2
23	$\underline{113}$	26	29	20	1.4883	1.4893		
	$80\bar{1}$			9		1.4759		
24	$\underline{020}$	26	23	23	1.4526	1.4530	440	2
	$71\bar{1}$			0		1.4570		
25	800	10	10	1	1.4264	1.4331		
	$\underline{710}$			9		1.4268		
	$51\bar{3}$			0		1.4207		
	213			0		1.4189		
	$80\bar{2}$			0		1.4165		
26	602	100	100	0	1.3883	1.4142		
	$\underline{220}$			0		1.4085		
	$20\bar{4}$			19		1.4062	440	2
	$\underline{403}$			2		1.3927		
	$71\bar{2}$			39		1.3894	440	4
	$\underline{512}$			39		1.3875	440	4
	$22\bar{1}$			1		1.3837		

through which an aluminum chloride of a 0.5-mol/*l* aqueous solution was neutralized with a 14% ammonia aqueous solution to pH 7.5; the gel thus precipitated was filtered out and rinsed. The gel was then aged in ethylenediamine, a 5% aqueous solution, for 3 days at 30—40°C, by which time it had crystallized into nordstrandite. This nordstrandite was then heated and dehydrated at 700°C in air for 1 hr; the η-alumina was thus obtained.

This η-alumina was treated hydrothermally at 500°C, under 150 atm, for 45 hr; quite well-crystallized θ-alumina was thus obtained. When this θ-alumina was heated again at 1000°C in air for 0.5 hr, it became highly well-crystallized θ-alumina.

Preparation of θ-Alumina from Boehmite. Well-crystallized boehmite was prepared from gibbsite by

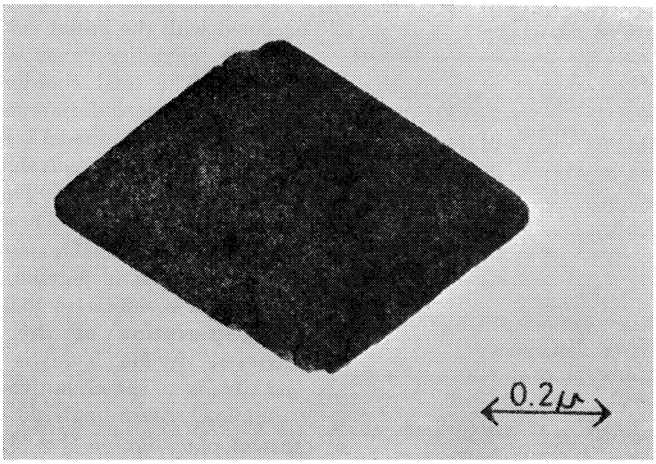


Fig. 2. Electron-micrograph of θ-alumina having the initial own shape of boehmite from well-crystallized boehmite.

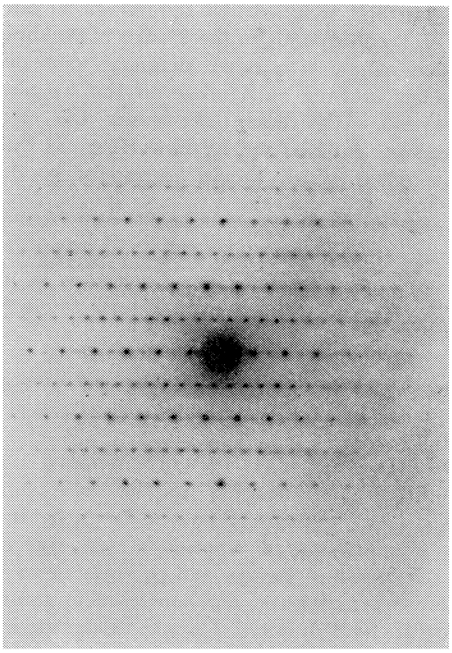


Fig. 3. Electron diffraction pattern of θ-alumina from well-crystallized boehmite.

hydrothermal treatment. This boehmite was heated at 1100°C in air for 2 hr, θ-alumina with the initial shape of boehmite was thus obtained.

X-Ray Powder Diffraction. The X-ray-powder diffraction pattern of θ-alumina from η-alumina was taken with a recording X-ray diffractometer, using Ni filtered Cu$K\alpha$ radiation, as is illustrated in Fig. 1. This pattern shows a fairly good crystallinity.

The numbers of the peaks and the relative intensities obtained from the areas of the peaks are given in the 1st and 3rd columns of Table 1 respectively.

Electron Diffraction. An electron-micrograph of θ-alumina with the shape of boehmite was taken, as is illustrated in Fig. 2. The electron-diffraction pattern of θ-alumina was also taken, as is illustrated in Fig. 3. In Fig. 2, the *a*-axis of boehmite lies in the direction of the short diagonal of the rhombus, the *b*-axis is parallel to the long diagonal, and the *c*-axis is parallel to the incident electron beam.

Results and Discussion

Analysis of the Lattice and Atomic Parameters and the Indexing of the Powder-diffraction Pattern. The programs for the calculation of the atomic and lattice parameters were written for the HITAC 5020E computer by the authors. On the basis of the structure of β-gallia,[10] the intensities were computed on the assumption that aluminum atoms occupy the positions of gallium atoms as substitutes. Moreover, the index of each peak and its overlapping state were confirmed, as is shown in Table 1.

The lattice parameters calculated by the least-squares method are given in Table 2.

TABLE 2. LATTICE DIMENSIONS OF θ-ALUMINA

Monoclinic	$C_{2h}-C_{2/m}$
$\alpha=$	11.813±0.010Å
$b=$	2.906±0.002Å
$c=$	5.625±0.005Å
$\beta=$	104.1 ±0.1°

The transformation matrix from the cubic lattice (HKL), that is, the lattice of spinel, to θ-alumina's monoclinic lattice (hkl) is given as follows:

$$\begin{pmatrix} h \\ k \\ l \end{pmatrix} = \begin{pmatrix} -1/4 & 1/4 & -3/2 \\ 1/4 & 1/4 & 0 \\ 1/2 & -1/2 & 0 \end{pmatrix} \begin{pmatrix} H \\ K \\ L \end{pmatrix}$$

The spinel indices corresponding to θ-alumina and their multiplicities are given in the 7th and 8th columns of Table 1.

TABLE 3. ATOMIC PARAMETERS AND THEIR STANDARD DEVIATIONS OF β-GALLIA

	x	*z*
Ga(1)	0.0904(2)	−0.2052(5)
Ga(2)	0.3414(2)	−0.3143(5)
O(1)	0.1674(19)	0.1011(41)
O(2)	0.4957(16)	0.2553(34)
O(3)	0.8279(15)	0.4365(34)

TABLE 4. ATOMIC PARAMETERS AND THEIR STANDARD DEVIATIONS OF θ-ALUMINA

	x	*z*
Al(1)	0.0843(19)	−0.2071(37)
Al(2)	0.3400(14)	−0.3168(33)
O(1)	0.1614(20)	0.1071(53)
O(2)	0.4980(19)	0.2602(35)
O(3)	0.8326(24)	0.4404(54)

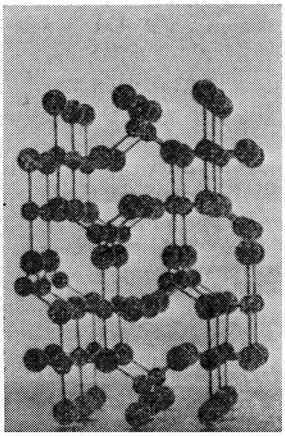


Fig. 4. Structure model of θ-alumina.
Large sphere: Oxygen
Small sphere: Aluminum

The least-squares refinement of the structure was executed with the initial value given in Table 3,[10] and the reliability factor was reduced from 0.17 to 0.08. The final coordinate, along with their estimated standard deviations, are given in Table 4, while the structure model is illustrated in Fig. 4.

This refinement reveals shifts of aluminum atoms from the ideal positions. The interatomic distances are given in Table 5. These interatomic distances show that the Al(1)O_4 tetrahedron is more distorted than that of β-gallia, but that the Al(2)O_6 octahedron is similar to that of β-gallia.

Interpretation of the Electron-diffraction Pattern. In Fig. 5, (a) is the shape of boehmite and (b) is a spinel lattice of the corresponding θ-alumina. Accordingly, in the electron-diffraction pattern of θ-alumina (Fig. 3), the horizontal direction corresponds to the *c*-axis of the spinel lattice of Fig. 5(b). This direction corresponds to one of the three diagonal directions of oxygen octahedrons in cubic closest packing of θ-alumina; it can thus be concluded that the horizontal direction in Fig. 2 corresponds to the *a**-axis of θ-alumina or to one of the two other diagonal axes perpendicularly crossing each other on the *b*-*c* plane of θ-alumina. Of these three cases, the electron-diffraction pattern clearly shows (Fig. 3) that the horizontal direction should correspond to the *a**-

TABLE 5. INTERATOMIC DISTANCES AND STANDARD DEVIATIONS

Atomic pair	Distance Å	σ Å
Tetrahedron		
Al(1)-O(1)	1.78	0.03
Al(1)-O(2)	1.73	0.02
Al(1)-O(3)	1.82	0.04
Octahedron		
Al(2)-O(1)	1.87	0.02
Al(2)-O(2)	1.86	0.03
Al(2)-O(3)	1.99	0.03
Al(2)-O(3)$_{\rm II}$	1.98	0.02

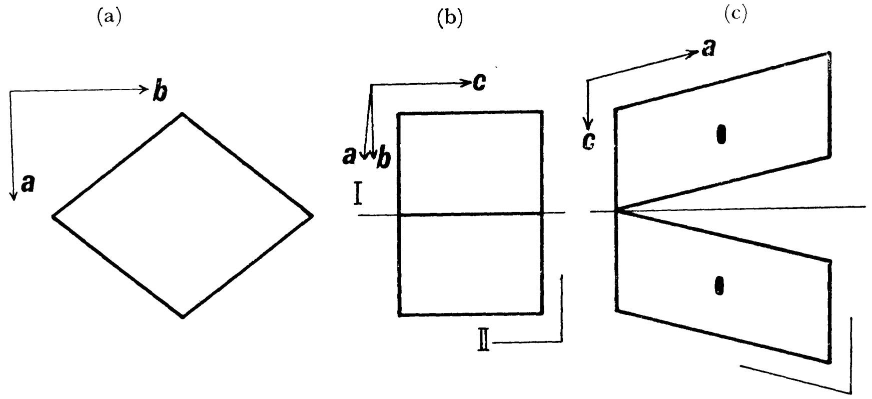


Fig. 5. Shape of θ-alumina from boehmite and lattices of spinel and θ-alumina with mirror planes.

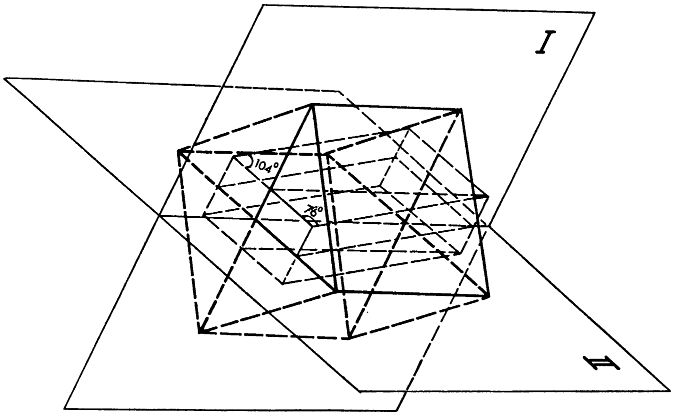
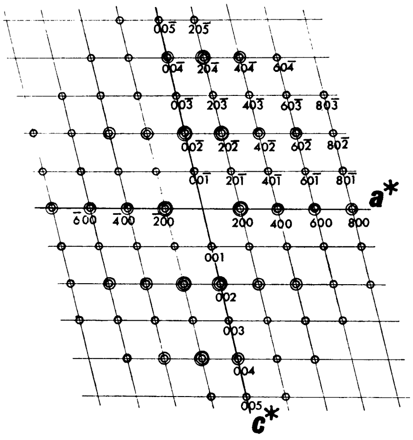
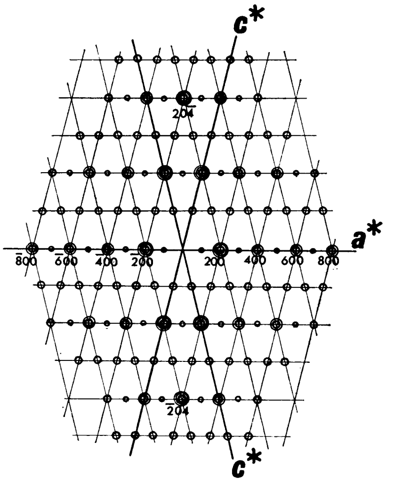


Fig. 6. Perspective drawing of the lattice of spinel with that of θ-alumina.



(a)

Fig. 7(a). Indices of electron diffraction pattern of θ-alumina from boehmite.



(b)

Fig. 7(b). Indices with the assumption of the twinning structure or the twinning like aggregate.

axis of θ-alumina, in view of the possible reflections of *h*0*l*. This relation is shown in Fig. 5(c) and Fig. 6.

In this case, θ-alumina has a twinning structure or a twinning-like aggregate structure. The twinning phenomenon can be explained as follows: there are mirror planes parallel to the (110) planes in the spinel lattice, as is shown in Fig. 6, and two mirror planes, I and II, perpendicularly crossing each other are to be considered. The other (110) plane need not be considered, because it is not a mirror planes in γ-alumina through which θ-alumina is formed from boehmite. If one of the two mirror plane, plane II, is conserved as a mirror plane in the θ-alumina ($C_{2h}C_{2/m}$) lattice, the other, plane I, can not become a mirror plane, but it can possibly become a twinning plane. On the assumption of this twinning structure, the reciprocal lattice of θ-alumina is illustrated in Fig. 7(b). This figure is in good agreement with the observed electron-diffraction pattern. Figure 7(a) represents the indices of θ-alumina without a twinning structure. The reason why the two planes do not alternate must be investigated in the future.

In the electron-diffraction pattern, weak spots are observed; they are shown in Fig. 3 and are expressed by the smallest circles in Fig. 7(b). These spots show the distortion of the crystal structure from $C_{2/m}$, but the X-ray-powder diffraction does not show any evidence for this distortion. Therefore, it can be said that the true space group is distorted from $C_{2/m}$, but that the atomic arrangement of the structure analyzed above with $C_{2/m}$ is almost true.

All the calculations were performed with a computer of the Computation Center of Tokyo University.