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Note added in proof: Recently we became aware of a similar structure refinement on NAH by Kiers, Piepenbroek & Vos (1978).

Our positional parameters are generally in good agreement with their results. Differences are at most twice the sum of the associated e.s.d.'s [O(3) atom]. The same applies for the bond lengths and angles, except for $\text{Na}''\text{—O}''(1) = 2.342 \text{ \AA}$ of Kiers, Piepenbroek & Vos, which seems to be a misprint. The corresponding distance determined in our study is 2.617 \AA .

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A Structural Investigation of $\alpha\text{-Al}_2\text{O}_3$ at 2170 K

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Abstract

The crystal structures of $\alpha\text{-Al}_2\text{O}_3$ at 300 and 2170 K were studied by three-dimensional X-ray data which were measured in the ranges $\sin \theta/\lambda < 1.08 \text{ \AA}^{-1}$ at 300 K and $\sin \theta/\lambda < 0.70 \text{ \AA}^{-1}$ at 2170 K on a four-circle diffractometer equipped with a gas-heating furnace. The structures were refined to conventional R values of 0.027 at 300 K and 0.038 at 2170 K. Significant changes in the positional parameters of the Al atoms and slight changes in those of the O atoms were observed. The distorted hexagonal-close-packed plane of O atoms becomes more regular at 2170 K and the Al atom moves towards the vacant octahedral interstice between the oxygen layers. The two independent Al—O bond lengths are 1.971 (2) and 1.852 (1) \AA at 300 K, while they are 2.024 (2) and 1.880 (1) \AA at 2170 K. Of the Al—Al distances, the largest expansion was observed in that across the shared face of the AlO_6 octahedra along the c axis (hexagonal setting).

Introduction

In corundum-type structures, the O atom is located at $(x, 0, \frac{1}{2})$ and the Al atom at $(0, 0, z)$ in the hexagonal

References

- ALMLÖF, J. & OTTERSEN, T. (1979). *Acta Cryst.* **A35**, 137–139.
 BERGLUND, B., LINDGREN, J. & TEGENFELDT, J. (1978). *J. Mol. Struct.* **43**, 179–191.
 BERTHOLD, I. & WEISS, A. (1967). *Z. Naturforsch. Teil A*, **22**, 1440–1451.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
 KETUDAT, S., BERTHOLD, I. & WEISS, A. (1967). *Z. Naturforsch. Teil A*, **22**, 1452–1457.
 KIERS, C. TH., PIEPENBROEK, A. & VOS, A. (1978). *Acta Cryst.* **B34**, 888–890.
 MARTÍNEZ, S., GARCÍA-BLANCO, S. & RIVOIR, L. (1956). *Acta Cryst.* **9**, 145–150.
 SODA, G. & CHIBA, T. (1969). *J. Chem. Phys.* **50**, 439–455.
 ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.
 ZWOLL, K. (1974). *Ber. Kernforschungsanlage Jülich*, No. 1057.

setting of $R\bar{3}c$. The O atoms arrange approximately in hexagonal close packing with metal atoms occupying two thirds of the octahedral interstices. The metal–metal distance along the threefold axis across the face shared by two MO_6 coordination octahedra is the shortest of the various metal–metal contacts in a corundum-type structure. Several studies have referred to changes in these structural parameters. Moss & Newnham (1964) reported that the Cr position in ruby ($\alpha\text{-Al}_2\text{O}_3$ with 4% Cr_2O_3) is shifted by 0.06 \AA from the normal Al position in the $\alpha\text{-Al}_2\text{O}_3$ structure. Rice & Robinson (1976, 1977) investigated the structural changes in Ti_2O_3 accompanying the semiconductor–metal transition when warmed through the temperature range 400–600 K and reported a large elongation of Ti–Ti distance across the threefold axis. d'Amour, Schiferl, Denner, Schulz & Hazapfel (1978) found that the positional parameters in ruby were constant up to $8.6 \times 10^3 \text{ MPa}$ in their study by high-pressure single-crystal X-ray diffractometry. Nukui, Tagai, Morikawa & Iwai (1976) investigated the structural conformation of molten alumina at 2370 K. Structural information on $\alpha\text{-Al}_2\text{O}_3$ at high temperatures has never been reported. The object of this study is to clarify structural changes of $\alpha\text{-Al}_2\text{O}_3$ at high

temperatures, particularly near the melting point (2323 K) of the crystal.

Experimental

The specimen was a transparent sapphire single crystal grown by the Verneuil method (Toshiba Ceramic Ltd). The top of the cylinder-shaped specimen, of diameter 0.4 mm and length 15 mm, was fused into a sphere of diameter 0.45 mm and cooled to permit crystallization. This spherical part of the specimen was confirmed to be a single crystal by the precession method. Gas-flame heating equipment attached to a four-circle diffractometer (Miyata, Ishizawa, Minato & Iwai, 1979) was employed to heat the specimen. The spherical part of the specimen was irradiated with X-rays. The cell dimensions were determined at 300 ± 1 K and 2170 ± 15 K by a least-squares procedure from ten 2θ values obtained on the four-circle diffractometer. They are given in Table 1. The intensity data were collected at 300 ± 1 K and 2170 ± 15 K with Mo $K\alpha$ radiation monochromated by a graphite plate. The ω - 2θ scan technique was employed with a scanning speed of 2° min^{-1} in ω . 260 and 82 independent reflexion data, whose $|F_o|$'s were $>3\sigma(|F_o|)$, were obtained in the ranges $\sin \theta/\lambda < 1.08 \text{ \AA}^{-1}$ at 300 K and $\sin \theta/\lambda < 0.70 \text{ \AA}^{-1}$ at 2170 K, respectively. Intensities were corrected for Lorentz and polarization effects. Absorption corrections were also made assuming a spherical crystal. The structures were refined with the full-matrix least-squares program *LINUS* (Coppens & Hamilton, 1970). The refinement was started from the atomic parameters of $\alpha\text{-Al}_2\text{O}_3$ given by Newnham & de Haan (1962). Secondary extinction was corrected for by Zachariassen's (1967) method. The extinction parameters obtained were 0.6×10^{-4} at 300 K and 0.4×10^{-4} at 2170 K. The largest correction factor was approximately 40% of the F values in both refinements. The atomic scattering factors used were those given in *International Tables for X-ray*

Table 1. Cell dimensions and atomic parameters for $\alpha\text{-Al}_2\text{O}_3$

	300 K	2170 K
a	4.754 (1) Å	4.844 (2) Å
c	12.99 (2)	13.27 (2)
z	0.35228 (5)	0.3533 (2)
U_{11}	0.0051 (2) Å ²	0.0299 (22) Å ²
U_{33}	0.0019 (2)	0.0255 (22)
B_{iso}	0.32	2.25
x	0.3064 (3)	0.307 (1)
U_{11}	0.0051 (3) Å ²	0.0282 (28) Å ²
U_{22}	0.0051 (4)	0.0290 (37)
U_{33}	0.0025 (3)	0.0275 (33)
U_{23}	0.0007 (2)	0.0046 (24)
B_{iso}	0.33	2.22

Table 2. Selected interatomic distances (Å) and their mean thermal-expansion coefficients ($\times 10^6 \text{ K}^{-1}$) and bond angles ($^\circ$), with their estimated standard deviations in parentheses

	300 K	2170 K	Thermal-expansion coefficient
Al ^I -O ⁱⁱ	1.971 (2)	2.024 (2)	14.4 (12)
Al ^I -O ^{ix}	1.852 (1)	1.880 (1)	8.1 (7)
Al ^I -Al ⁱⁱ	2.657 (4)	2.744 (4)	17.5 (17)
Al ^I -Al ⁱⁱⁱ	2.789 (1)	2.847 (1)	11.1 (5)
Al ^I -Al ^{iv}	3.214 (1)	3.262 (2)	8.0 (6)
Al ^I -Al ^v	3.496 (2)	3.565 (2)	10.6 (7)
O ⁱⁱ -O ^{vi}	2.522 (1)	2.577 (3)	11.7 (5)
O ⁱⁱ -O ^{vii}	2.863 (1)	2.913 (2)	9.4 (6)
O ⁱⁱ -O ^{viii}	2.619 (3)	2.675 (3)	11.4 (13)
O ⁱⁱ -O ^{ix}	2.724 (3)	2.779 (3)	10.8 (13)
Al ^I -O ⁱⁱ -Al ⁱⁱ	84.76 (10)	85.35 (13)	
Al ^I -O ^{vi} -Al ⁱⁱⁱ	93.61 (6)	93.58 (7)	
Al ^I -O ^{ix} -Al ^{iv}	120.38 (4)	120.41 (9)	
Al ^I -O ⁱⁱ -Al ^v	132.19 (3)	131.93 (5)	
O ⁱⁱ -Al ^I -O ^{vi}	79.53 (7)	79.09 (9)	
O ⁱⁱ -Al ^I -O ^{ix}	86.40 (6)	86.42 (9)	
O ^{ix} -Al ^I -O ⁱⁱⁱ	101.20 (5)	101.57 (9)	
O ⁱⁱ -Al ^I -O ⁱⁱⁱ	164.13 (3)	163.57 (7)	

Symmetry code

(i)	$\frac{1}{3} - x, \frac{2}{3} - y, \frac{2}{3} - z$	(vi)	$\frac{1}{3} - x + y, \frac{2}{3} + y, \frac{1}{6} + z$
(ii)	$\frac{1}{3} - y, \frac{2}{3} - x, \frac{1}{6} + z$	(vii)	$\frac{1}{3} - x + y, \frac{2}{3} + y, \frac{1}{6} + z$
(iii)	$x, 1 + y, z$	(viii)	$y, x, \frac{1}{2} - z$
(iv)	$\frac{2}{3} - y, \frac{1}{3} - x, -\frac{1}{6} + z$	(ix)	$1 - x + y, 1 - x, z$
(v)	$\frac{2}{3} + y, \frac{1}{3} + x, \frac{5}{6} - z$		

Crystallography (1974). Unit weight was allotted to all reflexions. At 2170 K the 030 reflexion, which was strongest and supposed to be affected by strong thermal diffuse scattering and extinction effects, was excluded from the final stage of refinement. The final R values were 0.027 for data obtained at 300 K and 0.038 for those obtained at 2170 K. The final atomic parameters are given in Table 1.* Selected interatomic distances and bond angles are given in Table 2. The mean thermal-expansion coefficients of the selected interatomic distances were calculated from $(d_{2170} - d_{300})/[d_{300} \times (2170 - 300)]$, where d_T is the interatomic distance at T K (Table 2).

Discussion

The structure of $\alpha\text{-Al}_2\text{O}_3$ is shown in Fig. 1. The cell dimensions and the positional parameters at 300 K agree well with those given by Newnham & de Haan (1962) within their estimated standard deviations. The

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34713 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

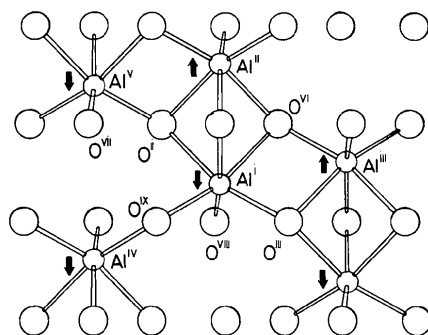


Fig. 1. The structure of α -Al₂O₃ projected on ($\bar{1}30$). The direction of the displacement of each Al atom at 2170 K is indicated by an arrow.

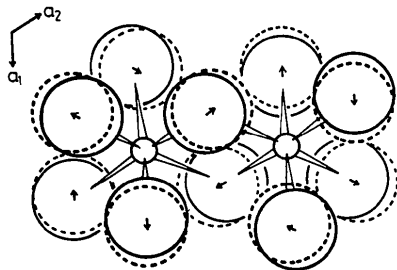


Fig. 2. The displacements of the O atoms projected along the c axis. Large solid circles show the positions of O atoms at 300 K ($x = 0.3064$) and dashed circles, those of O atoms in ideal hexagonal close packing ($x = \frac{1}{3}$). The small solid circle on the left is Al^I and that on the right is Al^{III}.

z parameter of the Al atom changes from 0.35228 (5) at 300 K to 0.3533 (2) at 2170 K, which means that the Al atom moves towards the vacant octahedral site on the threefold axis, as shown in Fig. 1. In the α -Al₂O₃ structure, each Al atom has ten nearest Al neighbours: one Al^I–Al^{II}, three Al^I–Al^{III} and six Al^I–Al^V (Table 1). The Al^I–Al^{II} bond, which is parallel to the c axis across the shared face of the coordination octahedra and is the shortest of all the Al–Al distances in the structure, increases most conspicuously from 2.657 (4) Å at 300 K to 2.744 (4) Å at 2170 K. The thermal-expansion coefficient of the distance, $17.5 (17) \times 10^{-6} \text{ K}^{-1}$, exceeds that of the c axis, $11.5 (18) \times 10^{-6} \text{ K}^{-1}$. The thermal-expansion coefficients of Al–Al distances decrease in the following order: distances across faces, distances across edges and distances across

corners. This implies that displacement of the Al atoms yields more uniform Al–Al distances between neighbouring Al atoms at high temperature.

The positional parameter x of the O atoms is 0.3064 (3) at 300 K and 0.307 (1) at 2170 K. The displacement of the O atom is less obvious than that of the Al atom. However, the shift makes the distorted close-packed plane of O atoms slightly more regular at high temperature, as shown in Fig. 2.

Two independent Al–O interatomic distances, Al^I–O^{II} and Al^I–O^{IX}, are present in the AlO₆ octahedron. The distances at 300 K are 1.971 (2) and 1.852 (1) Å and those at 2170 K are 2.024 (2) and 1.880 (1) Å, respectively. The expansion coefficient of Al^I–O^{II}, $14.4 (12) \times 10^{-6} \text{ K}^{-1}$, exceeds that of Al^I–O^{IX}, $8.1 (7) \times 10^{-6} \text{ K}^{-1}$, which indicates that the discordance in two different Al–O bond distances increases at high temperature. Since the thermal changes in the positional parameters of the O atoms are small, the increasing discordance in Al–O bond distances in an octahedron results from the increasing uniformity of neighbouring Al–Al distances. At this point, the structural change in α -Al₂O₃ differs from that of Ti₂O₃ (Rice & Robinson, 1976) in which the O atom moves in the opposite direction to that shown in Fig. 2 to minimize changes in Ti–O distances.

References

- D'AMOUR, H., SCHIFERL, D., DENNER, W., SCHULZ, H. & HAZAPFEL, W. B. (1978). Private communication.
- COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* A26, 71–83.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- MIYATA, T., ISHIZAWA, N., MINATO, I. & IWAI, S. (1979). *J. Appl. Cryst.* 12, 303–305.
- MOSS, S. C. & NEWNHAM, R. E. (1964). *Z. Kristallogr.* 120, 359–363.
- NEWNHAM, R. E. & DE HAAN, Y. M. (1962). *Z. Kristallogr.* 117, 235–237.
- NUKUI, A., TAGAI, H., MORIKAWA, H. & IWAI, S. (1976). *J. Am. Ceram. Soc.* 59, 534–536.
- RICE, C. E. & ROBINSON, W. R. (1976). *Mater. Res. Bull.* 11, 1355–1360.
- RICE, C. E. & ROBINSON, W. R. (1977). *Acta Cryst.* B33, 1342–1348.
- ZACHARIASEN, W. H. (1967). *Acta Cryst.* 23, 558–564.