

SHORT STRUCTURAL PAPERS

Papers intended for publication under this heading must be in the format prescribed in Notes for Authors, *Acta Cryst.* (1978). A34, 143–157.

Acta Cryst. (1982). B38, 889–891

Structure of Strontium Tetraaluminate β -SrAl₄O₇

BY KEN-ICHI MACHIDA, GIN-YA ADACHI* AND JIRO SHIOKAWA

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka, Suita, Osaka 565, Japan

AND MASAHIKO SHIMADA AND MITSUE KOIZUMI

Institute of Scientific and Industrial Research, Osaka University, Yamadaoka, Suita, Osaka 565, Japan

(Received 16 July 1981; accepted 10 September 1981)

Abstract. β -SrAl₄O₇ (high-pressure form), orthorhombic, *Cmma*, $a = 8.085$ (5), $b = 11.845$ (8), $c = 4.407$ (3) Å, $Z = 4$, $D_x = 4.84$, $D_m = 4.80$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 13.20$ mm⁻¹. The β -SrAl₄O₇ phase was obtained by the hydrothermal preparation method under high pressure, and the structure was determined from three-dimensional X-ray diffraction data ($R = 0.047$ for 324 observed reflections). The crystal lattice consists of a three-dimensional (Al₄O₇)_∞ network of Al(1)O₆ octahedra, and Al(2)O₄ and Al(3)O₄ tetrahedra; the Al–O bond lengths are 1.795 to 1.968 Å for the octahedra and 1.449 to 1.537 Å for the tetrahedra. These distances in AlO₄ units are considerably shorter than those in the other aluminates. Each Sr atom is surrounded by ten O atoms with interatomic distances from 2.503 to 2.664 Å.

Introduction. Some of the alkaline-earth borates, aluminates and gallates are transformed into high-pressure phases, anion units changing from triangles to tetrahedra or from tetrahedra to octahedra (Muller & Roy, 1974). The calcium metaaluminate, CaAl₂O₄, has been found to give various forms by high-pressure treatments (Reid & Ringwood, 1969; Ito, Suzuki, Inagaki & Naka, 1980). The structures of α -CaAl₄O₇ and α -SrAl₄O₇ (atmospheric-pressure form) consist of a three-dimensional (Al₄O₇)_∞ network of AlO₄ units (Boyko & Wisnyi, 1958; Goodwin & Lindop, 1970; Lindop & Goodwin, 1972). Consequently these aluminates can be expected to give a new high-pressure form of which the structural framework consists of AlO₆ octahedra. A new high-pressure phase was obtained as a by-product for runs in which single crystals of

SrAl₂O₄ were grown using water as a solvent at 3.5–5.0 MPa and 1273–1573 K. Its chemical composition was found to be SrAl₄O₇ from X-ray analyses, and thus we termed it β -SrAl₄O₇. In this paper we report the crystal structure of β -SrAl₄O₇.

The polycrystalline sample of β -SrAl₄O₇ was prepared with a cubic-anvil-type apparatus (Shimada, Ogawa, Koizumi, Dache & Roy, 1979) from a mixture of α -SrAl₄O₇ and water maintained at a pressure of 5.0 MPa and 1473 K for 60 min. In trials in which water was not included in the preparation, β -SrAl₄O₇ could not be obtained up to 5.0 MPa and unknown phases were formed. Powder X-ray diffraction and density measurements were made on the above-mentioned polycrystalline sample. The single crystals used for X-ray measurements were grown from a mixture of SrAl₂O₄ and water by cooling to 1073 K at a rate of about 2 K min⁻¹ after maintaining at 4.0 MPa and 1573 K for 60 min. Their Weissenberg photographs showed the following systematic absences: $h + k = 2n + 1$ for hkl ; $h = 2n + 1$ and $k = 2n + 1$ for $hk0$, which correspond to space group *Cmma*. The crystal data of β -SrAl₄O₇ are presented together with those of the α form in Table 1. The cell parameters were refined by the least-squares treatment of the X-ray powder diffraction pattern calibrated with high-purity Si as an internal standard.

The intensity data were measured on a Rigaku Denki automated four-circle diffractometer with Mo $K\alpha$ radiation monochromated by a graphite plate. Independent reflections within $2\theta = 60^\circ$ were collected using the ω - 2θ scan technique and among them, 324 reflections with $|F_o| > 3\sigma(|F_o|)$ were regarded as observed. The intensity data were corrected for Lorentz and polarization factors, but no correction was made for absorption.

* To whom correspondence should be addressed.

Table 1. *Crystal data for α - and β -SrAl₄O₇*(a) α form¹

$M_r = 307.54$	$c = 5.536$ (3) Å
Monoclinic	$\beta = 106.12^\circ$
Space group $C2/c$	$V = 624.9$ Å ³
$a = 13.039$ (9) Å	$Z = 4$
$b = 9.011$ (5)	$D_x = 3.268$ Mg m ⁻³

(b) β form

$M_r = 307.54$	$\lambda = 0.71069$ Å
Orthorhombic	$\mu(\text{Mo } K\alpha) = 13.20$ mm ⁻¹
Space group $Cmma$	$D_m = 4.80$ Mg m ⁻³
$a = 8.085$ (5) Å	$D_x = 4.84$
$b = 11.845$ (8)	$Z = 4$
$c = 4.407$ (3)	$F(000) = 584$
$V = 422.0$ (5) Å ³	Crystal size
	0.16 × 0.13 × 0.08 mm

(i) Lindop & Goodwin (1972).

Table 2. *Final positional and thermal parameters for β -SrAl₄O₇ with e.s.d.'s in parentheses*

	x	y	z	B (Å ²)
Sr	$\frac{1}{2}$	$\frac{1}{2}$	0	0.34 (1)
Al(1)	0	0	0	0.26 (5)
Al(2)	$\frac{1}{2}$	0	$\frac{1}{2}$	1.12 (7)
Al(3)	0	0.136 (4)	0.454 (4)	1.30 (5)
O(1)	0	$\frac{1}{4}$	0.335 (10)	0.45 (14)
O(2)	0	0.128 (7)	0.782 (7)	0.39 (9)
O(3)	0.144 (5)	0.073 (5)	0.302 (5)	0.33 (6)

The coordinate of the Sr atom was determined by a three-dimensional Patterson function, and the remaining Al and O atoms were located on successive Fourier maps. The O(3) atom is located at the general position [16(*o*) site] while the other atoms occupy the special positions: Sr, 4(*e*) site; Al(1), 4(*c*) site; Al(2), 4(*b*) site; Al(3) and O(2), 8(*m*) site; O(1), 4(*g*) site. Isotropic refinements were made on all atomic parameters by the block-diagonal least-squares method with *HBLS-V* (Ashida, 1979) to give $R = 0.047$ and $R_w = 0.061$. The atomic scattering factors for Sr, Al and O atoms were those listed in *International Tables for X-ray Crystallography* (1974). The weighting scheme $w = (F_m/F_o)^2$ for $F_o > F_m$ ($= 10.0$) and $w = 1.0$ for $F_o \leq F_m$ ($= 10.0$) was employed. The final positional and thermal parameters are listed in Table 2.*

Discussion. The interatomic distances and angles in β -SrAl₄O₇ are summarized in Table 3. The coordination number for a quarter of Al atoms increases from 4 to 6 by the high-pressure treatment, and hence

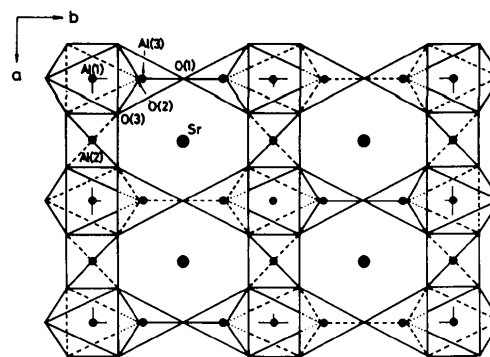
* Lists of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36385 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

there are two types of aluminate units, Al(1)O₆ octahedra, and Al(2)O₄ and Al(3)O₄ tetrahedra. These units are appreciably distorted from the regular octahedron and tetrahedron, the Al—O bond lengths and O—Al—O bond angles being 1.795–1.968 Å and 72.5–107.5° for the Al(1)O₆ unit and 1.449–1.537 Å and 98.5–115.0° for the Al(2)O₄ and Al(3)O₄ units. It is noticeable that the Al—O distances for the tetrahedral units are considerably shorter than those in some aluminates (atmospheric-pressure phases), e.g. 1.718–1.808 Å for α -SrAl₄O₇ (Lindop & Goodwin, 1972) and 1.728–1.779 Å for CaAl₂O₄ (Hörkner & Müller-Buschbaum, 1976).

A projection of the β -SrAl₄O₇ structure viewed along the *c* axis is shown in Fig. 1. The Al(1)O₆ and Al(3)O₄ units can be seen to have mirror symmetry on the (100) or (200) plane and the Al(2)O₄ tetrahedron shows the symmetry of twofold rotation around an axis parallel to the *c* axis. The structure consists of a three-dimensional (Al₄O₇)_∞ network of octahedral and

Table 3. *Interatomic distances (Å) and angles (°) in β -SrAl₄O₇ with e.s.d.'s in parentheses*

(a) The (Al ₄ O ₇) _∞ network			
Al(1) octahedron			
Al(1)—O(2)	1.795 (7) (×2)	O(2)—Al(1)—O(3)	89.5 (3) (×4)
—O(3)	1.968 (5) (×4)	O(3)—Al(1)—O(3)	90.5 (3) (×4)
			72.5 (2) (×2)
			107.5 (2) (×2)
Al(2) tetrahedron			
Al(2)—O(3)	1.498 (5) (×4)	O(3)—Al(2)—O(3)	108.7 (3) (×2)
			109.5 (3) (×2)
			110.2 (3) (×2)
Al(3) tetrahedron			
Al(3)—O(1)	1.449 (11)	O(1)—Al(3)—O(2)	115.0 (5)
—O(2)	1.449 (8)	O(1)—Al(3)—O(3)	107.2 (5) (×2)
—O(3)	1.537 (6) (×2)	O(2)—Al(3)—O(3)	113.8 (4) (×2)
		O(3)—Al(3)—O(3)	98.5 (3)
(b) Sr—O distances			
Sr—O(1)	2.503 (10) (×2)	Sr—O(3)	2.627 (5) (×4)
—O(2)	2.664 (7) (×4)		

Fig. 1. A projection of the β -SrAl₄O₇ structure viewed along the *c* axis.

tetrahedral units with shared corner O atoms, which is appreciably denser than the structural framework of α -SrAl₄O₇. This reflects the observation that the density of SrAl₄O₇ drastically increases with the phase transformation from α to β (see Table 1).

The structure viewed along the a axis is illustrated in Fig. 2. The units of Al(1)O₆ and Al(3)O₄ are linked together to form a kind of layer on the (100) or (200) plane, which is three-dimensionally connected with the other layers by Al(2)O₄ tetrahedra. The Sr atoms are located in tunnels of (Al₄O₇)_∞ network running parallel to the a axis.

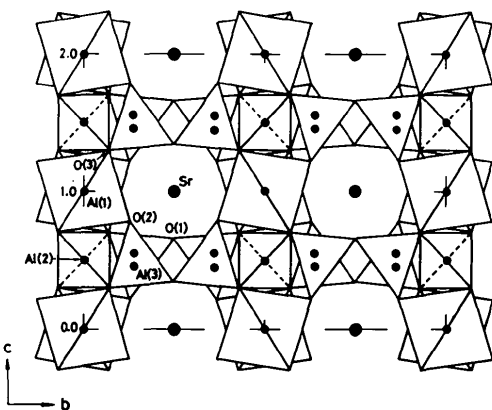


Fig. 2. A projection of the β -SrAl₄O₇ structure viewed along the a axis.

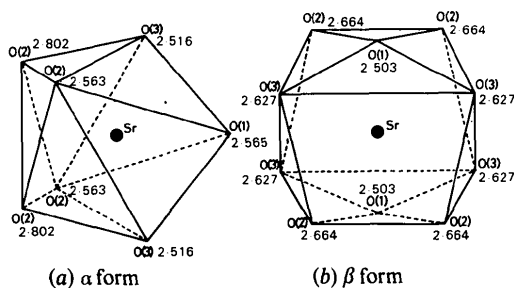


Fig. 3. Schematic illustration of the SrO_{*n*} polyhedra in the SrAl₄O₇ polymorphs. The numerical values represent the Sr—O distances between nearest neighbors (Å).

The anion environments around Sr atoms in α - and β -SrAl₄O₇ are illustrated in Fig. 3. The Sr atoms are surrounded by seven and ten O atoms for the α and β phases to form SrO₇ and SrO₁₀ polyhedra respectively. The Sr—O distances are closely similar to each other (mean values: 2.618 Å, α form; 2.617 Å, β form). The symmetry of SrO₁₀ is seen to be high compared with that of SrO₇ polyhedra, because the SrO₁₀ polyhedra have the symmetries of mirror and twofold rotation but the SrO₇ polyhedra show only that of twofold rotation around the Sr—O(1) axis.

The authors wish to thank Mr N Ogawa for the preparation of samples, and Drs N. Kasai, N. Yasuoka and K. Miki for their valuable suggestions on X-ray structural analyses. The computations were carried out on an ACOS series 77 NEAC System 700 Computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

References

- ASHIDA, T. (1979). *HBL5-V, The Universal Crystallographic Computing System* — Osaka, pp. 53–59. The Computation Center, Osaka Univ.
- BOYKO, E. R. & WISNYI, L. G. (1958). *Acta Cryst.* **11**, 444–445.
- GOODWIN, D. W. & LINDOP, A. J. (1970). *Acta Cryst.* **B26**, 1230–1235.
- HÖRKNER, W. & MÜLLER-BUSCHBAUM, H.K. (1976). *J. Inorg. Nucl. Chem.* **38**, 983–984.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- ITO, S., SUZUKI, K., INAGAKI, M. & NAKA, S. (1980). *Mater. Res. Bull.* **15**, 925–932.
- LINDOP, A. J. & GOODWIN, D. W. (1972). *Acta Cryst.* **B28**, 2625–2626.
- MULLER, O. & ROY, R. (1974). *The Major Ternary Structural Families*, pp. 62–63, 71, 78. New York: Springer-Verlag.
- REID, A. F. & RINGWOOD, A. E. (1969). *Earth Planet. Sci. Lett.* **6**, 205.
- SHIMADA, M., OGAWA, N., KOIZUMI, M., DACHILLE, F. & ROY, R. (1979). *Am. Ceram. Soc. Bull.* **58**, 519–521.