

Structure of Synthetic Potassium Zinc Silicate: $K_2Zn_2Si_8O_{19}$

BY A. KAWAHARA, S. KOHARA, N. KONISHI* AND J. HORIUCHI†

Department of Earth Sciences, Faculty of Science, Okayama University, Tsushima, Okayama 700, Japan

AND K. KAWAMURA

Chemical Institute, Faculty of Science, University of Kokkaido, Sapporo 060, Japan

(Received 12 March 1990; accepted 22 May 1990)

Abstract. Dipotassium dizinc octasilicate, $K_2Zn_2Si_8O_{19}$, $M_r = 737.7$, monoclinic, $C2$, $a = 13.769$ (3), $b = 5.079$ (1), $c = 12.403$ (4) Å, $\beta = 107.25$ (4)°, $V = 828.4$ (4) Å³, $Z = 2$, $D_x = 2.96$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 4.14$ mm⁻¹, $F(000) = 724$, $T = 298$ K, final $R = 0.047$ for 987 independent reflections. The structure contains three-dimensional SiO_4 networks having eight-, ten- and twelve-membered rings of SiO_4 tetrahedra with three kinds of non-bridging O atoms (mean Si—O: 1.607 Å). Zn atoms are connected to the non-bridging O atoms in tetrahedral coordination, thus constructing zigzag ZnO_4 chains along the twofold screw axes (mean Zn—O: 1.952 Å). This structure belongs to a new type of silicate and is expressed by the Liebau classification as $K_2Zn_2\{oB_3\}_\infty [{}^6Si_8O_{19}]$. K atoms have nine nearest O atom neighbours and are situated in the cavities of the Si, Zn and O frameworks (mean K—O: 2.964 Å).

Introduction. The systematization of SiO_4 polyanion configurations is important from the stereochemical viewpoint of the formation of silicates, and the common silicate frameworks have been investigated in detail. The structure of zinc silicate, unusual in silicate stereochemistry, has not been studied extensively. In zinc silicates, in contrast with zinc phosphates, Zn atoms are all tetrahedrally coordinated by O atoms. There is also controversy about whether Zn atoms should be included in silicate polyanion structures (Zoltai, 1960). The structures of non-alkali zinc silicates and sodium zinc silicates have been investigated by several authors (Klaska, Eck & Pohl, 1978; Marumo & Syono, 1968; Hesse, Liebau & Boehm, 1977; Plakhov & Belov, 1977, 1979; Simonov, Belokoneva & Belov, 1976; Simonov, Belokoneva & Belov, 1980). As regards potassium zinc silicates, however, only a few compounds have been studied.

* Present address: 1559, Tsujita, Mabicho, Kibigun, Okayama-710-11, Japan.

† Present address: Fuji Facom Corporation, Shinjuku-Koyama Building, 4-Chome 30-3, Yoyogi, Shibuya, Tokyo-151, Japan.

Too few structures have been determined for a systematic description of zinc silicates and so the synthesis of new phases is very important. In view of this, the authors tried to synthesize a series of potassium zinc silicates, $K_xZn_ySi_pO_q$, and several new phases have been obtained. The present paper reports the structure of one of these new phases obtained by hydrothermal synthesis.

Experimental. The title compound was synthesized hydrothermally with a test-tube-type apparatus (773 K, 1000 kg cm⁻², 96 h) from a mixture of K_2CO_3 , ZnO, SiO_2 (gels) and H_2O . The chemical composition of the reaction product was confirmed by X-ray microprobe analysis. The crystals of $K_2Zn_2Si_8O_{19}$, named tentatively phase *M*, were colourless and transparent with glassy lustre and gave no apparent euhedral forms. A crystal of dimensions 0.03 × 0.02 × 0.02 mm was used for intensity measurement. The intensity data were collected on a Philips four-circle diffractometer with the 2θ - ω -scan technique, Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å) and a graphite monochromator. Standard reflections: 311, 602, $\bar{5}36$; variation: 4.1%. Of the 1423 reflections collected up to $2\theta = 56^\circ$ ($-18 < h < 17$, $0 < k < 6$, $0 < l < 16$), 987 had $I > 3\sigma(I)$. The intensity data were corrected for Lorentz-polarization effects but not for absorption because of the minute crystal size. The lattice dimensions were calculated from 20 reflections with $5 < 2\theta < 25^\circ$. The powder diffraction data were collected on a Rigaku powder diffractometer with a graphite monochromator using Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å) with silicon as an internal standard. These data are listed in Table 1.

The Wilson statistical method and Patterson peaks in the (010) plane gave the space group as $C2$. Zn atoms were located by Patterson synthesis and the other atoms were located on subsequent Fourier maps. Full-matrix least-squares refinement with anisotropic temperature factors for Zn, K and Si and isotropic temperature factors for O, minimizing

Table 1. *X-ray powder data*

d_{obs}	I/I_0	h	k	l	d_{calc}
11.95	32	0	0	1	11.845
5.96	23	0	0	2	5.922
5.27	18	$\frac{2}{2}$	0	2	5.241
4.57	41	$\frac{1}{1}$	1	1	4.571
4.25	10	1	1	1	4.246
3.946	27	0	0	3	3.948
3.524	36	1	1	2	3.521
3.410	24	$\frac{3}{3}$	1	1	3.400
3.324	100	$\frac{3}{3}$	1	0	3.318
3.215	26	$\frac{3}{3}$	1	2	3.220
3.064	44	$\frac{2}{2}$	0	4	3.061
3.024	44	3	1	1	3.024
2.965	90	0	0	4	2.961
2.886	27	$\frac{3}{3}$	1	3	2.879
2.645	41	$\frac{1}{1}$	1	4	2.641
2.514	18	$\frac{3}{3}$	1	4	2.507
2.489	9	0	2	1	2.483
2.306	9	$\frac{3}{3}$	1	3	2.299
2.292	9	6	0	2	2.288
2.048	9	2	0	5	2.044
1.943	9	4	2	3	1.939
1.809	18	4	2	2	1.806

Table 2. *Atomic positional parameters* ($\times 10^5$ for Zn, $\times 10^4$ for other atoms) and *equivalent isotropic temperature factors* (B_{eq} for Zn, K and Si; B_{iso} for O) with *e.s.d.'s* in parentheses

$$B_{\text{eq}} = (4/3)(a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + abc\cos\gamma\beta_{12} + accos\beta\beta_{13} + bccos\alpha\beta_{23}).$$

	x	y	z	$B_{\text{eq}}/B_{\text{iso}}(\text{\AA}^2)$
Zn	19993 (7)	50000	41159 (8)	0.63 (2)
K	3768 (2)	312 (6)	3510 (2)	1.46 (5)
Si(1)	731 (2)	28 (7)	4246 (2)	0.62 (5)
Si(2)	2042 (2)	5914 (6)	1598 (2)	0.63 (5)
Si(3)	3743 (2)	8455 (6)	729 (2)	0.64 (5)
Si(4)	22 (2)	8567 (6)	1672 (2)	0.67 (5)
O(1)	4220 (5)	1215 (16)	1262 (6)	1.35 (12)
O(2)	2917 (5)	7803 (16)	1366 (6)	1.31 (12)
O(3)	1074 (5)	7835 (16)	1452 (6)	1.34 (12)
O(4)	2443 (5)	4671 (16)	2812 (5)	1.21 (12)
O(5)	134 (5)	8912 (15)	2989 (5)	0.99 (11)
O(6)	1812 (5)	8544 (15)	4663 (5)	0.78 (10)
O(7)	5000	4039 (20)	5000	1.12 (16)
O(8)	830 (5)	3129 (15)	4278 (6)	1.17 (12)
O(9)	1749 (5)	3700 (16)	608 (6)	1.22 (12)
O(10)	4592 (5)	6194 (15)	1008 (5)	1.17 (12)

$\sum w(\Delta F)^2$, reduced R to 0.043, $wR = 0.052$, $w = 1/\sigma(F)^2$, $S = 1.39$, $(\Delta/\sigma)_{\text{max}} = 0.15$, and $(\Delta\rho)_{\text{max,min}} = 1.49, -1.35 \text{ e \AA}^{-3}$.

Atomic scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Table 2 gives the final positional parameters and equivalent isotropic thermal factors* of the atoms.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53250 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The calculations were carried out at the Data Processing Centre of Okayama University using the modified programs of *UNICS* (Sakurai, 1971).

Discussion. The structure of phase *M* is shown stereographically in Fig. 1 using *ORTEP* (Johnson, 1965).

All the Si atoms lie in general positions. Si(3) and Si(4) tetrahedra share all their corners with other SiO_4 tetrahedra, while Si(2) shares three, and Si(1) two corners, respectively. These tetrahedra form layers with twelve-membered rings parallel to (010), which are stacked by sharing apex O atoms to construct a three-dimensional network structure having eight- and ten-membered SiO_4 rings. Zn atoms are in general positions and form distorted tetrahedra with the non-bridging O atoms of the SiO_4 tetrahedra, thus giving zigzag ZnO_4 chains along the twofold screw axes (mean Zn—O 1.952 \AA). In this case, the proposition that the Zn atoms should be included in the Si—O tetrahedral framework (Zoltai, 1960) can hardly be acceptable. This structure belongs to a new silicate type and is expressed as $\text{K}_2\text{Zn}_2\{\text{o}B_{\infty}^3\}[\text{Si}_8\text{O}_{19}]$ according to Liebau's classification (Liebau, 1985). Here, the symbol *oB* stands for 'open Branched', and ∞ represents 'three-dimensional frameworks'. The superscript 6 of ${}^6\text{Si}$ corresponds to the number of tetrahedra within one repeating unit of the linear part of the chain (periodicity 'sechser'). The structural scheme is illustrated in Fig. 2. K atoms located in the cavities of these Si—O frameworks have nine nearest neighbour O atoms.

The interatomic distances and bond angles are listed in Table 3. The Si—O distances are comparable with those in previous investigations (Marumo & Syono, 1968; Klaska, Eck & Pohl, 1978;

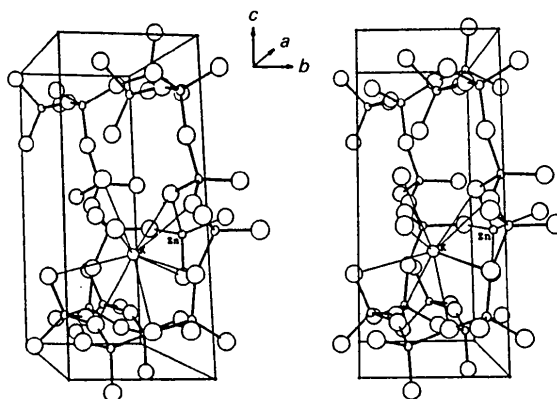


Fig. 1. Stereoscopic drawing of the structure of $\text{K}_2\text{Zn}_2\text{Si}_8\text{O}_{19}$. The figure represents one of the rings of SiO_4 tetrahedra with Zn and K atoms.

Egorov-Tismenko, Simonov & Belov, 1978; Plakhov & Belov, 1979; Yu, Smith & Austerman, 1978). The Si—O distances are significantly longer when the oxygen is shared with another Si atom than when shared with a Zn atom (1.611 and 1.588 Å on average). These bond lengths are comparable with those calculated from previous works (Plakhov & Belov, 1977; Hesse, Liebau & Boehm, 1977; Simonov, Belokoneva & Belov, 1976, 1980; Kohara & Kawahara, 1990). The average Si—O distances for the four kinds of SiO₄ tetrahedra are 1.617, 1.612, 1.602 and 1.598 Å, respectively. The O—Si—O bond angles are slightly distorted as compared with those in the idealized SiO₄ tetrahedron (distortion indices of SiO₄ tetrahedra 4.29×10^{-2} , 3.54×10^{-2} , 2.92×10^{-3} and 1.33×10^{-2} , respectively) (Liebau, 1985). The bonds in the K—O polyhedra are ionic and can absorb all the strains coming from the rather rigid Si, Zn—O frameworks. This explains why compounds A_xZn_ySi_pO_q (A = alkali metal) are more abundant than Zn_xSi_pO_q.

The employment of isotropic thermal parameters for O atoms in the final refinement and the rather high e.s.d. values of oxygen positional parameters in Table 2 are a result of the minute size of the crystal and crystallogenic problems. The synthesis of single crystals suitable for perfect structure analysis is difficult by hydrothermal methods currently available.

The sums of electrostatic charges calculated using the parameters of Brown & Wu (1976) are satisfactory, ranging from 1.88 to 2.18 for O, 2.06 for Zn, 1.02 for K and ranging from 4.07 to 4.27 v.u. for Si atoms.

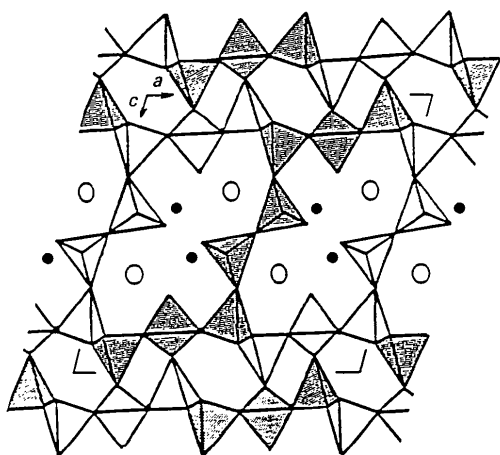


Fig. 2. Linkage of Si tetrahedra in the unit cell. The framework consists of such Si—O layers. The shaded tetrahedra are related to the white ones by 2_1 operations. The large open circles and the small closed ones correspond to K and Zn atoms, respectively.

Table 3. Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses

Si(1)—O(5)	1.633 (6)	Si(3)—O(9)	1.599 (7)
Si(1)—O(6)	1.611 (7)	Si(3)—O(10)	1.602 (8)
Si(1)—O(7)	1.643 (4)	Si(4)—O(1)	1.604 (8)
Si(1)—O(8)	1.580 (8)	Si(4)—O(3)	1.595 (9)
Si(2)—O(2)	1.631 (8)	Si(4)—O(5)	1.604 (7)
Si(2)—O(3)	1.618 (9)	Si(4)—O(10)	1.587 (8)
Si(2)—O(4)	1.574 (7)	Zn—O(4)	1.898 (7)
Si(2)—O(9)	1.625 (8)	Zn—O(6)	1.968 (8)
Si(3)—O(1)	1.605 (8)	Zn—O(6)'	2.012 (6)
Si(3)—O(2)	1.600 (9)	Zn—O(8)	1.931 (8)
K—O(1)	3.066 (9)	K—O(6)	3.089 (8)
K—O(2)	2.867 (8)	K—O(7)	2.831 (7)
K—O(4)	3.369 (8)	K—O(8)	2.931 (7)
K—O(4)''	2.836 (8)	K—O(8)'''	2.857 (8)
K—O(5)	2.832 (8)		
O(5)—Si(1)—O(6)	107.4 (4)	O(2)—Si(3)—O(9)	112.6 (4)
O(5)—Si(1)—O(7)	102.6 (3)	O(2)—Si(3)—O(10)	109.0 (4)
O(5)—Si(1)—O(8)	112.6 (4)	O(9)—Si(3)—O(10)	109.7 (4)
O(6)—Si(1)—O(7)	109.8 (4)	O(1)—Si(4)—O(3)	110.3 (4)
O(6)—Si(1)—O(8)	113.2 (4)	O(1)—Si(4)—O(5)	104.7 (4)
O(7)—Si(1)—O(8)	110.7 (5)	O(1)—Si(4)—O(10)	110.2 (4)
O(2)—Si(2)—O(3)	104.6 (4)	O(3)—Si(4)—O(5)	112.4 (4)
O(2)—Si(2)—O(4)	109.7 (4)	O(3)—Si(4)—O(10)	109.0 (4)
O(2)—Si(2)—O(9)	107.7 (4)	O(5)—Si(4)—O(10)	110.2 (4)
O(3)—Si(2)—O(4)	113.1 (4)	O(4)—Zn—O(6)	118.9 (3)
O(3)—Si(2)—O(9)	108.7 (4)	O(4)—Zn—O(6)'	102.4 (3)
O(4)—Si(2)—O(9)	112.5 (4)	O(4)—Zn—O(8)	122.3 (3)
O(1)—Si(3)—O(2)	104.0 (4)	O(6)—Zn—O(6)'	103.7 (3)
O(1)—Si(3)—O(9)	110.8 (4)	O(6)—Zn—O(8)	102.4 (3)
O(1)—Si(3)—O(10)	110.7 (4)	O(6)—Zn—O(8)	104.9 (3)

Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} + y, -z$; (ii) $x, -1 + y, z$; (iii) $\frac{1}{2} - x, \frac{1}{2} + y, -z$.

The authors thank Professor Y. Iitaka, Pharmaceutical Institute, University of Tokyo, for the four-circle diffractometer at the authors' disposal.

References

- BROWN, I. D. & WU, K. K. (1976). *Acta Cryst.* **B32**, 1957–1959.
- EGOROV-TISENKO, Y. K., SIMONOV, M. A. & BELOV, N. V. (1978). *Sov. Phys. Dokl.* **23**, 99–100.
- HESSE, K. F., LIEBAU, F. & BOEHM, H. (1977). *Acta Cryst.* **B33**, 1333–1337.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- KLASKA, K. H., ECK, J. C. & POHL, D. (1978). *Acta Cryst.* **B34**, 3324–3325.
- KOHARA, S. & KAWAHARA, A. (1990). *Acta Cryst.* **C46**, 1373–1376.
- LIEBAU, F. (1985). *Structural Chemistry of Silicates*, pp. 69–75, 250. Berlin: Springer-Verlag.
- MARUMO, F. & SYONO, Y. (1968). *Acta Cryst.* **B27**, 1868–1870.
- PLAKHOV, G. F. & BELOV, N. V. (1977). *Sov. Phys. Dokl.* **22**, 709–711.
- PLAKHOV, G. F. & BELOV, N. V. (1979). *Kristallografiya*, **24**, 1177–1183.
- SAKURAI, T. (1971). Editor. *Universal Crystallographic Computation Program System*. The Crystallographic Society of Japan, Tokyo, Japan.
- SIMONOV, M. A., BELOKONEVA, E. L. & BELOV, N. V. (1976). *Zh. Strukt. Khim.* **18**, 203–206.
- SIMONOV, M. A., BELOKONEVA, E. L. & BELOV, N. V. (1980). *Kristallografiya*, **25**, 1282–1284.
- YU, S. C., SMITH, D. K. & AUSTERMAN, S. B. (1978). *Am. Mineral.* **63**, 1241–1248.
- ZOLTAI, T. (1960). *Am. Mineral.* **45**, 960–973.