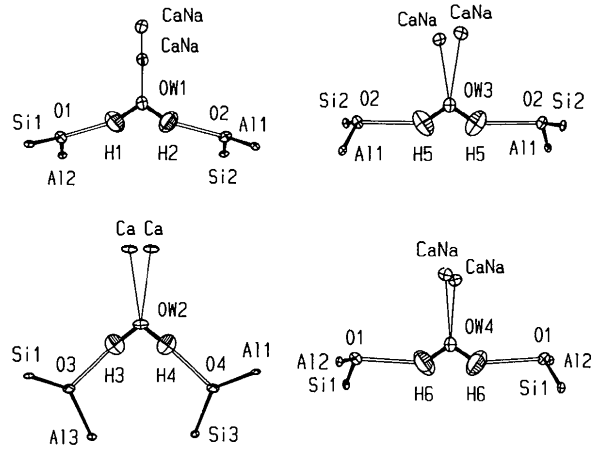

Fig. 2. The water coordination in thomsonite at 13 K. Thermal ellipsoids are scaled to include 75% probability. Only one of the Ca sites coordinating $OW(2)$ is occupied.

occupancy requirements. It results in the calculated occupancy factors 0·998 and 1·007, which are within 3 e.s.d.'s of the refined values, and a composition that is within the limits of error of the microprobe analysis.

The NaCa coordination is changed very little between 13 and 295 K except for NaCa—$OW(1)$: 2·433 (1) (13 *K*) and 2·452 (1) Å (295 K). The Ca coordination shows more significant changes. The Ca–Ca separation is larger at 13 K, 0·659 (2) Å as compared with 0·565 (2) Å at 295 K, resulting in a more asymmetric coordination at 13 K: Ca—O(8) and Ca—O(9) decrease by 0·031 Å while Ca—O(8)′ and Ca—O(9)′ increase by 0·047 Å on lowering the temperature to 13 K.

The shortest hydrogen bonds involving $OW(1)$ and $OW(2)$ become even shorter and increase their OW—H···O angles on cooling, while the opposite is true for the longer hydrogen bonds involving $OW(3)$ and $OW(4)$. The largest change is observed for H(5)···O(2), 1·965 (2) (13 K) to 1·945 (3) Å (295 K), and is accompanied by a large change in the water angle, 110·9 (2) (13 K) to 112·5 (4)° (295 K). The flexibility of the water angle is also demonstrated in the distribution of water angles in thomsonite, 104·6 (1) to 110·9 (2)°, which is highly correlated to the distance between the two hydrogen-bond acceptors (Kvick, 1986). A short acceptor–acceptor distance results in a small water angle as was also demonstrated in scolecite (Kvick *et al.*, 1985).

We wish to thank Mr J. Henriques for valuable technical assistance during data collection. KS thanks the Swedish Natural Sciences Research Council and JVS the US National Science Foundation (CHE 86) for their financial support.

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Acta Cryst. (1990). **C46**, 1373–1376

Structure of Synthetic Dipotassium Zinc Tetrasilicate

By S. Kohara and A. Kawahara

Department of Earth Sciences, Faculty of Science, Okayama University, Tsushima-Naka 1-1, *Okayama* 700, *Japan*

(*Received* 29 *August* 1989; *accepted* 30 *November* 1989)

Abstract. $K_2ZnSi_4O_{10}$, $M_r = 415·9$, orthorhombic, $P2_12_12_1$, $a = 10·0676$ (8), $b = 14·047$ (1), $c = 7·0673$ (8) Å, $V = 999·4$ (2) Å^3, $Z = 4$, $D_x = 2·76$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 3·85$ mm^{-1}, $F(000) = 816$, $T = 293$ K, final $R = 0·048$ for 1656 independent reflections. The structure is built from a tectosilicate framework containing SiO_4 (mean Si—O 1·618 Å) and ZnO_4 (mean Zn—O 1·950 Å) tetrahedra and large cavities for K atoms. The SiO_4 tetrahedra form three-dimensional frameworks built up by ten-membered rings parallel to the (100) plane connected to other rings by

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bridging apex O atoms of the tetrahedra. This structure belongs to the new silicate frameworks and can be described by the structural formula $K_4Zn_2\{oB,^3_\infty\}[^6Si_8O_{20}]$ after the classification symbol of Liebau [*Structural Chemistry of Silicates* (1985). Berlin: Springer]. The two kinds of K atoms gave eight and nine nearest neighbor O atoms (mean K—O 3·069 and 3·029 Å).

Introduction. The structure of Zn alkali silicates is important from the viewpoint of the classification of silicate framework structures. In zinc silicates, Zn atoms are all tetrahedrally coordinated by O atoms in contrast to Zn phosphates. There is also controversy as to whether Zn atoms can be included in the silicate anion structures in the systematization of the silicates (Zoltai, 1960). The non-alkali Zn silicates and Na–Zn silicates have been investigated by several authors.

The number of known structures is not sufficient to make a systematization of Zn silicates. Accordingly, the synthesis of new phases is very important. Hence, the authors tried to carry out the hydrothermal syntheses 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 which has been obtained by hydrothermal synthesis.

Experimental. The synthesis of the title compound was carried out with test-tube-type apparatus (873 K, 1000 kg cm^{-3}, 72 h) with a reagent mixture of K_2CO_3, ZnO, SiO_2 and H_2O. Crystals of $K_2ZnSi_4O_{10}$, with euhedral forms, were colorless, transparent and of glassy luster. They luminesce under ultraviolet light. The chemical composition was determined by EPMA analysis. A crystal measuring 0·3 × 0·1 × 0·1 mm was used for data collection. The intensities of the reflections were measured on a Rigaku diffractometer with graphite monochromated Mo $K\alpha$ radiation and 2θ–ω scans. 3 standard reflections monitored every 100 reflections, 3·0% variation. 1710 intensities were collected up to $2\theta = 56°$ ($0 < h < 14$, $0 < k < 19$, $0 < l < 9$); of these, 1656 intensities with $I > 3\sigma(I)$ were classified as observed. A Lorentz–polarization correction was made but no absorption correction. The lattice dimensions were calculated from 20 reflections with $57 < 2\theta < 61°$ using Cu $K\alpha$ ($\lambda = 1·5418$ Å). The powder-diffraction data were collected on a Rigaku powder diffractometer equipped with a graphite monochromator using Cu $K\alpha$ radiation. The specimen was mixed with a small amount of silicon powder as internal standard. Relevant data are in Table 1.

Table 1. *Powder-diffraction data*

d	*I*	*hkl*	*d*	*I*	*hkl*
8·261	16	110	3·276	54	310
7·075	24	001, 020	3·246	83	112
6·366	11	011	3·162	14	022, 041
5·824	13	120	3·087	21	231
5·007	11	021	3·010	27	122, 141
4·741	40	210	2·971	41	311
4·480	33	121	2·724	32	330, 132
4·101	32	201, 220	2·673	16	222, 241
3·914	30	031	2·547	37	331
3·645	29	131	2·421	16	142
3·510	71	040	2·233	10	023, 242
3·430	100	012, 230			

Table 2. *Atomic positional parameters* (× 10^4) *and equivalent isotropic thermal parameters, with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{3}{4}(a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab\cos\gamma.\beta_{12} + ac\cos\beta.\beta_{13} + bc\cos\alpha.\beta_{23}).$$

	x	*y*	*z*	B_{eq}
Zn	1934 (1)	3545 (1)	166 (2)	0·69 (2)
K(1)	3261 (3)	3998 (2)	5102 (4)	2·07 (5)
K(2)	3977 (3)	1178 (2)	2315 (4)	2·18 (6)
Si(1)	4825 (2)	4215 (2)	9690 (4)	0·61 (5)
Si(2)	973 (3)	2267 (2)	3259 (4)	0·66 (5)
Si(3)	4401 (2)	991 (2)	7336 (4)	0·64 (5)
Si(4)	3457 (2)	8209 (2)	2358 (4)	0·60 (5)
O(1)	753 (7)	9868 (5)	780 (10)	1·10 (14)
O(2)	1711 (7)	5510 (4)	4737 (12)	1·26 (14)
O(3)	4667 (7)	8821 (5)	3285 (10)	1·10 (14)
O(4)	60 (8)	1584 (5)	1905 (11)	1·68 (16)
O(5)	2267 (8)	2673 (5)	2279 (11)	1·39 (16)
O(6)	3648 (8)	8371 (4)	90 (10)	1·32 (14)
O(7)	38 (8)	8102 (5)	1074 (10)	1·21 (15)
O(8)	2092 (7)	8757 (5)	3045 (10)	1·32 (15)
O(9)	318 (7)	4259 (5)	919 (10)	0·90 (13)
O(10)	3452 (7)	7112 (5)	2833 (11)	1·13 (14)

The Zn atom was found from Patterson syntheses, and the other atoms were found on the subsequent Fourier maps. Full-matrix least-squares refinement with anisotropic temperature factors, minimizing $\sum w(\Delta F)^2$, gave $R = 0·048$, $wR = 0·067$, $w = 1$, $S = 2·53$, $(\Delta/\sigma)_{max} = 0·24$, $(\Delta/\sigma)_{av} = 0·07$ and $(\Delta\rho)_{max,min} = 1·17, -0·83$ e Å^{-3}.

Scattering factors corresponding to neutral atoms were used throughout the calculations (from *International Tables for X-ray Crystallography*, 1974). The final positional and equivalent isotropic temperature-factor parameters are shown in Table 2.*

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

Discussion. A stereographic figure of the structure of $K_2ZnSi_4O_{10}$ is shown in Fig. 1 (Johnson, 1965). The structure consists of three-dimensional SiO_4

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52813 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

frameworks built up by ten-membered rings of SiO_4 tetrahedra in the *bc* plane in the cell, connected by other ten-membered rings using apex O atoms of every four ring tetrahedra. The mode of linkage of these ten-membered rings of SiO_4 is illustrated in Fig. 2.

The SiO_4 frameworks can be described by the following structural formula: $K_4Zn_2\{oB,{}^3_\infty\}[{}^6Si_8O_{20}]$ after the classification symbol of Liebau (1985). Here, the symbols *oB* are the first letters of 'open Branched', and ${}^3_\infty$ indicates 'three-dimensional framework', while the superscript 6 on Si corresponds to the number of tetrahedra within one repeating unit of the linear part of the chain (periodicity 'sechser') within one period. This structure belongs to the new type of silicate. Zn atoms are tetrahedrally coordinated and are connected to Si–O rings by corner sharing. The ZnO_4 tetrahedron may be considered as part of three-dimensional SiO_4 frameworks (Zoltai, 1960). In this case, the tetrahedral frameworks of Si and Zn form a tectosilicate structure. K(1) and K(2) have eight and nine nearest neighbor O atoms, respectively. These coordination polyhedra are located in the cavities of these ten-membered rings.

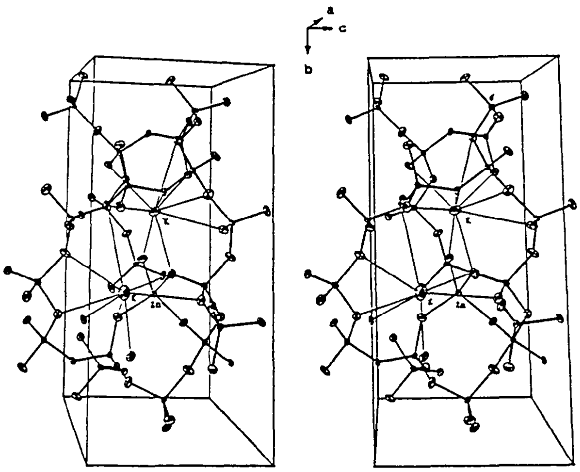

Fig. 1. Stereographic view of the structure of $K_2ZnSi_4O_{10}$. The figure shows one of the ten-membered rings of SiO_4 tetrahedra containing one Zn and two K atoms.

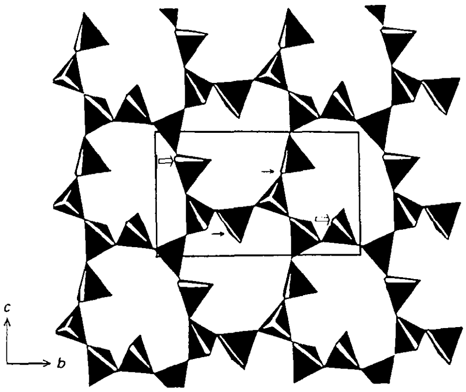

Fig. 2. The mode of linkage of SiO_4 tetrahedra. The framework structure is divided into layered Si–O networks. ⟹ represents O atoms linked to Si of the upper layer network, and → represents O atoms to those of the lower layer network.

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

Zn—O(2)	1·927 (7)	O(2)—Zn—O(5)	115·4 (3)
—O(5)	1·960 (8)	—O(9)	105·9 (3)
—O(9)	1·984 (7)	—O(10)	109·7 (3)
—O(10)	1·929 (8)	O(5)—Zn—O(9)	104·6 (3)
		—O(10)	112·7 (3)
		O(9)—Zn—O(10)	107·8 (3)
K(1)—O(2)^{i}	2·648 (7)	K(2)—O(1)	2·869 (8)
—O(2)$'^{i}$	3·348 (9)	—O(3)	3·452 (8)
—O(3)	3·185 (8)	—O(5)	2·716 (8)
—O(4)	2·902 (8)	—O(6)	3·351 (8)
—O(5)	2·906 (8)	—O(7)	3·011 (8)
—O(6)	3·237 (8)	—O(8)	3·205 (8)
—O(7)	3·479 (8)	—O(9)	2·725 (8)
—O(9)	2·894 (8)	—O(10)	2·904 (8)
—O(10)	3·022 (8)		
Si(1)—O(1)	1·626 (7)	Si(2)—O(4)	1·637 (8)
—O(2)	1·594 (7)	—O(5)	1·582 (8)
—O(3)	1·617 (8)	—O(6)	1·620 (7)
—O(4)	1·608 (8)	—O(7)	1·623 (8)
Si(3)—O(1)	1·640 (8)	Si(4)—O(3)	1·629 (7)
—O(7)	1·655 (8)	—O(6)	1·630 (8)
—O(8)	1·623 (7)	—O(8)	1·648 (7)
—O(9)	1·580 (8)	—O(10)	1·577 (8)
O(1)—Si(1)—O(2)	111·7 (4)	O(4)—Si(2)—O(5)	114·7 (4)
—O(3)	105·7 (4)	—O(6)	106·0 (4)
—O(4)	109·0 (4)	—O(7)	104·0 (4)
O(2)—Si(1)—O(3)	111·8 (4)	O(5)—Si(2)—O(6)	110·8 (4)
—O(4)	109·1 (4)	—O(7)	112·5 (4)
O(3)—Si(1)—O(4)	109·6 (4)	O(6)—Si(2)—O(7)	108·4 (4)
O(1)—Si(1)—O(7)	103·7 (4)	O(3)—Si(4)—O(6)	103·5 (4)
—O(8)	106·3 (4)	—O(8)	105·0 (4)
—O(9)	114·5 (4)	—O(10)	115·6 (4)
O(7)—Si(3)—O(8)	108·3 (4)	O(6)—Si(4)—O(8)	108·8 (4)
—O(9)	113·1 (4)	—O(10)	110·2 (4)
O(8)—Si(3)—O(9)	110·4 (4)	O(8)—Si(4)—O(10)	113·0 (4)

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

The interatomic distances and angles are listed in Table 3. Si—O and Zn—O distances agree with previous data (Marumo & Syono, 1968; Klaska, Eck & Pohl, 1978; Egorov-Tismenko, Simonov & Belov, 1978; Plakhov & Belov, 1979; Yu, Smith & Austerman, 1978). Si—O distances bridging with other Si atoms (mean 1·631 Å) are significantly longer than those bridging with Zn atoms (mean 1·583 Å), which is consistent with the values calculated from previous investigations (Plakhov & Belov, 1977; Hesse, Liebau & Böhm, 1977; Simonov, Belokoneva & Belov, 1976, 1980). The average Si—O distances for four SiO_4 tetrahedra are 1·612, 1·615, 1·625 and 1·621 Å, respectively, and the O—Si—O angles are slightly distorted compared with idealized SiO_4 tetrahedra (deviations from mean values $8{\cdot}67 \times 10^{-4}$, $9{\cdot}07 \times 10^{-2}$, $7{\cdot}75 \times 10^{-2}$ and $9{\cdot}55 \times 10^{-2\circ}$, respectively) (Liebau, 1985). The K—O polyhedra are irregular in shape and bondings are ionic. Thus, these polyhedra compensate for all the strains derived from the framework constructed by the rigid, rather covalent sp^3 configuration of SiO_4 and ZnO_4. This is consistent with the fact that compounds containing $A_xZn_ySi_pO_q$ (A = alkali metal) are more abundant than those containing only $Zn_xSi_pO_q$.

The rather large values of the standard deviations of the oxygen positional parameters in Table 2 may be attributed to both the small size of the crystal specimen and crystallogenetic problems. The syntheses of better single crystals for more precise structure analyses are still difficult by currently used hydrothermal methods.

The sum of electrostatic charges calculated with the parameters of Brown & Wu (1976) is satisfactory, ranging from 1·86 to 2·11 for O, 2·057 for Zn, from 0·804 to 0·805 for K and from 4·009 to 4·095 valence units for Si atoms.

The intensity measurements were carried out at the Research Center for Protein Engineering, Institute for Protein Research, Osaka University. The authors thank the staff at the Research Center for their kind help with the manipulation of the four-circle diffractometer.

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Acta Cryst. (1990). **C46**, 1376–1378

Room-Temperature Structure of $La_2O_2S_2$

By J. Ostoréro

Laboratoire de Magnétisme et d'Optique des Solides, CNRS, 1 *Place A. Briand,* 92190 *Meudon, France*

and M. Leblanc

Laboratoire des Fluorures, UA 449, *Faculté des Sciences,* 72017 *Le Mans CEDEX, France*

(*Received* 17 *May* 1989; *accepted* 30 *November* 1989)

Abstract. Lanthanum oxide sulfide $La_2O_2S_2$, M_r = 373·947, orthorhombic, $Cmca$, a = 13·215 (2), b = 5·943 (1), c = 5·938 (1) Å, V = 466·3 (2) Å^3, Z = 4, D_x = 5·32 Mg m^{-3}, Mo $K\alpha$, λ = 0·71069 Å, μ = 18·87 mm^{-1}, $F(000)$ = 648, R = 0·017, 582 unique observed reflections, flux growth, data corrected for twinning of the crystal. The structure is built from infinitive layers of LaO_4S_4 square antiprisms connected by edges; these layers share either oxygen or disulfide common planes. Short S—S distances [d = 2·103 (2) Å] correspond to S_2^{2-} entities.

Introduction. The rare-earth oxysulfides Ln_2O_2S form an important class of luminescent materials with numerous applications as phosphors (Klaassen, Van Leuken & Maessen, 1988) or as high-gain laser materials (Alves, Buchanan, Wickersheim & Yates, 1971). During the crystal growth by flux method of dilanthanum dioxide sulfide, formation of small yellow crystals occurs at low temperature (Ostoréro, Fadly & Makram, 1976). They were identified as dilanthanum dioxide disulfide. The crystal structure of these compounds does not seem to be precisely

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