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Synthetic Dipotassium Zinc Disilicate

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Abstract

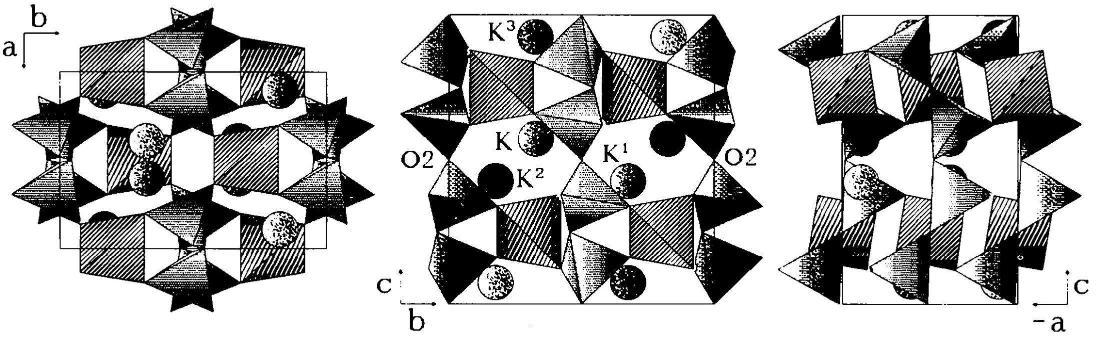
The structure of dipotassium zinc disilicate, $K_2ZnSi_2O_6$, comprises three-membered rings formed by two $[SiO_4]$ and one $[ZnO_4]$ tetrahedron, which are connected to form layers parallel to (001). Within the unit cell, one layer is connected by common O atoms to another layer, which is symmetry related to the first by a 2_1 axis along [001], thus forming a silicate *vierer* single chain with a large stretching factor of f_s = 96.8% and one unusually small Si—O—Si angle of 118.3 (2)°. The K atoms are coordinated by nine nearest O atoms and lie between the three-membered ring layers, forming a face-connected $[KO_3]$ network. The formula of this new potassium zinc silicate structure may be expressed, following the recommendations of the IUCr, as $K_4^{[9]}Zn_2^{[4t]}\{uB,1^1_\infty\}[^4Si_4O_{12}]$.

Comment

Recently, several new potassium zinc silicates have been synthesized (Dollase & Ross, 1993; Kawahara, Kohara, Konishi & Horiuchi, 1991; Kohara & Kawahara, 1990). Although several structures of zinc silicates, particularly the alkali and alkali earth zinc silicates, have been investigated (Hesse, Liebau & Boehm, 1977; Belekoneva, Egorov-Tismenko, Simonov & Belov, 1970; Plakhov & Belov, 1977; Hamilton & Finney, 1985), there are still too few known phases for a systematic description.

The new potassium zinc silicate described here was derived from work on the possibilities of substituting alkali and alkali earth cations for the water molecule in hemimorphite.

Projections of the structure of $K_2ZnSi_2O_6$ are shown in Fig. 1. The Zn and Si atoms are tetrahedrally coordinated by O atoms. Two $[SiO_4]$ and one $[ZnO_4]$ tetrahedron form a three-membered ring. The Si and Zn atoms of the three-membered ring are located on a plane roughly parallel to (101). The rings are condensed into a layer parallel to (001) such that seven-membered rings are created (Fig. 1*a*). Within the unit cell, one three-membered-ring layer is linked *via* the O2 atoms to another layer and the layers are symmetry related to each other by the 2_1 axis along [001]. Three additional and topologically different rings are formed about this connection: one seven-membered ring approximately parallel to (111) and two eight-membered rings approximately parallel to (010) and (110). The linkage of the two three-membered-ring layers within the unit cell creates very stretched silicate chains, with a large stretching factor of f_s = 96.8% (Fig. 1*c*).



(*a*) (*b*) (*c*)

Fig. 1. Projections of the structure of $K_4^{[9]}Zn_2^{[4t]}\{uB,1^1_\infty\}[^4Si_4O_{12}]$, showing the network of O-atom tetrahedra ($[ZnO_4]$ tetrahedra are striped, $[SiO_4]$ tetrahedra are dotted) and basic features such as the three-membered ring layers, the position of the K atoms within the plane of connection of two ring layers, and the very stretched *vierer* single chains parallel to **c**.

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Following the classification of Liebau (1985), the silicate chain can be described by the following structural formula: $\{uB,1^1_\infty\}[^4Si_4O_{12}]$. The formula denotes an unbranched (uB) single chain (1^1_∞) with a four-[SiO_4]-tetrahedron repetition unit, [$^4Si_4O_{12}$]. The [ZnO_4] tetrahedra connect these chains to form a framework. If the isolated [ZnO_4] tetrahedra are included in the [SiO_4] polyanion condensation units (Zoltai, 1960), the network of [TO_4] tetrahedra can be described as a loop-branched *zweier* framework, $\{lB,^3_\infty\}[^2(Zn_1Si_2)O_6]$.

The K^+ cations are coordinated by nine O atoms and lie almost on the plane of the O2 atoms, *i.e.* on the plane of the connection of two three-membered-ring layers (Figs. 1*b* and 1*c*). In Fig. 2, the [KO_9] polyhedron is shown within the unit cell as an *ORTEP* stereoplot (Johnson, 1965). The polyhedral planes, marked with F^1, F^2 and F^3, are common with the polyhedra of K–K^1, K–K^2 and K–K^3, respectively. The spiral-like arrangement of the K^+ cations along [001] is also emphasized. The faces F^1 and F^2 separating the K^+ cations within the plane of the connection of two three-membered-ring layers (O2 layer) are especially important for understanding the outstanding Si—O2—Si angle of 118.3 (2)° in the silicate chain. The small Si—O2—Si angle can be understood as a necessary arrangement to screen the charges of the K^+ cations within the K—O plane. Because of this need, the O3···O3″ distance within F^1 and the O3···O1 distance within F^2 are the smallest distances within their faces. As a consequence, this affects the Si—O2—Si angle as well as the corresponding Si···Si distance [2.876 (2) Å]. Compared with the literature (O'Keefe & Hyde, 1978), the short angle and the Si···Si distance should have the smallest values observed in silicates. The interatomic distances and angles are listed in Table 2.

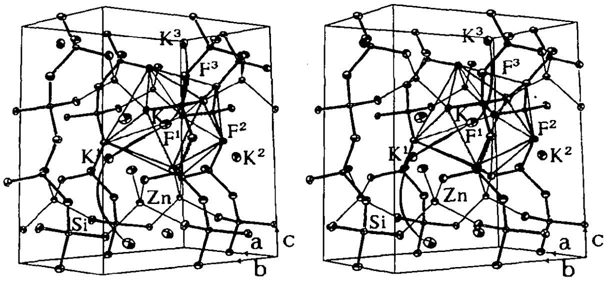

Fig. 2. Stereographic view of the structure of $K_4^{[9]}Zn_2^{[4t]}\{uB,1^1_\infty\}$-[$^4Si_4O_{12}$]. The figure shows the three-membered ring layers and the [KO_9] polyhedron with its face connection (F^1, F^2 and F^3 are shadowed) to other [KO_9] polyhedra, forming a face-connected [KO_3] network. The spiral-like arrangement of the K^+ cations along [001] is emphasized by the curved line. Displacement ellipsoids are plotted at the 50% probability level.

Although three-membered rings comprising two [ZnO_4] and one [SiO_4] tetrahedron are common in zinc silicates with high condensation units of [ZnO_4] tetrahedra (willemite: Simonov, Sandomirskii, Egorov-Tismenko & Belov, 1977; hemimorphite: McDonald & Cruickshank, 1966; hodgkinsonite: Rentzeperis, 1963; junitoite: Hamilton & Finney, 1985; clinohydrite: Simonov, Belekoneva, Egorov-Tismenko & Belov, 1977; $Na_2Zn_3Si_2O_8$: Plakhov, Simonov & Belov, 1975; $K_2Mn_2Zn_4Si_4O_{15}$: Pushcharovskii, Probedimskaya & Belov, 1969), the discovery of the reverse [ZnO_4]:[SiO_4] ratio within the three-membered ring of the title compound is novel for the zinc silicates. The new potassium zinc silicate has a stronger relationship to VPI7 (Annen, Davis, Higgins & Schlenker, 1991) than to the sodium pendant $Na_2ZnSi_2O_6$ (Belekoneva, Egorov-Tismenko, Simonov & Belov, 1970), because of the occurrence of three-membered rings. The authors of VPI7 noted that the *T*—O—*T* angle of *ca* 130° is necessary to form three-membered rings. In $K_2ZnSi_2O_6$, this angle can be found as an average value within the three-membered ring (129.97°) and as the Si—O3—Zn connecting angle of 129.8° within the three-membered ring layers.

The average Si—O distance (1.632 Å) is slightly increased when compared with values from previous investigations (Hesse, Liebau & Boehm, 1977; Belekoneva, Egorov-Tismenko, Simonov & Belov, 1970; Plakhov & Belov, 1977; Hamilton & Finney, 1985; Kawahara, Kohara, Konishi & Horiuchi, 1991; Kohara & Kawahara, 1990), whereas the average Zn—O distance (1.944 Å) is in the same range. The two Si—O distances Si—O2 and Si—O4 are significantly elongated within the silicate chain (mean 1.661 Å) compared with the two Si—O distances Si—O1 and Si—O3 in the three-membered ring (mean 1.604 Å), which is consistent with the fact that Si—O distances are longer in Si—O—Si than in Si—O—Zn. The average K—O distance (2.995 Å) is in good agreement with the values observed by Kawahara, Kohara, Konishi & Horiuchi (1991), Kohara & Kawahara (1990), and Dollase & Ross (1993).

The sums of electrostatic charges calculated with the parameters of Brown & Altermatt (1985) deviate somewhat from the theoretical values (Zn = 2.094, Si = 3.928, K = 0.988 and O = 1.958–2.032). The differences in the Si and Zn sums might indicate a little Si–Zn disorder between the two different [TO_4] sites, whereas from difference Fourier synthesis (*SHELX76*; Sheldrick, 1976) this indication could not be supported.

Experimental

Crystals of $K_2ZnSi_2O_6$ were grown under hydrothermal conditions (873 K, 800 bar, 168 h) from a mixture of ZnO (41.6 wt%), SiO_2 (gel) (15.4 wt%) and KOH (43 wt%). The chemical composition of the crystals was investigated by semi-quantitative energy-dispersive X-ray analysis using a transmission electron microscope. Only a few crystals besides probable unreacted fine-grained ZnO were formed.

Crystal data

$K_4Zn_2Si_4O_{12}$	Mo $K\alpha$ radiation
$M_r = 591.6$	$\lambda = 0.71069$ Å

Orthorhombic
$C222_1$
$a = 6.2983\ (3)$ Å
$b = 9.5537\ (9)$ Å
$c = 10.4499\ (6)$ Å
$V = 628.79\ (7)$ Å^3
$Z = 2$
$D_x = 3.12$ Mg m^{-3}

Cell parameters from 24 reflections
$\theta = 3.9$–$26.83°$
$\mu = 5.64$ mm^{-1}
$T = 293$ K
Brick
0.208 × 0.128 × 0.106 mm
Colourless

Data collection

Philips PW1100 diffractometer
$\omega/2\theta$ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
$T_{\min} = 0.19$, $T_{\max} = 0.25$
7149 measured reflections
1900 independent reflections

1890 observed reflections $[I > \sigma(I)]$
$R_{\rm int} = 0.0283$
$\theta_{\max} = 40°$
$h = -11 \rightarrow 11$
$k = -15 \rightarrow 15$
$l = -17 \rightarrow 17$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F
$R = 0.0541$
$wR = 0.0365$
$S = 6.016$
1890 reflections
54 parameters
$w = 3.339/\sigma^2(F)$
$(\Delta/\sigma)_{\max} < 0.0005$
$\Delta\rho_{\max} = 2.01$ e Å^{-3}
$\Delta\rho_{\min} = -2.08$ e Å^{-3}

Extinction correction: *SHELX76* (Sheldrick, 1976)
Extinction coefficient: 0.00058
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
Zn	0	0.1929 (1)	3/4	0.72 (2)
Si	0.1519 (1)	0.4827 (1)	0.6367 (1)	0.61 (3)
K	0.6092 (1)	0.3273 (1)	0.5755 (1)	1.59 (3)
O1	0.3019 (3)	0.1795 (3)	0.1638 (2)	1.04 (8)
O2	0.4849 (6)	0	0	0.96 (11)
O3	0.8603 (4)	0.0780 (2)	0.6240 (2)	0.96 (8)
O4	0	0.4519 (3)	1/4	1.18 (11)

Table 2. *Selected geometric parameters* (Å, °)

Zn—O1	1.962 (2)	K—O3′	2.905 (3)
Zn—O1′	1.962 (2)	K—O3′′	2.906 (3)
Zn—O3	1.926 (2)	K—O1′	2.924 (2)
Zn—O3′	1.926 (2)	K—O1′′	2.984 (2)
Si—O1	1.602 (3)	K—O2	3.144 (3)
Si—O2	1.676 (2)	K—O2′	3.278 (1)
Si—O3	1.605 (3)	K—O4	3.305 (3)
Si—O4	1.645 (1)	K···K^1	3.657 (2)
K—O1	2.751 (2)	K···K^2	3.819 (1)
K—O3	2.760 (2)	K···K^3	3.899 (2)
Si—O2—Si	118.3 (2)	O1—Si—O2	109.8 (1)
Si—O4—Si	135.4 (2)	O1—Si—O3	114.5 (1)
O1—Zn—O1′	103,2 (1)	O1—Si—O4	110.2 (1)
O1—Zn—O3	112.2 (1)	O2—Si—O3	107.1 (1)
O1—Zn—O3′	109.3 (1)	O2—Si—O4	106.1 (1)
O1′—Zn—O3′	112.2 (1)	O3—Si—O4	108.7 (1)
O3—Zn—O1′	109.3 (1)	Si—O3—Zn	129.8 (1)
O3—Zn—O3′	110.5 (1)	Si—O1—Zn	124.5 (1)

The space group was determined by the Weissenberg film technique and by measurements on the PW1100 diffractometer. Although there were very weak (001) reflections with $l = 2n + 1$ visible in the Weissenberg films, measurements on the PW1100 showed that the peak-to-background relations of those reflections was such that the (001) extinction condition $l = 2n$ is fulfilled, which led to the space group $C222_1$. The structure was determined using a Patterson synthesis (*SHELXS86*; Sheldrick, 1985) to find the three heavy atoms, Zn, K and Si, reducing the R value to 18%. After that the O atoms were found by difference Fourier synthesis (*SHELX76*; Sheldrick, 1976). Distances were calculated using *ORFFE* (Busing, Martin & Levy, 1964). Molecular graphics were produced using *ORTEP* (Johnson, 1965).

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Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: DU1113). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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