The crystal structure of $K_2Si^{VI}Si_3^{IV}O_9$

Donald K. Swanson and Charles T. Prewitt

Department of Earth and Space Sciences
State University of New York, Stony Brook, New York 11794

Abstract

The crystal structure of $K_2Si^{VI}Si_3^{IV}O_9$ has been refined in space group $P6_3/m$ to an $R = 2.02\%$ and is confirmed to be isotypic with wadeite ($K_2ZrSi_3O_9$). The atomic charges of Si^{VI}, Si^{IV}, $O(1)_{br}$ and $O(2)_{nbr}$ are $+3.3$, $+2.5$, -1.4 and -1.4, respectively, and suggest that an increase in the coordination number of a Si atom from 4 to 6 significantly increases the ionic character of that atom. The mean octahedral Si–O distance, 1.778Å, compares well with that predicted by an empirical equation, 1.781Å.

Introduction

The phase $K_2Si^{VI}Si_3^{IV}O_9$ was first synthesized by Kinomura, Kume and Koizumi (1975) at high temperature and pressure. They concluded that this phase has the wadeite structure because: (1) its X-ray powder pattern is similar to that of $K_2TiSi_3O_9$ (Choisnet, Deschanvres and Raveau, 1973) and (2) the a and c cell edges were found to agree with values predicted from a plot of the variations in the a and c cell edges with the radius of the octahedral cation for a variety of wadeite-type structures. Kinomura *et al.* (1975) discussed the geophysical significance of $K_2Si^{VI}Si_3^{IV}O_9$ in the Earth's mantle and suggested that this phase may be an intermediate step in the transition of feldspar to a hollandite-type phase.

The purpose of this study was to refine the crystal structure of $K_2Si^{VI}Si_3^{IV}O_9$ so that variations in the steric details and local bonding features between the Si^{VI}–O and Si^{IV}–O bond could be examined. In addition, because $K_2Si^{VI}Si_3^{IV}O_9$ contains both four and six-coordinated Si, it provides an excellent opportunity for studying the interactions present in an Si^{VI}–O–Si^{IV} linkage.[1]

Experimental details

Specimen preparation

Single crystals of $K_2Si^{VI}Si_3^{IV}O_9$ were synthesized by reacting crystalline potassium tetrasilicate ($K_2Si_4O_9$) at high temperature and pressure. The starting material, $K_2Si_4O_9$, was kindly provided to us by Professor David R. Wones who had synthesized the crystalline $K_2Si_4O_9$ in 1958 at the USGS laboratories according to the procedure described by Schairer and Bowen (1955). The potassium tetrasilicate was sealed in a Pt capsule and placed in a piston-cylinder apparatus. The sample was held at 24 kbar and 900°C for one hour. The resulting run product consisted of a mixture of crystalline material and glass. After careful optical examination of the crystalline material a clear single crystal, with approximate dimensions 45 × 60 × 85 μm, was chosen for X-ray diffraction study. Precession photographs verified that the crystal is untwinned and that its Laue symmetry is consistent with the space group of wadeite, $P6_3/m$.

Data collection

Integrated intensities were collected up to $2\theta = 80°$ in one quadrant of reciprocal space ($-h < 0 \leq +h$, $k \geq 0$, $l \geq 0$) using a Picker four-circle diffractometer with graphite-monochromatized MoKα radiation (.7107Å). The reflection data were measured using the $\omega - 2\theta$ scan mode with a scan width of $(2.0° + 0.7° \tan\theta)$ and $\sigma_I/I = 0.01$ for $0 < 2\theta \leq 65°$ and with a scan width of $(1.3° + 0.7° \tan\theta)$ and $\sigma_I/I = 0.01$ for $65 < 2\theta \leq 80°$. Cell parameters were determined by a least squares calculation on 23 reflections in the range $39° < 2\theta < 65°$ that were individually centered at eight equivalent positions on the diffractometer. Cell parameters and other crystallographic data are listed in Table 1.

Refinement procedure

All structure refinements were carried out using the full-matrix least-squares refinement program RADY (Sasaki, pers. comm.), a modified version of RADIEL (Coppens *et al.*, 1975). Reflections for which $I_{obs} < 3\sigma_I$ were considered unobservable and eliminated from the refinements. Based on this rejection criterion 432 of the 2419 observed data were excluded from the refinements. In addition, 109 reflections that had unequal backgrounds were also eliminated. Reflections were considered to have unequal backgrounds if

$$RB < BMIN \text{ or } RB > BMAX$$

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[1] $Si_5O[PO_4]_6$ also contains four and six-coordinated Si (Mayer, 1974), but none of the oxygen atoms in this phase are common to both Si^{IV} and Si^{VI}.

Table 1. Crystallographic data for $K_2Si^{VI}Si_3^{IV}O_9$

a	6.6124(9)* Å	Space Group P6₃/m-1
c	9.5102(8)	μ (MoKα) = 19.98 cm⁻¹
V	360.11(7) Å³	Z = 2

* Estimated standard deviations are given in parentheses.

Table 2. Atomic positional parameters, anisotropic temperature factors and equivalent isotropic temperature factors

	K	Si^{VI}	Si^{IV}	O(1)	O(2)
x	1/3	0	0.36532(7)*	0.49150(18)	0.23203(13)
y	2/3	0	0.23343(7)	0.07339(19)	0.20907(13)
z	0.05778(5)	0	1/4	1/4	0.10611(8)
β_{11}	0.01414(8)	0.00448(9)	0.00216(5)	0.00306(13)	0.00521(10)
β_{22}	β_{11}	β_{11}	0.00265(5)	0.00399(14)	0.00481(10)
β_{33}	0.00261(1)	0.00069(1)	0.00094(1)	0.00286(2)	0.00140(1)
β_{12}	β_{11}	β_{11}	0.00121(4)	0.00219(11)	0.00231(8)
β_{13}	0	0	0	0	-0.00141(3)
β_{23}	0	0	0	0	-0.00082(3)
B_{eq}	1.139(5)	0.344(6)	0.323(4)	0.629(12)	0.619(8)

* Estimated standard deviations are given in parentheses.

where RB is the ratio of the peak counts for the background on each side of a peak, BMIN = 0.5/SC, BMAX = 2.0*SC and SC = $\sqrt{85/BT}$. The SC parameter was defined to be the square root of the maximum counting time for background allowed during data collection (85 sec) divided by the counting time for background, BT, used on an individual reflection. Each of the remaining 1878 reflections was assigned a unit weight. The positional parameters and isotropic temperature factors of $K_2Ti Si_3O_9$ (Choisnet *et al.*, 1973) were used as starting parameters for the initial refinement. The atomic positional parameters and isotropic temperature factors, which were converted to anisotropic temperature factors during the first stage of refinement, were refined simultaneously with the valence shell populations of the Si and O atoms obtained according to the procedure outlined by Sasaki, Fujino, Takéuchi and Sadanaga (1980). The atomic scattering factor curves for K^+ and O^- were taken from the *International Tables for X-ray Crystallography, Vol. IV* (1974) and that for Si^{3+} from the *International Tables for X-ray Crystallography, Vol. III* (1962). The scattering factor curve for O^{2-} was obtained from Tokonami (1965) and that for Si^{2+} from Fukamachi (1971). The anomalous dispersion terms for each atom were obtained from the *International Tables for X-ray Crystallography, Vol. IV* (1974).

The $K_2Si^{VI}Si_3^{IV}O_9$ structure was refined initially using reflection data collected from the three asymmetric units of reciprocal space that had been corrected for Lorentz and polarization effects. The structure refinement converged to an R = 2.53% after four cycles.

The second stage of the structure refinement consisted of correcting the data for absorption effects by numerical integration (Finger, unpublished) and then refining these data without an extinction correction. The refinement converged to an R = 2.39% after three cycles. When a Type I isotropic extinction correction (Becker and Coppens, 1974) was applied the refinement converged to an R = 2.36%. The refined extinction parameter G = $0.1667 \cdot 10^{-4}$ is small and accounted for only one reflection having an extinction factor less than 0.95.

The final stage of refinement was carried out using symmetry-averaged data. The absorption and extinction corrected structure factors from the previous refinement were averaged among symmetry-equivalent reflections. This resulted in a total of 659 independent reflections. These data were then refined without an extinction correction and after four cycles converged to an R = 2.02%

(R_w = 2.29%). The atomic positional parameters and temperature factors obtained from this refinement are listed in Table 2. The calculated and observed structure factors are listed in Table 3[2]. It is important to note that the observed structure factors were corrected individually for extinction before being averaged and that the averaged data were then refined without an extinction correction. It is not appropriate to apply an extinction correction to averaged data since the path length through a crystal is not, in general, equal for symmetry-equivalent reflections.

Discussion

Description of structure

This study confirms the earlier work of Kinomura *et al.* (1975) that $K_2Si^{VI}Si_3^{IV}O_9$ has the wadeite structure with Si atoms occupying both octahedral and tetrahedral sites. $K_2Si^{VI}Si_3^{IV}O_9$ can be described as a framework structure consisting of parallel layers of Si_3O_9 rings that are arranged in an ABAB... stacking sequence along [001] and linked together by octahedrally-coordinated Si atoms. The monovalent K atoms occupy the large cages that occur between the A and B layers of Si_3O_9 and serve to charge balance the structure. A stereoscopic illustration of the $K_2Si^{VI}Si_3^{IV}O_9$ structure, prepared using the computer program ORTEP (Johnson, 1965), is given in Figure 1. Important interatomic distances and bond angles are listed in Table 4.

When the K atom is taken to be 9-coordinated the Pauling bond-strength sum of the bridging oxygen, p[O(1)], and the nonbridging oxygen, p[O(2)], are 2.22

[2] To receive a copy of Table 3, order Document AM-83-221 from the Office, Mineralogical Society of America, 2000 Florida N.W., Washington, D.C. 20009. Please remit $1.00 in advance for the microfiche.
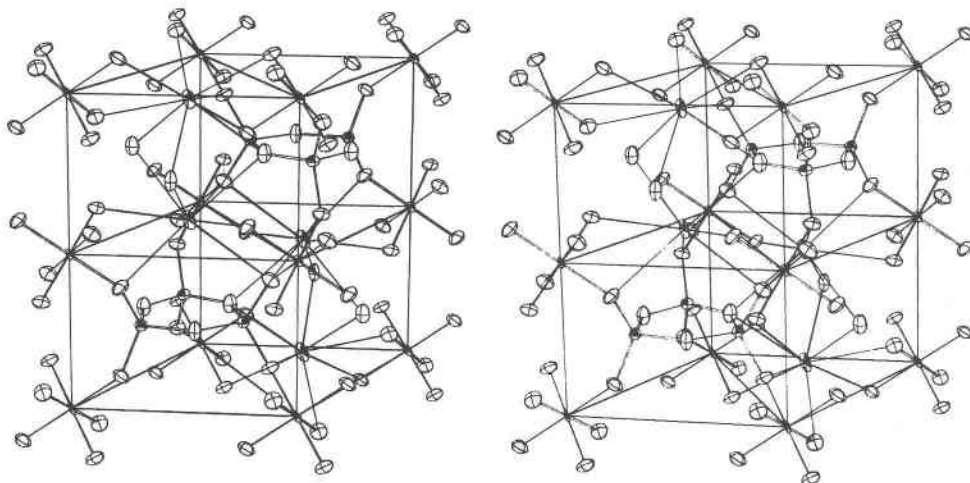
Fig. 1. A stereoscopic illustration of the $K_2Si^{VI}Si_3^{IV}O_9$ unit cell, prepared using the computer program ORTEP (Johnson, 1965).

and 1.89 respectively. Thus the Si^{IV}–O(1) bonds are expected to be longer than the Si^{IV}–O(2) bonds. Baur's (1970) empirical equation

$$d(Si–O) = 0.09p[O] + 1.44$$

predicts an Si^{IV}–O(1) distance of 1.64Å that compares well with the observed mean distance of 1.65Å. Furthermore, Chakoumakos, Hill and Gibbs (1981) have shown recently that the Si^{IV}–O distance in ring structures is linearly correlated with the percent fractional s-character of the bridging Si–O bond, denoted here as f_s. Their empirical equation for ring structures

Table 4. Interatomic distances and bond angles

	DISTANCES		ANGLES	
K-site				
K-O(2) [3]*	2.7908(4)$^!$ Å			
K-O(1) [3]	2.9758(3)			
K-O(2) [3]	3.0005(3)			
K-O(1) [3]	3.2974(2)			
Si octahedron				
Si-O(2) [6]	1.7783(1)	O(2)-Si-O(2) [6]	90.973(8)°	
		O(2)-Si-O(2) [6]	89.027(9)	
		O(2)-Si-O(2) [3]	180.	
Si tetrahedron				
Si-O(1) [1]	1.6429(2)	O(1)-Si-O(1) [1]	105.553(12)	
Si-O(1) [1]	1.6596(2)	O(1)-Si-O(2) [2]	103.983(5)	
Si-O(2) [2]	1.5916(1)	O(1)-Si-O(2) [2]	111.632(4)	
		O(2)-Si-O(2) [1]	118.579(8)	
		Si^{IV}-O(1)-Si^{IV}	= 134.447(5)	
		Si^{IV}-O(2)-Si^{VI}	= 141.760(4)	

* Multiplicities are given in brackets.

$^!$ Estimated standard deviations are given in parentheses.

$$d(Si–O) = -3.5 \cdot 10^{-3} f_s + 1.78$$

where $f_s = [100/(1 - \sec \measuredangle \text{ SiOSi})]$, also predicts an Si^{IV}–O(1) distance of 1.64Å. Baur's empirical equation, however, predicts a distance of 1.61Å for the Si^{IV}–O(2) bond, which is significantly longer than the observed distance of 1.59Å. One explanation for this discrepancy may be a result of the presence of the unusually large O(2)–Si–O(2) angle, 118.58°. Gibbs, Prewitt and Baldwin (1977) found that the Si–O distances in coesite are linearly dependent on the average of the three ⟨O–Si–O⟩ angles common to the bond, ⟨O–Si–O⟩$_3$, with larger ⟨O–Si–O⟩$_3$ angles associated with shorter Si–O distances. Although no empirical equation for estimating the influence of the ⟨O–Si–O⟩$_3$ angle on the Si–O distance is available, Gibbs *et al.* did observe that the shortest Si–O distance in coesite, 1.595Å, also had the largest ⟨O–Si–O⟩$_3$ angle, 109.86°. In $K_2Si^{VI}Si_3^{IV}O_9$ the observed ⟨O–Si–O⟩$_3$ angle for the Si–O(2) bond is significantly larger, 111.40°, and thus may account for the relatively short bond.

The bond lengths and angles listed in Table 4 for the SiO_6 coordination polyhedron show that this octahedron is very regular and approximates the point group symmetry O_h. In addition, the mean Si^{VI}–O bond length for this octahedron is in good agreement with that predicted by Baur's empirical equation (Baur, 1977). Baur arrived at an empirical equation for calculating the mean Si–O bond length in an octahedron based on a regression analysis of the mean Si–O distances in 13 observed octahedra. The equation

$$d(Si–O)_{mean} = 0.013CN + 1.729$$

where CN is the mean coordination number of the oxygen atoms in a given octahedron, predicts a mean Si^{VI}–O distance of 1.781Å, which agrees well with the observed mean Si^{VI}–O distance in $K_2Si^{VI}Si_3^{IV}O_9$ of 1.778Å.
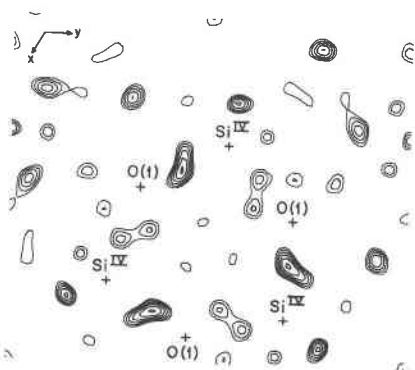
Fig. 2. Difference–Fourier section through the Si_3O_9 ring. Contours are drawn starting at $0.2e/Å^3$ and are at intervals of $0.05e/Å^3$.

Atomic charges

Atomic charges for Si^{VI}, Si^{IV}, $O(1)_{br}$ and $O(2)_{nbr}$ were calculated by refining the valence shell population of each atom. The scattering factor curves for Si and O were represented in the form

$$f(s/2) = f_M(s/2) + pf_{m-M}(s/2) + f' + if''$$

where $s = 2\sin\theta/\lambda$, f_M is the scattering factor of an atom in ionic state M, f_{m-M} is the difference between f's for two ionic states, m and M, and p the valence shell population parameter to be refined (Sasaki *et al.*, 1980). The total number of electrons was constrained during the refinements in order to maintain charge neutrality in the structure. The valence shell population of K^+ was not refined.

The refined atomic charges, with errors given in parentheses, are $Si^{VI} = +3.29(15)$, $Si^{IV} = +2.52(11)$, $O(1) = -1.43(8)$ and $O(2) = -1.43(4)$. The atomic charges sug-
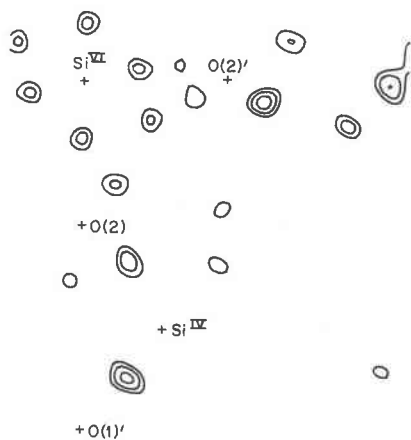
gest that an increase in the coordination number of the Si atom from four to six significantly increases the ionic character of that atom.

Difference-Fourier maps

A difference-Fourier section through the Si_3O_9 ring (z = 0.25) is presented in Figure 2. A peak height of $0.45e/Å^3$ is observed along the short Si–O(1) bond, 1.643Å, whereas a peak height of only $0.30e/Å^3$ is observed along the longer Si–O(1) bond, 1.660Å. A significant build-up of electron density is also observed outside the Si_3O_9 ring just behind the Si atom. This residual density has a peak height of $0.4e/Å^3$ and is located approximately at the intersection of the direction that bisects the obtuse O(1)–Si–O(1) angle and the O(2)–O(2) shared edge which is perpendicular to the ring.

A difference-Fourier section through the Si^{VI}–O(2)–Si^{IV} linkage is given in Figure 3. The Si^{IV}–O(2) bond is observed to have a peak with a height of only $0.25e/Å^3$ that occurs slightly off the bond vector. The Si^{VI}–O(2) bond also exhibits a peak with a height of only $0.25e/Å^3$, which lies on the bond vector.

Conclusions

The crystal structure of $K_2Si^{VI}Si_3^{IV}O_9$ has been refined in space group $P6_3/m$ and is isotypic with wadeite. The refined atomic charges of Si^{VI} and Si^{IV} are +3.3 and +2.5 and suggest that the octahedral Si atom has significantly more ionic character than the tetrahedral Si atom. Observed Si^{VI}–O and Si^{IV}–O distances conform with those predicted by empirical equations.

Further study on $K_2Si^{VI}Si_3^{IV}O_9$ should include a collection of accurate high-angle data so that the bonding features observed in the difference-Fourier maps can be better resolved and therefore deemed more significant.

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Fig. 3. Difference-Fourier section through the Si^{VI}–O(2)–Si^{IV} linkage. Contours are drawn starting at $0.2e/Å^3$ and are at intervals of $0.05e/Å^3$. The O(2)' and O(1)' atoms lie slightly out of the plane formed by the Si^{VI}–O(2)–Si^{IV} linkage.

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