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A mineral wadeite in glass, occurrence and crystal structure

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Crystals with a hexagonal lath–like morphology were found in glass products for cathode ray tubes. These crystals are preserved at the interfaces between glass and ZrO_2 ceramics in a glass melting tank. An electron microprobe analysis gives SiO_2: 45.6, ZrO_2: 31.5, K_2O: 19.0, Na_2O: 1.92, BaO: 1.46, SrO: 0.33, in wt%. These values and X–ray analyses indicated the crystals to be precipitated with the same structure as mineral wadeite, $K_2ZrSi_3O_9$, whose K atom sites are partially substituted by Ba, Sr or Na atoms. The structure is hexagonal with the space group $P6_3/m$, and the unit cell dimensions of a=6.918(2) and c=10.151(3) Å. The structure was refined using X–ray diffraction intensities from a single crystal. The bond distances and angles for Si_3O_9 rings are well comparable with those of benitoite, $BaTiSi_3O_9$, which is another example mineral including Si_3O_9 rings, with slight but significant difference in non–bridging Si–O bond distances. The mean square displacements of atoms in Si_3O_9 rings show that the tetrahedron is rigid for Si–O bond but strongly distorted for the O–O edges of non–bridging O atoms during thermal vibrations, coordinating to Zr and K. The thermal vibrational behaviors for the non–bridging oxygen are significantly different from those in benitoite.

Introduction

Wadeite, $K_2ZrSi_3O_9$, is a rare mineral containing Si_3O_9 rings, first reported by Prider (1939) for specimens from a suite of leucite–lamproites of the West Kimberley area of Western Australia, and next by Carmichael (1967) from the leucite hill, Wyoming, USA. According to Prider, the mineral is colorless and has hexagonal basal sections: optical properties are uniaxial positive with $\omega = 1.624$–1.627 and $\varepsilon = 1.655$–1.673 ($\varepsilon - \omega = 0.028$–$0.046$). On the other hand, crystals, which are well comparable with wadeite for their structures and chemical compositions, have been known to be occasionally generated in the glass manufacturing process in glass plants (Derabert, 1976; Takeuchi, 1987). Derabert (1976) studied such crystals occurred as reaction products between Al_2O_3–ZrO_2–SiO_2 refractory and lead glass. Takeuchi (1987) reported the occurrence of the crystals in the bulk of lead glass products.

There have been at least two structural studies, based on different hexagonal space groups, reported about natural wadeite. Henshaw (1955) refined the structure using intensity data measured for the specimen from the West Kimberley area of Western Australia in space group $P6_3/m$ with the lattice constants of a=6.893(4), c=10.172(2) Å and Z=2. Blinov et al. (1977) also studied natural specimens of high purity, recovered from their disposal, which showed no systematic absence in the 00l reflections in the X–ray diffractions, leading to space group P6, rather than $P6_3/m$.

So far no crystallographic study has been reported for the specimens of non–natural origins. In this paper, the occurrence of wadeite–like crystals in a Ba–Sr–alkaline–silicate glass is described and then the results of crystal structure analysis are reported. The differences between natural samples and artificial samples appeared

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in a glass manufacturing process are also discussed.

Occurrence and chemical compositions

Crystals are the most common problems to be avoided in glass manufacturing processes. There has been an effort contributed to eliminate the crystals. One of the important processes is the identification and characterization of such crystalline materials to know their origins. The crystalline materials are mostly identified to be in minerals because the glass is made from super-cooled silicate melts of mineral resources. One of such minerals is wadeite, crystallized as precipitates in a Ba-Sr-alkaline-silicate glass, which is to be used for the face plates of cathode ray tubes. The chemical compositions of such glass are shown in Table 1. This glass contains heavy metal ions such as Sr^{2+}, Ba^{2+}, Zr^{4+} for prevention of X-rays generated by cathode ray tubes, and also contains Sb^{3+} for eliminating blisters in glass.

The crystalline materials with the wadeite structure (abbreviated as wadeite-defects) in the glass sometimes appear in needle-like shapes with hexagonal cross sections. Figure 1 shows an image of optical microscope, and Figure 2 shows a cross section image obtained in an electron microprobe, both exhibiting hexagonal cross sections suggesting a hexagonal or trigonal symmetry.

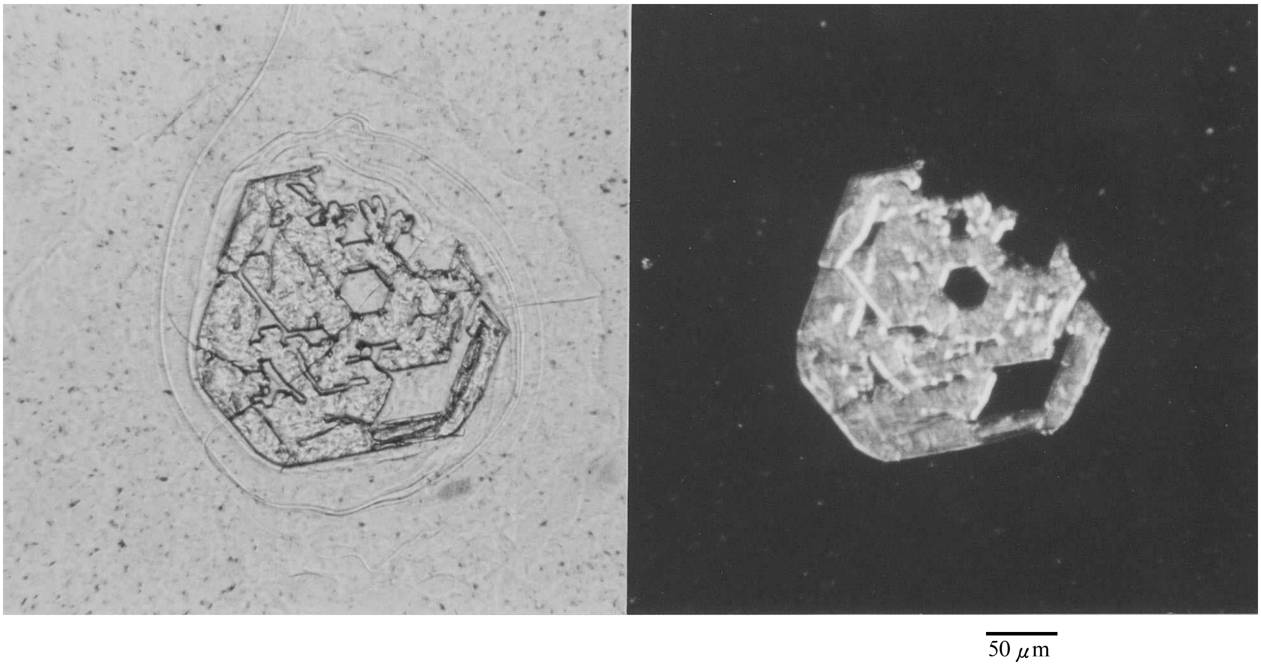
Chemical analyses were carrried out by using an electron microprobe analyzer, EPMA 1600 (Shimadzu corporation). Table 2 shows the chemical composi-

Table 1. Chemical composition of the Ba, Sr-alkaline silicate glass for cathode ray tube

	wt. %
SiO_2	61.0
Al_2O_3	2.0
Na_2O	7.5
K_2O	7.5
ZrO_2	2.3
SrO	8.5
BaO	8.5
Sb_2O_3	0.3
others	2.3

Table 2. Chemical composition of wadeite and its surrounding glass

	wadeite	(wt.%) surrounding glass
SiO_2	45.60	53.80
ZrO_2	31.50	12.90
K_2O	19.00	6.32
BaO	1.46	6.25
Na_2O	1.92	9.90
SrO	0.33	6.75
Al_2O_3	0.00	2.49



Open nicol crossed nicols

Figure 1. Optical micrograph of wadeite occurred in glass.

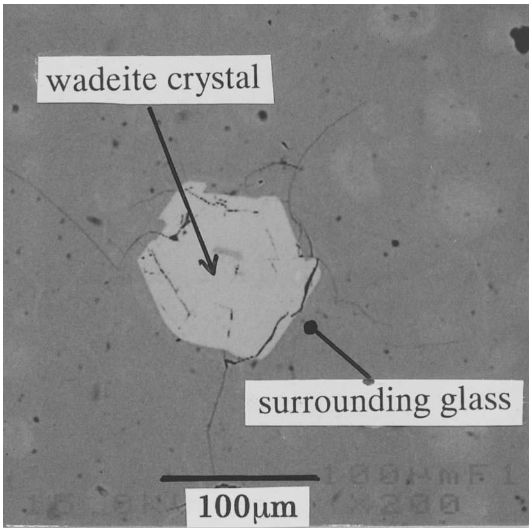


Figure 2. Back scattered electron image of wadeite occurred in glass.

Table 3. Typical refractory materials for glass industry

	AZS	ZFC (wt.%)
Al_2O_3	50.0	0.8
ZrO_2	33.0	94.0
SiO_2	16.0	4.5
Na_2O	1.1	0.4

tions of the present specimens and the glass surrounding them. The analyzing points are indicated in Figure 2. The compositions are almost equal to the theoretical values of wadeite with only small fluctuations through the specimens. The ZrO_2 content of the glass in contact with the precipitate crystals is higher than that of the mother glass, whereas other elements are less than those of the mother glass. This suggests that the wadeite is crystallized in ZrO_2-rich liquid.

In usual glass melting furnaces, ZrO_2 is the most common oxide used as a refractory material (Kino, 1992). Table 3 shows the chemical compositions of typical refractory materials used in the glass industry. The wadeite are sometimes found at the reaction zone of high ZrO_2 fused cast refractory (ZFC) as shown in Figure 3. It is considered that the wadeite gradually grew in a long period on ZFC refractory and was scratched out by glass flow to settle down on face plates as defects (Sakai, 1995).

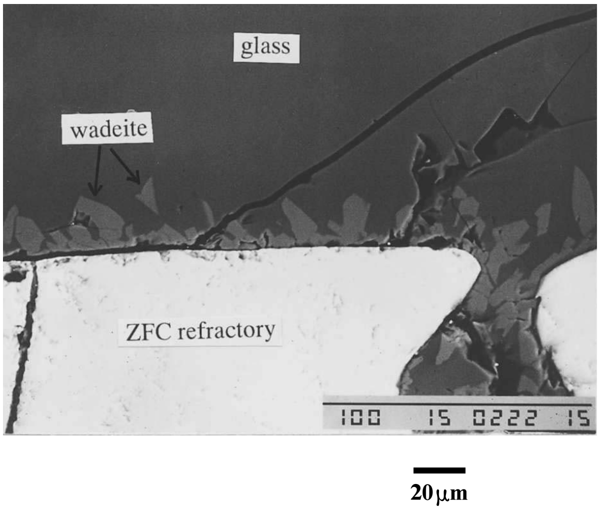


Figure 3. Wadeite crystals grown on ZFC refractory.

Table 4. Chemical composition of wadeite in glass and in natural

	in glass	in natural			theoretical (wt.%)
	this study	1	2	3	
SiO_2	45.60	39.40	48.80	47.40	45.30
ZrO_2	31.50	21.30	27.90	28.50	31.00
K_2O	19.00	18.40	19.70	21.50	23.70
BaO	1.46	1.20	0.10	0.10	
Na_2O	1.92	2.82	0.10	0.10	
SrO	0.33	0.16			
Al_2O_3	0.00	5.98	0.20	0.80	
FeO			0.40	0.60	
TiO_2		1.63	2.80	0.80	
CaO		5.22	0.10	0.10	
MgO	0.09	0.28			
P_2O_5		3.15			

1 Prider, 1939; 2 Carmichael, 1967; 3 Carmichael, 1967.

The present wadeite crystals contain Si, K, Zr, Na, Sr and Ba, among which main constituents are the first three: the chemical compositions are compared with those of three natural specimens and the theoretical values in Table 4. The contents of SiO_2 and ZrO_2 in our specimens are in good agreement with the theoretical values, whereas K_2O content is slightly lower than the theoretical value. It is supposed that K is partially substituted by the minor elements Na, Sr and Ba. The natural specimens show some varieties of compositions: in Prider (1939)' specimen, SiO_2 is much lower than other two natural specimens of Carmichael (1967), instead Al_2O_3 and CaO seem to conpensate the deficiency of SiO_2. The chemical compositions of our specimen are formulated as $K_2ZrSi_3O_9$ with a small amount of Ba, Na and Sr in the place of K. The natural samples contain Al_2O_3, FeO, TiO_2, CaO, MgO, P_2O_5 and so on, which are all absent in our specimens.

Table 5. Cell dimensions of wadeite in glass and in natural

	Henshow (1955)*	Blinov (1977)*	Present study
a (Å)	6.893(4)	6.926(1)	6.918(2)
c (Å)	10.172(2)	10.177(1)	10.151(3)

* Natural specimens

X-ray study

The crystalline materials were digged up from a thin section of the glass. It was possible to obtain transparent 1.0 mm-long specimens showing a sharp extinction under an optical microscope with crossed nicols. Because there have been two different structure reports for natural wadeite, we carefully examined the diffraction symmetry. An optically single crystal with the dimensions of about 200×100×50 μm was used in the X-ray single crystal study. The specimen showed sharp well-defined diffraction spots on X-ray oscillation photographs. Peak search and preliminary intensity measurements on a 4-circle diffractometer, Rigaku AFC7S diffractometer, with graphite monochromated MoKα radiation resulted in the Laue symmetry of 6/m and the lattice parameters of a=6.918(2) Å, c=10.151(3) Å and cell volume=420.7(2) Å^3, which are compared with those for the natural specimens in Table 5. The systematic absences were observed only in the 001 reflections with condition $1 \neq 2n$, indicating the possible space group to be either $P6_3$ or $P6_3/m$.

Intensity data were collected at room temperature using the ω-2θ scan mode to a maximum 2θ value of 80.0°. Scans of $(1.50+0.30 \tan \theta)°$ were made at a speed of 4.0°/min in ω. Weak reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of 3 scans) and the counts were accumulated to ensure good counting statistics. The intensities of three representative reflections were mea-

Table 6. Positional and thermal parameters of wadeite occurred in artificial glass in comparison with positional parameters for natural wadeite

	Ref.	Num. of sites etc.	x	y	z
Zr	(a)	2 b -3	0.0	0.0	0.5
	(b)		0.0	0.0	0.5
	(c)	1 a 6	0.0	0.0	0.4990(4)
K	(a)	4 f 3	0.3333	0.6666	0.4419(1)
	(b)		0.3333	0.6666	0.442
	(c)		0.3333	0.6666	0.447(4)
Si	(a)	6 h m	0.3865(1)	0.2583(1)	0.25
	(b)		0.389	0.255	0.25
	(c)		0.386(1)	0.259(1)	0.249(4)
O_1	(a)	6 h m	0.4875(3)	0.0899(3)	0.25
	(b)		0.500	0.100	0.25
	(c)		0.488(2)	0.090(2)	0.261(4)
O_2	(a)	12 i 1	0.7442(3)	0.7655(3)	0.6168(1)
	(b)		0.737	0.764	0.614
	(c)		0.756(2)	0.768(2)	0.620(5)

	B_{eq} (Å^2)	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zr	1.232(4)	0.0212(2)	0.0212	0.0045(2)	0.0106	0.0	0.0
K	1.601(8)	0.0202(2)	0.0202	0.0205(4)	0.0101	0.0	0.0
Si	0.72(1)	0.0075(3)	0.0072(3)	0.0138(3)	0.0045(2)	0.0	0.0
O_1	3.05(5)	0.0094(8)	0.0068(8)	0.0101(2)	0.0048(7)	0.0	0.0
O_2	2.21(3)	0.0310(8)	0.0371(9)	0.0120(5)	0.0142((7)	-0.0035(6)	0.0066(6)

(a) Present study with one-e.s.d.'s in parentheses, (b) Henshaw (1955) and (c) Blinov et al. (1977) with three-e.s.d.'s in parentheses. Space groups are $P6_3/m$ for (a) and (c), but P-6 for (c), where refinement was carried out in P3. Values in (c) are only for atoms corresponding to those in (a) or (b).

Thermal parameters U_{ij}'s are those used in a temperature factor expression:

$\exp[-2\pi^2(a^{*2}U_{11}h^2+b^{*2}\ U_{22}k^2+c^{*2}U_{33}\lambda^2+2a^*b^*hkU_{12}+2a^*c^*h\lambda U_{13}+2b^*c^*k\lambda U_{23}]]$.

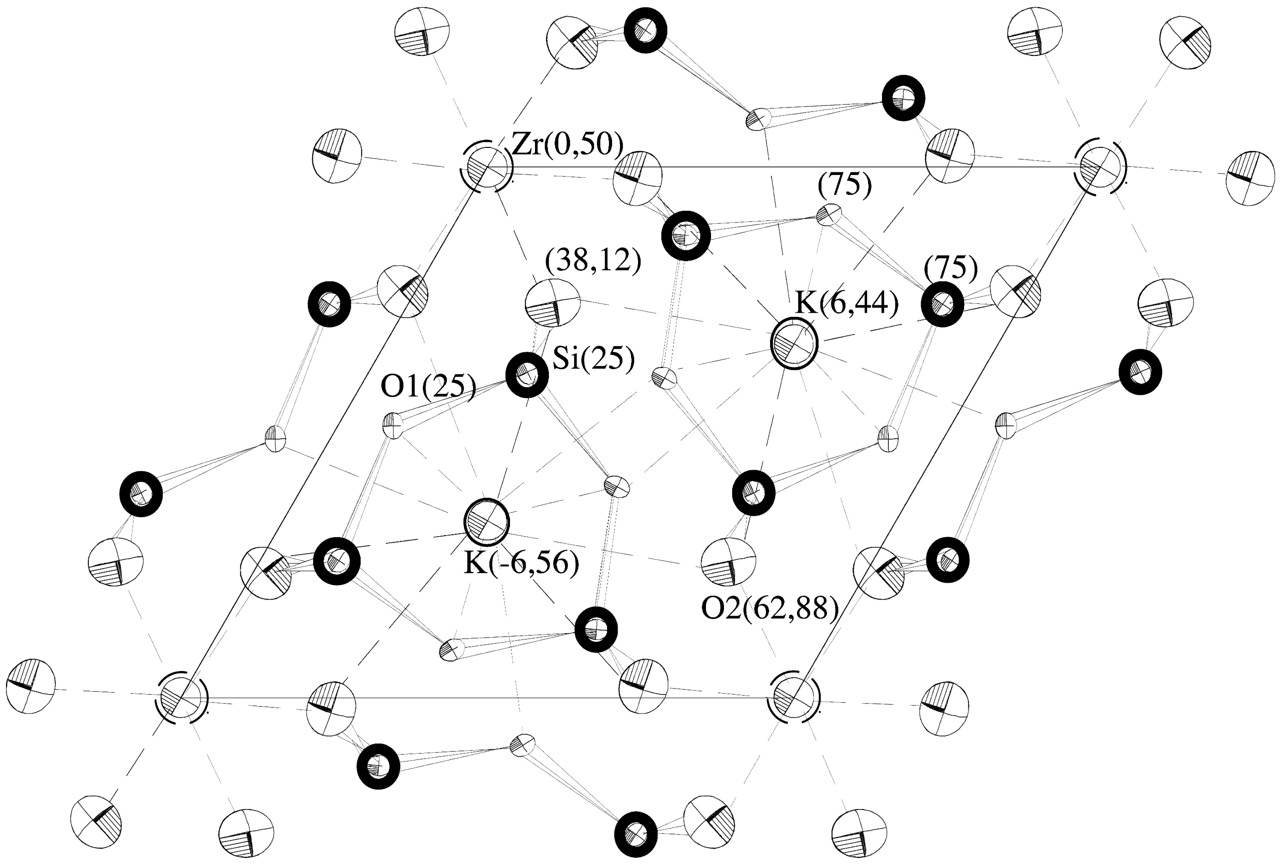


Figure 4. C-axis projection of wadeite in glass. Atoms are shown with thermal ellipsoids of 50% probability.

sured after every 150 reflections. Of the 4094 reflections collected, 703 were unique ($R_{int}=0.037$). The linear absorption coefficient, μ, for MoKα radiation is 27.238 cm^{-1}, resulting in μR ranging from 0.13 to 0.27 for the present specimen. The intensity data were converted to structure factors after correction for Lorentz and polarization effects.

In the N(z) test, a cumulative distribution curve for intensities agrees very well with that for the centric case. The probable space group was thus determined to be $P6_3/m$, equal with Henshaw (1955)'s, but not with Blinov et al. (1979)'s. The full matrix least-squares refinement of structure was commenced with a set of positional and isotropic temperature factors of atoms, obtained by combined application of direct method and Fourier syntheses. In total, five kinds of symmetrically independent atoms are involved: Si on (6h), Zr on (2b), K on (4f), O_2 on (12i) and O_1 on (6h), where (6h) etc indicate the number of positions in a cell and Wyckoff notation, respectively. The weighting scheme for the least squares refinements was based on counting statistics. Neutral atomic scattering factors were taken from Cromer and Waber (1974). The atomic scattering factors for the K site were approximated by mixing 0.83 of K, 0.13 of Na and 0.04 of Ba. Anomalous dispersion effects were included in F_{calc} (Ibers and Hamilton, 1964): the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley (1992). All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation(1997). The final cycle of refinement was based on 535 observed reflections ($I > 3.00\sigma(I)$) against 27 variable parameters including anisotropic temperature factors, and converged (largest parameter shift was 0.47 times its esd) with unweighted and weighted agreement factors of:

$$R=\Sigma \| Fo| - |Fc\| / \Sigma |Fo| = 0.023$$
$$R_w=[\Sigma_w(|Fo| - |Fc|)^2 / \Sigma_w Fo^2]^{1/2} = 0.024$$

The standard deviation of an observation of unit weight was 1.64. Listings observed and calculated structure factors, and standard deviations of the observed F's are available from the first author. The final positional and thermal parameters are compared with those by Henshaw (1955) and Blinov et al. (1977) in Table 6. It was found at this stage that our intensity data were measured with indices based on another possible setting of axes, which were the inverse of Henshaw's in the right-handed system. For comparison with the previ-

Table 7. Bond distances and angles in wadeite, of which tetrahedral bonds are compared with those in benitoite

(a) distances (Å)

	wadeite			benitoite	
	Present study	Blinov et al. (1977)*		Fisher (1969)	
	Si	Si_1	Si_2	Si	
Si - br O	O_1 1.631(3)	O_1 1.646	O_2 1.643	1.630 (3)	
Si - br O	O_1 1.642(2)	O_1 1.644	O_2 1.655	1.648 (3)	
Si - nobr O	O_2 1.589(2) x2	O_3 1.592, O_4 1.596	O_5 1.594, O_6 1.596	1.605 (2) x2	
average	1.613	1.621		1.622	
	Si	Si_1	Si_2	Si	
Si-Si	3.010(2)x2	Si_1 3.021	Si_2 3.021	3.005	
	Zr	Zr_1	Zr_2		
Zr-O	O_2 2.073(2)x6	O_3 2.069x3	O_4 2.100x3		
	---	O_6 2.085x3	O_5 2.059x3		
average	2.073	2.079			
	K	K_1	K_2	K_3	K_4
K-O	O_2 3.123(5)x3	O_4 3.057x3	O_3 3.180x3	O_6 3.053x3	O_5 3.179x3
	O_2 2.824(3)x3	O_5 2.821x3	O_6 2.863x3	O_3 2.801x3	O_4 2.830x3
	O_1 3.222(6)x3	O_2 3.287x3	O_2 3.176x3	O_1 3.291x3	O_1 3.192x3
	O_1 3.474(8)x3	O_1 3.398x3	O_1 3.544x3	O_2 3.383x3	O_2 3.548x3
average	3.161	3.141	3.191	3.132	3.187

(b) angles(°)

	Present study	Blinov et al.(1977)	benitoite (Fisher, 1969)
$Si-O_1-Si$	133.7(2)	133.35	132.9(1)
	---	132.70	---
average	133.7	133.0	132.9
O_2-Si-O_2	116.7(1)		113.1(2)
O_2-Si-O_1	106.06(9) x2		105.6(1) x2
O_2-Si-O_1	110.56(9) x2		112.3(1) x2
O_1-Si-O_1	106.3(2)		107.1(1)
average	109.4	109.2**	109.3

*: Values shown for Blinov et al. (1977) are those for space group P3, calculated here from given coordinates and cell dimensions. It must be noted that their structure belongs to P-6, but is refined in P3. Numbering for atoms are in no relation between the two studies.

**: Twelve values are given, but only their average is referred here.

ous results, our coordinates and anisotropic temperature factors in Table 6 are transformed applying a transformation (010/100/00-1). As Blinov et al.'s structure is in more general P-6 (they actually refined the structure in P3), we picked up, for comparison, only the atoms corresponding to the independent atoms in Henshaw's table.

Discussion of structure

The crystals precipitated in a Ba-Sr-alkaline silicate glass appear to be lath-like with hexagonal-shaped basal sections. The chemical compositions of the crystals in the glass are almost equal to the ideal values of wadeite for SiO_2 and ZrO_2, but K_2O content is slightly lower than the ideal value, suggesting that the K atom sites are partially occupied by Ba, Sr, Mg and Na atoms. The results of the structure refinements using X-ray intensities confirm the substitution scheme at the K sites.

The (001) projection of the present structure is shown in Figure 4. The Si-O, Zr-O and K-O distances, and Si-O-Si and tetrahedral angles are summarized in Table 7 in comparison with the previous study. The characteristic feature of the structure contains two Si_3O_9 rings and two Zr atoms in a cell. Three Si atoms and three O_1 atoms, lying on the mirror plane, form a ditrigonal-shaped ring with six O_2 atoms, located off from the mirror plane. Zr atoms, which lie on 6_3 axes, each separated by c/2, are octahedrally coordinated by O_2 atoms. Each K atom, which lies on a -6 axis,

Table 8. Mean square displacements of atoms and principal axis directions in (a) wadeite and (b) benitoite

(a)

Atoms	axis	$<u^2>$ (Å^2)	Angles(°)		
			from [210]	from [010]	from [001]
Zr	axis 1	0.02120	30.7	59.3	90.0
	axis 2	0.02120	120.7	30.7	90.0
	axis 3	0.00450	90.0	90.0	0.0
K	axis 1	0.02020	30.0	60.0	90.0
	axis 2	0.02020	120.0	30.0	90.0
	axis 3	0.02050	90.0	90.0	0.0
Si	axis 1	0.00791	25.5	64.5	90.0
	axis 2	0.00569	115.5	25.5	90.0
	axis 3	0.01380	90.0	90.0	0.0
O_1	axis 1	0.00940	1.8	88.2	90.0
	axis 2	0.00580	91.8	1.8	90.0
	axis 3	0.01010	90.0	90.0	0.0
O_2	axis 1	0.03092	13.1	77.6	94.0
	axis 2	0.04425	100.7	20.6	72.6
	axis 3	0.00869	82.5	106.2	17.9

(b)*

Atoms	axis	$<u^2>$ (Å^2)	Angles(°)		
			from [210]	from [010]	from [001]
Si	axis 1	0.0038(6)	13	77	90
	axis 2	0.0033(13)	103	13	90
	axis 3	0.0032(11)	90	90	0
O_1	axis 1	0.0064(9)	14	103	90
	axis 2	0.0054(9)	76	13	90
	axis 3	0.0135(12)	90	90	0
O_2	axis 1	0.0036(6)	45	95	134
	axis 2	0.0092(8)	78	11	87
	axis 3	0.0119(6)	46	100	45

*Fisher (1969) provided anisotropic temperature factors only for Si, O_1 and O_2, whcih are used to calculate $\langle u^2 \rangle$ and related angles here.

resides in a large polyhedron, elongated along the c-axis, of twelve O atoms; six (three O_1 and three O_2) belonging to the three neighboring rings and remaining six (three O_1 and three O_2) belonging to the ring just below or above itself. As the result, the polyhedron is each connected along the c-axis by sharing one larger trigonal face of O_1 at the bottom or the top and the other smaller trigonal face of, again, O_1 at the top or the bottom, respectively; both faces are just the mirror planes at z= 0.25 and 0.75. The K-O distances range from 2.82 to 3.48 Å.

The structure is comparable with that of benitoite in regard with that both minerals contain the Si_3O_9 rings. The Si-O-Si and the tetrahedral angles are compared with those in benitoite (Fisher, 1969) in Table 7. In these structures, 4-fold coordinated Si atoms form three symmetrically different Si-O bonds, two Si-O_1 and one Si-O_2. The two Si-O_1 bonds (bridging bond) are slightly different, 1.631(3) and 1.642(2) Å, each other, resulting in the slightly distorted ditrigonal rings of Si_3O_9. On the other hand, non-bridging bonds Si-O_2 of 1.589(2) Å are much shorter than the formers. In other words, the SiO_4 tetrahedra are not regular ones in these structures. The Si... Si separations in these structures, which are the shortest in silicates (Baur, 1971), are also close enough each other such as 3.010 Å for wadeite and 3.005 Å for benitoite. The non-bridging Si-O bond in wadeite is, however, slightly, but significantly shorter than the corresponding one in benitoite. This may suggest that the central loop of the Si_3O_9 ring, i.e., the bridging Si-O bond, is little affected by the difference in the surrounding cation distributions, but the outer parts, i.e., non-bridging Si-O bonds are affected to a certain extent.

The thermal vibrational parameters of atoms are highly anisotropic except for the K atom sites, which are almost perfectly isotropic (Table 8). The thermal ellipsoids for the Zr sites and the Si sites are oblate and prolate spheroidal with the shortest and the longest semi-axes along [001], respectively. The two kinds of those parameters of O atoms show considerably different sizes and shapes in the ellipsoids: the non-bridging O_2 ellipsoids is large and highly anisotropic with the shortest axis nearly in [001] and with other two axes in nearly equal lengths, whereas the bridging O_1 ellipsoid is small, rather comparable with that for Si, both of which have the longest axes in [001]. These features of the mean square displacements (msd) for the Si_3O_9 ring clearly indicate that the SiO_4 tetrahedra are strongly distorted mainly in the O_2-O_2 edges, perpendicular to the mirror plane, during thermal vibrations. On the other hand, the msd's of Si and O atoms in the both bridging and non-bridging Si-O bonds are in good agreements each other, suggesting that the Si-O bonds are rigid and move in tandem along the bonds (Dunitz et al., 1988): $\langle u^2 \rangle_{Si-O}=0.0119$ and 0.0119 Å^2 for Si and O_2, respectively, and 0.0057 and 0.0062 Å^2 for Si and O_1, respectively.

The thermal vibrational behaviors for atoms in Si_3O_9 rings in benitoite (Fisher, 1969) are much smaller than in wadeite (Table 8). In benitoite, Si atoms show almost isotropic msd's and the two kinds of O atoms, bridging (O_1) and non-bridging (O_2), are anisotropic but show no notable difference in amplitudes each other: the msd's are rather comparable with those of the bridging O atoms in wadeite. In other words, the thermal vibrations for the non-bridging Si-O bonds are notably different in these structures.

In spite of the different space groups employed, the two groups of structure analyses of wadeite, one by Henshaw (1955) or us and another by Blinov et al.

(1977), have provided essentially the same structure each other, with the small deviations of O atoms. According to Blinov et al. (1977), in their lower symmetry specimen, the cation distribution almost exactly obeys $P6_3/m$ pseudosymmetry, whereas the centrosymmetry is broken by the deviations of the O atoms from their ideal positions in $P6_3/m$. However, in comparison between our results and Blinov et al.'s, the differences seem to be too small to establish any definite displacement pattern between them (Table 6).

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