Zektzerite, NaLiZrSi₆O₁₅: a silicate with six-tetrahedral-repeat double chains

Subrata Ghose and Che'ng Wan

Department of Geological Sciences, University of Washington
Seattle, Washington 98195

Abstract

Zektzerite, $NaLiZrSi_6O_{15}$, is orthorhombic, space group *Cmca*, with cell dimensions: $a =$ 14.330(2), $b = 17.354(2)$, and $c = 10.164(2)$A; $Z = 8$. The crystal structure has been determined by the symbolic addition method and refined by the method of least squares to an R factor of 0.040 for 2389 reflections, measured on an automatic single-crystal diffractometer.

The crystal structure of zektzerite is a three-dimensional framework consisting of (a) edge-sharing Na-polyhedral chains, (b) octahedral-tetrahedral chains, formed by alternating Li tetrahedra and Zr octahedra sharing edges, and (c) corrugated double-silicate chains with six-tetrahedral repeat (*Sechser-Doppelkette*) and three different four-membered rings. The Li tetrahedron, with an average Li–O distance of 1.959A, shows strong angular distortion. The Zr octahedron is nearly regular, with an average Zr–O distance of 2.074A. The sodium atom occurs in an irregular cavity formed by the corrugation of the silicate double chains; it is coordinated to six oxygen atoms at distances of 2.37–2.67A, and four more oxygen atoms at distances of 3.12–3.23A. The average Si–O bond lengths within the Si(1), Si(2), and Si(3) tetrahedra are 1.614, 1.616, and 1.610A. The Si–O–Si bond angles involving oxygens lying on mirror planes average 155.7°, whereas those within the single silicate chain average 147.6°. The larger Si–O–Si angles are associated with shorter Si–O bonds. Zektzerite is isostructural with tuhualite, $(Na,K)Fe^{2+}Fe^{3+}Si_6O_{15}$, and synthetic $Na_2Mg_2Si_6O_{15}$. Provided the valence balance and coordination requirements are satisfied, a large number of silicates can crystallize within this structure type.

Introduction

Zektzerite, $LiNaZrSi_6O_{15}$, a new mineral found in miarolitic cavities of the Golden Horn batholith near Washington Pass, North Cascades, Washington, occurs in association with quartz, microcline, aegirine, riebeckite, astrophyllite, zircon, and elpidite. It is orthorhombic and occurs as translucent colorless stout prisms. Dunn *et al.* (1977) determined its optical properties, unit-cell dimensions and possible space groups; they also noted the similarity of its cell dimensions and chemical composition with those of tuhualite, $(Na,K)_2Fe_2^{2+}Fe_2^{3+}Si_{12}O_{30} \cdot H_2O$. The present structure determination shows that these two minerals are indeed isostructural, containing double silicate chains with six-tetrahedral repeat (*Sechser-Doppelkette*).[1]

---

[1] See Liebau (1972) for the terminology and a classification of silicate structures based on chain types.

Experimental

A sphere with a diameter of 0 44 mm was ground from a single crystal fragment using a sphere grinder (Bond, 1951). The single-crystal sphere was mounted on the computer-controlled automatic single-crystal X-ray diffractometer (Syntex PĪ), and the unit-cell dimensions were refined by the method of least squares, using 15 reflections measured with MoKα radiation with 2θ values between 30° and 40° (Table 1). The unit-cell dimensions are in good agreement with those determined by Dunn *et al.* (1977). The intensities of all reflections within a 2θ value of 65° were measured on the diffractometer, using MoKα radiation monochromatized by reflection from a graphite "single" crystal, and a scintillation counter. A variable scan rate was used, the minimum being 2°/min (50kV, 12.5 mA). Out of a total 2389 reflections, 316 were below $3\sigma(I)$, where $\sigma(I)$ is the standard deviation of the measurement of the intensity, I,

Table 1. Zektzerite: crystal data

Zektzerite, $NaLiZrSi_6O_{15}$:	Golden Horn batholith, N. Cascades, Washington

Colorless, translucent prisms

Orthorhombic, *mmm*	Cell Volume: 2527.6(7)$\overset{\circ}{A}^3$
$a(\overset{\circ}{A})$ = 14.330(2)	Cell content: 8[$NaLiZrSi_6O_{15}$]
$b(\overset{\circ}{A})$ = 17.354(2)	D_m: 2.79 g cm^{-3}
$c(\overset{\circ}{A})$ = 10.164(2)	D_c: 2.80 g cm^{-3}
Space group: *Cmca*	$\mu(MoK\alpha)$: 15.409 cm^{-1}

as derived from the counting statistics. The intensity data were corrected for Lorentz and polarization factors. No absorption corrections were made, since the linear absorption coefficient of zektzerite for $MoK\alpha$ radiation is small (Table 1).

Determination and refinement of the crystal structure

Dunn *et al.* (1977) could not distinguish between the two possible space groups *Cmca* and *C2ca*. The Wilson statistics of the measured intensities indicated the presence of a center of symmetry and *Cmca* as the correct space group. The crystal structure was determined directly by the symbolic addition method (Karle and Karle, 1966), using the computer program MULTAN (Germain *et al.*, 1971). The first E-map showed the positions of the sodium, zirconium, two silicon, and seven oxygen atoms. Structure-factor cal-

culation based on these atoms followed by difference Fourier synthesis yielded the positions of one silicon and two oxygen atoms. These atomic positions were refined by the method of least squares. The difference Fourier synthesis subsequently calculated revealed the position of the lithium atom.

All the atomic positional and thermal parameters were refined by the method of full-matrix least squares using the RFINE program (Finger, 1969). The observed structure factors (F_o's) were weighted by 1/$\sigma^2(F_o)$, where $\sigma(F_o)$ is the standard deviation of F_o, as determined by the counting statistics. The atomic scattering factors for Li, Na, Zr, Si, and O were taken from Cromer and Mann (1968), and corrected for anomalous dispersion (Cromer and Liberman, 1970). Three cycles of refinement using anisotropic temperature factors yielded a final *R*-factor of 0.040 for all reflections. 40 strong low-angle reflections (with F_o–F_c > 10.0 were believed to be suffering from extinction and were excluded from the refinement. The refinement converged at this stage, the average shift *vs.* error being 0.00. The final atomic positional and thermal parameters are listed in Table 2. Observed and calculated structure factors are listed in Table 3.[2] The bond lengths and angles, and the dimensions of

[2] To obtain a copy of this table, order Document AM-78-065 from the Business Office, Mineralogical Society of America, 1909 K Street, N.W., Washington, D.C. 20006. Please remit $1.00 in advance for the microfiche.

Table 2. Zektzerite: atomic positional and thermal parameters (standard deviations in parentheses)

Atom	x	y	z	B eq[†]	β_{11}*	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Na	0.25000	0.21648(8)	0.25000	2.10(3)	251(7)	78(4)	799(17)	0	209(1)	0
Li	0.24712(44)	0.00000	0.00000	1.12(8)	152(22)	107(15)	197(40)	0	0	-2(20)
Zr	0.25000	-0.08805(1)	0.25000	0.38(1)	53(1)	29(1)	88(2)	0	-1(1)	0
Si(1)	0.39091(4)	0.12869(3)	0.01792(5)	0.51(1)	59(2)	42(1)	129(4)	-6(2)	-9(3)	-1(2)
Si(2)	0.38965(4)	0.07306(3)	0.31148(5)	0.51(1)	63(2)	41(1)	129(4)	-8(1)	2(3)	-7(2)
Si(3)	0.39072(4)	0.19281(3)	0.54143(5)	0.53(1)	67(2)	39(1)	137(4)	-5(2)	7(3)	-9(2)
O(1)	0.37070(12)	0.21970(8)	-0.00542(16)	1.21(2)	222(8)	50(4)	289(14)	5(5)	-29(9)	-4(6)
O(2)	0.32801(10)	0.07851(8)	-0.07887(14)	0.73(2)	99(6)	56(4)	172(11)	-15(4)	-27(7)	-4(5)
O(3)	0.36177(11)	0.11174(9)	0.17054(15)	1.02(2)	136(7)	102(5)	172(12)	7(5)	-3(7)	35(6)
O(4)	0.32978(10)	-0.00240(8)	0.34095(14)	0.79(2)	102(6)	53(4)	217(12)	-27(4)	2(7)	-10(5)
O(5)	0.36064(11)	0.14017(8)	0.41591(15)	0.93(2)	136(7)	64(4)	221(13)	-1(4)	0(7)	-50(6)
O(6)	0.32984(11)	0.17405(8)	0.66829(14)	0.87(2)	121(6)	71(4)	184(12)	-16(4)	52(8)	-3(5)
O(7)	0.50000	0.11001(15)	-0.00132(24)	1.33(4)	56(9)	170(8)	362(21)	0	0	-31(11)
O(8)	0.50000	0.05683(13)	0.31751(24)	1.15(3)	41(8)	115(7)	419(22)	0	0	-1(10)
O(9)	0.50000	0.18146(14)	0.57081(25)	1.34(4)	72(9)	148(8)	400(22)	0	0	25(10)

[†]Equivalent isotropic B, calculated from anisotropic temperature factors

*Form of the anisotropic temperature factor ($\times 10^5$): exp $\{ \sum\limits_{i=1}^{3} \sum\limits_{j=1}^{3} h_i h_j \beta_{ij} \}$

Table 4. Zektzerite: interatomic distances (A) and angles (°) (standard deviations in parentheses)

The Na Polyhedron

Na – O(3)	2.554(2)(x2)	O(3) – Na – O(3')	89.24(8)
Na – O(5)	2.667(2)(x2)	O(3) – Na – O(5)	58.24(5)(x2)
Na – O(6)	2.368(2)(x2)	O(3) – Na – O(5')	79.60(5)(x2)
Na – O(1)	3.120(2)(x2)	O(3) – Na – O(6)	99.04(5)(x2)
Na – O(1')	3.225(2)(x2)	O(5) – Na – O(6)	109.45(5)(x2)
Mean of 6	2.530	O(6) – Na – O(6')	73.31(8)
Mean of 10	2.787	O(1) – Na – O(1')	109.76(5)(x2)
		O(1) – Na – O(3)	53.27(4)(x2)
O(3) – O(3')	3.587(3)	O(1) – Na – O(5)	101.86(5)(x2)
O(3) – O(5)	2.542(2)(x2)	O(1) – Na – O(6)	54.97(4)(x2)
O(3) – O(5')	3.342(2)(x2)	O(1') – Na – O(5)	50.52(4)(x2)
O(3) – O(6)	3.746(2)(x2)	O(1') – Na – O(6)	74.67(5)(x2)
O(5) – O(6)	4.114(2)(x2)		
O(6) – O(6')	2.827(3)		
O(1) – O(1')	3.618(3)(x2)		
O(1) – O(3)	2.593(2)(x2)		
O(1) – O(5)	3.704(2)(x2)		
O(1) – O(6)	2.619(2)(x2)		
O(1') – O(5)	2.564(2)(x2)		
O(1') – O(6)	3.460(2)(x2)		

The Li Tetrahedron

Li – O(2)	1.960(4)(x2)	O(2) – Li – O(2')	107.49(31)
Li – O(4)	1.957(4)(x2)	O(2) – Li – O(4)	133.28(6)(x2)
Mean	1.959	O(2) – Li – O(4')	88.88(6)(x2)
		O(4) – Li – O(4')	111.46(32)
O(2) – O(2')	3.161(3)	Mean	110.55
O(2) – O(4)	3.596(2)(x2)		
O(2) – O(4')	2.742(2)(x2)		
O(4) – O(4')	3.234(3)		
Mean	3.179		

The Zr Octahedron

Zr – O(2)	2.074(1)(x2)	O(2) – Zr – O(2')	170.84(7)
Zr – O(4)	2.091(1)(x2)	O(2) – Zr – O(4)	91.11(5)(x2)
Zr – O(6)	2.056(1)(x2)	O(2) – Zr – O(4')	82.36(5)(x2)
Mean	2.074	O(2) – Zr – O(6)	95.56(6)(x2)
		O(2) – Zr – O(6')	91.10(6)(x2)
O(2) – O(4)	2.973(2)(x2)	O(4) – Zr – O(4')	89.37(8)
O(2) – O(4')	2.742(2)(x2)	O(4) – Zr – O(6)	91.90(6)(x2)
O(2) – O(6)	3.059(2)(x2)	O(4) – Zr – O(6')	177.59(6)(x2)
O(2) – O(6')	2.948(2)(x2)	O(6) – Zr – O(6')	86.90(8)
O(4) – O(4')	2.940(3)	Mean of 12	90.03
O(4) – O(6)	2.980(2)(x2)		
O(6) – O(6')	2.827(3)		
Mean	2.931		

The Si(1) Tetrahedron

Si(1) – O(1)	1.623(2)	O(1) – Si(1) – O(2)	109.92(8)
Si(1) – O(2)	1.593(2)	O(1) – Si(1) – O(3)	105.57(8)
Si(1) – O(3)	1.633(2)	O(1) – Si(1) – O(7)	110.60(11)
Si(1) – O(7)	1.608(1)	O(2) – Si(1) – O(3)	110.08(8)
Mean	1.614	O(2) – Si(1) – O(7)	111.38(10)
		O(3) – Si(1) – O(7)	109.12(11)
O(1) – O(2)	2.633(2)	Mean	109.45
O(1) – O(3)	2.593(2)		
O(1) – O(7)	2.657(2)		
O(2) – O(3)	2.644(2)		
O(2) – O(7)	2.645(2)		
O(3) – O(7)	2.641(2)		
Mean	2.636		

The Si(2) Tetrahedron

Si(2) – O(3)	1.632(2)	O(3) – Si(2) – O(4)	111.79(8)
Si(2) – O(4)	1.594(2)	O(3) – Si(2) – O(5)	102.44(8)
Si(2) – O(5)	1.630(2)	O(3) – Si(2) – O(8)	110.27(11)
Si(2) – O(8)	1.607(1)	O(4) – Si(2) – O(5)	109.11(8)
Mean	1.616	O(4) – Si(2) – O(8)	112.24(10)
		O(5) – Si(2) – O(8)	110.57(10)
O(3) – O(4)	2.671(2)	Mean	109.40
O(3) – O(5)	2.542(2)		
O(3) – O(8)	2.658(2)		
O(4) – O(5)	2.626(2)		
O(4) – O(8)	2.659(2)		
O(5) – O(8)	2.661(2)		
Mean	2.636		

The Si(3) Tetrahedron

Si(3) – O(1)	1.617(2)	O(1) – Si(3) – O(5)	104.44(8)
Si(3) – O(5)	1.627(2)	O(1) – Si(3) – O(6)	109.49(8)
Si(3) – O(6)	1.590(2)	O(1) – Si(3) – O(9)	110.06(11)
Si(3) – O(9)	1.606(1)	O(5) – Si(3) – O(6)	112.05(8)
Mean	1.610	O(5) – Si(3) – O(9)	109.58(11)
		O(6) – Si(3) – O(9)	111.03(11)
O(1) – O(5)	2.564(2)	Mean	109.44
O(1) – O(6)	2.619(2)		
O(1) – O(9)	2.641(2)		
O(5) – O(6)	2.668(2)		
O(5) – O(9)	2.642(2)		
O(6) – O(9)	2.635(2)		
Mean	2.628		

Cation – Cation distances

Si(1) – Si(1')	3.1265(11)
Si(1) – Si(2)	3.1361(8)
Si(1) – Si(3)	3.1068(7)
Si(2) – Si(2')	3.1625(11)
Si(2) – Si(3)	3.1275(7)
Si(3) – Si(3')	3.1319(11)
Li – Zr	2.9654(2)(x2)
Li – Si(1)	3.044(4)(x2)
Zr – Si(2)	3.020(4)
Zr – Si(1)	3.4626(5)(x2)
Zr – Si(2')	3.4946(6)(x2)
Zr – Si(3)	3.4445(6)(x2)

Si – O – Si angles

Si(1) – O(1) – Si(3)	147.04(11)
Si(1) – O(3) – Si(2)	147.74(11)
Si(2) – O(5) – Si(3)	147.60(11)
Si(1) – O(7) – Si(1')	152.77(17)
Si(2) – O(8) – Si(2')	159.35(17)
Si(3) – O(9) – Si(3')	154.26(17)
Li – O(2) – Zr	94.58(12)
Li – O(4) – Zr	94.16(12)

the thermal ellipsoids with their standard deviations were calculated using the program ERROR (Finger, 1972, private communication). The bond lengths and angles are listed in Table 4 and the dimensions of thermal ellipsoids in Table 5. The average standard deviation in Li–O, Na–O, Zr–O, and Si–O bond lengths are 0.004, 0.002, 0.001, 0.002A and in O–Li–O, O–Na–O, O–Zr–O, and O–Si–O angles 0.20, 0.05, 0.06, 0.09° respectively.

Description of the structure

The crystal structure of zektzerite is a three-dimensional framework, consisting of three types of poly-hedral chains: (a) an edge-sharing Na polyhedral chain; (b) an octahedral-tetrahedral chain, formed by alternating LiO_4 tetrahedra and ZrO_6 octahedra sharing edges; and (c) a corrugated silicate double chain, with six-tetrahedral repeat (*Sechser-Doppelkette*) (Figs. 1 a,b,c).

The Na polyhedral chain

The sodium atoms occur within cylindrical channels, formed by the corrugation of the silicate double chains (Fig. 2). Of the ten Na–O bonds within 3.25A, six are comparatively short, ranging from 2.368A to 2.667A, forming a highly distorted octahedron;

Table 5. Zektzerite: thermal ellipsoids (standard deviations in parentheses)

Atom	Axis	rms amplitude (Å)	Angle (°) with respect to +a	+b	+c
Na	r1	0.109	90	0	90
	r2	0.129	32(7)	90	58(7)
	r3	0.226	122(2)	90	32(2)
Li	r1	0.102	90	88(17)	2(17)
	r2	0.126	0	90	90
	r3	0.128	90	2(17)	92(17)
Zr	r1	0.066	90	0	90
	r2	0.067	84(9)	90	174(9)
	r3	0.075	174(5)	90	96(5)
Si(1)	r1	0.073	139(11)	58(10)	67(8)
	r2	0.082	80(22)	42(22)	130(18)
	r3	0.085	51(27)	65(26)	49(29)
Si(2)	r1	0.072	126(10)	40(9)	75(7)
	r2	0.081	122(15)	97(11)	147(15)
	r3	0.088	128(20)	129(20)	62(20)
Si(3)	r1	0.074	104(9)	25(9)	70(6)
	r2	0.081	141(18)	89(13)	129(18)
	r3	0.090	125(10)	115(7)	46(8)
O(1)	r1	0.087	88(2)	3(4)	88(4)
	r2	0.121	76(5)	89(4)	166(5)
	r3	0.154	166(4)	88(2)	104(4)
O(2)	r1	0.081	126(19)	52(20)	58(21)
	r2	0.095	85(15)	46(11)	135(12)
	r3	0.111	144(11)	112(10)	117(10)
O(3)	r1	0.088	95(5)	112(4)	22(4)
	r2	0.118	14(12)	79(11)	81(7)
	r3	0.130	103(11)	25(7)	70(4)
O(4)	r1	0.075	124(7)	35(7)	84(5)
	r2	0.106	109(16)	96(11)	160(14)
	r3	0.115	140(19)	124(17)	71(15)
O(5)	r1	0.078	91(4)	39(6)	51(6)
	r2	0.119	3(28)	92(18)	87(22)
	r3	0.123	93(28)	129(5)	39(5)
O(6)	r1	0.082	54(10)	104(9)	39(10)
	r2	0.102	82(8)	156(8)	113(7)
	r3	0.126	143(7)	109(6)	60(6)
O(7)	r1	0.076	180	90	90
	r2	0.134	90	109(7)	161(7)
	r3	0.164	90	19(7)	109(7)
O(8)	r1	0.065	180	90	90
	r2	0.133	90	179(12)	91(12)
	r3	0.148	90	91(12)	1(12)
O(9)	r1	0.087	180	90	90
	r2	0.139	90	55(14)	145(14)
	r3	0.155	90	35(23)	55(23)

within the octahedron, the O–Na–O angles range from 58.2° to 117.6°. Four longer Na–O bonds ranging from 3.120Å to 3.225Å complete the Na polyhedron. Each Na polyhedron shares two opposite edges [O(1)–O(1')] with two adjacent Na polyhedra to form a chain parallel to the c axis (Fig. 1a).

The octahedral-tetrahedral chain

The Li tetrahedron shares two opposite edges [O(2)–O(4') 2.742Å] with two Zr octahedra on either side, thereby forming a chain parallel to the c axis,

with alternating LiO_4 tetrahedral and ZrO_6 octahedra (Fig. 1b). Within the chain the Li–Zr distance is 2.965Å. The Li–O distances (av. 1.959Å) within the LiO_4 tetrahedron show very little variation, whereas the O–Li–O angles show a large variation, ranging from 88.9° to 133.3°. The Zr octahedron is nearly regular, the Zr–O distances varying from 2.056 to 2.091Å (av. 2.074Å), and the O–Zr–O angles from 82.4° to 95.6°. It shares one edge [O(6)–O(6') 2.827Å] with an adjacent Na polyhedron.

The corrugated double-silicate chain with six-tetrahedral repeat

The most interesting part of the structure is the corrugated silicate chain with six-tetrahedral repeat parallel to the c axis. Such a single silicate chain is connected to an identical chain across a mirror-plane by sharing corners, giving rise to a double-silicate chain (*Sechser-Doppelkette*). These double chains contain three different four-membered tetrahedral rings (Fig. 1c).

The three-dimensional framework

Each octahedral-tetrahedral chain is connected to four adjacent silicate double chains by sharing corners. Likewise, each silicate double chain is connected to four adjacent octahedral-tetrahedral chains by corner-sharing. The Na polyhedral chains are connected to a pair of silicate double chains on the one side and an octahedral-tetrahedral chain on the other by sharing polyhedral edges and corners. A three-dimensional framework structure is formed in this fashion (Fig. 2). The two good cleavages {100} and {010} break the cation–oxygen bonds, leaving the silicate double chains intact (*cf.* amphiboles).

Anisotropic thermal vibration

The thermal vibration of the zirconium and the silicon atoms are nearly isotropic, whereas that of the lithium atom can be represented by a slightly oblate spheroid (Fig. 1b). Commensurate with its environment, the thermal vibration of the sodium atom is strongly anisotropic, the vibration ellipsoid being a strongly prolate spheroid (Fig. 1a). The oxygen atoms are mildly anisotropic, except those bridging oxygens on mirror planes, which are fairly strongly anisotropic, the maximum vibration direction being normal to the Si–O–Si plane (Fig. 1c).

Comparison with the tuhualite structure and the tuhualite structure type

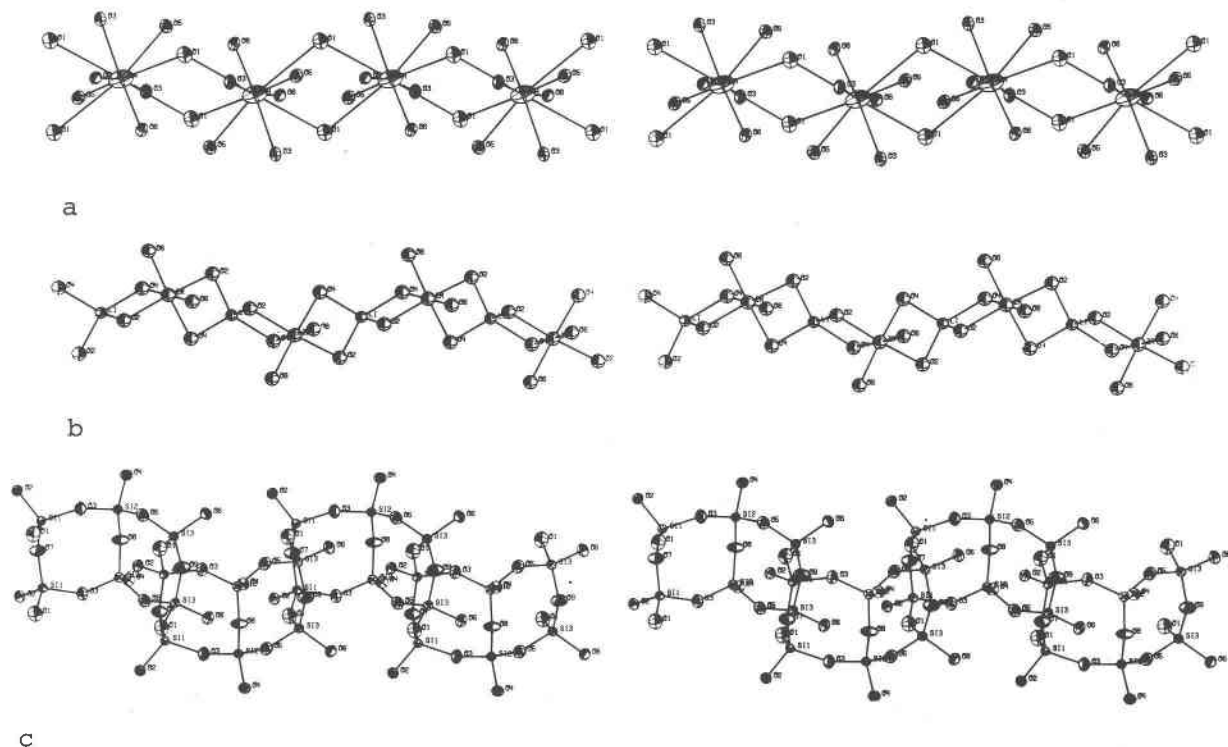Zektzerite is isostructural with tuhualite (Merlino,

Fig. 1. Zektzerite: stereoscopic views of the three structural components: (a) the Na-polyhedral chain; (b) the octahedral-tetrahedral chain, formed by alternating Li tetrahedra and Zr octahedra; and (c) the corrugated silicate double chain with six-tetrahedral repeat.

1969) and a synthetic orthorhombic phase $Na_2Mg_2Si_6O_{15}$ (Cradwick and Taylor, 1972). In tuhualite and in $Na_2Mg_2Si_6O_{15}$, the octahedral-tetrahedral chains consist of alternating Fe^{2+} tetrahedra and Fe^{3+} octahedra, and alternating Mg tetrahedra and Mg octahedra respectively. The angular distortion within the Fe^{2+} and Mg^{2+} tetrahedra respectively in these two structures are closely comparable to the angular distortion found within the Li tetrahedron in zektzerite. The coordination of Na [specifically Na(2) in $Na_2Mg_2Si_6O_{15}$] and the configuration of the silicate double chains are closely comparable in all three structures. In $Na_2Mg_2Si_6O_{15}$ there is an additional Na-position [Na(1): $x = 0.0000$, $y = 0.4099$, $z = 0.2568$], which is vacant in tuhualite and zektzerite. This Na site is nine-coordinated, with three short Na–O bonds ranging from 2.50 to 2.63A, and three pairs of long Na–O bonds ranging from 2.75 to 3.06A. The NaO_9 polyhedron is a tri-capped trigonal prism, the three closer oxygens occurring at the centers of the prism faces. Because of the larger average cation–oxygen distance (2.81A), this site is more suitable for potassium. In tuhualite K would presumably prefer this site over Na. The crystal-chemical rela-

tionships among phases isostructural with tuhualite can be shown in terms of the cation sites:

	M(1)	M(2)	M(3)	M(4)
Coordination number	9	10	4	6
$Na_2Mg_2Si_2O_{15}$	$Na^+(1)$	$Na^+(2)$	$Mg^{2+}(1)$	$Mg^{2+}(2)$
Tuhualite, $(Na,K)Fe^{2+}Fe^{3+}Si_6O_{15}$ $\cdot 0.5\,H_2O^3$	▢	Na^+,K^+	Fe^{2+}	Fe^{3+}
Zektzerite, $LiNaZrSi_6O_{15}$	▢	Na^+	Li^+	Zr^{4+}

where ▢ indicates a vacancy.

It is clear that provided the coordination and total valence balance requirements are satisfied, a large number of combinations of different cations can produce the same structure type. Some possible examples of other compounds of the tuhualite structure type are:

---

[3] The infrared spectra of tuhualite indicate the absence of water molecules in the structure (G. R. Rossman, 1977, private communication).
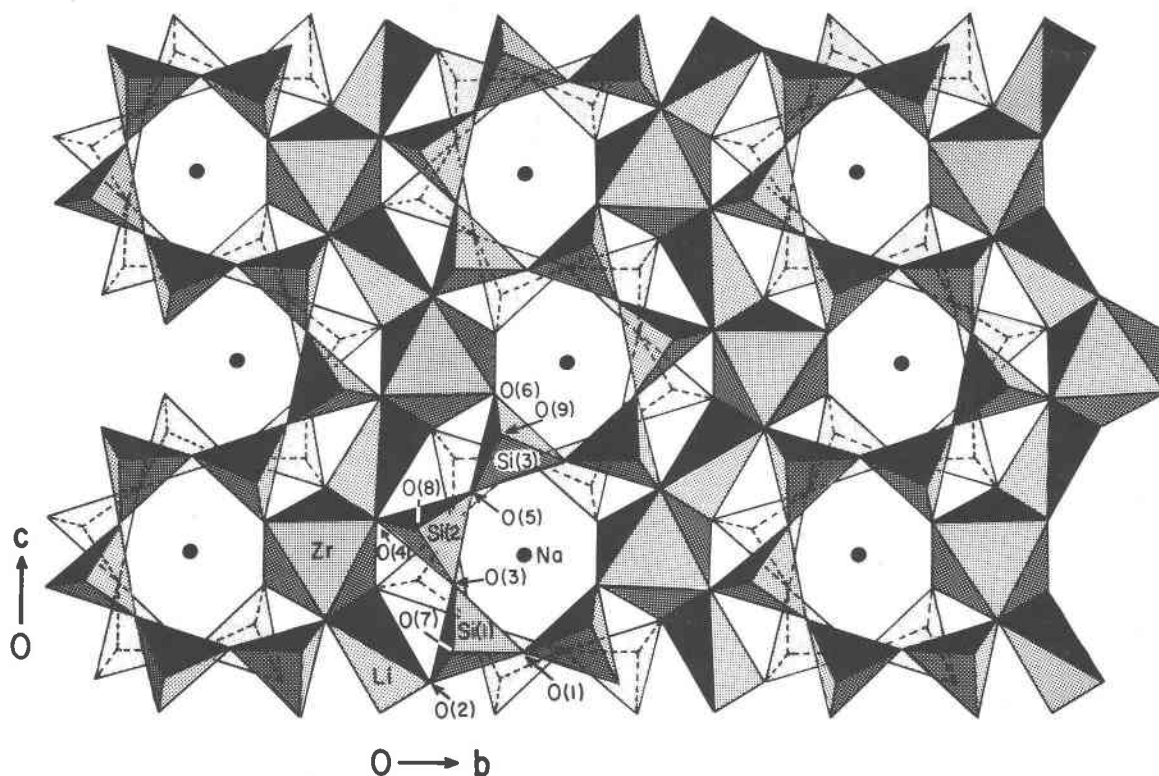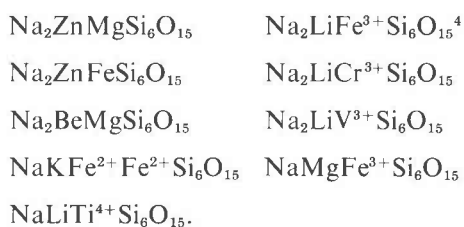
Fig. 2. A view of one-half of the zektzerite structure projected along [100]; the second half is obtained by reflection across a mirror plane (at $x = \frac{1}{2}$), passing through the oxygen atoms, O(7), O(8), and O(9), thereby doubling the silicate chain (*cf.* Fig. 1 in Merlino, 1969).

$Na_2ZnMgSi_6O_{15}$ $Na_2LiFe^{3+}Si_6O_{15}$[4]

$Na_2ZnFeSi_6O_{15}$ $Na_2LiCr^{3+}Si_6O_{15}$

$Na_2BeMgSi_6O_{15}$ $Na_2LiV^{3+}Si_6O_{15}$

$NaKFe^{2+}Fe^{2+}Si_6O_{15}$ $NaMgFe^{3+}Si_6O_{15}$

$NaLiTi^{4+}Si_6O_{15}$.

Discussion

The Si–O bond lengths and the Si–O–Si angles in zektzerite

The average Si–O bond lengths within Si(1), Si(2), and Si(3) tetrahedra are 1.614, 1.616, and 1.610A respectively. The variation of Si–O bond lengths within each silicate tetrahedron reflects bond strengths received by the oxygen atoms from other cations, in addition to the contribution from silicon.

On the basis of the oxygen coordination the Si–O

bonds can be classified into three types: (A) oxygens bonded to one Si + Zr + Li (or Na), (B) oxygens bonded to two Si only, (C) oxygens bonded to two Si + Na. The Si–O bonds involving oxygens of (A), (B), and (C) types average 1.593 ($\pm$ 0.003)A, 1.607 ($\pm$ 0.001)A, and 1.627 ($\pm$ 0.015)A respectively.

The larger degree of variation of the Si–O bond lengths involving oxygen atoms of the (C)-type can be further rationalized on the basis of the length of the Na–O bond; when the Na–O bond is longer, the Si–O bond is shorter and *vice versa.* The shortest Si–O bond [Si(3)–O(6), 1.590A] involves the most charge-deficient oxygen atom [O(6), e.s.v. sum 1.77], a phenomenon first noted by Merlino (1969) in tuhualite.

The Si–O–Si bond angles fall into two groups: those involving oxygens lying on mirror planes average 155.7° ($\pm$ 4.2°), whereas the other three within the single silicate chain average 147.6° ($\pm$ 0.6°). These angles are all larger than the average Si–O–Si angle (140°) found by Liebau (1961) in a large number of silicates. The larger Si–O–Si angles are associ-

[4] This compound has been synthesized during hydrothermal growth of quartz crystals at Bell Telephone Laboratories (K. Nassau and G. R. Rossman, 1977, private communication).

ated with shorter Si–O bonds, in agreement with the molecular orbital calculations on silicate chain fragments (Tossell and Gibbs, 1977).

Planarity of the corrugated single-silicate chain

The corrugated single-silicate chain has the sequence O(1)–Si(1)–0(3)–Si(2)–O(5)–Si(3)–O(1')–Si(1')–O(3')–Si(2')–O(5')–Si(3')–, the oxygen atoms being the bridging ones within the single-silicate chain (Fig. 1c). It is approximately planar, the plane being nearly parallel to the (100) plane. The minimum and maximum deviations of the bridging oxygen atoms from the least-squares plane defined by the silicon atoms only are 0.28A and 0.45A respectively. The degree of the corrugation of the chain is indicated by the ratio of the unit length of the corrugated chain $vs.$ the chain length when fully stretched out, which is 10.16A/16.80A = 0.60.

The planarity of the three crystallographically-distinct four-membered silicate rings

Within the double-silicate chains, three different rings can be discerned, which are:

(1) Si(1)–O(7)–Si(1')–O(3)–Si(2)–O(8)–Si(2')–O(3')

(2) Si(2)–O(8)–Si(2')–O(5)–Si(3)–O(9)–Si(3')–O(5')

(3) Si(1)–O(7)–Si(1')–O(1)–Si(3)–O(9)–Si(3')–O(1')

The average deviations of the bridging oxygen atoms from the least-squares planes passed through the silicon atoms only for rings (1), (2), and (3) are 0.17, 0.23, and 0.29A respectively. The acute angles between the rings (1) and (2), (2) and (3), and (3) and (1) are 59.6°, 52.8°, and 67.7° respectively.

Acknowledgments

References

Bond, W. L. (1951) Making small spheres. Rev. Sci. Instr., 22, 344–345.

Cradwick, M. E. and H. F. W. Taylor (1972) The crystal structure of $Na_2Mg_2Si_6O_{15}$. Acta Crystallogr., B28, 3583–3587.

Cromer, D. T. and D. Liberman (1970) Relativistic calculation of anomalous scattering factors for X-rays. J. Chem. Phys., 53, 1891–1898.

—— and J. B. Mann (1968) X-ray scattering factors computed from numerical Hartree-Fock wave functions. Acta Crystallogr., A24, 321–324.

Dunn, P. J., R. C. Rouse, B. Cannon and J. A. Nelen (1977) Zektzerite: a new lithium sodium zirconium silicate related to tuhualite and the osumilite group. Am. Mineral., 62, 416–420.

Finger, L. W. (1969) Determination of cation distribution by least squares refinement of single crystal X-ray data. Carnegie Inst. Wash. Year Book, 2, 216–217.

Germain, G., P. Main and M. M. Woolfson (1971) The application of phase relationships to complex structures. III. The optimum use of phase relationships. Acta Crystallogr., A27, 368–376.

Karle, J. and I. L. Karle (1966) The symbolic addition procedure for phase determination for centrosymmetric and non-centrosymmetric crystals. Acta Crystallogr., 21, 849–859.

Liebau, F. (1961) Untersuchungen über die Grösse des Si–O–Si-Valenzwinkels. Acta Crystallogr., 14, 1103–1109.

—— (1972) Crystal chemistry of silicon. In K. H. Wedepohl, Ed., Handbook of Geochemistry. Vol. II/3, 14-A-1–14-A-32, Springer-Verlag, Berlin.

Merlino, S. (1969) Tuhualite crystal structure. Science, 166, 1399–1401.

Tossell, J. A. and G. V. Gibbs (1977) Prediction of T–O–T angles from molecular orbital studies on corner-sharing mineral fragments (abstr.). Trans. Am. Geophys. Union, 58, 522.