Zektzerite, NaLiZrSi$_6$O$_{15}$: a silicate with six-tetrahedral-repeat double chains

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Abstract

Zektzerite, NaLiZrSi$_6$O$_{15}$, is orthorhombic, space group Cmca, with cell dimensions: $a = 14.330(2)$, $b = 17.354(2)$, and $c = 10.164(2)$ Å; $Z = 8$. 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 (Sechs-ber-Doppelkette) and three different four-membered rings. The Li tetrahedron, with an average Li-O distance of 1.959 Å, shows strong angular distortion. The Zr octahedron is nearly regular, with an average Zr-O distance of 2.074 Å. 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 2.37-2.67 Å, and four more oxygen atoms at distances of 3.12-3.23 Å. The average Si-O bond lengths within the Si(1), Si(2), and Si(3) tetrahedra are 1.614, 1.616, and 1.610 Å. 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)$_2$Fe$^{3+}$Fe$^{3+}$Si$_6$O$_{21}$, and synthetic Na$_2$Mg$_2$Si$_6$O$_{18}$. Provided the valence balance and coordination requirements are satisfied, a large number of silicates can crystallize within this structure type.

Introduction

Zektzerite, LiNaZrSi$_6$O$_{15}$, a new mineral found in mafic lavas 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)$_2$Fe$^{3+}$Fe$^{3+}$Si$_6$O$_{21}$. H$_2$O. The present structure determination shows that these two minerals are indeed isostructural, containing double silicate chains with six-tetrahedral repeat (Sechs-ber-Doppelkette). \(^1\)

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 P1), and the unit-cell dimensions were refined by the method of least squares, using 15 reflections measured with MoK$_\alpha$ radiation with $2\theta$ 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 $2\theta$ value of 65° were measured on the diffractometer, using MoK$_\alpha$ radiation monochromatized by reflection from a graphite "single" crystal, and a scintillation counter. A variable scan rate was used, the minimum being $2^\circ$/min (50kV, 12.5 mA). Out of a total 2389 reflections, 316 were below 3σ(I), where σ(I) is the standard deviation of the measurement of the intensity, I.
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 MoKa 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 calculation 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 REINE program (Finger, 1969). The observed structure factors (Fo's) were weighted by 1/\(\sigma^2(Fo)\), where \(\sigma(Fo)\) is the standard deviation of Fo, 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 Fo - Fe > 10.0 were believed to be suffering from extinction and were excluded from the refinement. The refinement converged at this stage, the average shift 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.

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### Table 1. Zektzerite: crystal data

<table>
<thead>
<tr>
<th>Zektzerite, NaLi2ZrSi015</th>
<th>Golden Horn batholith, N. Cascades, Washington</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orthorhombic, mm</td>
<td>Cell Volume: 2527.67(4) Å³</td>
</tr>
<tr>
<td>a (Å) = 14.330(2)</td>
<td>Cell content: 8[NaLi2ZrSi015]</td>
</tr>
<tr>
<td>b (Å) = 17.354(2)</td>
<td>D = 2.79 g cm⁻³</td>
</tr>
<tr>
<td>c (Å) = 10.164(2)</td>
<td>D = 2.80 g cm⁻³</td>
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<tr>
<td>Space group: Cmca</td>
<td>U(MoKα): 15.409 cm⁻¹</td>
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### Table 2. Zektzerite: atomic positional and thermal parameters (standard deviations in parentheses)

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>B eqt</th>
<th>β₁₁</th>
<th>β₂₂</th>
<th>β₃₃</th>
<th>β₁₂</th>
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<td>Na</td>
<td>0.25000</td>
<td>0.21648(8)</td>
<td>0.25000</td>
<td>2.10(3)</td>
<td>251.7</td>
<td>78.4</td>
<td>799.17</td>
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<td>209(1)</td>
<td>0</td>
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<tr>
<td>Li</td>
<td>0.2472(44)</td>
<td>0.00000</td>
<td>0.00000</td>
<td>1.12(8)</td>
<td>152(22)</td>
<td>107(15)</td>
<td>197(40)</td>
<td>0</td>
<td>0</td>
<td>-2(20)</td>
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<tr>
<td>Zr</td>
<td>0.25000</td>
<td>-0.08850(1)</td>
<td>0.25000</td>
<td>0.38(1)</td>
<td>53(1)</td>
<td>29(1)</td>
<td>88(2)</td>
<td>0</td>
<td>-1(1)</td>
<td>0</td>
</tr>
<tr>
<td>Si(1)</td>
<td>0.39094(4)</td>
<td>0.12869(3)</td>
<td>0.01792(5)</td>
<td>0.51(1)</td>
<td>59(2)</td>
<td>24(1)</td>
<td>129(4)</td>
<td>-6(2)</td>
<td>-9(3)</td>
<td>-1(2)</td>
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<tr>
<td>Si(1)</td>
<td>0.38965(4)</td>
<td>0.07306(3)</td>
<td>0.31148(5)</td>
<td>0.51(1)</td>
<td>63(2)</td>
<td>14(1)</td>
<td>129(4)</td>
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<td>Si(3)</td>
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<td>0.19288(3)</td>
<td>0.54143(5)</td>
<td>0.53(1)</td>
<td>67(2)</td>
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<td>0.21970(8)</td>
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<td>50(4)</td>
<td>289(14)</td>
<td>5(5)</td>
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<td>-4(6)</td>
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<tr>
<td>O(2)</td>
<td>0.32800(10)</td>
<td>0.07851(8)</td>
<td>-0.08788(14)</td>
<td>0.73(2)</td>
<td>99(6)</td>
<td>56(4)</td>
<td>172(11)</td>
<td>-15(4)</td>
<td>-27(7)</td>
<td>-4(5)</td>
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<tr>
<td>O(3)</td>
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<td>0.11174(9)</td>
<td>0.17054(15)</td>
<td>1.02(2)</td>
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<td>102(5)</td>
<td>172(12)</td>
<td>7(5)</td>
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<td>35(6)</td>
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<td>O(4)</td>
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<td>-0.00240(8)</td>
<td>0.34095(14)</td>
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<td>217(12)</td>
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<td>O(5)</td>
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<td>0.14017(8)</td>
<td>0.43591(15)</td>
<td>0.93(2)</td>
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<td>0.17405(8)</td>
<td>0.66289(14)</td>
<td>0.87(2)</td>
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<td>O(7)</td>
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<td>O(8)</td>
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<td>0</td>
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<td>O(9)</td>
<td>0.50000</td>
<td>0.18146(14)</td>
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<td>72(9)</td>
<td>148(8)</td>
<td>400(22)</td>
<td>0</td>
<td>0</td>
<td>25(10)</td>
</tr>
</tbody>
</table>

* Equivalent isotropic B, calculated from anisotropic temperature factors

* Form of the anisotropic temperature factor (x10⁵): \(\exp \left\{ \frac{1}{2} \sum_{i=1}^{3} \sum_{j=1}^{3} \beta_{ij} h_i h_j R_{ij} \right\} \)
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 angles are 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 polyhedral chains: (a) an edge-sharing Na polyhedral chain; (b) an octahedral-tetrahedral chain, formed by alternating LiO₄ tetrahedra and ZrO₆ 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 3.25Å, six are comparatively short, ranging from 2.368Å, to 2.667Å, forming a highly distorted octahedron;
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(l)–O(l')] 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')] with two Zr octahedra on either side, thereby forming a chain parallel to the c axis, with alternating LiO₆ tetrahedral and ZrO₆ octahedra (Fig. 1b). Within the chain the Li–Zr distance is 2.965Å. The Li–O distances (av. 1.959Å) within the LiO₆ 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$_2$Mg$_2$Si$_6$O$_{18}$ (Cradwick and Taylor, 1972). In tuhualite and in Na$_2$Mg$_2$Si$_6$O$_{18}$, 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$_2$Mg$_2$Si$_6$O$_{18}$] and the configuration of the silicate double chains are closely comparable in all three structures. In Na$_2$Mg$_2$Si$_6$O$_{18}$, 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 2.63Å, and three pairs of long Na–O bonds ranging from 2.75 to 3.06Å. The NaO$_6$ 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 (2.81Å), this site is more suitable for potassium. In tuhualite K would presumably prefer this site over Na. The crystal-chemical relationships among phases isostructural with tuhualite can be shown in terms of the cation sites:

$$\begin{array}{cccc}
M(1) & M(2) & M(3) & M(4) \\
\text{Coordination number} & 9 & 10 & 4 & 6 \\
\text{Na}_2\text{Mg}_2\text{Si}_6\text{O}_{18} & \text{Na}^{+}(1) & \text{Na}^{+}(2) & \text{Mg}^{2+}(1) & \text{Mg}^{2+}(2) \\
\text{Tuhualite,} & (\text{Na,K})\text{Fe}^{2+}\text{Fe}^{3+}\text{Si}_6\text{O}_{18} & \text{Na}^{+},\text{K}^{+} & \text{Fe}^{2+} & \text{Fe}^{3+} \\
\text{Zektzerite,} & \text{LiNaZrSi}_6\text{O}_{18} & \text{Na}^{+} & \text{Li}^{+} & \text{Zr}^{4+}
\end{array}$$

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).
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 1.610Å 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 (± 0.003)Å, 1.607 (± 0.001)Å, and 1.627 (± 0.015)Å 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), 1.590Å] 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° (± 4.2°), whereas the other three within the single silicate chain average 147.6° (± 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-

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Na₂ZnMgSi₅O₁₅ Na₂LiFe³⁺Si₆O₁₅
Na₂ZnFeSi₄O₁₅ Na₂LiCr³⁺Si₄O₁₅
Na₂BeMgSi₄O₁₅ Na₂LiV⁺Si₄O₁₅
NaKFe²⁺Fe²⁺Si₂O₁₅ NaMgFe³⁺Si₂O₁₅
NaLiTi⁺⁺Si₂O₁₅.

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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)-O(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 0.284 and 0.454 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

It is a pleasure to thank Russell Boggs, Seattle, Washington for the zektzerite crystals, Professor George R. Rossman, California Institute of Technology for discussions on the crystal chemistry of tuhualite, and Professor Charles T. Prewitt, State University of New York at Stony Brook, Dr. Ronald C. Rouse, University of Michigan, and Dr. Pete J. Dunn, Smithsonian Institution, Washington, D.C. for reviews of the paper. This research has been supported in part by the NSF grant EAR 76-13373 (Geochemistry).

References


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