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Abstract

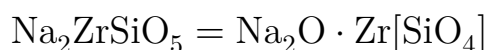
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CRYSTALLOGRAPHY

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CRYSTAL STRUCTURE OF Na, Zr-OXYORTHOSILICATE



The increasing demand for heat-resistant glazes, ceramics, and also adsorbents has aroused interest in the system $\text{A}_2\text{O}-\text{ZrO}_2-\text{SiO}_2$, where $\text{A} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$, and, in particular, in the preparation and investigation of the properties of "pure" sodium zirconium silicates $\text{Na}_2\text{ZrSiO}_5$, $\text{Na}_2\text{ZrSi}_2\text{O}_7$, $\text{Na}_4\text{Zr}_2\text{Si}_3\text{O}_{12}$, etc.

The object of our structural investigation was single crystals of $\text{Na}_2\text{ZrSiO}_5$, kindly provided by V. G. Chukhlantsev (S. M. Kirov Ural Polytechnic Institute).

The first syntheses of Na, Zr-oxyorthosilicate were carried out at the end of the last century ⁽¹⁾. Subsequently the individuality of this phase was established in the study of the system $\text{Na}_2\text{O}-\text{ZrO}_2-\text{SiO}_2$ ⁽²⁾. According to ⁽²⁾, confirming the results of ⁽¹⁾, $\text{Na}_2\text{ZrSiO}_5$ crystals are biaxial, optically negative, with a pseudohexagonal prismatic habit. $n_g = n_m = 1.790$, $n_p = 1.741$. Density (pycnometer, at 24°) = 3.605. The crystals were assigned to the rhombic system.

Later studies of single crystals ^(3,4) did not confirm the data obtained earlier. In ⁽⁴⁾, colorless biaxial crystals with a vitreous luster are described as positive, with a small angle between the optical axes. The refractive indices of the crystals differ from the data of ^(1,2): $n_g = 1.784 \pm 0.003$, $n_m = 1.755 \pm 0.003$, $n_p = 1.742 \pm 0.003$; density 3.621 (pycnometer, benzene, at 20°).

Single-crystal X-ray analysis established a monoclinic cell with parameters $a = 13.92$; $b = 5.46$; $c = 13.70 \text{ \AA}$, $\beta = 120^\circ$, and with $Z = 8$ units of $\text{Na}_2\text{ZrSiO}_5$. The Fedorov group $P2_1/c$ is determined quite unambiguously from the extinctions. From 1500 nonzero reflections $h0l-h4l$, $0kl-1kl$ (MoK_α radiation, $\max \sin \theta / \lambda = 1.3 \text{ \AA}^{-1}$, estimation of intensities by blackening standards with a step of $\sqrt{2}$), the three-dimensional Patterson function $P(uvw)$ was constructed. Analysis of the bond peaks by ⁽⁵⁾ and of interactions by ⁽⁶⁾ revealed the heavy Zr, medium Si atoms, and part of the lighter Na and O atoms. The remaining Na and O atoms were localized at the stage of electron-density syntheses $\rho(xyz)$. Least-squares refinement of the positional parameters reduced

Table 1

Coordinates of the basis atoms of Na, Zr-orthosilicate

Atoms	x/a	y/b	z/c	Atoms	x/a	y/b	z/c
Zr ₁	0.0647	0.7608	0.3719	O ₂	0.289	0.254	0.150
Zr ₂	0.4349	0.2612	0.3068	O ₃	0.408	0.789	0.041
Si ₁	0.1583	0.2277	0.0688	O ₄	0.211	0.714	0.362
Si ₂	0.3413	0.7711	0.4088	O ₅	0.091	0.303	0.129
Na ₁	0.314	0.741	0.145	O ₆	0.378	0.596	0.338
Na ₂	0.079	0.733	0.148	O ₇	0.134	0.937	0.027
Na ₃	0.184	0.264	0.330	O ₈	0.363	0.064	0.392
Na ₄	0.420	0.231	0.067	O ₉	0.007	0.474	0.271
O ₁	0.127	0.102	0.461	O ₁₀	0.492	0.966	0.265

R_{hkl} from 0.17 to 0.135 at $B = 0.4 \text{ \AA}^2$. Introduction of thermal (individual) factors reduced R_{hkl} to 0.131 ($\max \sin \theta / \lambda = 1.3 \text{ \AA}^{-1}$).

The final coordinates of the basis atoms are collected in Table 1, and the interatomic distances calculated from them are in Table 2.

As in all previously solved pure (and “mixed”) zirconosilicates—katapleite, seidozerite, lovozerite, wadeite, elpidite, dalyite, etc.—both independent Zr atoms are localized in an almost regular oxygen octahedron. The deviations of the six $Zr-O$ distances from the sum of the ionic radii do not exceed 10%: $Zr_1-O = 1.99-2.16 \text{ \AA}$ and $Zr_2-O = 2.00-2.17 \text{ \AA}$. The scatter of interatomic distances in the Si tetrahedra is also small: $Si_1-O = 1.58-1.66$, $Si_2-O = 1.60-1.67 \text{ \AA}$. There are four independent Na cations in the structure. In the environment of two of them (Na_3 and Na_4), five nearest O atoms can be distinguished at distances approximately equal to the sum of the ionic radii of Na + O; these constitute the first coordination sphere: $Na_1-O = 2.42-2.49 \text{ \AA}$ and $Na_2-O = 2.40-2.58 \text{ \AA}$. The sixth distances, which complete the five-vertex polyhedron to an octahedron, are considerably longer: 2.76 and 2.82 \AA , respectively. The next ligands are located beyond 3.00 \AA . The Na_2 octahedron is less distorted: of the six distances, three are very close to one another: 2.38; 2.39; 2.44 \AA , and the next are 2.55; 2.60; 2.75 \AA ; the seventh anion is removed to 3.13 \AA . In one more cation (Na_1), four close neighbors, 2.39-2.50 \AA , surround the central atom as a tetrahedron, and three more, more distant ones (2.68-2.83), complete the tetrahedron to a prism plus a half-octahedron.

Table 2

Interatomic distances in Na_2ZrSiO_5 (\AA)

Zr_1 octahedron (\AA)	Zr_2 octahedron (\AA)
$Zr_1-O_1 = 2.16$	$Zr_2-O_2 = 2.09$
$-O_5^* = 2.09$	$-O_3^* = 2.14$

Zr_1 octahedron (Å)	Zr_2 octahedron (Å)
— $O_4 = 2.14$	— $O_6 = 2.12$
— $O_7 = 2.16$	— $O_8 = 2.17$
— $O_9 = 2.08$	— $O_{10}^* = 2.06$
— $O_9^* = 1.99$	— $O_{10} = 2.00$

Si_1 tetrahedron	Si_2 tetrahedron
Si_1 — $O_1^* = 1.61$	Si_2 — $O_3^* = 1.63$
— $O_2 = 1.58$	— $O_4 = 1.60$
— $O_5 = 1.60$	— $O_6 = 1.62$
— $O_7 = 1.66$	— $O_8 = 1.67$
Average 1.618	Average 1.630

Na_1 polyhedron	Na_2 polyhedron
Na_1 — $O_2 = 2.68$	Na_2 — $O_1^* = 2.55$
— $O_2^* = 2.83$	— $O_4 = 2.60$
— $O_3 = 2.39$	— $O_5 = 2.38$
— $O_6 = 2.50$	— $O_5^* = 3.13$
— $O_7 = 2.42$	— $O_7 = 2.44$
— $O_{10} = 2.49$	— $O_9^* = 2.39$
— $O_{10}^* = 2.75$	— $O_9 = 2.75$

Na_3 polyhedron	Na_4 polyhedron
Na_3 — $O_1 = 2.47$	Na_4 — $O_2 = 2.58$
— $O_4 = 2.49$	— $O_3^* = 2.43$
— $O_5 = 2.44$	— $O_6^* = 2.51$
— $O_8 = 2.42$	— $O_8^* = 2.42$
— $O_9 = 2.42$	— $O_{10} = 2.40$
— $O_9^* = 2.76$	— $O_{10}^* = 2.82$
— $O_4^* = 3.03$	— $O_3 = 3.06$

Note. Atoms related to basis atoms by symmetry operations are marked with an asterisk.

The principal architectural elements in the structure of Na_2ZrSiO_5 should be regarded as chains-columns of Zr octahedra extending along the short b axis and connected with one another by shared vertices: $[ZrO_5]_\infty$ (Fig. 1). Such columns are common in Ti structures, but in a Zr silicate they have been encountered for the first time.* These columns are of the “frame” type, i.e., rocking; almost

Fig. 1. Na₂ZrSiO₅. Projection of the structure onto the *xy* plane in polyhedra. Chains of Zr₁ and Zr₂ octahedra, which are connected by Si tetrahedra, are shown

Figure 1: Fig. 1. Na₂ZrSiO₅. Projection of the structure onto the *xy* plane in polyhedra. Chains of Zr₁ and Zr₂ octahedra, which are connected by Si tetrahedra, are shown

Fig. 2. Na₂ZrSiO₅. Projection of the structure onto the *xz* plane in polyhedra. The lighter polyhedra are located at the level $y = 3/4 b$, the darker ones at $y = 1/4 b$. Centers of symmetry are indicated by small circles

Figure 2: Fig. 2. Na₂ZrSiO₅. Projection of the structure onto the *xz* plane in polyhedra. The lighter polyhedra are located at the level $y = 3/4 b$, the darker ones at $y = 1/4 b$. Centers of symmetry are indicated by small circles

exactly along the screw axes 2_1 , vertical oxygen edges of the Zr octahedra continue one another; the Zr atoms themselves (the bodies of the octahedra) are located on different sides of the oxygen axes, and per period b there are two Zr octahedra. In the full cell there are four Zr columns, divided into two crystallographically independent pairs: one along the 2_1 axes with $x = 0$, the other along 2_1 with $x = 1/2$.

The different orientation of those planes in which the Zr octahedra alternating in height remain in the two sorts of columns is striking. The axes** of these columns are arranged almost exactly at the vertices of a pseudohexagonal net (Fig. 2) with cell edge equal to $a/2 \approx c/2$. Along the pseudotri-

* In β - $K_2Zr_2O_5$ (7), columns of Zr octahedra are described with alternation of linkage sometimes by an edge, sometimes by faces (?).

** On them are strung the fifth atoms O_5 , which do not participate in the Si orthotetrahedra.

axes of this net, i.e., through the centers of the two triangles into which the elementary rhombus is divided, Si orthotetrahedra are located, each [SiO₄] among three Zr columns. With two Zr columns the Si tetrahedron has one common O vertex with each, and with one it has two. Each Zr column of the six neighboring ones is linked with two Si tetrahedra.

Fig. 1. Na₂ZrSiO₅. Projection of the structure onto the *xy* plane in polyhedra. Chains of Zr₁- and Zr₂-octahedra, which are connected by Si tetrahedra, are shown.

Fig. 2. Na₂ZrSiO₅. Projection of the structure onto the *xz* plane in polyhedra. The lighter polyhedra are located at the level $y \cong \frac{3}{4}b$, the darker ones at $y \cong \frac{1}{4}b$. Centers of symmetry are indicated by small circles.

In the open framework of Zr and Si polyhedra (Fig. 2), channels are formed,

but the Na atoms are not located along the axes of these channels; rather, they are situated beneath those two junctions of each Si tetrahedron with Zr columns where only one vertex is common (with the column). Thus the Na atoms, as it were, compact the walls of the channels—the wells of the structure.

The structure of Na, Zr oxoorthosilicate provides yet another example of the regularity previously noted in sphene, ramsayite, and other silicates: in a structure where “medium-sized” cations with increased charge (Ti^{4+} , Zr^{4+} , etc.) dominate, it is precisely the latter that determine its architecture, leaving to the large, loose cations the role of fillers of the three-dimensional framework.

In conclusion, the authors take this opportunity once again to express their deep gratitude to V. G. Chukhlantsev for his great assistance in synthesizing single crystals and in the subsequent work.

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