CRYSTAL STRUCTURE OF THE MONOCLINIC MODIFICATION OF K,Zr-DIORTHOSILICATE = K\$_{2}\$ZrSi\$_{2}\$O\$_{7}\$

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Abstract

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CRYSTAL STRUCTURE OF THE MONOCLINIC MODIFICATION OF K,Zr-DIORTHOSILICATE = $K_2ZrSi_2O_7$

The investigated crystals of the monoclinic modification $K_2ZrSi_2O_7$ (*1*) were obtained in a study of the system $K_2O-ZrO_2-SiO_2$ by V. G. Chukhantsev and Yu. M. Polezhaev (*2*) (S. M. Kirov Ural Polytechnic Institute).

In a cell with periods: $a = 9.54$, $b = 14.26$ (a distinct pseudoperiod $b' = b/2$), $c = 5.60$ Å, $\gamma = 116°31'$; $Z = 4$ units of $K_2ZrSi_2O_7$. The Fedorov group $C_{2h}^5 = P2_1/b$ is determined from the extinctions. In the array of experimental intensities there were ~ 1200 nonzero reflections $hk0-hk5$ and $h0l-h1l$ (Weissenberg goniometer, Mo radiation, $\max \sin\theta/\lambda = 0.95$ Å^{-1}, intensities estimated on a $\sqrt[4]{2}$-scale of blackening marks). Analysis of the three-dimensional Patterson function $P(uvw)$ according to (*3*) revealed the heavy Zr atoms and the intermediate Si and K, whose coordinates were taken as starting values for syntheses of the electron density $\rho(xyz)$. For the Si and K atoms, at the first stage the same scattering power ($\approx f_{\mathrm{Si}}$) was assumed. The light O atoms were localized from a series of electron-density syntheses, and at the last stage Si and K were separated.

Table 1

$K_2ZrSi_2O_7$. Coordinates of the basis atoms

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Zr	0.237	0.232	0.253	O_2	0.309	0.492	0.795
Si_1	0.172	0.369	0.744	O_3	0.476	0.316	0.232
Si_2	0.336	0.114	0.741	O_4	0.217	0.342	0.464
K_1	0.035	0.426	0.264	O_5	0.185	0.296	0.935
K_2	0.482	0.592	0.260	O_6	0.245	0.111	0.007
O_1	0.004	0.629	0.264	O_7	0.265	0.148	0.540

All the intermediate atoms, along with the heavier Zr, are displaced only slightly from the glide plane b (at the levels $\sim z/4$ and $3z/4$), and an ambiguity arises

Fig. 1. $K_2ZrSi_2O_7$. xy projection, parallel to glide plane b and normal to the 2_1 screw axes. Along [120] run chains of diorthogroups linked by Zr octahedra.

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in the arrangement between the b planes of four O atoms out of the seven (contained in the formula). Difference syntheses $\Delta\rho(xyz)$, as well as phase-weighted projections $\sigma_{\sin}$ and $\sigma_{\cos}$ according to (*4*), helped to distinguish their false and true positions. The discrepancy factor at this stage was 0.19. Refinement of the positional parameters by least squares reduced R to 0.15, and the introduction of isotropic individual corrections reduced it further to 0.14 ($\max \sin\theta/\lambda = 0.95$ Å^{-1}).

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

The Zr atom (as in most Zr silicates) has an almost regular octahedral environment: distances Zr–O = 2.06-2.26 Å, O–O within 2.83-3.14 Å. Each of the two independent Si atoms is surrounded tetrahedrally by 4 O atoms: Si_1–O = 1.53-1.70 Å at O–O = 2.62-2.72 Å, and Si_2–O = 1.52-1.70 at O–O = 2.54-2.85 Å. The Si_1 and Si_2 tetrahedra are combined into Si_2O_7 diortho groups in such a way that the triangular bases of the Si tetrahedra opposite the bridging vertex are mutually rotated by 60°; thus the polyhedron described around the diortho group becomes an elongated octahedron (similar to the environment of Si_2O_7 in Sc-thortveitite).

Large K atoms are located in rather loose eight-vertex polyhedra. For the K_1 cation, of the eight K—O distances, five (2.76-2.86 Å) are almost equal to the sum of the ionic radii $K^{1+} + O^{2-}$ ($\approx$ 2.70 Å), while the remaining three may be regarded as lying in the second coordination sphere (3.03-3.08 Å). A similar tendency of a large cation toward fivefold coordination has been noted for K (and its

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large analogues in Group I, Rb and Cs) in the structures of sulfates, chromates, and fluoroberyllates ([5]). In the looser K_2-polyhedron, two K_2—O distances (2.72 and 2.76 Å) are substantially shorter than the other six, which do not go outside the narrow limits 2.99-3.08 Å (see also ([5])).

Table 2

$K_2ZrSi_2O_7$. Interatomic distances (in Å)

Zr octahedron	**Zr octahedron**	**Zr octahedron**

$Zr—O_1^* = 2.11$	$O_1^*—O_4^* = 3.12$	$O_3—O_6 = 3.07$
$—O_3 = 2.06$	$—O_5^{**} = 2.83$	$—O_7 = 2.90$
$—O_4 = 2.06$	$—O_6 = 2.84$	$O_4—O_5^{**} = 3.05$
$—O_5^{**} = 2.16$	$—O_7 = 2.98$	$—O_7 = 3.00$
$—O_6 = 2.26$	$O_3—O_4 = 2.95$	$O_5^{**}—O_6 = 2.98$
$—O_7 = 2.07$	$O_3—O_5^{**} = 3.14$	$O_6—O_7 = 3.03$
Si_1 tetrahedron	**Si_1 tetrahedron**	**Si_1 tetrahedron**
$Si_1—O_1^* = 1.61$	$O_1^*—O_2 = 2.68$	$O_2—O_4 = 2.66$
$—O_2 = 1.69$	$—O_4 = 2.72$	$—O_5 = 2.63$
$—O_4 = 1.70$	$—O_5 = 2.62$	$O_4—O_5 = 2.68$
$—O_5 = 1.53$		
Si_2 tetrahedron	**Si_2 tetrahedron**	**Si_2 tetrahedron**
$Si_2—O_2^* = 1.66$	$O_2^*—O_3 = 2.61$	$O_3—O_6^* = 2.85$
$—O_3 = 1.64$	$O_6^* = 2.63$	$—O_7 = 2.54$
$—O_6^* = 1.70$	$O_7 = 2.63$	$O_6^*—O_7 = 2.66$
$—O_7 = 1.52$		
K_1-polyhedron	**K_2-polyhedron**	
$K_1—O_1 = 3.07$	$K_2—O_2 = 3.08$	
$—O_4 = 2.76$	$—O_2^* = 2.76$	
$—O_1^* = 2.76$	$—O_3^* = 3.08$	
$—O_1^* = 3.03$	$—O_3^* = 2.99$	
$—O_5^* = 3.08$	$—O_4^* = 3.00$	
$—O_6^* = 2.82$	$—O_5^* = 3.08$	
$—O_6^* = 2.83$	$—O_6^* = 2.72$	
$—O_7^* = 2.88$	$—O_7^* = 3.03$	

* Atoms obtained from the basic atoms by symmetry operations.
** Translationally identical atoms.

The structure of $K_2ZrSi_2O_7$ appears especially distinct in projection along the short axis c (Fig. 1), where it is completely resolved into four (per unit cell) parallel [$\bar{1}20$] chains with a link along the chain axis, consisting of a ZrO_6 octahedron and an Si_2O_7 diorthogroup. These chains are located at heights $c/4$ and $3c/4$, very close to the glide planes b situated at the same levels, by which the chains are also connected: the 1st and 3rd by one "proper" glide plane and likewise the 2nd and 4th by their "proper" one. Chains from different planes are connected to one another both by a center of symmetry and by screw axes 2_1. The Zr octahedra, through their vertices not occupied in the "proper" row, participate simultaneously in two translationally identical (along the z axis) rows located lower (higher) than the initial one by $c/2$ (Fig. 2).

Fig. 2. $K_2ZrSi_2O_7$. Projection yz in polyhedra. Two parallel (100) layers are distinguished, in which rows of diorthogroups are connected by Zr octahedra into openwork walls: the light ones are in the foreground, the darker ones in the background.

Fig. 2. K2ZrSi2O7. yz projection in polyhedra. Two parallel (100) layers are distinguished, in which rows of diorthogroups are connected by Zr octahedra into openwork walls: light ones are in the foreground, darker ones in the background

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Fig. 3. Na2ZrSi2O7. xy projection—analogous to the projection in Fig. 1, but replacement of K by Na distorts the motif and halves the period b, with disappearance of the glide plane b

Figure 3: Fig. 3. Na2ZrSi2O7. xy projection—analogous to the projection in Fig. 1, but replacement of K by Na distorts the motif and halves the period b, with disappearance of the glide plane b

Fig. 3. $Na_2ZrSi_2O_7$. Projection *xy*—analogous to the projection in Fig. 1, but replacement of K by Na distorts the motif and halves the period *b*, with disappearance of the glide plane *b*.

In this respect, the structure of $K_2ZrSi_2O_7$ is a packing of chain-beams, all of which are parallel to $[\bar{1}20]$. Their ends in the plane (100)

occur in a checkerboard order, i.e., the beams of some level (along *c*) are connected with those lying above and below by common edges.

From an architectural point of view it is more convenient to see in this structure parallel (100) openwork walls (two per cell at levels $x \approx a/4$ and $3a/4$ (Figs. 1 and 2). In these walls, two diortho groups lying in each glide plane *b* (at levels $c/4$ and $3c/4$) and the Zr octahedra connected with them fasten together with analogous groups in the upper and lower cell. Replacing the diortho group Si_2O_7 by an octahedron fitting into it (elongated), we find that in these walls as well there is a checkerboard alternation of occupied polyhedra (octahedra) with voids. The latter, along [101] and $[\bar{1}01]$, are joined into channels, on the walls of which the cations K_1 and K_2 are located (at the same levels $\approx c/4$ and $3c/4$).

Table 3

$K_2ZrSi_2O_7$. Valence balance

Atoms	O_1	O_2	O_3	O_4	O_5	O_6	O_7
Zr	$^2/_3$	–	$^2/_3$	$^2/_3$	$^2/_3$	$^2/_3$	$^2/_3$
Si_1	1	1	–	1	1	–	–
Si_2	–	1	1	–	–	1	1
K_1	$^3/_8$	–	–	$^1/_8$	$^1/_8$	$^2/_8$	$^1/_8$

Atoms	O_1	O_2	O_3	O_4	O_5	O_6	O_7
K_2	–	$^{2}/_{8}$	$^{2}/_{8}$	$^{1}/_{8}$	$^{1}/_{8}$	$^{1}/_{8}$	$^{1}/_{8}$
$\sum n_i^{\omega_i}$	$2^{1}/_{24}$	$2^{1}/_{4}$	$1^{11}/_{12}$	$1^{11}/_{22}$	$1^{11}/_{12}$	$2^{1}/_{24}$	$1^{11}/_{12}$

If, conversely, the Zr octahedra are replaced by the group Si_2O_7 (almost equal to them in size), then we obtain a net with alternating eight-membered and four-membered rings, as in apophyllite. Each Zr octahedron is connected with six different Si_2O_7 groups, and conversely. This makes it possible to regard $(ZrSi_2O_7)^{2-}_{\infty\infty\infty}$ as a single anionic framework, opposed by two K cations, and to speak emphatically of a K-zirconosilicate.

A comparison of the structures of $K_2Zr[Si_2O_7]$ and the recently deciphered ([6]) natural $Na_2Zr[Si_2O_7]$ shows (Fig. 3) the unity of the motif, but replacement of the large K ($r = 1.33$ Å) by the considerably smaller Na ($r = 0.98$ Å) leads to narrowing (and elongation) of the continuous channels of Fig. 1. More substantial is the twofold shortening of the long period b: in their openwork walls the groups Si_2O_7 (and the Zr octahedra) are connected no longer by a glide plane, but simply by translation.

Of considerable interest is the comparison of the two structures $K_2ZrSi_2O_7$ and $Na_2ZrSi_2O_7$ with the structure of $Na_3Sc[Si_2O_7]$ ([7]), in which 4-valent Zr is replaced by trivalent scandium, which has an almost identical ionic radius (Zr –0.81 (0.79), Sc –0.81 according to Goldschmidt and Arens). The replacement requires the introduction of a third cation (Na) into the formula. The place for this additional cation is freed by the "transfer of the diortho group" from the octahedron into a trigonal prism, which causes the transformation of the one-and-a-half-story net ([8]) $ZrO_6 + Si_2O_7$ into a single-story one in the Sc silicate.

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