

The crystal structure of kukisvumite, $\text{Na}_6\text{ZnTi}_4(\text{Si}_2\text{O}_6)_4\text{O}_4 \cdot 4\text{H}_2\text{O}$

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Received September 17, 1999; accepted January 13, 2000

Abstract. The crystal structure of kukisvumite, a rare mineral from Kola peninsula, Russia, has been refined in the *Pccn* space group with X-ray single-crystal data to $R = 0.055$. Kukisvumite, ideally $\text{Na}_6\text{ZnTi}_4(\text{Si}_2\text{O}_6)_4\text{O}_4 \cdot 4\text{H}_2\text{O}$, has $a = 29.029(4)$ Å, $b = 8.595(1)$ Å, $c = 5.209(1)$ Å, and $Z = 2$. Its crystal structure is closely related to that of lintisite; the latter mineral is obtained from kukisvumite through the substitution $\text{Zn}^{2+} + \square = 2\text{Li}^+$. In the *Pccn* space group an average structural model is realized, resulting in columns of half-occupied $[\text{ZnO}_4]$ tetrahedra and in zig-zag chains of half-occupied Na-centered octahedra. The actual structure of kukisvumite would imply a concerted ordering of zinc and sodium in neighbour cells. The polysomatic relationships of kukisvumite with the minerals of the lintisite family are shortly outlined.

Introduction

Kukisvumite was described by Yakovenchuk, Pakhomovskii and Bogdanova (1991) from an arfvedsonite-microcline pegmatite vein in the Kukisvumtschorr deposit, Khibiny alkaline massif, Kola peninsula, Russia. Microprobe analyses of kukisvumite gave the following simplified chemical formula: $\text{Na}_6\text{ZnTi}_4\text{Si}_8\text{O}_{28} \cdot 4\text{H}_2\text{O}$. The chemical composition of kukisvumite is very similar to that of lintisite, a mineral newly described from the nearby Lovozero massif (Khomyakov, Polezhaeva, Merlino, Pasero, 1990; Merlino, Pasero, Khomyakov, 1990). The chemical formula of lintisite can be written as $\text{Na}_6\text{Li}_2\text{Ti}_4\text{Si}_8\text{O}_{28} \cdot 4\text{H}_2\text{O}$, that is, the two minerals are related by the simple substitution $\text{Zn}^{2+} + \square = 2\text{Li}^+$.

The unit cell parameters of the two minerals are also closely related in spite of the different crystal systems, and the X-ray powder patterns are almost identical in all the strongest lines.

It seemed likely that close structural relationships exist between kukisvumite and lintisite. Therefore we undertook a structural study of kukisvumite from the type locality to clarify its relationships with lintisite. A preliminary account of the basic structural features of kukisvumite has been shortly outlined by Merlino and Pasero (1997). In this paper a full description of the kukisvumite structure is given.

Experimental

Preliminary Weissenberg photographs taken on selected crystals of kukisvumite confirmed the orthorhombic symmetry and the space group *Pccn*. The following unit cell parameters for the crystal eventually chosen for the intensity data collection (dimensions $0.44 \times 0.06 \times 0.02$ mm) were refined at the four-circle diffractometer: $a = 29.029(4)$, $b = 8.595(1)$, $c = 5.209(1)$ Å.

The intensity data set was collected with a Siemens four-circle diffractometer. Operating conditions were the following: room temperature, 50 kV, 40 mA, MoK_α , $\lambda = 0.71069$ Å, scan mode $\theta - 2\theta$, scan speed $2^\circ/\text{min}$, maximum $2\theta = 50^\circ$, $-1 \leq h \leq 34$, $-1 \leq k \leq 10$, $-1 \leq l \leq 6$, refinement carried out against squared structure amplitudes (1138 independent reflections) with SHELXL-93 (Sheldrick, 1993) computer package, absorption effects accounted for through XABS2 (Parkin, Moezzi, Hope, 1995).

Structure refinement

On the basis of the reasonable hypothesis that kukisvumite was structurally very similar to lintisite, a starting set of fractional coordinates for kukisvumite was obtained on the basis of the monoclinic structure of lintisite, which has an approximately pseudo-orthorhombic metric ($\beta \approx 91^\circ$), by taking into account the different origin and space group symmetry. The site occupancy factors of some atoms were lowered on the basis of crystal-chemical considerations. Therefore a zinc atoms with 50% occupancy was placed in the same site which is occupied by lithium in lintisite. Moreover, also the occupancy of Na2 atom was fixed at 50%, because the space group *Pccn* resulted in two incompatible equivalent positions for Na2, 2.60 Å apart. For the same reason, we fixed 50% occupancy for the water molecule, too: owing to the different symmetry in kukisvumite there are two independent, half occupied sites, O81 and O82, instead of a single O8 site in lintisite. The full occupancy at those sites, too, would have implied some additional impossible interatomic distances, e.g., 1.02 Å between O81 and O82.

Such a structural model was refined smoothly. The final reliability indices for the anisotropic model were $R1$ (conventional R factor) = 0.055 for 588 reflections with

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$F_o > 4\sigma(F_o)$ and 0.146 for all 1138 reflections, $wR2$ (weighted R factor on F^2) = 0.148; weighting scheme = $1/[\sigma^2(F_o^2) + (0.0531P)^2 + 0.00P]$, where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$.

The maximum and minimum electron density maxima in the final difference Fourier synthesis were $+0.67$ and $-0.64 \text{ e}/\text{\AA}^3$, with all major positive electron density maxima in the surroundings of O81 and O82. Owing to the disordered nature of kukisvumite the hydrogen atoms were included in the refinement in calculated positions, and the relevant O—H and H...O distances were constrained to reasonable values during the refinement.

The final fractional coordinates and displacement parameters for kukisvumite are listed in Table 1. Selected bond distances are given in Table 2, and are compared with the corresponding distances in lintisite. The valence bond balance is reported in Table 3.

Table 1a. Final fractional coordinates and U_{eq} displacement parameters for kukisvumite; e.s.d.'s are given in parentheses and refer to the last digit.

Atom	x	y	z	U_{eq}
Ti	0.5830(1)	0.8450(4)	0.1322(7)	0.0055(8)
Si1	0.4863(2)	0.8418(7)	0.7887(9)	0.005(1)
Si2	0.6557(2)	0.1484(6)	0.0514(9)	0.007(1)
Zn ^a	$3/4$	$1/4$	0.791(2)	0.024(2)
Na1	0.5840(3)	0.0615(8)	0.623(2)	0.015(2)
Na2 ^a	0.7500(7)	0.591(2)	0.786(3)	0.031(4)
O1	0.4652(4)	0.763(1)	0.050(3)	0.009(3)
O2	0.4641(4)	0.011(1)	0.754(3)	0.007(3)
O3	0.6223(4)	0.000(1)	0.006(2)	0.009(3)
O4	0.7917(4)	1.108(1)	0.539(3)	0.022(4)
O5	0.8879(4)	0.820(1)	0.939(3)	0.006(3)
O6	0.6398(4)	0.274(1)	0.825(2)	0.011(3)
O7	0.5420(4)	0.833(1)	0.793(2)	0.007(3)
O81 ^a	0.7922(8)	0.851(4)	0.934(5)	0.016(6)
O82 ^a	0.7965(9)	0.849(4)	1.128(6)	0.025(7)
H1 ^a	0.792	0.93	0.80	0.05
H2 ^a	0.825	0.81	0.94	0.05
H3 ^a	0.797	0.95	1.24	0.05
H4 ^a	0.828	0.85	1.04	0.05

a: *s.o.f.* 0.5 (see text for explanation).

Table 1b. Anisotropic displacement parameters for kukisvumite.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ti	0.008(2)	0.005(2)	0.004(2)	0.001(2)	0.000(1)	0.001(2)
Si1	0.004(3)	0.005(2)	0.006(2)	-0.001(3)	0.000(2)	0.002(3)
Si2	0.006(2)	0.007(2)	0.008(2)	0.000(3)	-0.001(2)	0.001(3)
Zn	0.024(4)	0.025(4)	0.022(4)	0	0	0.001(4)
Na1	0.020(4)	0.012(4)	0.013(4)	-0.001(4)	-0.001(4)	-0.001(4)
Na2	0.030(10)	0.042(11)	0.022(9)	-0.001(9)	0.007(9)	-0.009(11)
O1	0.004(6)	0.011(6)	0.010(6)	0.003(7)	-0.003(6)	-0.003(7)
O2	0.008(7)	0.003(6)	0.012(7)	-0.003(7)	-0.005(7)	0.002(6)
O3	0.006(6)	0.013(7)	0.009(8)	0.001(6)	0.005(6)	0.001(5)
O4	0.007(7)	0.009(7)	0.050(10)	-0.001(7)	0.002(8)	0.006(6)
O5	0.004(7)	0.007(7)	0.006(6)	0.001(6)	0.000(5)	-0.002(5)
O6	0.010(7)	0.009(7)	0.014(8)	0.009(6)	0.001(6)	0.002(6)
O7	0.006(6)	0.006(7)	0.008(6)	-0.001(7)	0.002(5)	-0.005(6)
O81	0.004(14)	0.023(16)	0.021(16)	0.008(21)	0.003(12)	-0.007(16)
O82	0.009(14)	0.039(18)	0.027(18)	-0.017(24)	-0.005(15)	0.003(18)

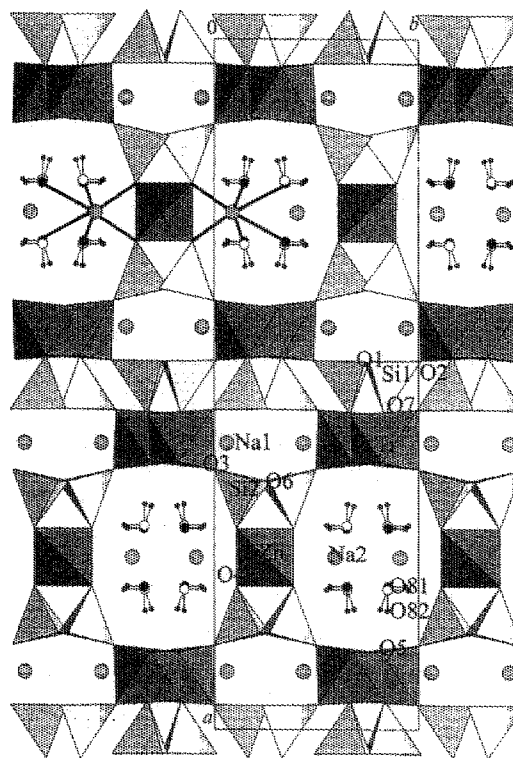


Fig. 1. The crystal structure of kukisvumite, as seen along [001]. The unit cell is outlined. The coordination of Na2 is sketched only twice, to avoid confusion with the atom labels, which are in keeping with the fractional coordinates of Table 1.

Description of the structure

The structure of kukisvumite (depicted in Fig. 1) is closely related to that of lintisite (Merlino, et al., 1990). All coordination polyhedra are similar in the two structures (cf. Table 2). The titanium is octahedrally coordinated by six oxygen atoms, the octahedra giving rise to zig-zag chains through sharing of edges. The titanium atoms occupy eccentric positions within the coordination polyhedra. The two independent silicon atoms occur within tetrahedra arranged in pyroxene-like chains, having O—O—O angles of 171° (Si1 chains) and 162° (Si2 chains). Zinc is in tetrahedral coordination as well. Unlike lithium in lintisite, in

Table 2a. Bond lengths (Å) in kukisvumite. The corresponding distances in lintsite (Merlino, et al., 1990) are reported for the sake of comparison.

	kukisvumite	lintsite
Ti polyhedron		
O5	1.82(1)	1.807(3)
O3a	1.87(1)	1.874(3)
O5b	1.93(1)	1.923(3)
O2c	1.94(1)	1.956(3)
O7b	2.11(1)	2.116(3)
O7d	2.13(1)	2.141(3)
(Ti—O)	1.968	1.969
Si1 polyhedron		
O2e	1.60(1)	1.597(3)
O7d	1.62(1)	1.628(3)
O1	1.64(1)	1.638(3)
O1b	1.65(1)	1.648(3)
(Si1—O)	1.628	1.628
Si2 polyhedron		
O4a	1.56(1)	1.586(3)
O3a	1.62(1)	1.629(3)
O6b	1.64(1)	1.653(3)
O6e	1.66(1)	1.663(3)
(Si2—O)	1.622	1.633
Zn polyhedron		
		(Li-polyhedron)
O4f	2.15(1)	2.013(7)
O4a	2.15(1)	2.013(7)
O4g	2.16(1)	2.014(6)
O4b	2.16(1)	2.014(6)
(Zn—O)	2.154	2.014
Na1 polyhedron		
O3a	2.34(1)	2.355(4)
O1h	2.42(1)	2.419(3)
O5d	2.43(1)	2.448(3)
O7d	2.47(1)	2.464(3)
O2i	2.49(1)	2.500(4)
O6j	2.65(1)	2.589(3)
O6e	2.66(1)	2.649(3)
O1k	2.69(1)	2.687(3)
(Na1—O)	2.519	2.514
Na2 polyhedron		
O81l	2.26(3)	2.328(4)
O82m	2.29(4)	2.328(4)
O4g	2.46(2)	2.513(3)
O4a	2.48(2)	2.513(3)
O81n	2.66(4)	2.638(4)
O82n	2.72(4)	2.638(4)
(Na2—O)	2.481	2.493

which columns of edge-sharing [LiO₄] tetrahedra occur, in the case of kukisvumite every second tetrahedral site is empty. This is related to the electrostatic valence balance, Zn²⁺ having a doubled charge with respect to Li⁺, and is accomplished, as stated above, by setting 50% occupancy at the zinc site, in close agreement with the chemical composition of kukisvumite. Of the two sodium atoms, Na1 is eight-fold coordinated by eight oxygens, Na2 is octahedrally coordinated by two oxygen atoms and four water molecules [NaO₂(H₂O)₄], giving rise to zigzag chains. In this latter case, too, the occupancy of sodium (Na2) and water molecules (O81 and O82) is halved.

Therefore the only major difference is the presence, in kukisvumite, of a zinc and sodium slab, instead of a lithium and sodium slab as in lintsite. These two structural units are compared in Fig. 2.

Table 2b. Distances (Å) and angles (°) involving water molecules in kukisvumite.

	O—H distance	O...O distance	O—H—O angle
<i>O81 water molecule</i>			
O81—H1...O4	1.00	3.02(3)	178
O81—H2...O5	1.00	2.79(3)	142
H1—O81—H2 angle			104
<i>O82 water molecule</i>			
O82—H3...O4 ⁿ	1.04	3.10(3)	178
O82—H4...O5	1.01	2.84(3)	158
H3—O82—H4 angle			105

Symmetry codes for equivalent positions: a: $x, y + 1, z$; b: $x, -y + 3/2, z - 1/2$; c: $-x + 1, -y + 1, -z + 1$; d: $x, y, z - 1$; e: $x, y + 1, z - 1$; f: $-x + 3/2, -y + 3/2, z$; g: $-x + 3/2, y + 1, z - 1/2$; h: $-x + 1, y + 1/2, -z - 1/2$; i: $-x + 1, -y + 1, -z$; j: $x, -y + 3/2, z - 3/2$; k: $-x + 1, -y + 2, -z$; l: $-x + 3/2, y, z - 3/2$; m: $-x + 3/2, y, z - 1/2$; n: $-x + 3/2, -y + 3/2, z - 1$; o: $x, y, z + 1$.

The half-occupancy of some atoms (Zn, Na2, O81, O82) in the structure of kukisvumite means that the real symmetry of the mineral is lower than *Pccn*, and that the average structure only can be assessed in this space group, in which two different, although geometrically equivalent, configurations are in superposition. In the actual structure either of these two configurations occurs at every single unit cell. As an hypothesis, the possible ordering of the two configurations should give rise to the doubling of the *b* cell parameter. However, careful inspection of long-exposed Weissenberg photographs, and of a number of selected area electron diffraction patterns, did not provide evidences of long-range ordering in kukisvumite. Therefore the disordered model better describes the real structure of the mineral.

It is worth noting that, unlike the other cations, the average (Zn—O) distance is significantly longer than ex-

Table 3. Bond valence balance given in conventional valence units (v.u.) and computed according to Brese & O'Keeffe (1992). The contribution of hydrogen bonds has been computed following Ferraris & Ivaldi (1988). Left and right superscripts indicate the number of equivalent bonds for each cation and each anion, respectively.

	Ti	Si1	Si2	Zn	Na1	Na2	H-bonds Σ_v
O1		0.95			0.19		2.16
		0.93			0.09		
O2	0.72	1.07			0.15		1.94
O3	0.85		1.01		0.23		2.09
O4			1.18	² 0.30 ^{0.5} ² 0.29 ^{0.5}		0.17 ^{0.5} 0.16 ^{0.5}	0.13 ^{0.5} 0.11 ^{0.5}
O5	0.99				0.18		0.19 ^{0.5} 0.17 ^{0.5}
	0.73						2.08
O6			0.95		0.10		2.05
			0.90		0.10		
O7	0.45	1.02			0.16		2.05
	0.42						
O81						0.28	-0.13
						0.10	-0.19
O82						0.26	-0.11
						0.08	-0.17
$\Sigma_{c,v}$	4.16	3.97	4.04	1.18	1.20	1.05	

