American Mineralogist, Volume 85, pages 1516–1520, 2000

Tumchaite $Na_2(Zr,Sn)Si_4O_{11}\cdot 2H_2O$—A new mineral from carbonatites of the Vuoriyarvi alkali-ultrabasic massif, Murmansk Region, Russia

VICTOR V. SUBBOTIN,[1,]* STEFANO MERLINO,[2] DMITRY YU. PUSHCHAROVSKY,[3]
YAKOV A. PAKHOMOVSKY,[1] ORAZIO FERRO,[2] ALLA N. BOGDANOVA,[1] ANATOLY V. VOLOSHIN,[1]
NATALIA V. SOROKHTINA,[1] AND NATALIA V. ZUBKOVA[3]

[1]Geological Institute, Kola Science Centre of the Russian Academy of Sciences, Fersman Street 14, 184200 Apatity, Russia
[2]Department of Earth Sciences, University of Pisa, Via S. Maria 53, I-56126 Pisa, Italy
[3]Department of Crystallography, Geological Faculty, Moscow State University, 119899 Moscow, Russia

ABSTRACT

Tumchaite, $Na_2(Zr,Sn)Si_4O_{11}\cdot 2H_2O$, is a new species from the Vuoriyarvi alkali-ultrabasic massif, Murmansk Region, Russia, where it occurs as colorless to white tabular monoclinic crystals associated with calcite, dolomite, a mineral of the serpentine group and pyrite in the late dolomite-calcite carbonatites. It is transparent to translucent; with vitreous luster; and perfect cleavage on (100). Mohs hardness is 4.5, D_{meas} is 2.78 (2) g/cm^3. Tumchaite is optically biaxial (-), with $\alpha = 1.570$ (2), $\beta = 1.588$ (2), $\gamma = 1.594$ (2), $2V_{meas} = 60$ (5)°, and elongation positive, $Y = b$, $c \wedge Z = 3°$. Pleochroism exists, with $Y = Z$ = colorless, X = greenish-gray. Electron microprobe analysis gave (wt%): Na_2O 13.72, CaO 0.15, SiO_2 52.71, TiO_2 0.35, ZrO_2 20.41, SnO_2 5.73, HfO_2 0.60, H_2O (computed assuming $2H_2O$ pfu.) 7.86, total 101.53. The X-ray study pointed to space group $P2_1/c$, $a = 9.144$ (4), $b = 8.818$ (3), $c = 7.537$ (3) Å, $\beta = 113.22$ (3)°, $V = 558.49$ Å^3, $Z = 2$. The strongest lines of the powder diffraction pattern [d in Å (I) (hkl)] are: 8.40 (10) (100), 5.38 (9) ($11\bar{1}$), 4.00 (8) (111), 3.401 (9) ($20\bar{2}$), 2.902 (9) (211), 2.691 (9) ($13\bar{1}$). The crystal structure of tumchaite was refined to R = 0.043 for 865 $F_o > 4\sigma(F_o)$. The mineral is isotypic with penkvilksite-1M. The structure is characterized by silicate sheets parallel (100), formed by alternating clockwise- and counterclockwise-growing spiral chains of corner-sharing SiO_4 tetrahedra. The sheets are connected by octahedra occupied by (Zr, Sn) at 0, 1/2, 0. The Zr/Sn ratio in the octahedra is 4. Water molecules and Na cations are placed in the cavities of the polyhedral framework. The ideal crystal-chemical formula is $Na_2(Zr_{0.8}Sn_{0.2})[Si_4O_{11}]\cdot 2H_2O$. The mineral is named tumchaite for the river Tumcha near Vuoriyarvi massif.

INTRODUCTION

A new hydrous silicate of Na, Zr, and Sn was found in carbonatites of the alkaline-ultramafic Vuoriyarvi massif, the Murmansk Region, Russia. The mineral is named tumchaite for the river Tumcha near Vuoriyarvi alkali-ultrabasic massif. The new mineral species and its name were approved by the IMA Commission on New Minerals and New Mineral Names. Type material (holotype) is deposited at the Gorniy Museum of St. Petersburg Mining Institute (Technical University), St. Petersburg, Russia under catalogue number 3123.

OCCURRENCE AND PARAGENESIS

The Vuoriyarvi alkali-ultrabasic massif is located in the North Karelia on the north shore of the Vuoriyarvi lake and occupies an area of about 19.5 km^2. The rocks of the massif are represented by dunites, pyroxenites, ijolite-melteigites, phoscorites, and carbonatites (Kukharenko et al. 1965; Kogarko et al. 1995).

The mineral has been found as lens-like segregation of 0.5 × 1.0 × 1.5 cm^3 in size in core sample from bore hole, which crosscuts veined dolomite-calcite carbonatites occurring in pyroxenites from the central part of the Vuoriyarvi massif. The mineral, which is associated with calcite, dolomite, a mineral of the serpentine group and pyrite, formed in the hydrothermal alteration of carbonatites.

PHYSICAL AND OPTICAL PROPERTIES

Tumchaite occurs as tabular monoclinic crystals (Fig. 1). The size of individual crystals is up to 0.2 × 1.2 × 2.5 mm^3. The mineral is colorless to white, transparent to translucent, with a vitreous luster. The color of the power is white. Cleavage is perfect on (100), and very brittle, with uneven fracture. Parting is not observed. The Mohs hardness is close to 4.5. The Vickers hardness number with a 40 g load ranged from 365 to 445 (mean 410) kg/mm^2. The density, determined by flotation of the mineral using a dilute Clerici-H_2O solution, is 2.78 (2) g/cm^3, to compare with the value 2.77 g/cm^3, calculated on the basis of empirical formula.

In transmitted light ($\lambda = 589$ nm), the mineral is colorless, biaxial negative, $\alpha = 1.570$ (2), $\beta = 1.588$ (2), $\gamma = 1.594$ (2), and the measured $2V = 60$ (5)° compared to a calculated value of 59.4°. $Y = b$, $c \wedge Z = 3°$, and elongation is positive. Pleochroism consists of $Y = Z$ = colorless, X = greenish-gray. Twin-

---

* E-mail: sub@geo.kolasc.net.ru

ning on (100) was observed. Tumchaite does not luminesce under ultraviolet light or cathode rays. It is not dissolved by dilute hydrochloric acid.

The IR spectrum of tumchaite was recorded from powdered sample dispersed in KBr using the Specord-M80 spectrophotometer and shows the following absorption bands (the strongest starred): 3500*, 3450*, 1634*, 1158*, 1072, 992*, 958, 926, 776, 720, 668, 585, 560*, 540, 484*, 438*, 420, 400, 356, 335, 305, 288 cm^{-1}. The IR spectrum is similar to that of penkvilksite from the Lovozero massif, but the latter differs slightly in the positions and relative intensities of the majority of absorption bands. Differences are observed for the bending and stretching frequencies of H_2O molecules at 1634, 3450, and 3500 cm^{-1} in tumchaite compared to 1582, 1640, 3420, and 3550 cm^{-1} in penkvilksite.

CHEMICAL COMPOSITION

Quantitative electron microprobe analysis was performed with MS 46 CAMECA instrument operated at 20 kV (30 kV for Zr) and sample current 15–30 nA. The following standards were used for the elements shown in parentheses: lorenzenite (for Na and Ti), diopside (Ca and Si), wadeite (Zr), hematite (Fe), $MnCO_3$ (Mn), $Y_3Al_5O_{12}$ (Y), metallic Sn, Hf, and Nb.

Six different crystals of tumchaite were analyzed. The analyses, obtained from 6 to 10 analytical points in each crystal, indicated a constant chemical composition. Table 1 gives the chemical data for the crystal presenting a chemical composition closest to the average, as well as the whole compositional range. Water contents could not be determined owing to little quantity of homogeneous material. The presence of molecular water in the mineral, indicated by IR spectroscopy (above) was confirmed by the refinement of the crystal structure. The Empirical formula, calculated on the basis of 13 O atoms is $(Na_{2.03}Ca_{0.01})(Zr_{0.76}Sn_{0.17}Ti_{0.02}Hf_{0.01})Si_{4.02}O_{11}\cdot 2H_2O$, which simplifies to $Na_2(Zr,Sn)Si_4O_{11}\cdot 2H_2O$.

X-RAY CRYSTALLOGRAPHY

A single crystal with approximate dimensions 0.20 × 0.20 × 0.20 mm^3 was selected for X-ray study, which was carried out on a Siemens P4 four circle diffractometer, using graphite monochromatized Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å). The unit cell parameters were derived through a least square fit using 25 medium θ reflections: $a = 9.144$ (4), $b = 8.818$ (3), $c = 7.537$ (3) Å, $\beta = 113.22$ (3)°, $V = 558.49$ $Å^3$, $Z = 2$. The powder diffraction pattern of tumchaite (Debye-Scherrer camera with diameter 114.6 mm, Fe$K\alpha$ radiation) indexed on the basis of these parameters is shown in Table 2. The monoclinic symmetry and the lattice dimensions of tumchaite clearly indicated its close relationships with penkvilksite-1*M* (Merlino et al. 1994), which was subsequently confirmed by single-crystal study.

A total of 2095 reflections was collected with minimum $2\theta = 4°$ and maximum $2\theta = 70.23°$: $0 \le h \le 10$, $-10 \le k \le 10$, $-8 \le l \le 8$. The intensity of three standard reflections, measured every 97 observations, did not show any fluctuation larger than 3%. After merging ($R_{int} = 0.05$), the number of reflections decreased to 982. All intensities were corrected for absorption by

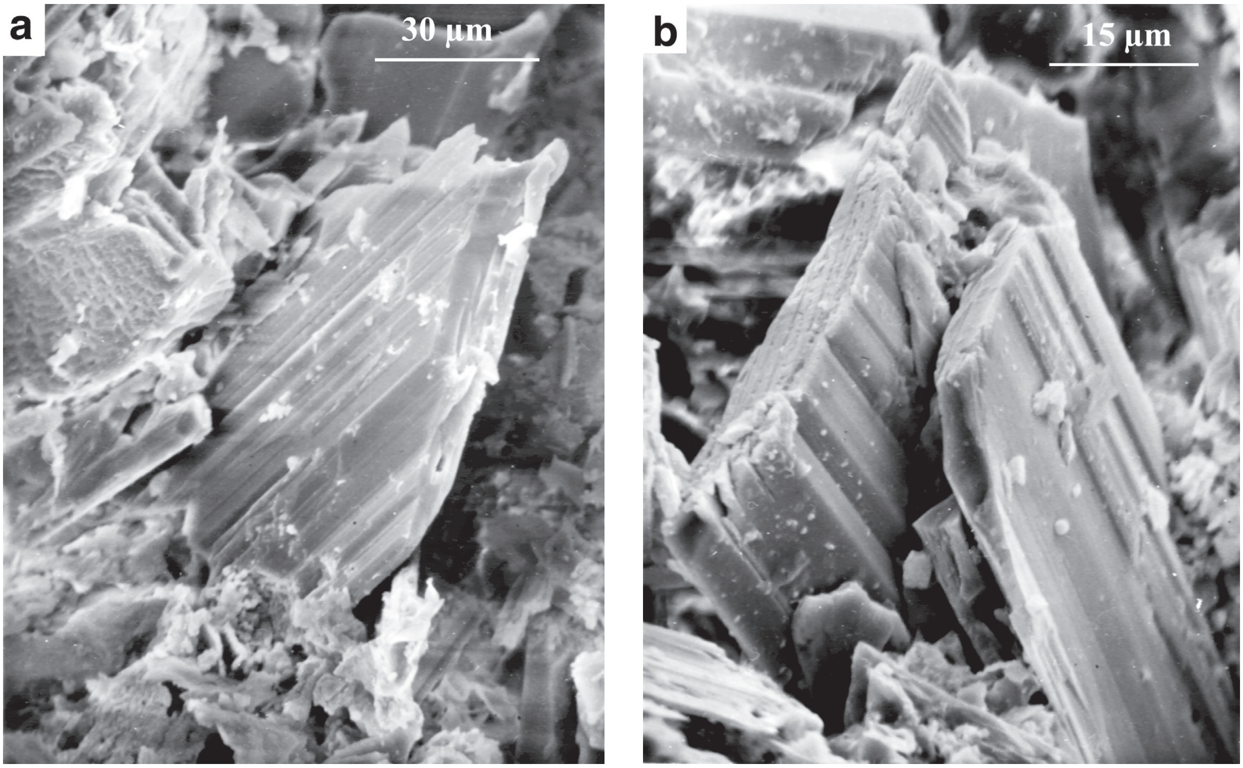

FIGURE 1. (**a** and **b**) SEM photomicrograph of typical tumchaite crystals shaped by the prism {*hkl*}, and by two pinacoids {100} and {*h*0*l*}. Grains are tabular on (100), elongated along [001].

TABLE 1. Chemical composition of tumchaite (wt%)

	Typical crystal	Range†
Na_2O	13.72	13.3–14.1
CaO	0.15	0.10–0.34
MnO	<0.02	0.00–0.02
FeO	<0.02	<0.02–0.04
Y_2O_3	<0.1	<0.1–0.2
SiO_2	52.71	52.6–54.2
TiO_2	0.35	0.10–0.35
ZrO_2	20.41	18.2–21.0
SnO_2	5.73	4.14–6.18
HfO_2	0.60	0.58–0.87
Nb_2O_5	<0.05	<0.05–0.15
H_2O by difference	7.86*	
Total	101.53	

* Computed assuming $2H_2O$ pfu.
† For six different crystals.

ψ-scan procedure and reduced to $|F|^2$. Crystal structure refinement, carried with a starting model based on the structure of penkvilksite-1*M*, was performed in the space group $P2_1/c$, using reflections with $I > 2\sigma(I)$, using the software package SHELX-97 (Sheldrick 1997). The structure determination was completed through a $\Delta\rho$ synthesis that determined the sites of H atoms. Thus the formula of the compound, $Na_2(Zr_{0.8}Sn_{0.2})[Si_4O_{11}]\cdot 2H_2O$, which fits with the chemical data, was established as a result of its structural investigation. The refinement of the structure with anisotropic displacement parameters for all atoms (except H) and with isotropic displacement parameters for H atoms decreased the *R* to 0.043 for 865 $F_o > 4\sigma(F_o)$ and the *R* to 0.051 for all 982 data; wR (F^2) = 0.104. The final electron density map was featureless: maximum $\Delta\rho = 0.89$ e/Å^3, minimum $\Delta\rho = -0.74$ e/Å^3. Refined atomic coordinates and interatomic distances are given in Tables 3 and 4. Intensity calculations (Yvon et al. 1977) for tumchaite (Table 2) demonstrated a good correspondence with powder diffraction data.

DESCRIPTION OF THE STRUCTURE

Tumchaite is isotypic with penkvilksite-1*M* and is chemically related to vlasovite. As in both 1*M* and 2*O* polytypes of penkvilksite, the dominant structural feature of tumchaite is the silicate sheet $[Si_4O_{11}]$ parallel to (100), which can be considered as a result of condensation of the tetrahedral spiral chains running along [010] with six tetrahedra in the repeat unit (Fig. 2). Adjacent spirals are oriented in alternate clockwise and counterclockwise way. The silicate sheets revealed in penkvilksite and in tumchaite extend our ideas about polymorphism of tetrahedral complexes $[Si_4O_{11}]$ (Pushcharovsky 1986), which were reported before as bands (amphiboles, vlasovite) or as framework (neptunite). Topologically related phosphate tetrahedral sheets were also found in the structure of synthetic magnesium ultraphosphate MgP_4O_{11} (Yakubovich et al. 1993). Tumchaite contains two symmetrically independent SiO_4 tetrahedra: Si1 and Si2 have two and three bridging O atoms, respectively. Similarly to other silicates, Si-O$_{br}$ distances are elongated (avg. Si-O$_{br}$ = 1.637 Å) as compared with Si-O$_{nbr}$ distances (avg. 1.598 Å).

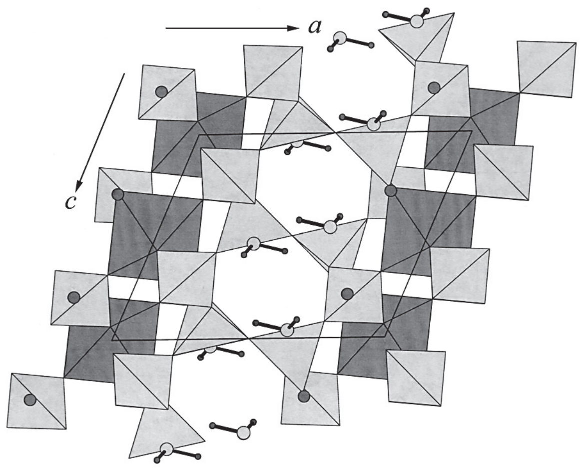

FIGURE 2. Perspective view of tumchaite along [010] (Dowty 1995). Filled, darker circles correspond to Na cations, ZrO_6 octahedra are dark gray, SiO_4 tetrahedra are shown as light gray, water molecules are shown as light gray circles (O-anions) connected by bold lines with small black circles (H-cations).

The tetrahedral silicate sheets are connected by cationic octahedra with a disordered distribution of Zr and Sn (at 0, 1/2, 0). The Zr/Sn ratio in these octahedra is 4. According to the value of ionic radii, Zr (r = 0.72 Å) is in between two groups of elements: (1) typically octahedral cations Mg^{2+}, Fe^{2+}, Ti^{4+}, Nb^{5+}, etc. with ionic radii 0.6–0.7 Å; (2) relatively large cations Ca^{2+}, Y^{3+}, U^{4+}, Th^{4+} with r = 0.9–1.0 Å (Pyatenko et al. 1999). The difference in valence of 2 vu seems too large to allow easy isomorphous replacement of Zr by bivalent cations. In addition, Zr always exhibits the tendency to be located in isolated octahedra. So far, on the basis of both these aspects, Hf^{4+} (r = 0.71 Å) has been considered a good isomorphic partner for Zr^{4+} in octahedra. However Sn^{4+}, with r = 0.69 Å and with the tendency to form isolated SnO_6 octahedra in silicates [for example pabstite, $Ba(Sn,Ti)Si_3O_9$, sorensenite, $Na_4SnBe_2Si_6O_{18}\cdot 2H_2O$] is also appropriate for substitution of Zr, but this substitution was not reported previously. The average distances Zr-O = 2.079 Å are very similar to those (2.08 Å) reported by Voronkov et al. (1978) for ZrO_6 octahedra in oxysalts. In the terminology of Liebau (1985), tumchaite has an unbranched single sheet with the fundamental vierer chains running parallel [001]. The structural formula of tumchaite, following IUCr recommendation (Lima-de-Faria et al. 1990), can be presented in the form: $Na_2^{[6]}Zr^{[6o]}\{\boldsymbol{uB}, 1^2_\infty\}[^4(Si_2^{[4t]\,[1;3]}\,Si_2^{[4t]\,[2;2]})O_{11}]\cdot 2H_2O$.

The 3-dimensional heteropolyhedral framework of tumchaite belongs to the series of typical mixed frameworks with general formula: $M_mT_nO_{3m+2n}$ (M and T octahedrally and tetrahedrally coordinated cations, respectively) (Voronkov et al. 1978). In these frameworks tetrahedra and octahedra are connected only through vertices, each vertex being shared only by two polyhedra. The mixed frameworks of zirconosilicates which belong to this category are characterized by the formula: $[Zr_mSi_nO_{3m+2n}]^{-2m}$. If the negative charge of the mixed framework is compensated only by alkaline cations, one obtains the following general formula of corresponding compounds: $A^+_{2m}Zr_mSi_nO_{3m+2n}$. This series comprises about 20 minerals and synthetic compounds, namely Na-containing vlasovite, tumchaite, gaidonnayite, hilairite, elpidite, etc. The mixed frameworks in

TABLE 2. X-ray powder diffraction pattern of tumchaite

I_{obs}	I_{calc}	d_{obs}	d_{calc}	*h k l*	I_{obs}	I_{calc}	d_{obs}	d_{calc}	*h k l*
10	100	8.40	8.4033	1 0 0	4	4	1.642	1.6438	1 5 1
9	68	5.38	5.3981	1 1 $\bar{1}$	2	1	1.573	1.5716	0 5 2
5	13	4.41	4.4090	0 2 0	5	4	1.543	1.5461	4 0 2
1	4	4.18	4.2017	2 0 0	2	3	1.528	1.5320	2 5 1
8	53	4.00	4.0353	1 1 1	2	3	1.518	1.5208	4 4 0
2	11	3.889	3.9042	1 2 0	3	5	1.502	1.5054	2 3 3
9	60	3.401	3.4133	2 0 $\bar{2}$	3	5	1.477	1.4773	$\bar{3}$ 1 5
4	15	3.143	3.1624	1 2 1	2	2	1.456	1.4590	5 3 0
9	56	2.902	2.9180	2 1 1	4	2	1.438	1.4394	1 5 $\bar{3}$
7	24	2.772	2.7784	3 0 $\bar{2}$	2	1	1.428	1.4292	$\bar{4}$ 1 5
9	50	2.691	2.6997	1 3 $\bar{1}$	2	2	1.412	1.4153	1 4 $\bar{4}$
3	12	2.449*	2.4534	2 3 $\bar{1}$	4	3	1.400	1.4006	6 0 0
2	3	2.309	2.3175	$\bar{1}$ $\bar{3}$ 2	2	1	1.394	1.3940	$\bar{3}$ 5 3
2	4	2.267	2.2692	2 0 2	2	2	1.366	1.3685	0 1 5
4	8	2.214	2.2045	0 4 0	3	2	1.347	1.3451	3 3 3
7	12	2.190	2.2034	3 1 $\bar{3}$	1	2	1.335	1.3383	5 3 1
	4		2.2028	4 1 $\bar{1}$					
3	4	2.126	2.1323	1 4 0	1	2	1.328	1.3303	6 3 $\bar{1}$
3	3	2.091	2.1008	4 0 0	1	3	1.319	1.3094	1 3 $\bar{5}$
1	1	2.024	2.0216	4 2 $\bar{1}$	3	1	1.307	1.3066	5 1 2
3	6	1.940	1.9445	4 1 $\bar{3}$	2	1	1.297	1.2991	3 6 $\bar{2}$
3	4	1.900	1.8965	4 2 0	3	4	1.251	1.2531	0 3 5
	2		1.8942	2 3 $\bar{3}$					6 4 $\bar{2}$
3	5	1.881	1.8597	0 4 2	1	2	1.237	1.2383	5 3 $\bar{5}$
	4		1.8519	2 4 $\bar{2}$					
5	9	1.847	1.8502	3 0 2	3	3	1.163	1.1659	7 3 $\bar{1}$
3	3	1.805	1.8068	1 1 $\bar{4}$	3	3	1.149	1.1488	5 1 3
5	11	1.793	1.7994	3 3 $\bar{3}$	2	2	1.135	1.1359	6 5 $\bar{3}$
3	6	1.762	1.7678	5 1 $\bar{1}$	2	2	1.120	1.1205	0 6 4
5	12	1.728	1.7324	2 2 $\bar{4}$	2	1	1.112	1.1130	6 2 2
	5		1.7323	3 4 0					
4	4	1.702	1.7067	4 0 $\bar{4}$	2	1	1.105	1.1049	3 7 1
2	2	1.676	1.6756	4 1 $\bar{4}$	2	3	1.098	1.0988	4 2 4
2	5	1.668	1.6710	1 3 3	1	0.4	1.089	1.0913	3 4 $\bar{6}$

* Superposition of β-reflection.

TABLE 3. Final positional and displacement parameters (Å^2) for tumchaite

Atom	x	y	z	U^*
Zr,Sn	0	0.5	0	0.0076(3)
Si1	0.1669(2)	0.1582(2)	0.1993(3)	0.0093(4)
Si2	0.3176(1)	0.4421(2)	0.4124(3)	0.0093(4)
Na	0.2051(4)	0.6884(3)	0.7109(4)	0.0243(7)
O1	0.3148(5)	0.2659(5)	0.3454(7)	0.0129(10)
O2	0.1164(6)	0.0346(5)	0.3187(7)	0.0126(10)
O3	0.0260(6)	0.2676(5)	0.0660(7)	0.0131(10)
O4	0.2471(6)	0.0543(5)	0.0791(7)	0.0131(10)
O5	0.2145(6)	0.5425(5)	0.2299(7)	0.0120(10)
O6	0.5	0	0	0.0157(14)
OW	0.3709(7)	0.6921(7)	0.0371(9)	0.0317(14)
H1	0.498	0.684	0.075	0.05
H2	0.352	0.602	0.090	0.05

* The equivalent isotropic displacement was converted from the anisotropic parameters (with the exception of the H atoms). The anisotropic displacement parameters are available from the authors.

TABLE 4. Selected interatomic distances (Å) and angles (°) for tumchaite

Zr-O2 ×2	2.060(5)	Si2-O5	1.594(5)
Zr-O5 ×2	2.076(5)	Si2-O6	1.616(2)
Zr-O3 ×2	2.100(5)	Si2-O4	1.623(5)
Avg.	2.079	Si2-O1	1.631(5)
Si1-O2	1.593(5)	Avg.	1.616
Si1-O3	1.607(5)	O1-Si2-O4	107.2(3)
Si1-O4	1.649(5)	O1-Si2-O5	109.3(3)
Si1-O1	1.664(5)	O1-Si2-O6	108.4(2)
Avg.	1.628	O4-Si2-O5	112.2(3)
O1-Si1-O2	111.0(3)	O4-Si2-O6	109.8(2)
O1-Si1-O3	108.3(3)	O5-Si2-O6	109.9(2)
O1-Si1-O4	105.1(3)	Avg.	109.5
O2-Si1-O3	115.1(3)	Na-OW	2.325(7)
O2-Si1-O4	102.8(3)	Na-O5	2.377(6)
O3-Si1-O4	114.3(3)	Na-O2	2.388(6)
Avg.	109.4	Na-O3	2.414(6)
		Na-O4	2.453(6)
		Na-OW	2.586(7)
		Avg.	2.424
		OW-H1	1.081
		OW-H2	0.930

their structures are characterized by the formation of the almost equivalent bonds Si-O-Si or Si-O-Zr, which determine the stability of such polyhedral configurations.

Note that Zr and Ti atoms lead to the crystallization of natural alkaline silicates from ultra-agpaitic media, when the formation of feldspars and of nepheline is impossible due to the lack of Al atoms (Pyatenko et al. 1999); hence the variety of zirconosilicates and titanosilicates observed in ultra-agpaitic rocks (Khibina and Lovozero, Kola peninsula, Russia; Mont Saint Hilaire, Quebec, Canada). The composition of hydrothermally altered carbonatites of the alkaline-ultramafic Vuoriyarvi massif is close to that of the ultra-agpaitic rocks and consequently both mineral systems contain a similar association of Zr- and Ti-minerals (catapleiite, gaidonnayite, georgechaoite, hilairite, komkovite, elpidite, lorenzenite, etc.)

The bond valence calculation (Brown and Shannon 1973) allowed the assignment of O and H_2O to oxygen positions (Table 5). Similarly with penkvilksite the H_2O molecule is linked only to Na^+ and form H bonds with O1 and O5 atoms. The calculation of O-H···O bonds improved the bond-balance sum for O1 and O5.

TABLE 5. Bond valence strength calculations for tumchaite

	Zr	Si1	Si2	Na	H bonds	Σ
O1		0.90	0.98		0.10	1.98
O2	0.70	1.09		0.21		2.00
O3	0.63	1.05		0.19		1.87
O4		0.93	1.00	0.17		2.10
O5	0.67		1.08	0.21	0.05	2.01
O6			1.02 ×2			2.04
OW				0.24,0.12	–0.15	0.21

Water molecules and Na^+ cations are localized in the wide cavities and tunnels of the mixed heteropolyhedral framework. The topology of the mixed framework allows tumchaite to be considered as a novel microporous zirconosilicate. Both natural and synthetic polytypes of penkvilksite-1*M* and -2*O* (Merlino et al. 1994; Liu et al. 1999) as well as another titanosilicate zorite (Sandomirsky and Belov 1979) also belong to this mineralogical series.

The structural similarity between tumchaite and penkvilksite is of interest because of a very limited isostructurality among Zr- and Ti-containing mineralogical analogues (Pyatenko et al. 1999). This peculiarity of their crystal chemical behavior is due to the different chemical nature of Zr and Ti, in particular to the increase of effective charge of Zr and consequently to the formation of more ionic and equidistant Zr-O bonds as compared with substantially unequal bonds Ti-O. The other examples of Zr- and Ti-containing isostructural minerals are: wadeite, $K_2ZrSi_3O_9$, and natural Ti-wadeite, $K_2TiSi_3O_9$, described by Kim and Pankov (1989); bazirite, $BaZrSi_3O_9$, and benitoite, $BaTiSi_3O_9$; dalyite, $K_2ZrSi_6O_{15}$, and davanite, $K_2TiSi_6O_{15}$; eudialyte, $Na_4(Ca,Ce)_2(Fe,Mn,Y)ZrSi_8O_{22}(OH,Cl)_2$, and alluaivite, $Na_{19}(Ca,Mn)_6(Ti,Nb)_3(Si_3O_9)_2(Si_{10}O_{28})_2Cl\cdot 2H_2O$; and zircophyllite, $(K,Na,Ca)_3(Mn,Fe)_7(Zr,Nb)_2Si_8O_{27}(OH,F)_4$, and astrophyllite, $(K,Na)_3(Fe,Mn)_7Ti_2Si_8O_{24}(O,OH)_7$.

ACKNOWLEDGMENTS

The authors are grateful to N.V. Chukanov for the analysis of IR spectrum, to Yu.P.Men'shikov who provided the sample of penkvilksite from the Lovozero massif for comparative study, to F. Liebau for evaluation of structural formula, and to J.W. Downs and to W. Dollase for helpful suggestions. This work was supported in part by the grants RFBR (98-05-64365, 99-05-65524, 99-05-39019, and 00-05-65399), the Russian Universities Program and by INTAS (project 97-0722).

REFERENCES CITED

Brown, I.D. and Shannon, R.D. (1973) Empirical bond-strength—bond-length curves for oxides. Acta Crystallographica, A29, 266–282.

Dowty, E. (1995) Atoms 3.2. A computer program for displaying atomic structures. Kingsport, TN 37663.

Kim, A.A. and Pankov, V.Yu. (1989) First find of potassic titanium silicate in the platinoid mineral assemblage of Inagli massif. Doklady Akademii Nauk SSSR, 309, 3, 690–692 (in Russian).

Kogarko, L.N., Kononova, V.A., Orlova, M.P., and Woolley, A.R. (1995) Alkaline Rocks and Carbonatites of the World. Part 2: Former USSR, 226 p. Chapman and Hall, London.

Kukharenko, A.A., Orlova, M.P., Bulakh, A.G., Bagdasarov, E.A., Rimskaya-Korsakova, O.M., Nefedov, E.I., Ilyinskiy, G.A., Sergeev, A.C., and Abakumova, N.B. (1965) The Caledonian complex of the ultrabasic alkalic rocks and carbonatites of the Kola Peninsula and northern Karelia, 772 p. Nedra, Moscow (in Russian).

Liebau, F. (1985) Structural Chemistry of Silicates. Structure Bonding and Classification, 347 p. Springer Verlag, Berlin.

Lima-de-Faria, J., Hellner, E., Liebau, F., Makovicky, E., and Parthe', E. (1990) Nomenclature of inorganic structure types. Acta Crystallographica, A46, 1–11.

Liu, Yu., Du, H., Xu, Y., Ding, H., Pang, W., and Yue, Y. (1999) Synthesis and characterization of a novel microporous titanisilicate with a structure of penkvilksite-1*M*. Microporous and Mesoporous Materials, 28, 511–517.

Merlino, S., Pasero, M., Artioli, G., and Khomyakov, A.P. (1994) Penkvilksite, a new kind of silicate structure: OD character, X-ray single-crystal (1*M*), and powder Rietveld (2*O*) refinements of two MDO polytypes. American Mineralogist, 79, 1185–1193.

Pushcharovsky, D.Yu. (1986) Structural mineralogy of silicates, 160 p. Nedra, Moscow (in Russian).

Pyatenko, Yu.A., Kurova, T.A., Chernitsova, N.M., Pudovkina, Z.V., Blinov, V.A., and Maksimova, N.V. (1999) Niobium, tantalum and zirconium in minerals, 213 p. IMGRE, Moscow (in Russian).

Sandomirsky, P.A. and Belov, N.V. (1979) The OD structure of zorite. Kristallografiya, 24(6), 1198–1210.

Sheldrick, G.M. (1997) SHELX-97: Program for the solution and refinement of crystal structures. Siemens Energy and Automation, Madison, WI.

Voronkov, A.A., Shumyatskaya, N.G., and Pyatenko, Yu.A. (1978) Crystalchemistry of zirconium minerals and their synthetic analogues, 183 p. Nauka, Moscow (in Russian).

Yakubovich, O.V., Dimitrova, O.V., and Vidrevich, A.I. (1993) Magnesium ultraphosphate MgP_4O_{11}: Growth and crystal structure. Crystallography Reports, 38, 176–180 (translated from Kristallografiya, 38, 77–85, 1993).

Yvon, K., Jeitschko, W., and Parthe, E. (1977) Lazy Pulverix—a computer program, for calculating X-ray and neutron diffraction powder patterns. Journal of Applied Crystallography, 10, 73–74.

MANUSCRIPT RECEIVED FEBRUARY 7, 2000
MANUSCRIPT ACCEPTED MAY 18, 2000
PAPER HANDLED BY JAMES W. DOWNS