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SENKEVICHITE, CsKNaCa₂TiO[Si₇O₁₈(OH)], A NEW MINERAL

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Senkevichite is a new cesium mineral, which has been found in the alkaline massif of Darai-Piyoz (Tajikistan). The mineral forms intergrowths of elongated board-like grains up to 1 mm in light in quartz-pectolite aggregates from blocks consisting mainly of granulated massive quartz. When transparent, the mineral is colourless, otherwise, white. The fracture is brittle. The Mohs hardness is 5.5-6. Measured density is 3.12 g/cm³. The mineral is biaxial, optically positive; $\alpha_p = 1.616(2)$, $\beta_m = 1.645(2)$, $\gamma_g = 1.683(2)$. Triclinic, space group P-1; $a = 10.4191(4)$ Å, $b = 12.2408(5)$ Å, $c = 7.0569(3)$ Å, $V = 887.8(1)$ Å³, $Z = 2$. Chemical composition is as follows (electron microprobe analysis; H₂O is calculated, wt %): SiO₂ – 50.48, TiO₂ – 8.94, Nb₂O₅ – 0.64, FeO – 0.50, MnO – 2.59, CaO – 11.09, Na₂O – 3.73, K₂O – 6.13, Cs₂O – 15.28, H₂O (calc) – 1.09, total – 100.47. Empirical formula of the mineral is Cs_{0.90}K_{1.09}Na_{1.00}(Ca_{1.65}Mn_{0.30}Fe_{0.06})_{2.01}(Ti_{0.93}Nb_{0.04})_{0.97}O_{0.97}[Si₇O₁₈(OH)]. Ideal formula is CsKNaCa₂TiO[Si₇O₁₈(OH)]. Strong lines on X-ray powder diagram are following (d, I): 4.08 (13), 3.33 (11), 3.25(25), 3.14 (21), 3.06 (100), 2.959 (20), 2.038 (17). Crystal structure is solved with R=4.5%. The type specimen of the new mineral is kept in the Fersman Mineralogical Museum RAS (Moscow, Russia).
3 tables, 4 figures, 7 references

Senkevichite, a new member of the cesium natural silicates with the formula CsKNaCa₂TiO[Si₇O₁₈(OH)], has been found at the Darai-Piyoz glacier (Tajikistan) in a moraine line with the same name as the alkaline massif. The mineral was encountered in a block of granulated quartz in assemblage with aegirine, pectolite, stillwellite-(Ce), polyolithionite, leucosphenite, neptunite, baratovite, fluorite, pekovite, zeravshanite, etc. Senkevichite was named in honour of Yurii Alekseevich Senkevich (1937-2003), outstanding Russian traveller, medical officer, researcher of the behaviour of the human organism in extreme conditions, famous TV reporter and journalist. Senkevichite is Cs analogue of tinaksite (Rogov, 1965).

Occurrence and mineral assemblage

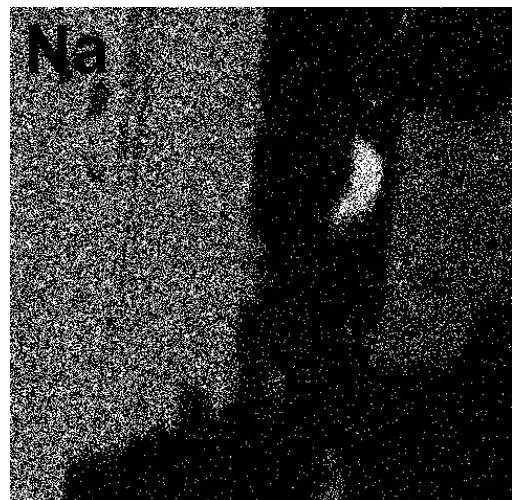
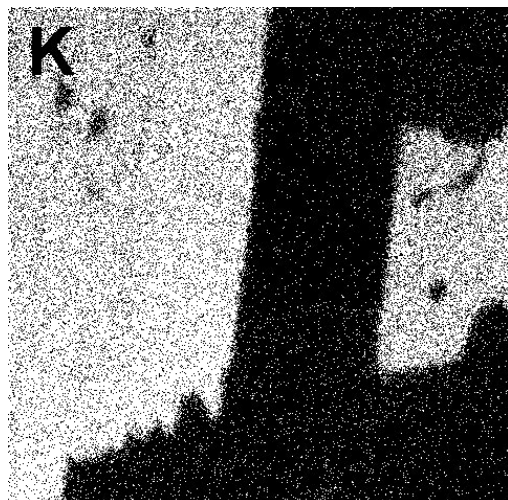
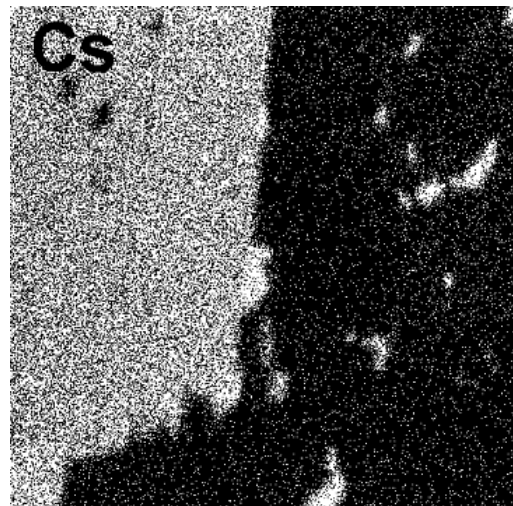
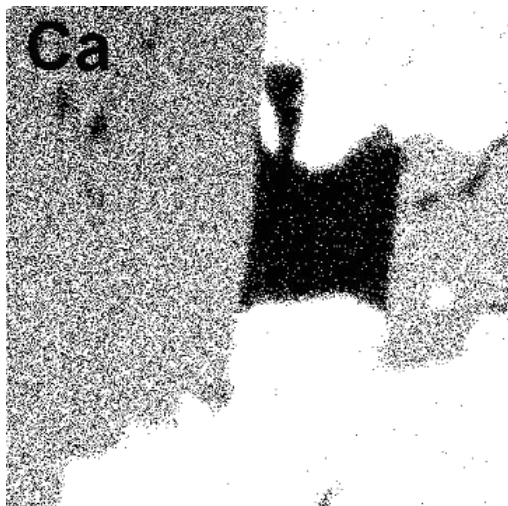
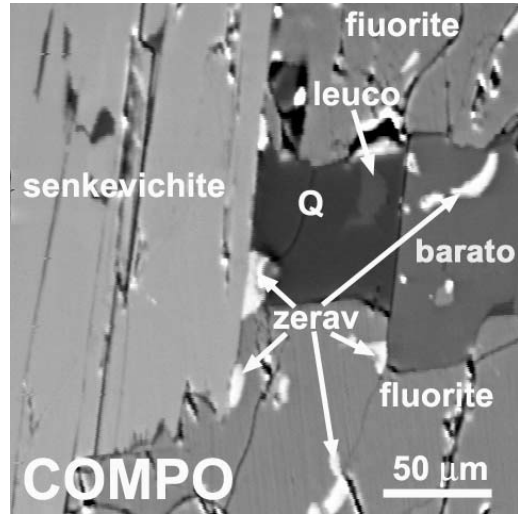
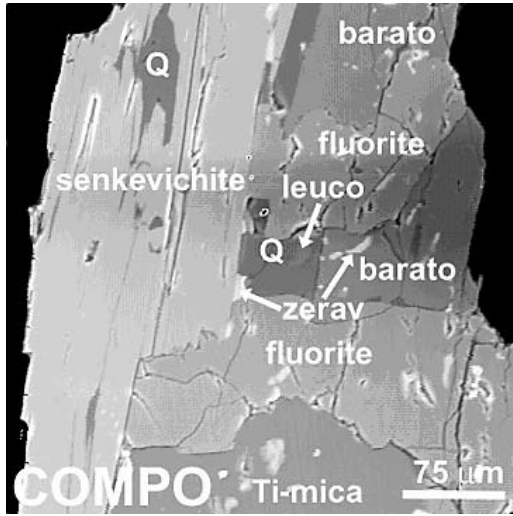
Senkevichite has been found in the rocks samples from the Upper Darai-Piyoz alkaline massif, which were collected at the moraine of the Darai-Piyoz glacier (Garm region, Central Tajikistan). A number of publications have been devoted to the geology and mineralogy of the

massif (Dusmatov, 1968, 1971; Belakovsky, 1991; etc.). The Darai-Piyoz massif is difficult to access because of complicated mountain relief; therefore the main part of mineralogical studies have been carried out on material collected in moraine deposits of the glacier cutting the massif. Diversity of proper cesium minerals is one of the peculiarities of the Darai-Piyoz alkaline massif. At present, in the rocks of this massif, the following minerals of cesium have been discovered: cesium kupletskite, telyushenkoite, zeravshanite, sokolovaite, and senkevichite. Probably, the list of cesium minerals will be expanded during further study of the mineralogy of the massif.

Senkevichite has been found in so called «quartz block», composed predominantly by granulated quartz. It was written about this unusual rock in detail earlier (Pautov, 2004). The mineral was found in a polymineral brown aggregate, which sometimes occurs in «quartz blocks». The aggregate consists mainly of pectolite with minor amounts of quartz. Besides these minerals there are accessory amounts of aegirine, fluorite, polyolithionite, neptunite, hyalotekite, baratovite in the aggregate; extremely rare sokolovaite and pekovite occur in it. Senkevichite intergrows with

* The mineral was considered and recommended for publication by the Russian Mineralogical Society Commission on New Minerals and Mineral Names and approved by the IMA Commission on New Minerals and Mineral Names on July 13, 2004

** The name of the gorge, where the alkaline massif of the same name is located, is translated from Tajik as «onion pie» and has the English version «darai-piyoz». In the first publications, the geographic name of the alkaline massif was also Darai-Piyoz. Below the authors will follow the same orthography



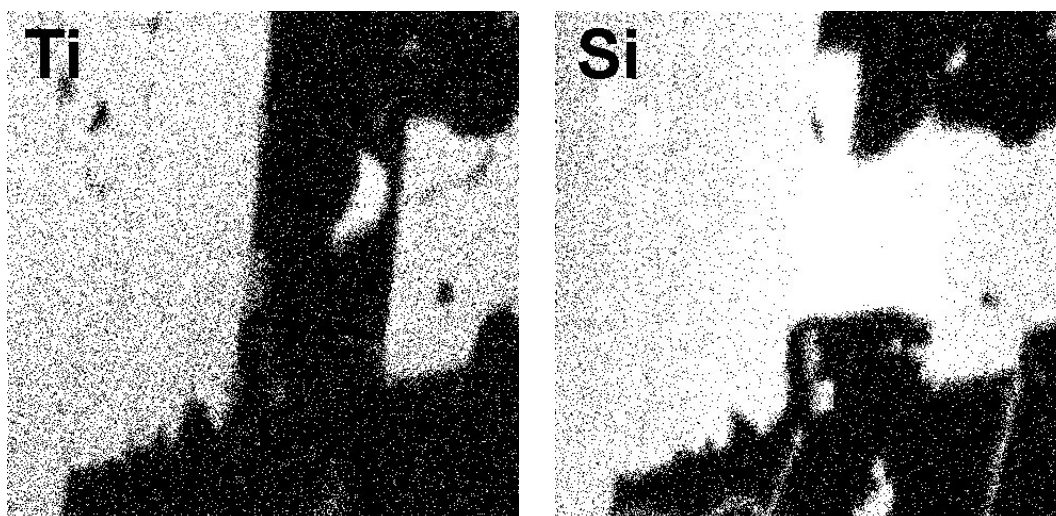


Fig. 1. Intergrowth of senkevichite with fluorite (fluorite), quartz (Q), zeravshanite (zerav), leucosphenite (leuco), baratovite (barato), and presumably new mineral, titanium mica (Ti-mica). Image in COMPO regime and characteristic emanation of indicated elements

neptunite, baratovite, quartz, pectolite, leucosphenite, fluorite, and a potentially new titanium mica (Fig. 1).

Physical properties

Senkevichite is a colourless, transparent mineral with strong vitreous lustre. It often looks white because of cracks. The mineral forms intergrowths of elongated board-like grains up to 1 mm in size. The Mohs hardness is 5.5-6. Micro-indentation measurements with a VHN load of 100g gave a mean value of 650 kg/mm² (20 measurements with the range from 611 to 708 kg/mm²). The mineral is brittle. Mineral density was determined by grain balancing in Clerici solution. Measured density of the mineral is 3.12(2) g/cm³; calculated density is 3.13 g/cm³. Senkevichite is optically positive, biaxial. Refraction indexes obtained by immersion method (at 589 nm) are as follows: $\alpha_p = 1.616(2)$, $\beta_m = 1.645(2)$, $\gamma_g = 1.683(2)$. Angle measured on Fedorov's stage $2V = 85(2)^\circ$, calculated angle is 84° . Dispersion is strong, $r < v$. The mineral is insoluble in water and HCl (1:1). The IR spectrum of senkevichite obtained with Specord-75IR instrument (the sample is a tablet of mineral with KBr) is close to the IR spectrum of tinaksite (Fig. 2); it is characterized by the following absorption bands (cm⁻¹): 3450, 3380, 1262(sh), 1092, 1065, 1035, 965, 880, 780, 718(sh), 703, 678, 652, 638, 541, 508, 480, 467.

Chemical composition

Chemical composition of senkevichite was analyzed with JCXA-50A (JEOL) electron microprobe instrument equipped with an energy dispersive spectrometer and three wave spectrometers. Analyses were obtained on an energy dispersive spectrometer at accelerating voltage of 20 kV and electron microprobe current of 20 nA. The standards used are as follows: microcline USNM143966 (Si, K), synthetic jadeite NaAlSi₂O₆ (Na), synthetic CsTb(PO₃)₄ (Cs), ilmenite USNM 96189 (Ti). It was not possible to detect water by direct method because of the small amount of material; its content was calculated. Concentrations were calculated by program of ZAF correction. Homogeneity of grains was checked with wave spectrometers. 6 grains were analysed. The average chemical composition of the analysed grains (Table 1) can be calculated for Si=7 on empirical formula: Cs_{0.96}K_{1.08}Na_{1.00}(Ca_{1.65}Mn_{0.30}Fe_{0.06})_{2.01}(Ti_{0.93}Nb_{0.04})_{0.97}O_{0.97}[Si₇O₁₈(OH)]. Ideal formula of senkevichite is CsKNaCa₂TiO[Si₇O₁₈(OH)]. The compatibility index of coincidence of properties is $(1-K_p/K_c) = 0.017$, that is superior category.

X-ray data

X-ray powder diagram of senkevichite was obtained with DRON-2 diffractometer instrument (Table 2); it is individual and well-indicated

Table 1. Chemical composition senkevichite (wt %)

	1	2	3	4	5	6	7	8	Average
SiO ₂	50.92	49.94	50.36	50.83	50.87	50.51	50.42	50.00	50.48
TiO ₂	8.52	8.90	9.41	9.14	8.83	8.73	8.71	9.28	8.94
Nb ₂ O ₅	0.61	0.59	0.39	0.46	0.59	0.89	0.85	0.72	0.64
FeO	0.36	0.73	0.47	0.61	0.48	0.45	0.45	0.43	0.50
MnO	2.47	3.40	2.29	2.60	2.26	2.67	2.66	2.39	2.59
CaO	11.20	9.82	11.04	11.81	11.24	11.62	11.60	10.38	11.09
Na ₂ O	3.70	3.84	3.56	3.75	3.78	3.90	3.58	3.74	3.73
K ₂ O	6.12	5.78	6.34	6.22	6.02	6.12	6.15	6.25	6.13
Cs ₂ O	15.68	15.51	14.77	14.78	14.92	15.56	15.57	15.46	15.28
H ₂ O _{calc.}	1.09	1.09	1.09	1.09	1.09	1.09	1.09	1.09	1.09
Total	100.57	100.80	99.83	100.45	100.23	101.05	100.32	100.39	100.47

Note: analysts A.A. Agakhanov and L.A. Pautov.

in suggested parameters of unit cell of triclinic system: $a = 10.4191(4)\text{\AA}$, $b = 12.2408(5)\text{\AA}$, $c = 7.0569(3)\text{\AA}$, $\alpha = 90.857(1)^\circ$, $\beta = 99.193(1)^\circ$, $\gamma = 91.895(1)^\circ$, $V = 887.8(1)\text{\AA}^3$, space group P-1, $Z = 2$.

Crystal structure of senkevichite was refined to an R_1 index of 4.5% for 4872 unique reflexes (Bruker P4 diffractometer with four-circle CCD detector, MoK α -radiation) (Sokolova *et al.*, 2005 in press). General, the crystal structure of senkevichite represents a mixed framework construction formed by silica-oxide chains and bands of Na-polyhedra and octahedra of Ti and Ca; there are Cs and K atoms in the cavities of the framework. There are seven tetrahedral Si sites ($\langle\text{Si-O}\rangle = 1.623\text{\AA}$); six of these tetrahedra are surrounded by oxygen atoms, one tetrahedron, Si(7), is surrounded by three oxygen atoms and an (OH) group. Also there are three sites M in sixfold coordination: M(1) is occupied predominantly by Ti with small portion of Nb ($\langle\text{M}(1)\text{-O}\rangle = 1.985\text{\AA}$), M(2) is filled up solely by

Ca ($\langle\text{M}(2)\text{-O}\rangle = 2.382\text{\AA}$), and M(3) is occupied by Ca with small portion of Fe²⁺ and Mn²⁺ ($\langle\text{M}(3)\text{-O}\rangle = 2.317\text{\AA}$ sites: there are a site of Na-polyhedron with sevenfold coordination ($\langle\text{Na-O}\rangle = 2.504\text{\AA}$) and two A sites. Among them [12]-coordinated A(1) is occupied predominantly by Cs (with a small portion of K) ($\langle\text{A}(1)\text{-O}\rangle = 3.318\text{\AA}$), [10]-coordinated A(2) is filled up by K ($\langle\text{A}(2)\text{-O}\rangle = 2.986\text{\AA}$). In senkevichite, silica-oxide chains represent an infinite chain of hybrid clusters $[\text{Si}_7\text{O}_{18}(\text{OH})]^{9-}$, composed of two wollastonite-like chains joined by common oxygen atom and additional Si-tetrahedron (Fig. 3a). M(1) octahedra and Na-polyhedra are connected by common edges and form a band with two polyhedra width; M(2) and M(3) octahedra joining by common edges form another band with width also in two polyhedra (Fig. 3b). These bands extend along the c axis and, joined by common vertices, form the layers parallel to (011). Hybrid doubled chains $[\text{Si}_7\text{O}_{18}(\text{OH})]^{9-}$, M(2) and M(3) octahedra, and

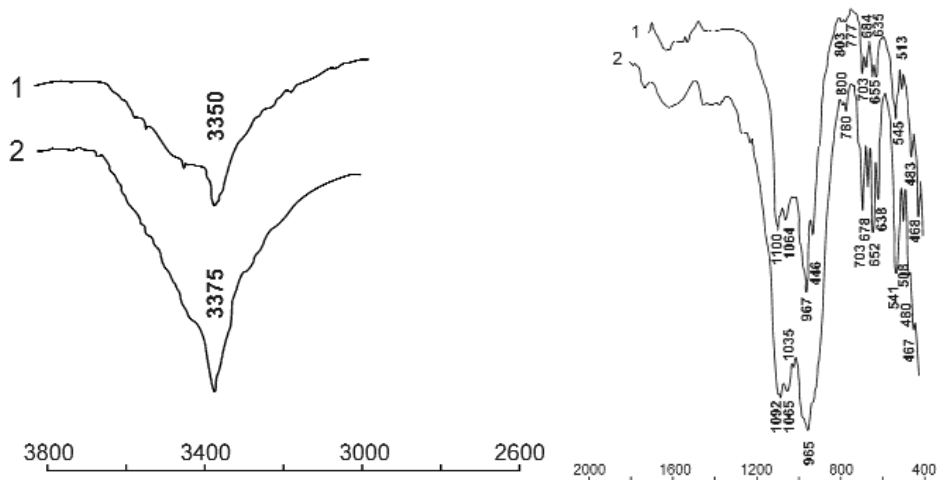


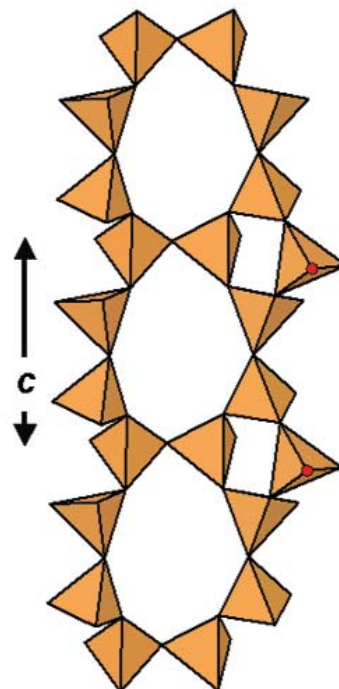
Fig. 2. The IR-spectra of tinaksite (1) and senkevichite (2). Analysts: N.V. Chukanov, L.A. Pautov

Table 2. X-ray powder diffraction data of senkevichite

<i>l</i>	<i>d</i> _{meas.}	<i>d</i> _{calc.}	<i>h k l</i>
3	10.30	10.28	1 0 0
5	5.16	5.17	2 0 0
3	4.97	4.99	1 -1 1
3	4.67	4.68	2 1 0
		4.64	0 2 -1
4	4.49	4.49	2 0 -1
4	4.36	4.38	1 -2 -1
5	4.16	4.19	2 1 -1
13	4.08	4.08	0 3 0
7	4.01	4.01	2 -2 0
3	3.88	3.87	2 2 0
		3.85	2 0 1
3	3.60	3.63	2 1 1
3	3.54	3.55	0 3 -1
3	3.43	3.43	3 0 0
11	3.33	3.35	1 1 -2
		3.33	0 1 2
		3.33	3 -1 0
4	3.28	3.27	3 1 0
16	3.25	3.25	2 -3 0
21	3.14	3.14	2 3 0
		3.15	1 0 2
100	3.06	3.06	0 4 0
		3.07	2 0 -2
		3.05	2 -3 -1
		3.04	3 -2 0
		3.03	2 -1 -2
20	2.959	2.96	1 -4 0
7	2.904	2.903	1 4 0
5	2.673	2.675	0 3 -2
		2.671	3 -3 0
7	2.578	2.579	3 2 1
		2.578	3 3 0
3	2.453	2.454	3 -2 -2
3	2.401	2.406	3 -3 1
4	2.323	2.323	3 -4 0
4	2.241	2.242	3 4 0
17	2.038	2.039	0 6 0
7	2.014	2.014	1 -6 0
3	1.985	1.986	2 4 2
3	1.937	1.940	3 5 -1
		1.940	1 -6 -1
5	1.826	1.827	5 -2 1
		1.826	4 -4 -2
6	1.712	1.713	1 7 0
5	1.673	1.673	2 -7 0
1	1.667	1.667	0 5 3
		1.666	2 -2 -4
5	1.637	1.637	5 -4 -2
1	1.631	1.629	3 -6 -2
2	1.616	1.616	5 -2 2
3	1.602	1.602	4 4 2
3	1.542	1.542	4 -5 2
		1.542	3 3 -4
	1.520	1.520	1 -8 0
2	1.468	1.468	7 0 0
3	1.439	1.440	7 -2 0
4	1.379	1.380	6 5 0
4	1.358	1.359	0 9 0
2	1.331	1.331	2 3 -5

Note: DRON-2 diffractometer, Fe anode, graphite monochromator, counter rate is 1 grad/min, the internal standard is quartz. Analyst A.A. Agakhanov The strong lines are marked by semi-bold

a



b

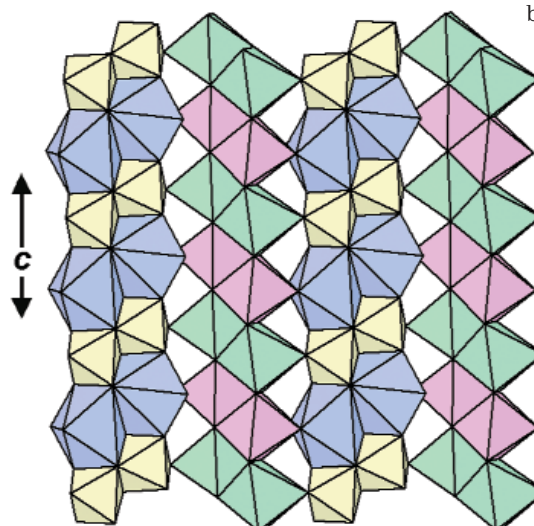


Fig. 3. a) hybrid doubled chain, $[Si_7O_{18}(OH)]^{6-}$, one of the main constituent elements of senkevichite crystal structure; (OH)-group is marked by red circle; b) layers composed by M(1), M(2), M(3) octahedra and Na-polyhedra; M(1) octahedra are marked by yellow colour, M(2) - green, M(3) - pink, Na-polyhedra - blue

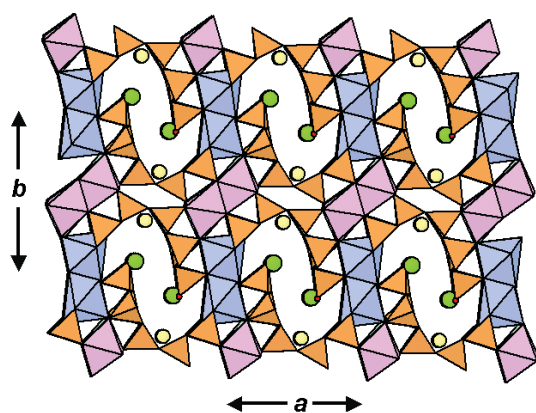


Fig. 4. Crystal structure of senkevichite in projection on (110). Si-tetrahedra are coloured by orange, Na-polyhedra - by blue, atoms A(1) are marked by green circles, atoms A(2) - by yellow circles, (OH)-groups - by small red circles

Table 3. Comparative characteristic of senkevichite and tinaksite

Chemical formula	senkevichite $\text{CsKNa Ca}_2\text{TiO}[\text{Si}_7\text{O}_{18}(\text{OH})]$	tinaksite $\text{NaK}_2\text{Ca}_2\text{TiO}[\text{Si}_7\text{O}_{18}(\text{OH})]$
Space group	<i>P</i> -1	<i>P</i> 1, <i>P</i> -1
<i>a</i> , Å	10.4191	10.35
<i>b</i> , Å	12.2408	12.17
<i>c</i> , Å	7.0569	7.05
α , °	90.857	91.00
β , °	99.193	99.20
γ , °	91.895	92.30
Z	2	2
Strong lines of X-ray powder diagram:		
<i>d</i> _{meas.} Å(<i>h</i>)	5.16(5)	5.09(30)
	4.08(13)	4.04(30)
	3.33(11)	3.32(30)
	3.25(16)	3.25(80)
	3.14(21)	3.09(50)
	3.06(100)	3.03(100)
	2.959(20)	2.952(50)
	2.904(7)	2.865(50)
	2.038(17)	2.002(45)
Density (meas), g/cm ³	3.13	2.82
	biaxial (+)	biaxial (+)
<i>n</i> _p	1.616	1.593
<i>n</i> _m	1.645	1.621
<i>n</i> _y	1.683	1.666

Na-polyhedra, joined by mutual vertices, form mixed framework with mutual cluster $[\text{NaCa}_2\text{Ti}(\text{Si}_7\text{O}_{18}(\text{OH})\text{O})]^{2-}$. The latter concludes the large cells occupied by A(1) and A(2) atoms (Fig. 4). Senkevichite is a Cs analogue of tinaksite, $\text{K}_2\text{NaCa}_2\text{Ti}(\text{Si}_7\text{O}_{18})\text{O}(\text{OH})$, (Petrunina *et al.*, 1971) and Cs-Na-Ti oxianalogue of tokkoite, $\text{K}_2\text{Ca}_4\text{Si}_7\text{O}_{18}(\text{OH})\text{F}$, (Rozhdestvenskaya *et al.*, 1989).

Comparative characteristic of senkevichite and tinaksite is given in Table 3.

The sample of senkevichite is deposited at (the Fersman Mineralogical Museum, Russian Academy of Sciences (Moscow)).

Acknowledgements

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