THE CRYSTAL CHEMISTRY OF SENKEVICHITE, Cs K Na Ca$_2$ Ti O [Si$_7$O$_{18}$(OH)], FROM THE DARA-I-PIOZ ALKALINE MASSIF, NORTHERN TAJIKISTAN

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Abstract

The crystal structure of senkevichite, ideally Cs K Na Ca$_2$ Ti^{4+} O [Si$_7$O$_{18}$(OH)], triclinic, $P\bar{1}$, *a* 10.4191(4), *b* 12.2408(5), *c* 7.0569(3) Å, α 90.857(1), β 99.193(1), γ 91.895(1)°, *V* 887.8(1) Å^3, *Z* = 2, D_{calc} 3.125 g/cm^3, from Dara-i-Pioz, Tien-Shan Mountains, Tajikistan, has been refined to R_1 = 4.5% for 4872 unique ($F_o > 4\sigma F$) reflections collected on a Bruker single-crystal *P*4 diffractometer equipped with a 4K CCD detector and Mo$K\alpha$ X-radiation. Electron-microprobe analysis gave SiO$_2$ 51.08, TiO$_2$ 8.94, FeO 0.50, MnO 2.59, CaO 10.98, K$_2$O 6.13, Na$_2$O 3.76, Nb$_2$O$_5$ 0.64, Cs$_2$O 15.28, (H$_2$O)$_{calc}$ 1.09, sum 100.99 wt.%, and (H$_2$O) was determined from crystal-structure analysis. Senkevichite is isostructural with tinaksite and tokkoite. There are seven tetrahedrally coordinated *Si* sites with a grand <*Si*–O> distance of 1.623 Å. Six of these sites are coordinated by O atoms, and the *Si*(7) site is coordinated by three O atoms and one (OH) group, *i.e.*, this is an acid silicate group. There are three [6]-coordinated *M* sites. The *M*(1) site is occupied primarily by Ti^{4+} (with minor Nb), with <*M*(1)–O> = 1.985 Å. The *M*(2) site is occupied solely by Ca, with <*M*(2)–O> = 2.382 Å, and the *M*(3) site is occupied by Ca (with minor Fe^{2+} and Mn^{2+}), with <*M*(3)–O> = 2.317 Å. There is one [7]-coordinated *Na* site with <*Na*–O> = 2.504 Å. There are two *A* sites, the [12]-coordinated *A*(1) site, occupied mainly by Cs (with minor K), with <*A*(1)–O> = 3.318 Å, and the [10]-coordinated *A*(2) site, occupied solely by K, with <*A*(2)–O> = 2.987Å. Senkevichite is a Cs-analogue of tinaksite, K$_2$ Na Ca$_2$ Ti^{4+} O [Si$_7$O$_{18}$(OH)], and a Cs–Na–Ti^{4+} oxyanalogue of tokkoite, K$_2$ Ca$_4$ F [Si$_7$O$_{18}$(OH)].

Keywords: senkevichite, tinaksite, tokkoite, crystal-structure refinement, acid silicate group.

Sommaire

Nous avons affiné la structure cristalline de la senkevichite, de composition idéale Cs K Na Ca$_2$ Ti^{4+} O [Si$_7$O$_{18}$(OH)], triclinique, $P\bar{1}$, *a* 10.4191(4), *b* 12.2408(5), *c* 7.0569(3) Å, α 90.857(1), β 99.193(1), γ 91.895(1)°, *V* 887.8(1) Å^3, *Z* = 2, D_{calc} 3.125 g/cm^3, provenant du complexe de Dara-i-Pioz, dans les montagnes Tien-Shan, au Tajikistan, jusqu'à un résidu R_1 de 4.5% en utilisant 4872 réflexions uniques ($F_o > 4\sigma F$) prélevées avec un diffractomètre à monocristal Bruker *P*4 muni d'un détecteur CCD 4K et rayonnement Mo$K\alpha$. Les analyses effectuées avec une microsonde électronique ont donné SiO$_2$ 51.08, TiO$_2$ 8.94, FeO 0.50, MnO 2.59, CaO 10.98, K$_2$O 6.13, Na$_2$O 3.76, Nb$_2$O$_5$ 0.64, Cs$_2$O 15.28, (H$_2$O)$_{calc}$ 1.09, pour un total de 100.99% (poids), et la proportion de (H$_2$O) a été établie par analyse de la structure. La senkevichite est isostructurale avec la tinaksite et la tokkoïte. La structure contient sept sites *Si* à coordinence tétraédrique, avec une distance moyenne <*Si*–O> de 1.623 Å. Six de ces sites sont coordonnés par des atomes d'oxygène, et le site *Si*(7) est coordonné par trois atomes d'oxygène et un groupe (OH). Il s'agit donc d'un groupe silicate acide. Il y a trois sites *M* à coordinence [6]. Le site *M*(1) contient surtout Ti^{4+} (et un peu de Nb), avec <*M*(1)–O> = 1.985 Å. Le site *M*(2) contient uniquement Ca, avec <*M*(2)–O> = 2.382 Å, et le site *M*(3) contient Ca (et des quantités mineures de Fe^{2+} et Mn^{2+}), avec <*M*(3)–O> = 2.317 Å. Il y a un site *Na* à coordinence [7], avec <*Na*–O> = 2.504 Å. Il y a deux sites *A*, le site *A*(1) à coordinence [12], contenant surtout le césium (et un peu de K), avec <*A*(1)–O> = 3.318 Å, et le site *A*(2), à coordinence [10], contenant uniquement le K, avec <*A*(2)–O> = 2.987Å. La senkevichite est l'analogue à Cs de la tinaksite, K$_2$ Na Ca$_2$ Ti^{4+} O [Si$_7$O$_{18}$(OH)], et l'oxyanalogue à Cs–Na–Ti^{4+} de la tokkoïte, K$_2$ Ca$_4$ F [Si$_7$O$_{18}$(OH)].

(Traduit par la Rédaction)

Mots-clés: senkevichite, tinaksite, tokkoïte, affinement de la structure cristalline, groupe silicate acide.

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INTRODUCTION

Senkevichite, Cs K Na Ca$_2$ Ti^{4+} O [Si$_7$O$_{18}$(OH)], is a new mineral species from the moraine of the Dara-i-Pioz glacier, the Alai mountain ridge, Tien-Shan Mountains, northern Tajikistan (Agakhanov *et al.* 2005). The mineral occurs as aggregates of elongate platy crystals up to 1 mm in length. Senkevichite was found in a quartz–pectolite boulder, in association with aegirine, fluorite, polylithionite, neptunite, hyalotekite, baratovite, sokolovaite, pectolite and a Ti^{4+}-rich mica. Senkevichite is the fifth cesium silicate mineral described from the Dara-i-Pioz moraine, after kupletskite-(Cs), (Cs,K,Na)$_3$ (Mn,Fe^{2+})$_7$ (Ti^{4+},Nb)$_2$ (Si$_8$O$_{24}$) (O,OH)$_7$ (Yefimov *et al.* 1971), telyushenkoite, Cs Na$_6$ [Be$_2$ Al$_3$ Si$_{15}$ O$_{39}$ F$_2$] (Sokolova *et al.* 2002, Agakhanov *et al.* 2003), zeravshanite, Cs$_4$ Na$_2$ Zr$_3$ (Si$_{18}$O$_{45}$) (H$_2$O)$_2$ (Uvarova *et al.* 2004), and sokolovaite, Cs Li$_2$ Al Si$_4$ O$_{10}$ F$_2$ (IMA–CMNMN 2004–012). Here, we report on the crystal structure and crystal chemistry of senkevichite.

COLLECTION OF X-RAY DATA AND STRUCTURE REFINEMENT

X-ray-diffraction data for senkevichite were collected with a Bruker *P4* diffractometer equipped with a 4K CCD detector (Mo*K*α radiation) from a single crystal with dimensions 0.14 × 0.08 × 0.06 mm. The intensities of 8690 reflections with $\overline{14} < h < 14$, $\overline{17} < k < 16$, $\overline{9} < l < 9$ were collected to 59.99° 2θ using 30 s per 0.2° frame, and an empirical absorption correction (SADABS, Sheldrick 1998) was applied. The refined unit-cell parameters were obtained from 6593 reflections with $I > 20\ \sigma I$. Using the atom coordinates of tinaksite (Bissert 1980), the crystal structure of senkevichite was refined to $R_1 = 4.5\%$ and a Go*F* value of 1.220 for 4872 independent reflections (308 refined parameters including extinction) with the SHELXTL version 5.1 system of programs (Bruker 1997). Site occupancies were refined for three *M* sites (one occupied by Ti^{4+} + Nb, one occupied by Ca, and the third occupied by Ca + Mn^{2+}), one *Na* site, and two *A* sites (primarily occupied by K and Cs).

Details of the data collection and structure refinement are given in Table 1, final atom-parameters are given in Table 2, selected interatomic distances and angles in Table 3, refined site-scattering values and assigned populations for selected sites in Table 4, and bond-valence values in Table 5. A table of structure factors may be obtained from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

CHEMICAL COMPOSITION

The crystal of senkevichite used for collection of the X-ray intensity data was mounted in epoxy, ground, polished and analyzed with a JEOL JCXA–50A electron microprobe operating at 20 kV and 20 nA with an energy-dispersion spectrometer and three wavelength-dispersion spectrometers. The following standards were used for *K*, *L* or *M* X-ray lines: Na: synthetic jadeite, Si, K: microcline USNM 43966; Cs: synthetic CsTb(PO$_3$)$_4$; Ti: ilmenite USNM 96189. Data were reduced using the (φρZ) procedure of Pouchou & Pichoir (1985). The amount of H$_2$O was calculated from the crystal-structure refinement. Table 6 gives the chemical composition and empirical formula-unit based on 20 anions including 1 OH group *pfu* (per formula unit): Cs$_{0.90}$K$_{1.08}$Na$_{1.00}$ (Ca$_{1.62}$Mn$_{0.30}$Fe$_{0.06}$)$_{\Sigma1.98}$ (Ti$_{0.93}$Nb$_{0.04}$)$_{\Sigma0.97}$ O [Si$_7$O$_{18}$ (OH)].

DESCRIPTION OF THE STRUCTURE

Cation sites

There are seven tetrahedrally coordinated *Si* sites with a grand <*Si*–O> distance of 1.623 Å, in accord with complete occupancy of each site by Si. One of the silicate tetrahedra, Si(7), is an acid silicate group [SiO$_3$(OH)]. There are three octahedrally coordinated *M* sites. The *M*(1) site is occupied primarily by Ti, with minor Nb: 0.93 Ti^{4+} + 0.04 Nb, with <*M*(1)–O> = 1.985 Å. The *M*(2) site is occupied solely by Ca, with <*M*(2)–O> = 2.382 Å, and the *M*(3) site is occupied by Ca, Mn^{2+} and minor Fe^{2+}: 0.62 Ca + 0.30 Mn^{2+} + 0.06 Fe^{2+}, with <*M*(3) – O> = 2.317 Å. There is one [7]-coordinated *Na* site, with <*Na*–O> = 2.504 Å. There are two *A* sites, [12]- and [10]-coordinated, respectively, and they are occupied by Cs with minor K: 0.90 Cs + 0.08 K, and 1.00 K, respectively, with <*A*(1)–O> = 3.318 and <*A*(2)–O> = 2.987 Å. The refined and calculated site-scattering values and the observed and calculated <*X*–φ> distances (φ: unspecified anion) indicate the site populations given in Table 4.

Topology of the structure

In the crystal structure of senkevichite, Si tetrahedra link together to form a *hybrid dreier double-chain*

TABLE 1. MISCELLANEOUS DATA CONCERNING THE REFINEMENT OF THE STRUCTURE OF SENKEVICHITE

a (Å)	10.4191(4)	Radiation/filter	MoKα/graphite
b	12.2408(5)	2θ range for data	
c	7.0569(3)	collection (°)	59.99
α (°)	90.857(1)	*R*(int) (%)	2.11
β	99.193(1)	Reflections collected	15,448
γ	91.895(1)	Unique reflections	8,690
V (Å^3)	887.8(1)	Independent reflections	5166
Space group	*P*1̄	$F_o > 4\sigma F$	4872
Z	2	Refinement method	
Absorption		Full-matrix least squares on F^2,	
coefficient (mm^{-1})	3.87	fixed weights proportional to $1/\sigma F_o^2$	
F(000)	807.2	Goodness of fit on F^2	1.22
D_{calc} (g/cm^3)	3.125	Final R_{obs} (%)	$R_1 = 4.50$
Crystal size (mm)	0.14 × 0.08 × 0.06	$[F_o > 4\sigma F]$	
		R indices (all data) (%)	$R_1 = 4.83$
			$wR_2 = 9.85$

TABLE 2. FINAL POSITIONS AND DISPLACEMENT PARAMETERS (Å^2) OF ATOMS IN SENKEVICHITE

	x	y	z	U_{eq}*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
$A(1)$	0.63686(3)	0.89743(3)	0.77051(4)	0.0182(1)	0.0157(2)	0.0169(2)	0.0219(2)	−0.0031(1)	0.0034(1)	−0.0015(1)
$A(2)$	0.55314(9)	0.64832(8)	0.2707(1)	0.0185(3)	0.0162(5)	0.0230(6)	0.0165(5)	0.0006(3)	0.0025(3)	0.0017(4)
Na	0.0195(2)	0.8883(1)	0.3891(2)	0.0149(5)	0.0143(9)	0.0144(9)	0.0162(9)	0.0024(6)	0.0016(6)	0.0038(6)
$M(1)$	0.00917(6)	0.89850(5)	0.89618(9)	0.0066(2)	0.0061(3)	0.0070(3)	0.0068(3)	0.0004(2)	0.0013(2)	−0.0003(2)
$M(2)$	0.11883(7)	0.59094(6)	0.9095(1)	0.0085(2)	0.0075(4)	0.0091(4)	0.0087(4)	0.0008(3)	0.0014(3)	0.0001(3)
$M(3)$	0.12262(6)	0.57715(6)	0.40821(9)	0.0091(2)	0.0081(3)	0.0101(4)	0.0090(3)	0.0002(2)	0.0012(2)	0.0004(2)
$Si(1)$	0.1318(1)	0.30739(8)	0.8740(1)	0.0062(2)	0.0063(4)	0.0076(5)	0.0046(4)	0.0000(3)	0.0009(3)	0.0006(3)
$Si(2)$	0.1304(1)	0.30134(8)	0.4266(1)	0.0066(2)	0.0065(4)	0.0083(5)	0.0049(4)	0.0006(3)	0.0007(3)	0.0004(3)
$Si(3)$	0.31497(9)	0.41614(8)	0.1982(1)	0.0067(2)	0.0042(4)	0.0085(5)	0.0072(4)	0.0009(3)	0.0002(3)	0.0008(3)
$Si(4)$	0.6883(1)	0.18824(9)	−0.0015(1)	0.0080(2)	0.0079(4)	0.0093(5)	0.0068(4)	−0.0004(3)	0.0013(3)	0.0005(4)
$Si(5)$	0.6952(1)	0.19562(9)	0.5723(1)	0.0097(2)	0.0093(5)	0.0116(5)	0.0080(4)	0.0013(4)	0.0009(4)	0.0014(4)
$Si(6)$	0.6055(1)	0.35742(9)	0.2699(1)	0.0074(2)	0.0063(4)	0.0090(5)	0.0072(4)	0.0006(3)	0.0011(3)	0.0013(4)
$Si(7)$	0.7286(1)	0.01788(9)	0.2834(1)	0.0082(2)	0.0084(5)	0.0085(5)	0.0079(4)	0.0011(3)	0.0020(3)	0.0010(4)
O(1)	0.2751(3)	0.3433(2)	0.9991(4)	0.0107(5)	0.0077(12)	0.0142(14)	0.0093(11)	−0.0027(10)	−0.0008(9)	−0.0002(10)
O(2)	0.0833(3)	0.1924(2)	0.9472(4)	0.0129(5)	0.0125(14)	0.0134(14)	0.0138(13)	0.0045(10)	0.0053(10)	−0.0018(11)
O(3)	0.0346(3)	0.4055(2)	0.8730(4)	0.0101(5)	0.0089(12)	0.0109(13)	0.0101(12)	0.0004(9)	−0.0001(10)	0.0020(10)
O(4)	0.1680(3)	0.2824(2)	0.6601(4)	0.0108(5)	0.0134(13)	0.0151(14)	0.0044(11)	0.0023(9)	0.0023(9)	0.0044(11)
O(5)	0.0841(3)	0.1844(2)	0.3328(4)	0.0123(5)	0.0138(13)	0.0108(13)	0.0109(12)	−0.0039(10)	−0.0013(10)	−0.0015(10)
O(6)	0.0312(3)	0.3984(2)	0.3829(4)	0.0113(5)	0.0113(13)	0.0121(13)	0.0110(12)	0.0016(10)	0.0025(10)	0.0044(10)
O(7)	0.2725(3)	0.3402(2)	0.3698(4)	0.0115(5)	0.0095(12)	0.0139(14)	0.0120(12)	0.0040(10)	0.0041(10)	0.0012(10)
O(8)	0.2535(3)	0.5326(2)	0.1887(4)	0.0111(5)	0.0099(12)	0.0109(13)	0.0123(12)	0.0009(10)	0.0003(10)	0.0037(10)
O(9)	0.4738(3)	0.4277(2)	0.2401(4)	0.0100(5)	0.0036(11)	0.0117(13)	0.0145(12)	0.0002(10)	0.0010(9)	0.0010(9)
O(10)	0.5995(3)	0.2828(3)	0.0741(4)	0.0144(6)	0.0181(14)	0.0176(15)	0.0076(12)	−0.0032(10)	0.0014(10)	0.0083(11)
O(11)	0.6480(3)	0.0732(2)	0.0918(4)	0.0115(5)	0.0076(12)	0.0145(14)	0.0118(12)	0.0058(10)	−0.0008(10)	0.0001(10)
O(12)	0.8395(3)	0.2177(2)	0.0594(4)	0.0110(5)	0.0087(12)	0.0109(13)	0.0134(12)	−0.0012(10)	0.0015(10)	−0.0003(10)
O(13)	0.6359(3)	0.1776(2)	0.7702(4)	0.0124(5)	0.0119(13)	0.0180(15)	0.0079(11)	0.0000(10)	0.0034(10)	0.0005(11)
O(14)	0.8366(3)	0.2455(3)	0.5958(4)	0.0147(6)	0.0091(13)	0.0173(15)	0.0172(13)	0.0012(11)	0.0004(10)	0.0014(11)
O(15)	0.6793(3)	0.0749(2)	0.4679(4)	0.0141(6)	0.0174(14)	0.0142(14)	0.0124(12)	−0.0009(10)	0.0078(11)	0.0004(11)
O(16)	0.5896(3)	0.2739(2)	0.4448(4)	0.0114(5)	0.0098(12)	0.0143(14)	0.0099(12)	0.0057(10)	0.0007(10)	0.0019(10)
O(17)	0.7321(3)	0.4346(2)	0.3090(4)	0.0119(5)	0.0050(12)	0.0159(14)	0.0145(12)	0.0007(10)	0.0015(10)	−0.0025(10)
O(18)	0.6737(3)	0.8920(3)	0.2783(5)	0.0180(6)	0.0111(13)	0.0130(15)	0.0297(16)	0.0014(12)	0.0023(12)	0.0008(11)
O(19)	0.8822(3)	0.0310(2)	0.2909(4)	0.0104(5)	0.0077(12)	0.0133(13)	0.0106(12)	0.0003(10)	0.0021(10)	0.0014(10)
O(20)	0.9025(3)	0.0144(2)	0.8809(4)	0.0087(5)	0.0058(11)	0.0096(13)	0.0106(11)	−0.0002(9)	0.0010(9)	0.0006(9)
H	0.738(4)	0.844(4)	0.298(8)		0.0216(12)					

* $U_{eq} = (1/3) \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* a_i a_j$.

(Liebau 1985) of composition [Si$_7$O$_{18}$(OH)]$^{9-}$. This double chain is constructed of an [Si$_3$O$_9$]$^{6-}$ wollastonite-type chain and an [Si$_4$O$_{11}$]$^{6-}$ vlasovite-type chain, both of which extend in the *c* direction (Fig. 1a). The double chain contains both four- and eight-membered rings; the four-membered ring is a component of the vlasovite-type chain, and the eight-membered ring is formed by linking of both types of chain.

The *M*(1) octahedra and *Na* polyhedra share common edges to form a ribbon two polyhedra wide that extends in the *c* direction (Fig. 1b). The *M*(2) and *M*(3) octahedra share common edges to form another ribbon two polyhedra wide that also extends along the *c* direction. These two ribbons are connected through common vertices to form a sheet parallel to (100) (Fig. 1b). Hybrid *dreier* double-chains [Si$_7$O$_{18}$(OH)]$^{9-}_\infty$ and *M*(2), *M*(3) and *Na* polyhedra share common vertices to form a mixed framework, [Na Ca$_2$ Ti^{4+} (Si$_7$O$_{18}$(OH)O]$^{2-}$, with large cages that contain Cs and K at the *A*(1) and *A*(2) sites, respectively (Fig. 2).

Hydrogen bonding

There is one unique H site in the crystal structure of senkevichite; details of its local stereochemistry are given in Table 3 and in Figure 3. Hydrogen is bonded to the O(18) anion of the silicate tetrahedron, forming an acid [SiO$_3$(OH)] group. The D(donor)–H(hydrogen) distance is 0.91 Å, as forced by the soft-constraint method of the refinement procedure for hydrogen positions. The H(hydrogen)...A(acceptor) distance is 1.86 Å, which indicates significant hydrogen bonding. The D–H...A angle is 164°, which is typical for weak to moderate hydrogen bonding. The O(18) anion is bonded to Si at the *Si*(7) site, and large alkali cations Cs and K at the *A*(1) and *A*(2) sites, together with its associated H atom. Inspection of Figure 3 shows that the *Si*(7) tetrahedron is attached to the shared edge of the Na polyhedron (shown blue in Fig. 3) and that the O(18) corner of the tetrahedron projects out into a large cavity that is sandwiched between two of the sheets

depicted in Figure 1b. Accordingly, the O(18) anion bonds to the large monovalent cations occupying this cavity. The arrangement of polyhedra in this region of the structure is such that the $Si(7)$ tetrahedron cannot adjust its position such that the O(18) anion can bond to any of the higher-valence cations within the structure. Hence the topological and geometrical details of the senkevichite structure are such that only the attachment of a H atom to the O(18) anion can satisfy its bond-valence requirements.
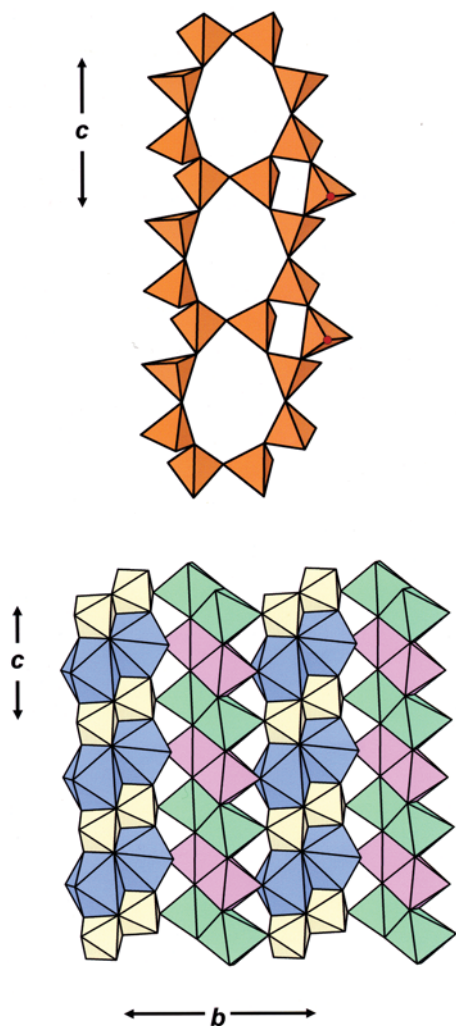

(a)

(b)

FIG. 1. (a) The hybrid $[Si_7O_{18}(OH)]^{9-}_\infty$ *dreier* double-chain in the crystal structure of senkevichite, (b) (011) sheets of $M(1)$, $M(2)$, $M(3)$ and Na polyhedra. Si tetrahedra are orange, $M(1)$ octahedra are yellow, $M(2)$ octahedra are green, $M(3)$ octahedra are pink, Na polyhedra are blue, and (OH) groups are red circles.

DISCUSSION

Senkevichite is a Cs-analogue of tinaksite, K_2 Na Ca_2 Ti (Si_7O_{18}) O (OH) (Petrunina *et al*. 1973), and a Cs–Na–Ti oxyanalogue of tokkoite, K_2 Ca_4 $[Si_7O_{18}(OH)]$ F (Rozhdestvenskaya *et al*. 1989). The crystal structure of tinaksite was first determined by Petrunina *et al*. (1973) in space group $P1$. Later, the structure was re-refined by Bissert (1980) in space group $P\bar{1}$. In the crystal structure of tinaksite, silicon–oxygen tetrahedra form a $[Si_7O_{18}(OH)]^{9-}$ hybrid *dreier* double-chain (Liebau 1985) of eight- and four-membered rings that extend along the [001] direction. The $M(1)$ octahedra and Na polyhedra share common edges to form a band two polyhedra wide; $M(2)$ and $M(3)$ octahedra share common edges to form another band two polyhedra wide. These bands extend along the c axis and are connected through common vertices to form a sheet parallel to (011). Hybrid *dreier* $[Si_7O_{18}(OH)]^{9-}_\infty$ double-chains and $M(2)$, $M(3)$ and Na polyhedra share common vertices to form a mixed framework, $[Na\ Ca_2$
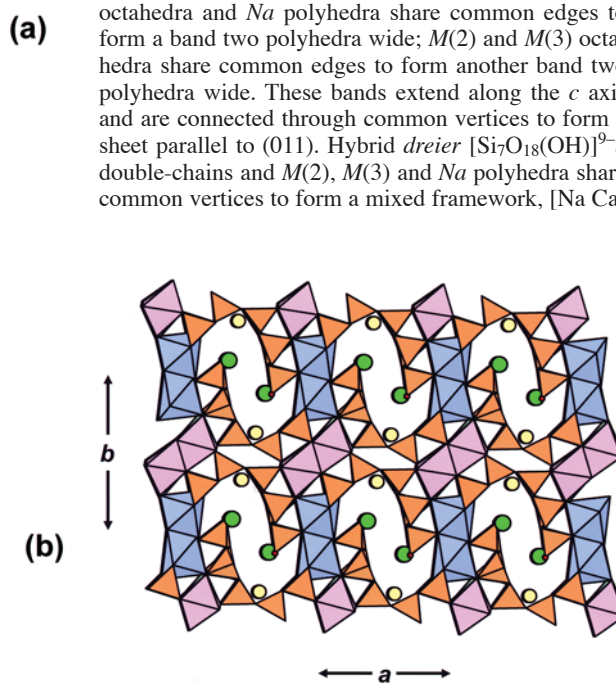

FIG. 2. The crystal structure of senkevichite projected onto (110). Legend as in Figure 1. The $A(1)$ atoms are shown as green circles, $A(2)$ atoms are shown as yellow circles.
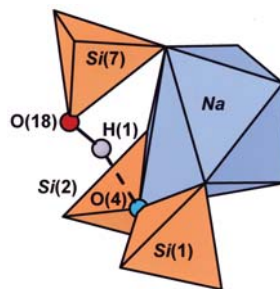

FIG. 3. The hydrogen-bonding arrangement in the crystal structure of senkevichite; legend as in Figure 1.

Ti $(Si_7O_{18}(OH)O]^{2-}$, with large cages that contain $A(1)$ and $A(2)$ atoms. In tinaksite, the relationship $A(1) = A(2) = K$ applies, whereas in senkevichite, $A(1)$ corresponds to Cs, and $A(2)$, to K.

The crystal structure of tokkoite, $K_2 Ca_4 [Si_7O_{18}(OH)]$ F, described by Rozhdestvenskaya *et al.* (1989), is related to both tinaksite and senkevichite. Its general geometry is the same, but instead of a band of $M(1)$ and *Na* polyhedra [where $M(1) = Ti$], tokkoite has a band of $Ca(1)$ and $Ca(2)$ octahedra. Also, tokkoite contains both (OH) and F, whereas tinaksite contains (OH) and not F.

Rozhdestvenskaya *et al.* (1989) suggested that tinaksite and tokkoite are end-members of the isomorphous series $K_2 Ca_4 [Si_7O_{18}(OH)]$ (O,OH,F) – K_2 Na Ca_2Ti $[Si_7O_{18}(OH)]$ O, in which the following substitutions take place simultaneously: $2 Ca^{2+} \rightleftharpoons Ti^{4+} + Na^+$ and $(F,OH)^- \rightleftharpoons O^{2-}$.

There is an interesting parallel in the the silicate motifs in the crystal structures of senkevichite, hubeite (Cooper & Hawthorne 2004) and inesite (Wan & Ghose 1978). In the structure of hubeite, the acid silicate group terminates one end of a $[Si_4O_{12}(OH)]$ group. These
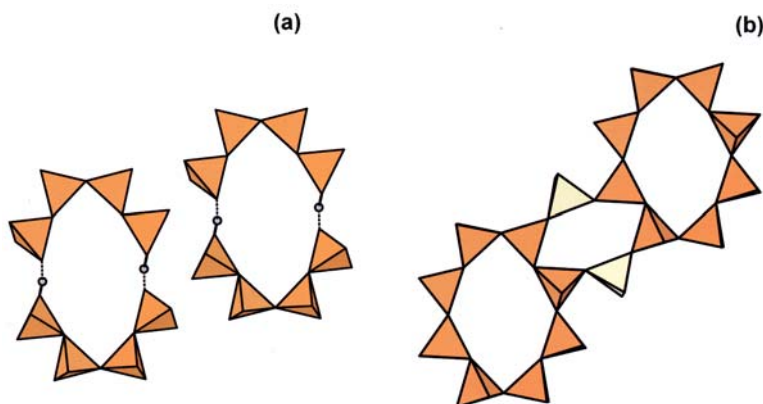

FIG. 4. Fragments of the crystal structure of hubeite and inesite: (a) hubeite: $[Si_4\phi_{13}]$ groups projected onto (001); (b) inesite: $[Si_{10}O_{30}]$ silicate group consisting of eight-membered rings connected by additional silicate tetrahedra. Si tetrahedra are orange and yellow, hydrogen atoms are shown as small gray circles, hydrogen bonds are shown as dashed lines.
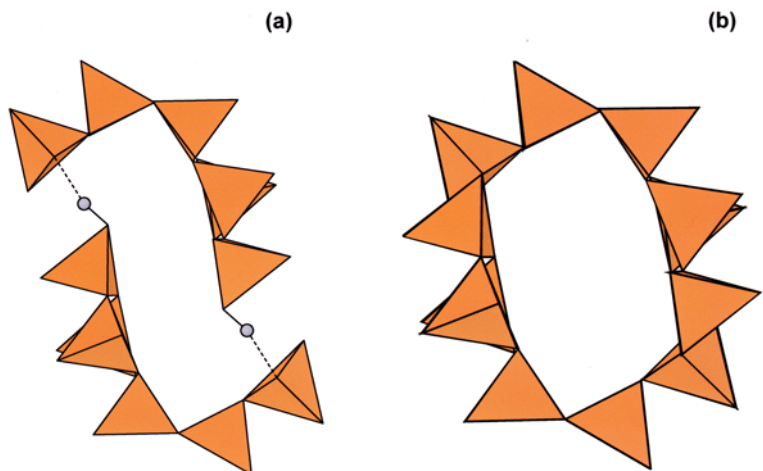

FIG. 5. (a) Double chains in the crystal structure of senkevichite projected onto (001); (b) an $[Si_{10}O_{30}]$ ring formed by loss of H atoms and subsequent coordination of the arrangement in (a).

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR SENKEVICHITE

Si(1)–O(1)	1.651(3)	Si(2)–O(4)	1.653(3)	Si(3)–O(1)a	1.642(3)	Si(4)–O(10)	1.641(3)
Si(1)–O(2)	1.600(3)	Si(2)–O(5)	1.595(3)	Si(3)–O(7)	1.644(3)	Si(4)–O(11)	1.635(3)
Si(1)–O(3)	1.595(3)	Si(2)–O(6)	1.602(3)	Si(3)–O(8)	1.581(3)	Si(4)–O(12)	1.593(3)
Si(1)–O(4)	1.640(3)	Si(2)–O(7)	1.652(3)	Si(3)–O(9)	1.635(3)	Si(4)–O(13)a	1.618(3)
<Si(1)–O>	1.622	<Si(2)–O>	1.626	<Si(3)–O>	1.626	<Si(4)–O>	1.622
Si(5)–O(13)	1.630(3)	Si(6)–O(9)	1.630(3)	Si(7)–O(11)	1.641(3)	A(1)–O(1)	3.466(3)
Si(5)–O(14)	1.559(3)	Si(6)–O(10)	1.636(3)	Si(7)–O(15)	1.630(3)	A(1)–O(2)	3.479(3)
Si(5)–O(15)	1.633(3)	Si(6)–O(16)	1.640(3)	Si(7)–O(18)b	1.624(3)	A(1)–O(5)	3.292(3)
Si(5)–O(16)	1.649(3)	Si(6)–O(17)	1.582(3)	Si(7)–O(19)	1.595(3)	A(1)–O(7)	3.275(3)
						A(1)–O(11)	3.088(3)
<Si(5)–O>	1.618	<Si(6)–O>	1.622	<Si(7)–O>	1.623	A(1)–O(11)c	3.296(3)
						A(1)–O(13)	3.429(3)
Si(1)-O(1)-Si(3)	131.3(2)	Na–O(2)	2.609(3)	A(2)–O(1)	2.814(3)	A(1)–O(15)	3.139(3)
Si(1)-O(4)-Si(2)	146.6(2)	Na–O(4)	2.793(3)	A(2)–O(4)	2.961(3)	A(1)–O(15)c	3.480(3)
Si(2)-O(7)-Si(3)	133.2(2)	Na–O(5)	2.545(3)	A(2)–O(7)	2.873(3)	A(1)–O(16)	3.272(3)
Si(3)-O(9)-Si(6)	143.2(2)	Na–O(14)	2.250(3)	A(2)–O(8)	3.346(3)	A(1)–O(18)	3.544(3)
Si(4)-O(10)-Si(6)	136.0(2)	Na–O(19)	2.337(3)	A(2)–O(9)	2.794(3)	A(1)–O(20)	3.055(3)
Si(4)-O(11)-Si(7)	125.5(2)	Na–O(19)c	2.500(3)	A(2)–O(10)	2.842(3)		
Si(4)-O(13)-Si(5)	137.1(2)	Na–O(20)	2.491(3)	A(2)–O(13)	2.936(3)	<A(1)–O>	3.318
Si(5)-O(15)-Si(7)	136.1(2)			A(2)–O(16)	2.853(3)		
Si(5)-O(16)-Si(6)	131.1(2)	<Na–O>	2.504	A(2)–O(17)	3.252(3)		
				A(2)–O(18)	3.194(3)		
				<A(2)–O>	2.987	D–H...A	O(18)–H...O(4)
M(1)–O(2)	1.922(3)	M(2)–O(3)	2.402(3)	M(3)–O(3)	2.380(3)	D–A (Å)	2.739(4)
M(1)–O(5)	1.992(3)	M(2)–O(3)e	2.388(3)	M(3)–O(6)	2.351(3)	D–H (Å)	0.91(1)
M(1)–O(12)	2.147(3)	M(2)–O(6)	2.389(3)	M(3)–O(6)c	2.367(3)	H...A (Å)	1.86(2)
M(1)–O(19)	2.054(3)	M(2)–O(8)	2.363(3)	M(3)–O(8)	2.292(3)	∠D–H...A (°)	164(5)
M(1)–O(20)	1.825(3)	M(2)–O(12)	2.369(3)	M(3)–O(14)	2.199(3)		
M(1)–O(20)d	1.970(3)	M(2)–O(17)	2.381(3)	M(3)–O(17)	2.314(3)		
<M(1)–O>	1.985	<M(2)–O>	2.382	<M(3)–O>	2.317		

a: x, y, $z - 1$; b: x, $y - 1$, z; c: $-x + 1$, $-y + 1$, $-z + 1$; d: $-x + 1$, $-y + 1$, $-z + 2$; e: $-x$, $-y + 1$; $-z + 2$.

TABLE 4. REFINED SITE-SCATTERING VALUES (*epfu*)
AND ASSIGNED SITE-POPULATIONS (*apfu*) FOR SENKEVICHITE

	Refined site-scattering	Site population	Calculated site-scattering	<X–φ> calc.*	<X–φ> obs.
A(1)	48.96(11)	0.90 Cs + 0.08 K	51.02	3.176	3.318
A(2)	18.56(9)	1.00 K	19	2.97	2.987
Na	10.95(9)	1.00 Na	11	2.5	2.504
M(1)	22.45(9)	0.93 Ti + 0.04 Nb	22.1	1.927	1.985
M(2)	19.74(9)	1.00 Ca	20	2.38	2.382
M(3)	22.41(9)	0.62 Ca + 0.30 Mn + 0.06 Fe	21.46	2.268	2.317

* Calculated by summing constituent ionic radii; values from Shannon (1976).

groups are arranged in pairs such that each H-atom hydrogen bonds to the other (non-acid) end of the other $[Si_4O_{12}(OH)]$ group (Fig. 4a). In the related structure of inesite, eight-membered rings of silicate tetrahedra (Fig. 4b) resemble pairs of $[Si_4O_{12}(OH)]$ groups with the H atoms removed, and the groups joined to satisfy the bond-valence requirements at the O atoms of the erstwhile (OH) groups. A similar situation emerges for senkevichite. Here, the acid silicate group terminates one end of a $[Si_5O_{15}(OH)]$ fragment, and these fragments are arranged in pairs such that each H atom hydrogen-bonds to the other (non-acid) end of the other $[Si_5O_{15}(OH)]$ group (Fig. 5a). Removal of the H-atoms and condensation of the two fragments along the O(donor)–O(acceptor) vectors result in a ten-membered ring of the form $[Si_{10}O_{30}]$ (Fig. 5b) that has not yet been found in mineral structures. It is intriguing how such complicated arrangements as senkevichite and hubeite contain convoluted silicate fragments that can be condensed into graphically compact arrangements.

TABLE 5. BOND-VALENCE TABLE FOR SENKEVICHITE

	$A(1)$**	$A(2)$**	Na**	$M(1)$*	$M(2)$*	$M(3)$**	$Si(1)$*	$Si(2)$*	$Si(3)$*	$Si(4)$*	$Si(5)$*	$Si(6)$*	$Si(7)$*	H	Σ
O(1)	0.07	0.15					0.93		0.96						2.11
O(2)	0.07		0.13	0.74			1.07								2.01
O(3)					0.63	0.26	1.08								1.97
O(4)		0.09	0.10				0.96	0.92						0.10	2.17
O(5)	0.10		0.14	0.61				1.08							1.93
O(6)					0.32	0.53		1.06							1.91
O(7)	0.10	0.12						0.93	0.95						2.10
O(8)		0.03			0.34	0.32			1.13						1.82
O(9)		0.16							0.97			0.98			2.11
O(10)		0.13								0.96		0.97			2.06
O(11)	0.25									0.97			0.96		2.18
O(12)					0.40	0.34				1.09					1.83
O(13)	0.07	0.10								1.02	0.98				2.17
O(14)			0.25			0.40					1.19				1.84
O(15)	0.20										0.98		0.98		2.16
O(16)	0.10	0.13									0.93	0.96			2.12
O(17)		0.04			0.33	0.30						1.12			1.79
O(18)	0.06	0.05											1.00	0.90	2.01
O(19)			0.21	0.52									1.08		1.97
			0.16												
O(20)	0.16		0.16	1.61											1.93
Σ	1.18	1.00	1.15	3.88	1.96	1.81	4.04	3.99	4.01	4.04	4.08	4.03	4.02	1.00	

* bond-valence parameters (vu) from Brown & Altermatt (1985); ** bond-valence parameters (vu) from Brown (1981).

TABLE 6. CHEMICAL COMPOSITION* (wt.%) AND UNIT FORMULA ($apfu$) OF SENKEVICHITE

SiO_2	51.08	Si	7.00
TiO_2	8.94		
Nb_2O_5	0.64	Ti^{4+}	0.93
CaO	10.98	Nb	0.04
MnO	2.59	$ΣM(1)$	0.97
FeO	0.50		
Cs_2O	15.28	Ca	1.62
K_2O	6.13	Mn	0.30
Na_2O	3.76	Fe^{2+}	0.06
H_2O**	1.09	$ΣM(2) + M(3)$	1.98
Total	100.99		
		Cs	0.90
		K	1.08
		$ΣA(1) + A(2)$	1.98
		Na	1.00
		H^+	1.00

* mean of eight determinations; ** calculated from the structure refinement.

ACKNOWLEDGEMENTS

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