Yakovenchukite-(Y), K₃NaCaY₂(Si₁₂O₃₀)(H₂O)₄, a new mineral from the Khibiny massif, Kola Peninsula, Russia: A novel type of octahedral-tetrahedral open-framework structure

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ABSTRACT

Yakovenchukite-(Y), K₃NaCaY₂[Si₁₂O₃₀](H₂O)₄, is a new REE silicate found in a thin (3–4 cm) sodalite-aegirine-microcline veinlet cutting ijolite-urtite at Mt. Kukisvumchorr, Khibiny alkaline massif, Kola Peninsula, Russia. The mineral occurs as small prismatic crystals in intimate association with microcline, aegirine, calcite, catapleiite, donnayite-(Y), fluorapophyllite, fluorite, galena, lead, litharge, molybdenite, natrolite–gonnardite, pyrochlore, rinkite, strontianite, and vuorijarvite-K. Yakovenchukite-(Y) is creamy to colorless, with vitreous luster. The streak is white. The mineral is transparent, non-fluorescent. The Mohs hardness is about 5. The mineral is brittle. Cleavage is perfect on {100}, distinct on {010}, fracture is stepped. Densities are 2.83 g/cm³ (measured by sink/float in heavy liquids) and 2.72 g/cm³ (calculated). Yakovenchukite-(Y) is biaxial (+): n_α = 1.520(5), n_β = 1.525(5), n_γ = 1.538(5) (589 nm), 2V(meas.) = 60 ± 5°, 2V(calc.) = 61.86°. The optical orientation is Y = **c**, X = **a**, Z = **b**, pleochroism is not observed. Chemical analysis by electron microprobe (wt%): Na₂O 4.32, K₂O 10.73, CaO 3.42, Y₂O₃ 15.49, Ce₂O₃ 0.10, Dy₂O₃ 0.68, Er₂O₃ 0.88, Tm₂O₃ 0.18, Yb₂O₃ 1.53, ThO₂ 0.62, SiO₂ 57.55, H₂O (by the Penfield method) 4.70, total 100.20. The empirical formula (based on Si = 12 apfu) is (K₂.₈₅ Na₀.₁₅)Σ₃.₀₀ Na₁.₀₀ (Ca₀.₇₁ Na₀.₆₀)Σ₁.₃₁ (Y₁.₇₂ Yb₀.₁₀ Er₀.₀₆ Dy₀.₀₅ Th₀.₀₃ Ce₀.₀₁ Tm₀.₀₁ Ca₀.₀₅)Σ₂.₀₃ [Si₁₂ O₃₀.₀₂]·3.27H₂O. According to single-crystal X-ray study yakovenchukite-(Y) is orthorhombic, *Pcca*, *a* = 14.972(8), *b* = 14.137(7), *c* = 14.594(8) Å, *V* = 3089(3) Å³, *Z* = 4. The strongest lines of the X-ray powder diffraction pattern are [*d*bs(Å) (*I*obs) (*hkl*)]: 7.00 (40) (020), 6.57 (60) (102), 4.20 (50) (222), 3.337 (100) (331), 3.248 (90) (024), 3.101 (40) (142), 3.014 (80) (422), 2.608 (40) (404). The crystal structure of yakovenchukite-(Y) belongs to a new structure type of minerals and inorganic compounds. It is based on microporous octahedral-tetrahedral framework of SiO₄-tetrahedra and YO₆-octahedra. Silicate tetrahedra share corners to form unprecedented [Si₁₂O₃₀] sheets consisting of 4-, 6-, and 14-membered rings. The sheets are parallel to (001) and are linked into 3D framework through YO₆ octahedra. Ca²⁺, K⁺, and Na⁺ cations are located within the framework cavities. The octahedral-tetrahedral framework possess channels extended along the **a** axis. The channel dimensions are 4.9 × 6.2 Å, which means the free crystallographic diameter of 2.2 × 3.5 Å, that allows classifying yakovenchukite-(Y) as a microporous material. Yakovenchukite-(Y) is the latest low-temperature hydrothermal mineral, formed by alteration of earlier REE-rich minerals (pyrochlore, rinkite, etc.). The mineral is named in honor of Victor N. Yakovenchuk, a mineralogist at the Geological Institute of the Kola Science Centre of the Russian Academy of Sciences, for his outstanding contribution to the mineralogy of alkaline and alkaline-ultrabasic massifs.

Keywords: Yakovenchukite-(Y), new mineral, REE-silicate, crystal structure, ultra-alkaline hydrothermal vein, Khibiny massif, Kola Peninsula

INTRODUCTION

The Khibiny massif is the world's largest intrusion of nepheline syenite and foidolite as well as a "world champion" of mineral diversity. More than 440 mineral species have been reported there, including 91 new mineral species (Yakovenchuk et al. 2006b). Yttrium minerals are not so widespread in the massif,

and only six species have been identified here so far: fergusonite-(Y), yttropyrochlore-(Y), pyatenkoite-(Y), sazykinaite-(Y), donnayite-(Y), and mckelveyite-(Y). The seventh yttrium mineral was found in 2005 by the first author during precise structural investigations of vuoriyarvite-K from specimens selected by V.N. Yakovenchuk from a veinlet within ijolite-urtite at Mt. Kukisvumchorr (the Kirov Mine, horizon +252 m). The mineral was identified as new and was named in honor of Victor Nest-erovich Yakovenchuk (b. 1950), researcher at the Laboratory of

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Self-Organization in Mineral Systems, the Geological Institute of the Kola Science Centre Russian Academy of Sciences, for his significant contributions to the study of minerals of alkaline and alkaline-ultrabasic massifs (Yakovenchuk et al. 1997, 1999, 2003, 2006a, 2006b; Ivanyuk et al. 2002, etc.). Both the mineral and mineral name has been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association (proposal 2005-035). The holotype specimen of yakovenchukite-(Y) has been deposited in the Mineralogical museum of St. Petersburg State University, Russia, registration number 1/19174.

OCCURRENCE

The apatite deposit at Mt. Kukisvumchorr (Khibiny massif, Kola Peninsula, Russia) consists of the main (40–180 m thick and 1850 m long) and the secondary (5–30 m wide) lenses of apatite-nepheline rock dipping northeast at 26 to 32° within a conical ring-like foidolite intrusion in foyaite. The main lens is accompanied by the conical 0.2–2.5 m wide shear-zone which dips at an angle of about 45° to the center of the massif and is marked by gneissic apatite-nepheline rocks, brecciated zones, layers of ijolite, juvite, and malignite, and also pegmatite and hydrothermal veins. Most of the veins are localized in overburden feldspar-bearing ijolite-urtite, malignite, and rischorrite, while the position of ultra-alkaline low-temperature hydrothermal veins and of the veinlet with yakovenchukite-(Y) is controlled by the radial Kukisvumchorr fault (Ivanyuk et al. 1996).

Yakovenchukite-(Y) was identified in a sodalite-aegirine-microcline veinlet in ijolite-urtite described in detail by Yakovenchuk et al. (2006b) (vein no. 46). It is a thin (3–4 cm) veinlet with several swellings (up to 20 cm) and a symmetric-zoned structure. The selvages (up to 2 cm, but not always present) are made of black, thin-prismatic aegirine crystals (up to 2 cm long). The axial zone (up to 20 cm) is composed of white tabular crystals of microcline (up to 5 cm diameter). The interstices are filled with aggregates of nepheline, sodalite, and natrolite, which contain inclusions of rinkite, fluorite, pectolite, lorenzenite, and fersmanite. Voids produced by leaching of fersmanite are encrusted by light-pink, prismatic vuorijarvite-K and tsepinite-K. In other voids, microcline is a substrate for box-shaped crystals of natrolite, acicular aegirine, thin-tabular catapleiite, prismatic pectolite, equant crystals of fluorapophyllite, aggregates of disk-shaped calcite, pyramidal crystals of donnayite-(Y), spherulites of strontianite, and flattened-prismatic crystals of yakovenchukite-(Y) (Fig. 1). Rinkite crystals exposed in voids are encrusted by small prismatic crystals of vuorijarvite-K. Microcline, fersmanite, lorenzenite, and sphalerite are overgrown by loose clusters of rhombic dodecahedra of pyrochlore covered by a "parquet-like" aggregate of prismatic vuorijarvite-K. Galena grains occur amongst microcline crystals. The alteration of galena results in the formation of aggregates of litharge together with small balls of native lead. At the borders of the microcline crystals, there are slender molybdenite lamellae.

Physical and optical properties

Yakovenchukite-(Y) forms flattened long-prismatic crystals with pinacoidal {100} (dominant), {010}, and rhombic prismatic {101} forms (see Fig. 1) covering the surface of small druses.

No twinning was observed. Macroscopically, yakovenchukite-(Y) is pale white, creamy with a vitreous luster. The mineral is transparent. Streak is white. Cleavage is perfect on {100}, distinct on {010}. Yakovenchukite-(Y) is brittle and has a stepped fracture. Mohs hardness is about 5. The density determined by the float and sink method in Clerici solution is 2.83 g/cm³; the density calculated on the basis of the empirical formula and cell dimensions obtained from X-ray powder diffraction data is 2.72 g/cm³.

Yakovenchukite-(Y) is biaxial (+): n_α = 1.520(5), n_β = 1.525(5), n_γ = 1.538(5) (589 nm), $2V_Z$(meas.) = 60 ± 5°, $2V_Z$(calc.) = 61.86°, optical orientation: Y = **c**, X = **a**, Z = **b**. In transmitted light, the mineral is colorless, without notable dispersion. The Gladstone-Dale relationship provides a compatibility index of 0.017, superior (with unit-cell volume from X-ray single-crystal data and D_{calc}).

Chemical composition

Chemical composition of yakovenchukite-(Y) was studied using a Cameca MS-46 electron microprobe operating at 20 kV, 20–30 nA, 20 μm beam diameter. 10 different points were analyzed (Table 1). The following standards were used: lorenzenite (for Na), wadeite (for K), wollastonite (for Ca and Si), synthetic $Y_3Al_5O_{12}$ (for Y), synthetic CeS (for Ce), synthetic $LiDy(WO_4)_2$ (for Dy), synthetic $LiEr(MoO_4)_2$ (for Er), synthetic $Tm_3Al_5O_{12}$ (for Tm), synthetic $LiYb(MoO_4)_2$ (for Yb), and thorite (for Th). Analytical difficulties due to the mineral instability under the electron beam were partially overcome by defocusing the beam and moving it slowly during the analysis. Concentration of H_2O was determined by the Penfield's method. The empirical formula, calculated from an average composition on the basis of Si = 12 apfu, is: $(K_{2.85}Na_{0.15})_{\Sigma3.00}Na_{1.00}(Ca_{0.71}Na_{0.60})_{\Sigma1.31}$ $(Y_{1.72}Yb_{0.10}Er_{0.06}Dy_{0.05}$ $Th_{0.03}Ce_{0.01}Tm_{0.01}Ca_{0.05})_{\Sigma2.03}$ $[Si_{12}O_{30.02}]\cdot3.27H_2O$, yielding the simplified formula $K_3NaCaY_2[Si_{12}O_{30}](H_2O)_4$, which requires K_2O 11.33, Na_2O 2.49, CaO 4.50, Y_2O_3 18.10, SiO_2 57.80, H_2O 5.78, total 100.00 wt%.

X-ray powder diffraction pattern

The powder X-ray diffraction pattern of yakovenchukite-(Y) was obtained by means of the URS-1 instrument operated at 40 kV and 30 mA with a 114.7 mm Debye-Scherrer camera and Fe$K\alpha$ radiation. The calculated powder pattern for Debye-Scherrer geometry and Cu$K\alpha$ radiation was determined with the program LAZY PULVERIX (Yvon et al. 1977) from atomic coordinates and occupancies of the refined single-crystal X-ray structure. Measured powder X-ray diffraction data (Table 2) were indexed on the basis of the calculated pattern. Refinement

TABLE 1. Chemical composition of yakovenchukite-(Y) (wt%)

	Mean	Range	Standard deviation
Na_2O	4.32	4.2–4.4	0.10
K_2O	10.73	10.5–10.9	0.20
CaO	3.42	3.34–3.50	0.08
Y_2O_3	15.49	15.25–15.75	0.25
Ce_2O_3	0.10	0.05–0.15	0.05
Dy_2O_3	0.68	0.60–0.75	0.07
Er_2O_3	0.88	0.80–0.95	0.07
Tm_2O_3	0.18	0.10–0.25	0.08
Yb_2O_3	1.53	1.47–1.60	0.05
ThO_2	0.62	0.5–0.7	0.10
SiO_2	57.55	56.9–58.2	0.60
H_2O	4.70		
Total	100.20		

TABLE 2. Powder X-ray diffraction data for yakovenchukite-(Y)

h	k	l	d_{calc}	I_{calc} (%)	d_{obs}	I/I_0
0	1	0	14.1370	11		
1	1	1	8.4037	10		
2	0	0	7.4860	25	7.37	20
0	2	0	7.0685	100	7.00	40
1	0	2	6.5594	52	6.57	60
2	0	2	5.2253	13	5.25	30
2	2	0	5.1394	11		
0	2	2	5.0770	18		
2	1	2	4.9012	15		
1	2	2	4.8081	17		
1	1	3	4.3971	5		
2	2	2	4.2018	28	4.20	50
2	3	0	3.9880	6		
4	0	0	3.7430	8		
0	4	0	3.5343	5		
2	3	2	3.4995	5		
3	1	3	3.3824	10		
3	3	1	3.3356	18		
4	0	2	3.3304	58	3.337	100
4	2	0	3.3079	14		
1	3	3	3.3014	7		
2	0	4	3.2797	36		
0	2	4	3.2421	74	3.248	90
2	4	0	3.1960	33		
0	4	2	3.1808	13		
1	2	4	3.1686	11		
1	4	2	3.1114	86	3.101	40
2	3	3	3.0841	8		
4	2	2	3.0128	72	3.014	80
2	2	4	2.9751	8		
2	4	2	2.9275	5		
5	1	1	2.8721	13	2.874	30
5	0	2	2.7702	12	2.772	20
3	2	4	2.7188	14		
3	4	2	2.6823	16	2.685	10
2	1	5	2.6704	5		
4	0	4	2.6126	22	2.608	40
4	4	0	2.5697	10		
0	4	4	2.5385	28	2.537	20
4	4	2	2.4238	10	2.398	10
0	2	6	2.3000	8		
0	6	2	2.2422	9		
6	2	2	2.2395	10	2.238	30
3	3	5	2.2219	5		
2	2	6	2.1985	7	2.190	30
4	4	4	2.1009	25	2.098	30
6	0	4	2.0597	7	2.060	20
7	0	2	2.0525	5		
4	6	0	1.9940	10		
4	2	6	1.9596	17	1.961	30
5	4	4	1.9363	52	1.929	20
4	6	2	1.9235	18		
8	0	0	1.8715	11	1.870	30
0	0	8	1.8242	7	1.815	30
8	2	0	1.8092	7		
6	4	4	1.7795	9		
0	8	0	1.7671	13		
4	4	6	1.7665	16		
8	2	2	1.7560	8		
4	6	4	1.7497	7		
3	0	8	1.7134	5		
0	6	6	1.6923	12		
1	6	6	1.6816	5		
6	6	2	1.6678	5		
8	0	4	1.6652	6		
8	4	0	1.6539	5		
2	6	6	1.6507	5		
8	2	4	1.6208	6		
2	4	8	1.5843	11		
4	8	2	1.5610	8		
4	4	8	1.4875	6		
8	6	2	1.4368	5		
0	4	10	1.3489	5		
0	10	4	1.3182	6		

Notes: Calculated pattern (Yvon et al. 1977) for Debye-Scherrer geometry and CuKα radiation from results of single-crystal structure refinement. Only intensities of 5% and stronger are listed.

of unit-cell parameters from powder data yielded: a = 14.96(5), b = 14.17(7), c = 14.56(5) Å, V = 3086(30) Å^3, Z = 4.

CRYSTAL STRUCTURE

Experimental methods

A prismatic crystal fragment of yakovenchukite was mounted on a Bruker AXS three-circle diffractometer (equipped with a CCD 1 K area detector and a flat graphite monochromator). More than a hemisphere of data was collected using an exposure time of 180 s and framewidths of 0.3° in ω. The unit-cell parameters (Table 3) were refined using least-squares techniques on the basis of 2212 reflections. The data were reduced and filtered for statistical outliers using the Bruker program SAINT, and were corrected for Lorentz, polarization, background, and absorption effects. Additional information pertinent to the data collection is given in Table 3.

The Bruker SHELXTL Version 5 system of programs was used for the determination and refinement of the structure. The structure was solved in the orthorhombic *Pcca* space group and refined on the basis of F^2 for all unique data. The final refinement included positional and anisotropic displacement parameters of all atoms, and included a weighting scheme of the structure factors. The refinement of the structure converged to an agreement index (R1) of 0.051, which was calculated for the 1269 unique observed reflections ($F_o \geq 4\sigma_{F_o}$). Final positional

FIGURE 1. Druse of yakovenchukite-(Y) crystals (field of view 3.0 × 2.4 mm) in a void within sodalite-aegirine-microcline veinlet in ijolite-urtite at Mt. Kukisvumchorr (Khibiny Massif).

TABLE 3. Crystallographic data and refinement parameters for yakovenchukite-(Y)

a (Å)	14.972(8)
b (Å)	14.137(7)
c (Å)	14.594(8)
V (Å^3)	3089(3)
Space group	*Pcca*
F_{000}	2457
μ (cm^{-1})	52.87
Z	4
D_{calc} (g/cm^3)	2.72
Crystal size (mm)	0.22 × 0.04 × 0.01
Radiation	MoKα
Total Ref.	16919
Unique Ref.	3588
Unique $|F_o| \geq 4\sigma_F$	1269
R_1	0.051
wR_2	0.077
S	0.788

Note: $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2)+(aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$; $s = \{\Sigma[w(F_o^2 - F_c^2)]/(n - p)\}^{1/2}$ where n is the number of reflections and p is the number of refined parameters.

TABLE 4. Atomic coordinates and displacement parameters for yakovenchukite-(Y)*

Atom	Occupancy	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Y1	$Y_{0.84}Yb_{0.16}$	0	1/2	1/2	0.0137(5)	0.0103(8)	0.0159(9)	0.0151(8)	0.0006(8)	0.0008(6)	−0.0002(7)
Y2	$Y_{0.82}Yb_{0.18}$	0	0	1/2	0.0143(5)	0.0099(7)	0.0176(9)	0.0154(8)	0.0013(8)	0.0014(6)	0.0008(8)
Si1		0.1252(2)	0.3588(3)	0.3440(2)	0.0149(9)	0.010(2)	0.011(2)	0.024(2)	−0.0027(17)	−0.0027(16)	−0.0004(14)
Si2		0.1215(2)	0.1434(3)	0.3510(2)	0.0161(9)	0.014(2)	0.019(2)	0.015(2)	−0.0013(16)	0.0012(16)	−0.0007(15)
Si3		0.1699(2)	0.6402(2)	0.3768(3)	0.0169(8)	0.0121(19)	0.019(2)	0.020(2)	−0.0023(17)	0.0013(15)	−0.0023(16)
Si4		0.1759(2)	−0.1359(2)	0.3717(3)	0.0141(8)	0.0120(19)	0.011(2)	0.020(2)	−0.0021(16)	−0.0002(15)	0.0003(16)
Si5		0.0972(2)	−0.0264(2)	0.2175(2)	0.0158(7)	0.0144(14)	0.017(2)	0.016(2)	0.0015(12)	0.0003(13)	−0.0007(13)
Si6		0.1452(2)	0.5182(2)	0.2019(2)	0.0207(8)	0.0159(16)	0.026(2)	0.020(2)	−0.0009(15)	0.0001(14)	0.0008(14)
O1		0	−0.0642(6)	1/4	0.022(2)	0.013(5)	0.022(5)	0.030(6)	0.000	−0.005(5)	0.000
O2		0.1407(5)	0.6031(5)	0.2768(6)	0.025(2)	0.027(5)	0.025(5)	0.024(5)	−0.007(4)	−0.004(4)	0.000(3)
O3		0.1150(5)	0.0775(5)	0.2608(5)	0.019(2)	0.029(5)	0.015(4)	0.013(5)	0.007(4)	−0.005(4)	0.005(4)
O4		0.1142(5)	0.4183(5)	0.2503(5)	0.025(2)	0.019(5)	0.024(5)	0.031(5)	0.006(5)	−0.008(4)	−0.003(4)
O5		0.1667(4)	−0.1019(5)	0.2656(5)	0.017(2)	0.015(4)	0.026(4)	0.009(4)	−0.006(3)	0.000(3)	0.003(3)
O6		0.2233(5)	0.3810(5)	0.3887(5)	0.020(2)	0.016(5)	0.023(5)	0.020(5)	−0.009(4)	0.004(4)	−0.004(4)
O7		0.1234(3)	0.2500(7)	0.3074(4)	0.020(1)	0.019(3)	0.015(3)	0.025(3)	−0.004(6)	0.006(3)	−0.005(4)
O8		0.2185(5)	0.1219(5)	0.4007(5)	0.019(2)	0.005(5)	0.023(5)	0.030(5)	0.000(4)	−0.003(4)	−0.003(3)
O9		0.0445(5)	0.1289(5)	0.4250(5)	0.021(2)	0.016(5)	0.020(5)	0.027(5)	0.004(4)	0.006(4)	−0.005(4)
O10		0.0499(5)	0.3799(5)	0.4176(5)	0.020(2)	0.015(5)	0.030(5)	0.016(5)	−0.003(4)	0.002(4)	−0.007(4)
O11		0.1508(3)	0.7520(7)	0.3767(4)	0.022(1)	0.013(5)	0.019(3)	0.035(4)	0.004(6)	0.003(3)	0.003(5)
O12		0.0906(5)	0.5452(5)	0.1147(5)	0.028(2)	0.025(4)	0.039(5)	0.020(5)	0.002(4)	−0.007(4)	−0.007(4)
O13		0.1075(5)	−0.0264(5)	0.1103(5)	0.024(2)	0.031(5)	0.032(5)	0.010(4)	0.005(4)	−0.004(3)	0.005(4)
O14		0.1188(5)	0.5910(5)	0.4586(5)	0.023(2)	0.022(5)	0.022(5)	0.024(5)	0.007(4)	0.003(4)	−0.002(4)
O15		1/4	1/2	0.1732(5)	0.028(2)	0.021(5)	0.048(7)	0.017(5)	0.000	0.000	−0.002(6)
O16		0.1198(5)	−0.0744(5)	0.4401(5)	0.020(2)	0.015(4)	0.025(5)	0.018(4)	−0.005(4)	0.002(3)	0.007(4)
H_2O17		0.4059(5)	0.2524(8)	0.0825(5)	0.057(2)	0.069(6)	0.038(4)	0.064(5)	0.009(7)	0.002(4)	0.008(8)
H_2O18		0.2429(5)	0.1640(5)	0.1046(4)	0.041(2)	0.035(5)	0.059(5)	0.030(4)	0.003(4)	−0.006(4)	0.020(5)
Na		1/4	1/2	0.0128(4)	0.042(2)	0.047(4)	0.053(5)	0.027(4)	0.000	0.000	−0.014(5)
Ca1		1/4	0	0.0300(2)	0.0157(7)	0.0096(15)	0.020(2)	0.017(2)	0.000	0.000	0.0040(19)
K1	$K_{0.88}$	1/2	0.2677(3)	1/4	0.041(1)	0.0308(19)	0.026(3)	0.065(3)	0.000	0.026(2)	0.000
K2	$K_{0.94}$	0.0896(2)	0.2619(3)	0.1022(2)	0.0384(8)	0.0180(12)	0.037(2)	0.061(2)	0.0041(19)	0.0013(12)	0.0046(16)
Ca2	$Ca_{0.06}$	0.0392(16)	0.244(3)	0.006(2)	0.013(6)						

Note: O atoms of the H_2O groups have been identified on the basis of bond valence analysis.

and displacement parameters of atoms and selected interatomic distances are in Tables 4 and 5, respectively.

RESULTS

The structure of yakovenchukite-(Y) (Fig. 2) contains two symmetry-independent Y sites, both octahedrally coordinated by six O atoms. The average <Y-O> bond lengths are 2.25 and 2.26 Å for Y1 and Y2, respectively, and are typical for the Y^{3+} cations. There are six Si sites, all tetrahedrally coordinated by O atoms. Silicate tetrahedra share corners to form unprecedented $(Si_{12}O_{30})$ sheets consisting of 4-, 6-, and 14-membered rings (see Fig. 3a). The sheets are parallel to (001) and are linked into a three-dimensional (3-D) framework via YO_6 octahedra. The octahedral-tetrahedral framework in the structure of yakovenchukite-(Y) possess channels extended along the **a** axis. The channels correspond to the locations of linkage between silicate sheets and Y-centered octahedra; their dimensions can be estimated as 4.9×6.2 Å, which means the free crystallographic diameter of 2.2×3.5 Å, that allows classifying yakovenchukite-(Y) as microporous material. Extra-framework content is represented by one Na, two Ca, two K, and two H_2O sites.

DISCUSSION

The structure of yakovenchukite-(Y) belongs to a new structure type of minerals and inorganic compounds. It is based upon a novel type of a microporous octahedral-tetrahedral framework. The basis of the framework is a silicate sheet of unique topology shown in Figures 3 and 4. The sheet consists of 4-, 6-, and 14-membered rings. Its topological structure can be described using nodal representation: all Si tetrahedra are symbolized by
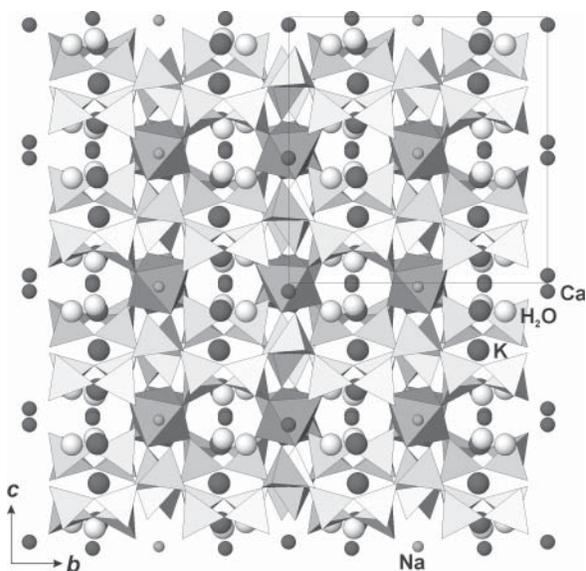
FIGURE 2. Crystal structure of yakovenchukite-(Y) projected along the **a** axis. Si tetrahedra and Y octahedra are light and gray, respectively. Large white and gray circles correspond to K^+ cations and H_2O molecules, respectively; smaller dark-gray and light-gray circles are Ca^{2+} and Na^+ cations, respectively.

vertices and vertices are linked when two respective tetrahedra share common corners. The 2-D net corresponding to the silicate sheet in yakovenchukite-(Y) is shown in Figure 4a. Its ring symbol (several polygons comprising the polyhedron specified

TABLE 5. Selected bond lengths (Å) in the structure of yakovenchukite-(Y)

Y1-O10	2.211(7) ×2	Si4-O16	1.568(8)	Ca1-O13	2.463(7) ×2
Y1-O12	2.248(7) ×2	Si4-O5	1.627(8)	Ca1-H$_2$O18	2.563(8) ×2
Y1-O14	2.277(7) ×2	Si4-O11	1.630(10)	Ca1-O16	2.574(7) ×2
<Y1-O>	2.25	Si4-O8	1.649(8)	Ca1-O8	2.598(8) ×2
		<Si4-O>	1.62	<Ca1-O>	2.55
Y2-O9	2.228(7) ×2				
Y2-O16	2.256(7) ×2	Si5-O13	1.572(7)	Ca2-O9	2.29(4)
Y2-O13	2.306(7) ×2	Si5-O1	1.622(4)	Ca2-H$_2$O17	2.38(3)
<Y2-O>	2.26	Si5-O3	1.622(8)	Ca2-O11	2.52(3)
Si1-O10	1.585(8)	Si5-O5	1.648(7)	Ca2-O10	2.59(4)
Si1-O4	1.614(8)	<Si5-O>	1.62	Ca2-O14	2.71(4)
Si1-O7	1.629(9)			Ca2-O16	2.86(4)
Si1-O6	1.638(8)	Si6-O12	1.559(7)	<Ca2-O>	2.56
<Si1-O>	1.62	Si6-O2	1.625(8)		
		Si6-O15	1.644(4)	K1-O2	2.815(8) ×2
Si2-O9	1.594(8)	Si6-O4	1.646(8)	K1-H$_2$O17	2.830(7) ×2
Si2-O3	1.615(8)	<Si6-O>	1.62	K1-O1	2.877(9)
Si2-O7	1.636(9)			K1-O11	2.931(5) ×2
Si2-O8	1.651(7)	Na-O15	2.342(10)	<K1-O>	2.86
<Si2-O>	1.62	Na-O14	2.478(8) ×2		
		Na-O6	2.504(8) ×2	K2-H$_2$O18	2.681(8)
		Na-O12	2.884(8) ×2	K2-O10	2.689(8)
Si3O14	1.579(8)	<Na-O>	2.58	K2-O9	2.777(8)
Si3O11	1.607(10)			K2-O14	2.985(8)
Si3O2	1.610(9)			K2-O7	3.043(6)
Si3O6	1.635(8)			K2-O4	3.114(8)
<Si3-O>	1.61			<K2-O>	2.88

by the number of their vertices) can be written as $14^{1}6^{1}4^{3}$.

Elpidite, Na$_2$ZrSi$_6$O$_{15}$(H$_2$O)$_3$ (Neronova and Belov 1963, 1964; Cannillo et al. 1973; Sapozhnikov and Kashaev 1978), displays a crystal structure with a topology closely related to yakovenchukite-(Y). Both mineral structures are based on an open framework of corner-sharing octahedra and tetrahedra. However, silicate tetrahedra in elpidite form 1-D chains of four-membered rings of tetrahedra (Fig. 4b). Transformation from elpidite to yakovenchukite-(Y) can be described using a nodal approach. To transform the elpidite net into the yakovenchukite-(Y) net, one has to break the links between two vertices of the same chain and to establish a new link between the adjacent chains (Fig. 4c). This leads to doubling of the unit-cell parameter parallel to the extension of the chains. Thus, the elpidite unit cell (*Pbcm*, $a = 7.14$, $b = 14.68$, $c = 14.65$ Å, $V = 1536$ Å^3; Cannillo et al. 1973) is approximately two times smaller than the yakovenchukite unit cell (*Pcca*, $a = 14.972$, $b = 14.137$, $c = 14.594$ Å, $V = 3089$ Å^3), taking into account that the silicate chains are parallel to the **a** axis in elpidite and to the **b** axis in yakovenchukite-(Y).

In general, yakovenchukite-(Y) belongs to the group of Zr-, Ti-, and REE-silicates based upon silicate sheets interlinked via metal octahedra (Krivovichev 2005). Other members of this group are: monteregianite and its synthetic analogs, Na$_2$[Y(Si$_8$O$_{19}$)](H$_2$O)$_5$ and Na$_2$[Ce(Si$_8$O$_{19}$)](H$_2$O)$_5$ (Ghose et al. 1987; Rocha et al. 1997, 2000), armstrongite (Kashaev and Sapozhnikov 1978; Kabalov et al. 2000), and sazhinite-(Ce) (Shumyatskaya et al. 1980).

Yakovenchukite-(Y) is a low-temperature hydrothermal mineral formed as a result of alteration of earlier minerals such as REE-rich rinkite and pyrochlore under exposure of alkaline solutions. As predicted by Tuttle and Bowen (1958) and confirmed by Kogarko (1977), hydrothermal solutions formed as a result of evolution of an alkaline melt may dissolve and alter early stage pegmatite minerals. Thus, cooling of villiaumite-bearing pegmatites is accompanied by the dissolution of villiaumite that
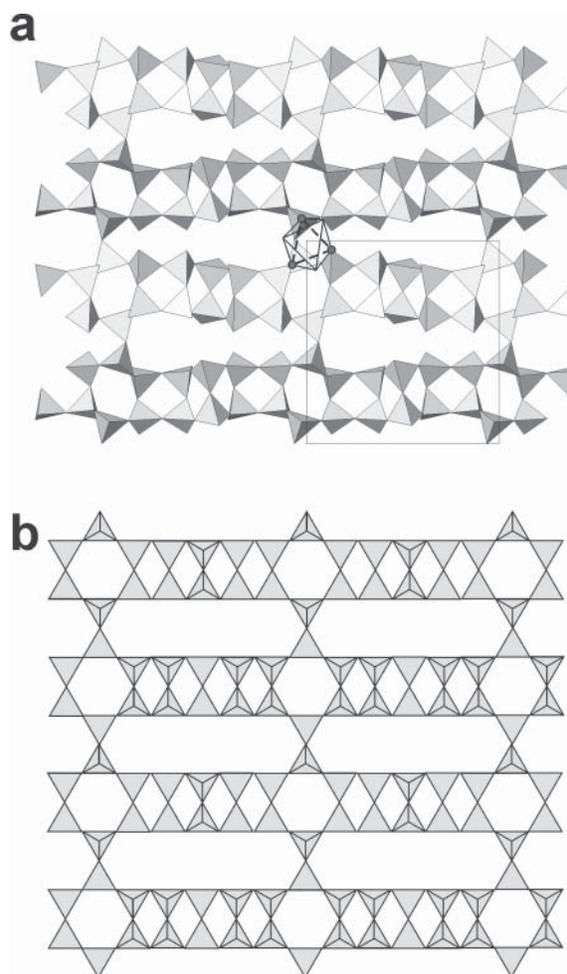
FIGURE 3. Silicate sheet in the structure of yakovenchukite-(Y) [parallel to (001)] in its real (**a**) and idealized (**b**) presentations. Connection of silicate tetrahedra to YO$_6$ octahedron is schematically shown in **a**.
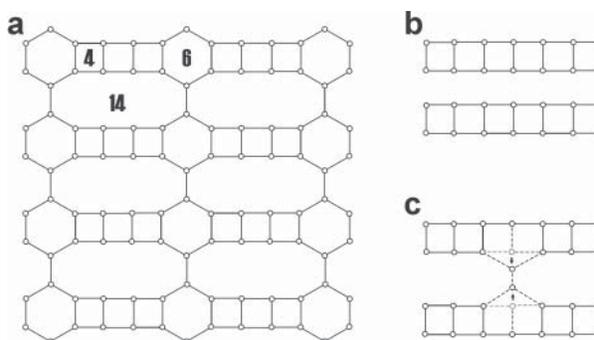
FIGURE 4. 2-D net corresponding to the topology of silicate sheet in yakovenchukite-(Y) (**a**). In elpidite, Si tetrahedra form isolated chains of 4-membered rings (**b**); to obtain 2-D net shown in **a**, one has to disjoint two adjacent vertices of the same chain and to establish a new link between two adjacent chains (**c**).

reinforces chemical activity of Na- and F-rich solutions (Ivanyuk et al. 1996). These solutions dissolve microcline, nepheline, fersmanite, rinkite, pyrochlore, etc. and become enriched in potassium, calcium, REE, and silica. If concentrations of these elements exceed the nucleation level, microporous mineral phases such as members of the labuntsovite group, yakovenchukite-(Y), zorite-chivruaiite series, etc. crystallize within interstices and leached voids of primary rocks. Thus, microporous minerals are formed as a result of hydrothermal alteration of precursor phases that, in turn, crystallize from alkaline-enriched melts. This sequence of phase transformations in nature can be of interest to material scientists in their efforts to obtain new microporous materials under laboratory conditions. The possible experimental protocol may include high-temperature synthesis of precursor phases (e.g., solid-state reactions, crystallization from melts, etc.) and their subsequent hydrothermal treatment under low-pressure and low-temperature conditions.

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