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Ivanyukite-Na-*T*, ivanyukite-Na-*C*, ivanyukite-K, and ivanyukite-Cu: New microporous titanosilicates from the Khibiny massif (Kola Peninsula, Russia) and crystal structure of ivanyukite-Na-*T*

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Abstract

Ivanyukite-Na-*T*, $Na_3[Ti_4(OH)O_3(SiO_4)_3]\cdot7H_2O$, ivanyukite-Na-*C*, $Na_2[Ti_4O_2(OH)_2(SiO_4)_3]\cdot6H_2O$, ivanyukite-K, $K_2[Ti_4(OH)_2O_2(SiO_4)_3]\cdot9H_2O$, and ivanyukite-Cu, $Cu[Ti_4(OH)_2O_2(SiO_4)_3]\cdot7H_2O$, are new microporous titanosilicates found in a natrolitized microcline-aegirine-sodalite lens in the orthoclase-bearing urtite at the Koashva Mountain (Khibiny Massif, Kola Peninsula, Russia). The minerals occur as well-shaped colorless (ivanyukite-Na-*T*), pale-orange (ivanyukite-Na-*C*), pale-blue (ivanyukite-K), and green (ivanyukite-Cu) cubic crystals (up to 1.5 mm in diameter) grown on microcline, vinogradovite, sazykinaite-(Y), natrolite, and djerfisherite. The minerals have vitreous luster and white streak. They are transparent and non-fluorescent. The Mohs hardness is estimated as ~4. The minerals are brittle. Cleavage is perfect on {100} (ivanyukite-Na-*C*, ivanyukite-K, and ivanyukite-Cu) or on $\{10\bar{1}1\}$ (ivanyukite-Na-*T*), fracture is stepped. Density, measured by the sink/float method in heavy liquids, ranges from 2.60 (ivanyukite-Na-*C*) to 2.70 g/cm^3 (ivanyukite-Na-*T*, ivanyukite-K, and ivanyukite-Cu), whereas calculated densities are: 2.58 (ivanyukite-Na-*T*), 2.39 (ivanyukite-Na-*C*), 2.69 (ivanyukite-K), and 2.46 g/cm^3 (ivanyukite-Cu). Ivanyukite-Na-*T* is uniaxial (+), $n_\omega = 1.76(1)$, $n_\varepsilon = 1.85(9)$ (589 nm), and the other minerals are isotropic, $n = 1.73(1)$. Chemical analysis by electron microprobe gave (wt% for ivanyukite-Na-*T*, ivanyukite-Na-*C*, ivanyukite-K, and ivanyukite-Cu, respectively): Na_2O 7.46, 5.19, 0.27, and 0.17; Al_2O_3 0.07, 0.21, 0.18, and 0.07; SiO_2 23.75, 25.47, 23.16, and 24.80; SO_3 0.00, 0.00, 0.00, and 0.20; K_2O 5.89, 6.34, 7.09, and 6.81; CaO 0.21, 0.14, 0.95, and 0.23; TiO_2 38.89, 37.81, 36.14, and 38.36; MnO 0.05, 0.33, 0.68, and 0.28; FeO 0.54, 2.17, 0.37, and 0.73; CuO 0.00, 0.00, 2.21, and 6.81; SrO 0.00, 0.00, 0.19, and 0.00; Nb_2O_5 2.99, 2.90, 3.62, and 3.02; BaO 0.14, 0.00, 0.00, and 0.00; H_2O (by the Penfield method) 19.00, 19.15, 25.00, and 21.50; total 98.99, 99.71, 99.86, and 98.97. The empirical formulae (based on Si+Al = 3 apfu) are $(Na_{1.82}K_{0.95}Ca_{0.03}Ba_{0.01})_{\Sigma2.81}[(Ti_{3.68}Nb_{0.17}Fe_{0.06}Mn_{0.01})_{\Sigma3.92}(Si_{2.99}Al_{0.01})_{\Sigma3.00}O_{14.59}(OH)_{1.37}]\cdot7.29H_2O$ (ivanyukite-Na-*T*), $(Na_{1.17}K_{0.94}Ca_{0.03})_{\Sigma2.14}[(Ti_{3.32}Fe_{0.21}Nb_{0.15}Mn_{0.03})_{\Sigma3.71}(Si_{2.97}Al_{0.03})_{\Sigma3.00}O_{12.89}(OH)_{2.87}]\cdot6.01H_2O$ (ivanyukite-Na-*C*), $(K_{1.16}Cu_{0.21}Ca_{0.13}Na_{0.07}Sr_{0.01})_{\Sigma1.58}[(Ti_{3.49}Nb_{0.21}Mn_{0.07}Fe_{0.04})_{\Sigma3.81}(Si_{2.97}Al_{0.03})_{\Sigma3.00}O_{13.19}(OH)_{2.75}]\cdot9.32H_2O$ (ivanyukite-K), and $(Cu_{0.62}K_{0.43}Na_{0.04}Ca_{0.03})_{\Sigma1.12}[(Ti_{3.48}Nb_{0.16}Fe_{0.07}Mn_{0.03})_{\Sigma3.74}(Si_{2.99}Al_{0.01})_{\Sigma3.00}O_{12.88}(OH)_{2.88}(SO_4)_{0.02}]\cdot7.21H_2O$ (ivanyukite-Cu). Ivanyukite-Na-*T* is trigonal, *R*3*m*, $a = 10.94(2)$, $c = 13.97(4)$ Å, $Z = 3$. Other minerals are cubic, $P\bar{4}3m$ $a = 7.856(6)$ (ivanyukite-Na-*C*), 7.808(2) (ivanyukite-K), and 7.850(7) Å (ivanyukite-Cu); Z = 1. The strongest lines in the powder X-ray diffraction pattern [d_{bs}(Å) (I_{obs}) *hkl*] are: 7.88(100)(011), 3.277(60)(014), 3.175(80)(212), 2.730(50)(220), 2.607(70)(303), 2.471(50)(124), 1.960(60)(044), 1.916(50)(135) (ivanyukite-Na-*T*); 7.88(100)(100), 4.53(30)(111), 3.205(80)(211), 2.774(30)(220), 2.622(40)(221, 300), 2.478(40)(310), 1.960(30)(400), 1.843(30)(330, 411) (ivanyukite-Na-*C*); 7.85(100)(100), 3.91(20)(200), 3.201(80)(211), 2.765(20)(220), 2.602(30)(221, 300), 2.471(40)(310), 1.951(30)(400), 1.839(30)(330, 411) (ivanyukite-K); 7.87(100)(100), 3.94(20)(200), 3.205(80)(211), 2.774(20)(220), 2.616(30)(221, 300), 2.481(30)(310), 1.960(30)(400), 1.843(30)(330, 411) (ivanyukite-Cu). The crystal structure of ivanyukite-Na-*T* [trigonal, *R*3*m*, $a = 10.921(3)$, $c = 13.885(4)$ Å, $V = 1434.2(7)$ Å^3] has been solved from highly mosaic crystal and refined to $R_1 = 0.147$ on the basis of 723 unique observed reflections. The crystal structures of ivanyukite-group minerals are based upon a 3-dimensional framework of the pharmacosiderite type, consisting of four edge-sharing TiO_6-octahedra interlinked by SiO_4 tetrahedra. The framework has a 3-dimensional system of channels defined by 8-membered rings with an effective channel width of 3.5 Å (calculated as the distance between O atoms across the channels minus 2.7 Å). The channels are occupied by Na^+ and K^+ cations and H_2O molecules. The infrared spectra of the ivanyukite group minerals show 14 absorption bands caused by vibrations of Si-O and Ti-O bonds, molecular water, and $(OH)^-$ groups. Ivanyukite-

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Na-*T* formed as a late-stage, hydrothermal phase of ultra-agpaitic hydrothermalites; ivanyukite-Na-*C* is produced by partial hydration of ivanyukite-Na-*T*, and both ivanyukite-K and ivanyukite-Cu are produced by partial hydration of ivanyukite-Na-*T* and natural cation exchange of Cu for Na near dissolved djerfisherite and chalcopyrite grains. Nomenclature of the ivanyukite group is based on the dominant extraframework cation and symmetry of the crystal structure. The minerals are named in honor of Gregory Yur'evich Ivanyuk, Russian mineralogist and petrologist, head of the Laboratory of Self-Organized Mineral Systems in the Geological Institute of the Kola Science Centre of the Russian Academy of Sciences, for his contributions to the petrology and mineralogy of banded iron-formations, alkaline, and alkaline-ultrabasic massifs.

Keywords: Ivanyukite-Na-*T*, ivanyukite-Na-*C*, ivanyukite-K, ivanyukite-Cu, new mineral, microporous titanosilicate, crystal structure, ultra-alkaline hydrothermalite, cation exchange, Khibiny massif, Kola Peninsula