Ivanyukite-group minerals: crystal structure and cation-exchange properties

V.N. Yakovenchuk, E.A. Selivanova, S.V. Krivovichev, Ya.A. Pakhomovsky, D.V. Spiridonova, A.G. Kasikov, G.Yu. Ivanyuk

Kola Science Centre, Russian Academy of Sciences
E-mail: yakovenchuk@geoksc.apatity.ru

Ivanyukite-Na-*T*, $Na_3[Ti_4(OH)O_3(SiO_4)_3]\cdot 7H_2O$, ivanyukite-Na-*C*, $Na_2[Ti_4O_2(OH)_2(SiO_4)_3]\cdot 6H_2O$, ivanyukite-K, $K_2[Ti_4(OH)_2O_2(SiO_4)_3]\cdot 9H_2O$, and ivanyukite-Cu, $Cu[Ti_4(OH)_2O_2(SiO_4)_3]\cdot 7H_2O$, are new microporous titanosilicates found in a natrolitised microcline-aegirine-sodalite lens in the orthoclase-bearing urtite at Mt. Koashva (Yakovenchuk et al., 2009). Ivanyukite-Na-*T* is 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 Na to Cu near dissolved djerfisherite and chalcopyrite grains.

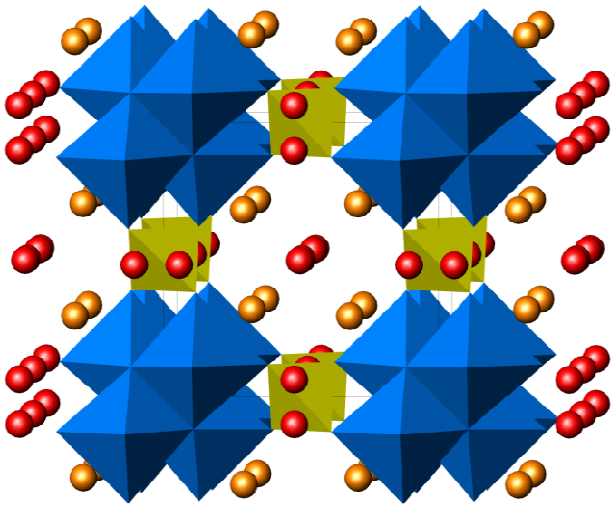

Fig. 1. Crystal structure of ivanyukite-K.

The crystal structure of ivanyukite-group minerals are based upon 3-dimensional framework of the pharmacosiderite type, consisting of four edge-sharing TiO_6-octahedra interlinked by SiO_4 tetrahedra (Fig. 1). The framework has a 3-dimensional system of channels defined by 8-membered rings with the crystallographic free diameter of 3.5 Å. The channels are occupied by Na^+ and K^+ cations and H_2O molecules. Na-rich ivanyukite has rhombohedral distortion due to interaction between cubanite-like clusters of $[Ti_4(O,OH)_4]$ and sodium cations.

Earlier it was established (Yakovenchuk et al., 2008) that all members of ivanyukite group have well cation-exchange properties and can absorb up to 55 wt. % Tl, 35 wt. % Cs, 27 wt. % Rb and 1.3 wt. % Cu from 1M cold water solution during 12 h. Also, we found that Cs-substituted ivanyukite cannot be decationized under ambient conditions, which permits us to offer this mineral for selective removal of ^{137}Cs from radioactive waste solutions.

Resent investigations show that ivanyukite can absorb from cold water solutions about 15 wt. % $(NH_4)^+$, 6 wt. % Co and Pd, 4 wt. % La, 1 wt. % Ni and Rh. Also, ivanyukite rapidly absorbs molecules of thiourea, methylene iodide, and hydrazine without the framework destroying. Large cations (Rb, Tl, Cs etc.) and molecules occupy central positions within 8-faced channels, and force out water molecules. Small and medium-sized cations are distributed within the canals both along the axes, and near $[Ti_4(O,OH)_4]$-clusters (like K^+ at Fig. 1).

This work was supported by the Russian Federal Programme 'Scientific and Education Cadres of Innovative Russia' (to DVS and SVK, state contract no. 02.740.11.0326) and

President of Russian Federation grant for young doctors of sciences (to SVK, grant no. MD 407.2009.5).

References

Yakovenchuk, V.N., Nikolaev A.P., Selivanova E.A., Pakhomovsky Ya.A. Korchak J.A., Spiridonova D.V., Zalkind O.A. Krivovichev S.V. (2009): 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 // *American Mineralogist*, **94**, 1450–1458.

Yakovenchuk V.N., Selivanova E.A., Ivanyuk G.Yu., Pakhomovsky Ya.A., Spiridonova D.V., Krivovichev S.V. (2008): First natural pharmacosiderite-related titanosilicates and their ion-exchange properties // *Minerals as Advanced Materials I* (Ed. S. Krivovichev). Springer-Verlag Berlin Heidelberg, 27-35.