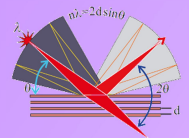




Crystal chemistry and ion-exchange properties of natural titanosilicates: zorite, ivanyukite and lintisite and their synthetic analogues

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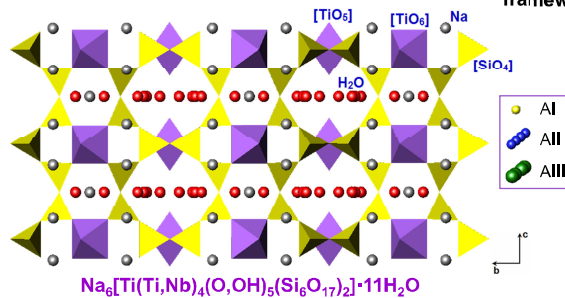
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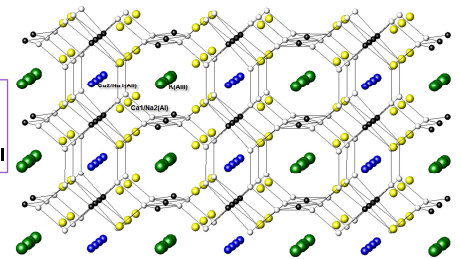
Zorite

In this work, we report data on exchange with Ti^{IV} , Cs^+ , Ag^+ , Rb^+ cations in zorite and structural characteristics of the ion-exchanged forms compared with forms investigated earlier. Crystals of Ti , Cs , Ag , Rb -forms of zorite were mounted on an STOE IPDS II diffractometer (MoK α) (Ti -zorite, Ag -zorite) and a SMART 1K CCD diffractometer (Cs -, Rb -zorite). The unit cell parameters were determined by the least squares method: Ti -zorite: space group $Cmmm$, $a = 7.250(3)$, $b = 23.406(12)$, $c = 7.035(3)$ Å, $V = 1193.8(9)$ Å³, $R(F) = 0.1280$; Cs -zorite: $a = 7.229(5)$, $b = 23.277(5)$, $c = 6.969(5)$ Å, $V = 1172.7(12)$ Å³, $R(F) = 0.0605$; Ag -zorite: $a = 7.2394(12)$, $b = 23.249(5)$, $c = 6.9211(11)$ Å, $V = 1164.9(4)$ Å³, $R(F) = 0.0704$; Rb -zorite: $a = 7.221(2)$, $b = 23.251(7)$, $c = 6.9631(19)$ Å, $V = 1169.1(6)$ Å³, $R(F) = 0.0582$.

Crystal structure of zorite

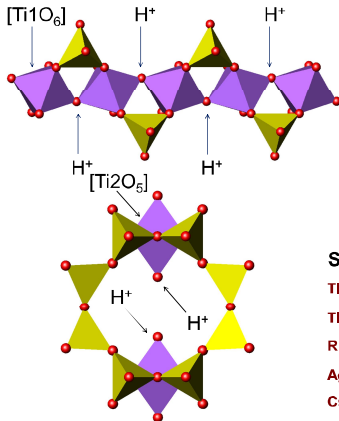


Nodal representation of titanosilicate framework of chivruaiite (Ca1, Ca2, K)/zorite (Na1, Na2)

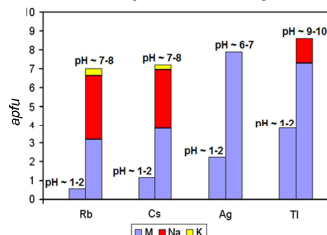


The results obtained allowed to classify extra-framework cation positions into three groups AI, AII, AIII. It has also been shown that the ion-exchange capacity depends upon pH of the solution used for ion-exchange experiments.

Protonation/deprotonation of the titanosilicate framework



Chemical analysis of examples of Ti-, Cs-, Ag-, Rb-exchanged zorite



Structural formulas of Ti-, Cs-, Ag-, Rb-zorite

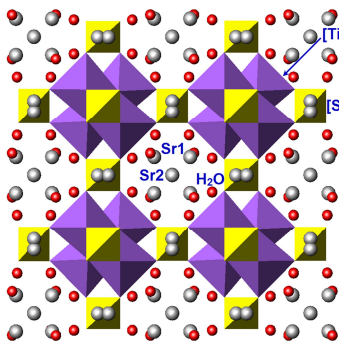
- $Ti_{7.58}Na_{1.43}[Ti_{4.12}Nb_{0.82}O_{4.59}(OH)_{0.41}(Si_6O_{17})_2] \cdot 5.85H_2O$ pH > 7
- $Ti_{3.82}H_{0.45}[Ti_{4.22}Nb_{0.57}(OH)_4(H_2O)_2](Si_6O_{17})_2] \cdot 3.97H_2O$ pH < 7
- $Rb_{3.69}Na_{3.67}[Ti_{4.43}Nb_{0.57}O_{2.93}(OH)_{2.07}(Si_6O_{17})_2] \cdot 10.08H_2O$ pH ≥ 7
- $Ag_{7.89}[Ti_{4.01}Nb_{0.69}(OH)_{2.62}O_{2.38}(Si_6O_{17})_2] \cdot H_2O$ pH ≥ 7
- $Cs_{3.61}Na_{3.49}[Ti_{4.41}Nb_{0.54}(OH)_{2.56}O_{2.44}(Si_6O_{17})_2] \cdot 10.43H_2O$ pH ≥ 7

Ivanyukite

The natural ivanyukite- $Na-T$ easily exchanges Na^+ cations with different monovalent and divalent cations (NH_4^+ , Cs^+ , Rb^+ , Ti^+ , Ag^+ , Cu^{2+} , Co^{2+} , Ni^{2+} and Sr^{2+}) from aqueous solutions at ambient conditions. We have studied two structures of ion-exchanged forms of ivanyukite (Rb -form and Sr -form). The crystal structures are based upon mixed three-dimensional octahedral-tetrahedral framework of pharmacosiderite type with channels occupied by Rb^+ and Sr^{2+} cations, and water molecules.

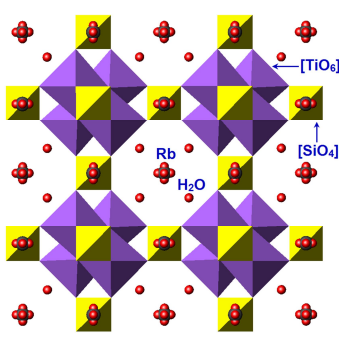
In a result of ion-exchange Na^+ and K^+ cations by Rb^+ and Sr^{2+} cations a space group change from $R3m$ to $P43m$ is observed. Deviation of ivanyukite- $Na-T$ crystal structure from cubic symmetry may be related to the presence of the K^+ cations, which occupy separate position and are responsible for the framework distortion. The K^+ cations interaction with oxygen atoms of cubane-like $Ti_4(O,OH)_4$ clusters of titanosilicate framework results framework stretch in 3-axis direction that is accompanied by decreasing of $Ti-O/OH-Ti$ (α) angle, of $Ti-Ti$ distance and increasing of $O/OH-Ti-O/OH$ (β) angle, of $O/OH-O/OH$ distance in comparison with corresponding parameters of Rb - and Sr -exchanged forms crystal structures.

Sr - exchanged form of ivanyukite



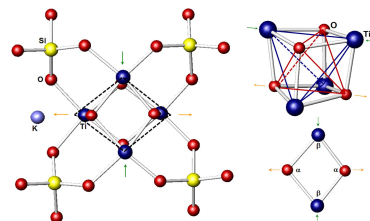
$Sr_{0.87}[Ti_4(OH)_{2.26}O_{1.74}(SiO_4)_3] \cdot 4.36H_2O$
Space group $P43m$
 $a = 7.834(5)$ Å

Rb - exchanged form of ivanyukite



$Rb_{2.16}[Ti_4O_{2.16}(OH)_{1.64}(SiO_4)_3] \cdot 5.5H_2O$
Space group $P43m$
 $a = 7.809(5)$ Å

Distortion of ivanyukite- $Na-T$ titanosilicate framework

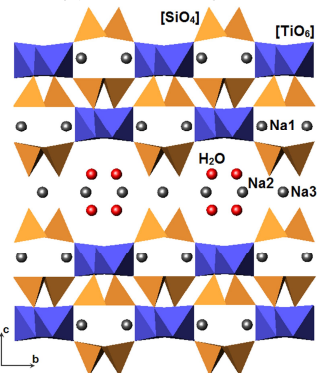


$R3m$ (ivanyukite- $Na-T$) \rightarrow $P43m$ (Rb -, Sr -forms of ivanyukite)

Geometric parameters of cubane-like cluster of TS framework

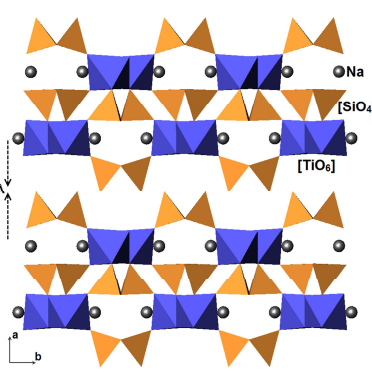
compound	bond length, Å		angle, °	
	O/OH-O/OH	Ti-Ti	α	β
ivanyukite- $Na-T$	2.532 (2.515)	3.064 (3.044)	98.32	78.80
Rb -ivanyukite	2.480	3.136	102.36	76.07
Sr -ivanyukite	2.460	3.146	102.91	75.38

AM-4 (synthetic analogue of lintisite)



$Na_3(Na,H)Ti_2O_2(Si_2O_6)_2(H_2O)_2$
Space group $A2/a$
 $a = 5.2012(8)$ Å, $b = 8.573(2)$ Å, $c = 29.300(6)$ Å,
 $V = 1306.4(4)$ Å³, $\beta = 89.26^\circ$

AM-4 after decationization



$Ti_2(OH)_2[Si_4O_{10}(OH)_2](H_2O)_2$
Space group $P2_1/c$
 $a = 11.962(1)$ Å, $b = 8.762(1)$ Å, $c = 5.2182(2)$ Å,
 $V = 536.98(5)$ Å³, $\beta = 100.95^\circ$

AM-4 (synthetic analogue of lintisite)

Within recent years, much attention has been devoted to synthesis and research of new materials, which show high thermal and radioactive stability and also ion-exchange properties. One of such materials is titanosilicate AM-4, which is the synthetic analogue of mineral lintisite. In this research AM-4 has been used to obtain new layered titanosilicate $Ti_2(OH)_2[Si_4O_{10}(OH)_2](H_2O)_2$. Decationization of AM-4 has been carried out by holding the sample in 0.5 M HCl during 3 hours. The crystal structure of new compound has been investigated by Rietveld method. In basis of this structure there are titanosilicate layers, which consist of octahedra TiO_6 and tetrahedra SiO_4 . As a result of sample holding in hydrochloric acid total removal of sodium had been observed, which caused layers displacement approximately per 4.5 Å. In this structure layers are joined just by hydrogenous bonds. New layered titanosilicate can be used for getting new intercalated materials with fixed properties.