

МИНЕРАЛОГИЧЕСКАЯ КРИСТАЛЛОГРАФИЯ

THE NEW NATURAL TUBULAR SILICATE $K_2NaCa_2[Si_2O_4(OH)]_4(OH)_3 \cdot 5H_2O$ FROM THE EIFEL PALEOVOLCANIC REGION, GERMANY

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Abstract. The new natural hydrous tubular silicate (NHTS) has been discovered in cavities of alkaline basalt from the basalt quarry Graulai, near Hillesheim, Eifel Mountains, Germany. The chemical composition is (wt. %, electron microprobe, H_2O content is calculated by total difference): Na_2O 4.10, K_2O 8.64, CaO 12.74, FeO 0.12, SrO 0.08, BaO 0.10, Al_2O_3 0.05, SiO_2 51.56, H_2O 22.62, total 100.00. Associated minerals are fluorapophyllite-(Na), quartz, calcite, clinopyroxene, and unidentified Na,K,Ca-silicates. NHTS occurs as aggregates of flattened long-prismatic crystals up to $0.02 \times 0.09 \times 1.5$ mm in cavities as well as curved fibrous crystals embedded in aggregates of unidentified hydrous Na,K,Ca-silicates. Perfect cleavage on (101) is observed. The mineral is white, with silky lustre. The calculated density is $1.994 \text{ g} \cdot \text{cm}^{-3}$. NHTS is a triclinic twin, space group $P-1$, the unit-cell parameters are: $a = 10.2995(4)$, $b = 7.0156(2)$, $c = 11.2824(3)$ Å, $\alpha = 108.114(7)$, $\beta = 94.990(3)$, $\gamma = 109.912(1)^\circ$, $V = 711.3(1)$ Å³. Equal-volume components of the twin are related by a 180° rotation around the b axis. The simplified chemical formula corresponding to the charge-balanced structural model is $K_2NaCa_2[Si_2O_4(OH)]_4(OH)_3 \cdot 5H_2O$ ($Z = 1$). The crystal structure of NHTS is based on silicate tubes $Si_4O_8(OH)_2$ joined together by edge sharing $CaO_4(H_2O)_2$ octahedra. The strongest lines of the powder X-ray diffraction pattern [d , Å (I , %) (hkl)] are: 9.46 (100) (101), 3.51 (81) (-240 , 020 , -303), 2.907 (90) (-222 , -411 , 015 , -123) and 2.817 (62) (222, 123). NHTS is optically biaxial (–); $\alpha = 1.503(2)$, $\beta = 1.505(2)$, $\gamma = 1.506(2)$; $2V = 60(10)^\circ$. NHTS is chemically and structurally (as well as by the IR spectrum) related to calcinaksite, $KNa[Ca(H_2O)](Si_4O_{10})$, and may be a product of its hydrolysis under hydrothermal conditions.

Keywords: hydrous tubular silicate, calcinaksite, crystal structure, IR spectroscopy, Graulai, Eifel

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INTRODUCTION

Minerals whose crystal structures contain tubular silicate polyanions are quite rare and are represented by a small number of mineral species. Natural silicates of this topological type include charoite, agrellite, miserite (Rozhdestvenskaya et al., 2011), canasite, $K_3Na_3Ca_5Si_{12}O_{30}(OH)_4$ (Dorfman et al., 1959; Rozhdestvenskaya et al., 1987), fluorcanasite, $K_3Na_3Ca_5Si_{12}O_{30}F_4 \cdot H_2O$ (Khomyakov et al., 2009), frankamenite, $K_3Na_3Ca_5Si_{12}O_{30}(F, OH)_4 \cdot H_2O$ (Nikishova et al., 1996; Rozhdestvenskaya et al., 1996), patynite, $NaKC_4(Si_9O_{23})$ (Kasatkin et al., 2019), as well as members of the litidionite group, manaksite, $KNaMn^{2+}(Si_4O_{10})$ (Khomyakov et al., 1992; Karimova, Burns, 2008), fenaksite $KNaFe^{2+}(Si_4O_{10})$ (Dorfman et al., 1959), litidionite, $KNaCu^{2+}(Si_4O_{10})$ (Pozas et al., 1975), and calcinaksite, $KNa[Ca(H_2O)](Si_4O_{10})$ (Aksenov et al., 2014; Chukanov et al., 2015). A specific feature of the silicate tube in patynite is its branched structure.

The lateral surface of the tube in litidionite-group minerals is formed by four- and eight-membered tetrahedral rings (Fig. 1). In these minerals, the silicate tubes are joined together by edge sharing MO_5O octahedra ($M = Mn^{2+}, Fe^{2+}, Cu^{2+}$ or Ca^{2+} ; $O = O$ or H_2O) and NaO_5 polyhedra. The K^+ cations occur within a large cavity of the silicate tube. The potentially new tubular hydrous silicate described in this paper is chemically and structurally related to calcinaksite. Its crystal structure is also based on litidionite-type silicate tubes.

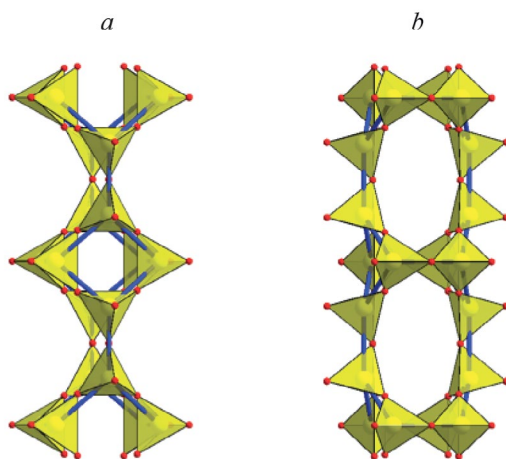


Fig. 1. A silicate tube occurring in the structures of litidionite-group minerals, presented in two projections (*a*, *b*), differing by a 90-degree rotation around the tube axis. Four- and eight-membered rings of tetrahedral are highlighted with blue lines

Рис. 1. Силикатная трубка в структурах минералов группы литидионита, представленная в двух проекциях (*a*, *b*), отличающихся поворотом на 90 градусов вокруг оси трубки. Четырех- и восьмичленные кольца тетраэдров выделены синими линиями

OCCURRENCE, GENERAL APPEARANCE AND PHYSICAL PROPERTIES

The new natural hydrous tubular silicate (NHTS) studied in this work originates from Si-rich xenolith hosted by alkaline basalt at the basalt quarry Graulai, near the town of Hillesheim, Eifel Mountains, Rhineland-Palatinate, Germany. Associated minerals are fluorapophyllite-(Na), quartz, calcite, clinopyroxene, as well as unidentified Na,K,Ca-silicates. NHTS occurs as aggregates of flattened long-prismatic crystals up to 1.5 mm long, up to 90 μm across and up to 20 μm thick in cavities (Fig. 2) and curved fibrous crystals embedded in aggregates of unidentified hydrous Na,K,Ca-silicates (Fig. 3). Perfect cleavage on (101) is observed.

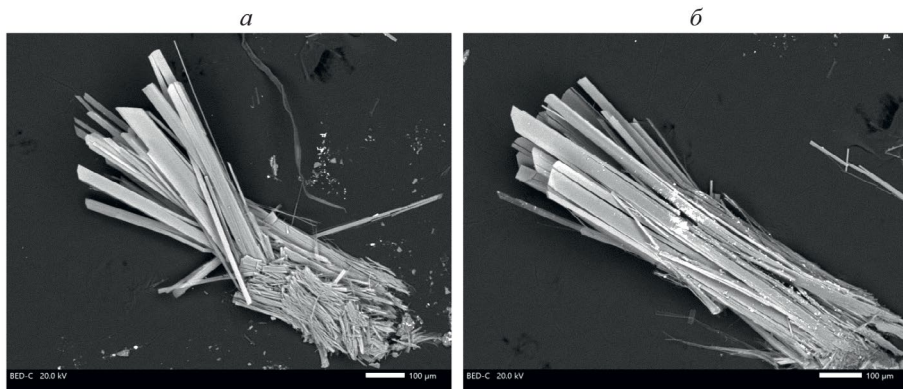


Fig. 2. Scanning electron microscopy images of NHTS aggregates. SEM (BSE) images

Рис. 2. Агрегаты водного трубчатого силиката. Изображения под сканирующим электронным микроскопом в отраженных электронах



Fig. 3. Fibrous aggregate of NHTS intergrown with unidentified hydrous Na, K, Ca-silicates. SEM (BSE) image of a polished section

Рис. 3. Волокнистый агрегат водного трубчатого силиката в сростании с не идентифицированными водными Na, K, Ca-силикатами. Изображение аншлифа под сканирующим электронным микроскопом в отраженных электронах

The mineral is white, with silky lustre. Density calculated using the empirical formula and unit-cell volume refined from single crystal X-ray structural data equals to $2.174 \text{ g}\cdot\text{cm}^{-3}$.

METHODS

Chemical composition. Chemical analyses were carried out using a digital scanning electron microscope Tescan VEGA-II XMU equipped by energy-dispersive spectrometer (EDS) INCA Energy 450 with semiconducting Si (Li) detector Link INCA Energy at an accelerating voltage of 20 kV, electron current of 190 pA and electron beam diameter of 160–180 nm. Attempts to use WDS were unsuccessful due to the instability of the highly hydrous mineral under the electron beam with the beam current necessary for WDS. H_2O was analysed by gas chromatography of products of the thermolysis at 1200°C in oxygen with a Vario Micro cube analyzer (Elementar GmbH, Germany).

X-ray diffraction. Powder X-ray diffraction data of aggregates mainly composed of NHTS were collected with a Rigaku R-Axis Rapid II diffractometer (Debye-Scherrer geometry, $d = 127.4 \text{ mm}$) equipped with a rotating anode X-ray source ($\text{CoK}\alpha$, $\lambda = 1.79021 \text{ \AA}$) and a curved image plate detector. The data were integrated using the software package Osc2Tab/SQRay (Britvin et al., 2017).

The single-crystal diffraction data were collected at a temperature of 293 K on an XtaLAB Synergy-DW X-ray diffractometer with a HyPix-Arc 150° photon counting detector. The diffraction reflections from a single flattened crystal (see Fig. 2) were too weak. Therefore an aggregate of several subparallel platelets strongly elongated in the [010] direction was selected for X-ray diffraction studies. Integration of diffraction peaks, correction for the Lorentz factor and radiation polarization were performed using the CrysAlis Pro 1.171.43.99a program.

Infrared spectroscopy. In order to obtain infrared (IR) absorption spectra, powdered samples have been mixed with dried KBr, pelletized, and analyzed using an ALPHA FTIR spectrometer (Bruker Optics) in the range of $3800\text{--}360 \text{ cm}^{-1}$ with a resolution of 4 cm^{-1} . A total of 16 scans were collected. IR spectrum of an analogous pellet of pure KBr was used as a reference.

Optical properties. Optical properties were studied in immersion liquids using in plane polarized transmitted light with $\lambda = 589 \text{ nm}$.

RESULTS

Infrared spectroscopy. In the region of silicate tube vibrations ($400\text{--}1200 \text{ cm}^{-1}$), the IR spectrum of NHTS (Fig. 4) is close to the spectrum of calcinaksite, but differs from the latter in poorer band resolution. Absorption in the ranges of $400\text{--}500$, $500\text{--}800$, $900\text{--}1000$ and $1000\text{--}1150 \text{ cm}^{-1}$ is related to Si–O–Si bending, O–Si–O bending, Si–O stretching (involving apical Si–O bonds) modes and antisymmetric vibrations of Si–O–Si groups, respectively. The band at 1683 cm^{-1} and strong absorption in the range of $3000\text{--}3620 \text{ cm}^{-1}$ correspond to bending and stretching vibrations of non-equivalent H_2O molecules, respectively. Among several thousand hydrous minerals and synthetic inorganic compounds, the IR spectra of which are cited in the reference books by Chukanov and Chervonnyi (2016) and Chukanov and Vigasina (2020), in almost all cases, the wavenumbers of H_2O bending vibrations are in the range of $1610\text{--}1680 \text{ cm}^{-1}$, whereas according to numerous works on quantum chemical calculations, bands in the range of $1700\text{--}1800 \text{ cm}^{-1}$ are attributed to hydronium H_3O^+ or the Zundel cation H_5O_2^+ . Taking into account these facts, bands in the range of $1700\text{--}3000 \text{ cm}^{-1}$ were assigned to vibrations of acid groups (presumably, H_3O^+ cations). In the IR spectrum of calcinaksite, bands in this range are not observed.

The presence of hydronium in a structure containing silanol groups Si–OH (see below) and water molecules is quite natural, since acidic silanol groups tend to dissociate, which

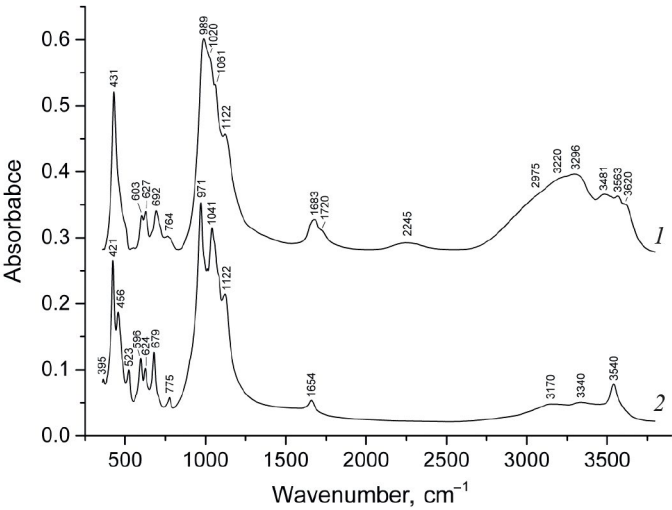


Fig. 4. IR spectra of NHTS (1) and calcinaksite (2)
Рис. 4. ИК-спектры водного трубчатого силиката (1) и кальцинаксита (2)

makes possible a dynamic acid-base equilibrium, which is characteristic of any acid in the presence of water: $\text{Si-OH}^{+\delta} + \text{H}_2\text{O} \leftrightarrow \text{Si-O} + \text{H}_3\text{O}^+$.

Optical properties. Under the microscope, NHTS is colorless, nonpleochroic. The mineral is biaxial, optically negative, with $\alpha = 1.503(2)$, $\beta = 1.505(2)$, $\gamma = 1.506(2)$. The $2V$ angle estimated from conoscopic sections is equal to $60(10)^\circ$.

Extinction is direct. Elongation is positive. Perfect cleavage is observed perpendicular to the direction of the acute bisector of $2V$ angle. The other two directions of less perfect cleavage are nearly perpendicular to the better cleavage and to each other.

Chemical composition. Chemical data of NHTS based on three spot analyses are given in Table 1. The contents of other elements with atomic numbers higher than that of C are below their detection limits. The H_2O content in the pure mineral could not be measured

Table 1. Chemical composition of NHTS (wt. %)
Таблица 1. Химический состав водного трубчатого силиката (мас. %)

Constituent	Content	Range	Probe Standard
Na ₂ O	4.10	3.64–4.65	Albite
K ₂ O	8.64	8.45–8.97	Orthoclase
CaO	12.74	12.18–13.54	Wollastonite
FeO	0.12	0.01–0.19	Fe
SrO	0.08	0–0.25	SrF ₂
BaO	0.10	0–0.30	BaSO ₄
Al ₂ O ₃	0.05	0–0.14	Albite
SiO ₂	51.56	50.46–52.27	Quartz
H ₂ O _{calc} *	22.62	—	
Total	100.00		

* Calculated by total difference.

because it is intimately intergrown with other hydrous Na, K, Ca-silicates. The gross H₂O content in the polymineralic aggregate is 22.4 wt.%. The CO₂ content was not measured because no bands of C-bearing groups are observed in the infrared spectrum. Taking into account the structural data (see below), the charge-balanced simplified formula of NHTS can be written as K₂NaCa₂[Si₂O₄(OH)]₄(OH)₃·5H₂O (*Z* = 1).

The Gladstone–Dale compatibility index $1 - (K_p/K_c)$ is equal to 0.017, which is rated as *superior* (Mandarino, 1981).

X-ray crystallography and crystal structure. The experimentally obtained powder X-ray diffraction (PXRD) data were indexed (Table 2) in a monoclinic lattice with the unit-cell parameters $a = 12.86(1)$, $b = 7.017(6)$, $c = 15.84(1)$ Å, $\beta = 96.18(7)^\circ$, $V = 1421(3)$ Å³.

The intensities of X-ray diffraction reflections from the single-crystal sample are strong enough to search for a structural model. However, the lattices of the plates do not match perfectly, which affects the quality of the measured diffraction pattern and complicates the structural analysis. We also cannot rule out that, despite all efforts, the sample could not be completely cleaned from other unidentified silicates that contributed to the diffraction pattern. Its quality can be judged by the quality of reflections in the $k = 0$ plane (Fig. 5) of the reciprocal lattice of a monoclinic crystal with the unit-cell parameters $a = 12.8039(6)$, $b = 7.0156(2)$, $c = 15.9244(5)$ Å, $\beta = 95.972(4)^\circ$, $V = 1422.7(1)$ Å³, which are selected in CrysAlisPro and are close to the values obtained by the PXRD method.

Table 2. Powder X-ray diffraction data for NHTS

Таблица 2. Результаты расчета порошковой рентгенограммы трубчатого водного силиката

I_{obs}	$d_{\text{obs}}, \text{\AA}$	$d_{\text{calc}}, \text{\AA}^*$	$h k l$
38	10.5	10.471	–101
100	9.46	9.456	101
34	6.43	6.414, 6.367	011, 200
13	6.15	6.145	110
10	4.73	4.741, 4.707	112, 103
2	4.42	4.427	211
18	3.96	3.977, 3.959	301, 004
35	3.67	3.659	–213
81	3.51	3.531, 3.508, 3.490	–204, 020, –303
32	3.29	3.289	121
31	3.21	3.216	204
24	3.14	3.152, 3.152	303, –105
90	2.907	2.914, 2.901, 2.887, 2.884	–222, –411, 015, –123
62	2.817	2.817, 2.813	222, 123
12	2.698	2.695	–321
13	2.357	2.364, 2.356	404, –512
33	2.138	2.153, 2.127	017, –325
11	2.030	2.022	521
20	1.962	1.960, 1.954	424, 226
7	1.789	1.795, 1.788	–327, –507
9	1.743	1.737	622
5	1.480	1.487, 1.481	138, 4.0.10

* Calculated from unit-cell parameters obtained on single crystal. The strongest reflections are marked in boldtype.

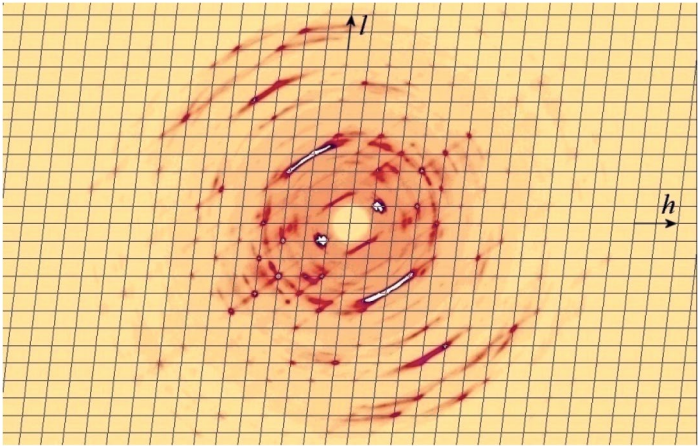


Fig. 5. Section of the diffraction pattern by the plane $k = 0$
Рис. 5. Сечение дифракционной картины плоскостью $k = 0$

The crystal structure of NHTS was first studied as monoclinic in the space group $I2/m$ using the Jana2006 program (Petříček et al., 2014) based on single crystal X-ray diffraction data. The structure model was refined using isotropic atomic displacement parameters and rejecting unsuitable reflections according to the criterion $|F_{\text{obs}} - F_{\text{calc}}| > 3\sigma(F_{\text{obs}})$. The need for strict rejection is explained by the distortion of the measured reflection intensities by contributions from several platelets having a significantly different orientation and, possibly, other unidentified silicates occurring in the studied sample (see above).

The positions of almost all atoms were found within the $I2/m$ group, but a problem arose with Na, the supposed position of which did not obey monoclinic symmetry. A transition was made from the monoclinic I -cell to the reduced cell with the parameters $a = 10.2995(4)$, $b = 7.0156(2)$, $c = 11.2824(3)$ Å, $\alpha = 108.114(7)$, $\beta = 94.990(3)$, $\gamma = 109.912(1)^\circ$, $V = 711.3(1)$ Å³, and the structure was refined again in the P -1 group. The idea of twinning of a triclinic crystal by a 180° rotation around the monoclinic axis of the I -cell was tested and confirmed. The refined volumes of the twin components were practically equal.

Basic information about the crystal, data collection parameters, and the results of the structural analysis are presented in Table 3. Table 4 contains information on the site coordinates, isotropic atomic displacement parameters, site occupancies and the bond valence sums calculated using the Jana2006 program. Selected interatomic distances are presented in Table 5.

Table 3. Crystal data, data collection information and structure refinement details

Таблица 3. Кристаллографические характеристики, данные монокристалльного эксперимента и параметры уточнения структурной модели

Chemical formula ($Z = 1$)	$\text{K}_2\text{NaCa}_2[\text{Si}_2\text{O}_4(\text{OH})]_4(\text{OH})_3 \cdot 5\text{H}_2\text{O}$
$a, b, c, \text{Å}$	10.2995(4), 7.0156(2), 11.2824(3)
$\alpha, \beta, \gamma, ^\circ$	108.114(7), 94.990(3), 109.912(1)
$V, \text{Å}^3$	711.3(1)
Space group, Z	P -1, 1
T, K	293
Diffractometer	XtaLAB Synergy-DW HyPix-Arc 150°
Radiation, λ (Å)	MoK_α , 0.71073
Scanning mode	ω

Table 3. End**Таблица 3.** Окончание

Crystal size (mm)	0.36×0.08×0.03
Absorption correction	Numerical, Gaussian
μ , mm ⁻¹	1.15
Data range, θ (°)	1.94–46.63
h, k, l ranges	$-20 \leq h \leq 20$; $-10 \leq k \leq 13$; $-22 \leq l \leq 18$
Reflections measured (obs, $I > 3\sigma(I)$ / all)	20 883/40 837
R_{int}	0.1109
Structure refinement	
Refinement based on	F
Weighting scheme	$w = 1/(s^2(F) + 0.0004F^2)$
Independent reflections used to refine the structural model (with $I > 3\sigma(I)$ / all)	1504/4647
Refined parameters	82
$R(F_{\text{obs}}) / wR(F_{\text{obs}})$	0.0930/0.0775
S_{obs}	1.70
$\Delta\rho_{\text{min}}/\Delta\rho_{\text{max}}$, e/Å ³	–2.32/2.52

Table 4. Atomic coordinates, isotropic displacement parameters, site occupancy factors and bond valence sums for atoms**Таблица 4.** Координаты атомов, изотропные параметры атомных смещений, заселенности позиций и суммы валентных усилий на атомах

Atom	x/a	y/b	z/c	U_{iso} , Å ²	S.O.F.	Bond valence sum
Ca1	0.5033(3)	0.2525(6)	0.0064(2)	0.0109(5)	1	2.22(3)
K1	0.7406(4)	0.1197(8)	0.5420(4)	0.0293(9)		1.13(2)
Si1	0.5137(4)	0.8876(7)	0.718764(4)	0.0071(5)		4.09(7)
Si2	0.4935(4)	0.3115(7)	0.7107(3)	0.0071(5)		4.06(7)
Si3	0.2628(4)	0.4231(10)	0.5963(4)	0.0170(8)		3.93(6)
Si4	0.2627(4)	0.2989(9)	0.3160(3)	0.0144(7)		4.01(7)
Na1	0.826(2)	0.165(3)	0.938(2)	0.038(4)	0.5	0.80(3)
O1	0.507(1)	0.940(2)	0.864(1)	0.019(1)	1	1.93(4)
O2	0.501(1)	0.409(2)	0.861(1)	0.019(1)		1.79(4)
O3	0.361(1)	0.168(2)	0.341(1)	0.017(1)		2.20(5)
O4	0.358(1)	0.527(2)	0.315(1)	0.017(1)		2.11(5)
O5	0.351(1)	0.284(2)	0.631(1)	0.017(2)		2.31(5)
O6	0.382(1)	0.662(2)	0.616(1)	0.017(2)		1.91(4)
O7	0.499(1)	0.071(2)	0.668(1)	0.016(2)		2.29(5)
O8	0.194(1)	0.296(2)	0.444(1)	0.021(2)		1.95(4)
Oh1*	0.140(1)	0.213(2)	0.190(1)	0.024(3)		1.07(3)
Oh2*	0.142(1)	0.391(2)	0.678(1)	0.018(2)		1.05(3)
Ow1**	0.258(2)	0.055(4)	0.955(2)	0.066(6)		0.48(2)
Ow2**	0.753(1)	0.433(2)	0.069(1)	0.022(2)		0.41(1)
Ow3**	0.909(2)	0.303(4)	0.765(2)	0.078(6)		0.33(2)
Ow4**	0.894(2)	0.931(3)	0.235(2)	0.057(5)		0.02(1)

* OH; ** H₂O

Table 5. Selected interatomic distances in the structure of NHTS

Таблица 5. Некоторые межатомные расстояния (Å) в структуре водного трубчатого силиката

Ca1-O1 (i)	2.30(1)	Si1-O1	1.58(1)
Ca1-O1 (ii)	2.26(2)	Si1-O3 (ii)	1.61(1)
Ca1-O2 (iii)	2.24(1)	Si1-O6	1.67(1)
Ca1-O2 (ii)	2.40(1)	Si1-O7 (v)	1.60(1)
Ca1-Ow1 (iii)	2.34(2)	—	
Ca1-Ow2	2.38(1)	Si2-O2	1.60(1)
		Si2-O4 (ii)	1.67(1)
K1-O3 (iv)	2.72(1)	Si2-O5	1.57(1)
K1-O4 (ii)	3.05(1)	Si2-O7	1.63(1)
K1-O5 (iv)	2.68(1)	—	
K1-O6 (ii)	3.12(2)	Si3-O5	1.64(2)
K1-O7	2.94(1)	Si3-O6	1.64(1)
K1-O7 (iv)	2.88(1)	Si3-O8	1.63(1)
K1-Ow3	2.59(2)	Si3-Oh2	1.61(1)
Na1-Oh1 (iv)	2.76(3)	Si4-O3	1.64(1)
Na1-Ow1 (vii)	2.24(3)	Si4-O4	1.57(1)
Na1-Ow2 (viii)	2.39(3)	Si4-O8	1.67(1)
Na1-Ow3	2.53(4)	Si4-Oh1	1.62(1)
Oh1-Ow1 (ii)	3.07(3)	Oh2-Ow4 (ii)	2.66(3)
Oh2-Ow2 (ii)	2.68(1)	Ow1-Ow4 (ii)	2.59(3)
Oh2-Ow3 (xii)	2.62(3)	Ow2-Ow4	3.13(2)
Oh1-Ow4 (xi)	2.84(2)	Ow3-Ow4 (xiii)	3.02(4)

(i) $x, y-1, z-1$; (ii) $-x+1, -y+1, -z+1$; (iii) $x, y, z-1$; (iv) $-x+1, -y, -z+1$; (v) $x, y+1, z$; (vi) $x, y-1, z$; (vii) $-x+1, -y, -z+2$; (viii) $x, y, z+1$; (ix) $-x+1, -y+2, -z+2$; (x) $-x+1, -y+1, -z+2$; (xi) $x-1, y-1, z$; (xii) $x-1, y, z$.

DISCUSSION

NHTS has much in common, and not only in chemical composition, with calcinaksite, $\text{KNa}[\text{Ca}(\text{H}_2\text{O})](\text{Si}_4\text{O}_{10})$ (Aksenov et al., 2014; Chukanov et al., 2015). whose structure (Fig. 6) is formed by tubes of SiO_4 tetrahedra and paired columns consisting of edge-shared calcium octahedra alternating with sodium pentahedra. Almost all the vertices of these polyhedra participate in coordination of two polyhedra and are occupied by O atoms. The only vertex of the Ca octahedron, not linked to other polyhedra, is occupied by a water molecule.

Tubes of Si tetrahedra are also present in the NHTS structure (Fig. 7a, b). However, unlike calcinaksite, the columns between the tubes are not paired and consist solely of Ca octahedra. The layers formed by tubes of Si tetrahedra and columns of Ca octahedra are separated from each other by spaces occupied by Na^+ ions and water molecules. Large cavities inside the silicate tubes are occupied by K^+ cations. Two vertices, Ow1 and Ow2, of each Ca octahedron, which are not linked to the Si tetrahedra, are presumably occupied by H_2O molecules (see Tables 4 and 5). The “external” vertices of the Si tetrahedra, which are not linked to other Si tetrahedra or Ca octahedra, are occupied by OH^- groups, judging by the bond valence sums on the corresponding oxygen atoms Oh1, Oh2 (Table 4). Each Na^+ ion is in a nearly flat environment of three water molecules (two of them are the vertices of adjacent Ca octahedra in one column) and one OH^- group at the vertex of a Si tetrahedron. The 50 % occupancy of the Na1 position was chosen taking into account the data of chemical

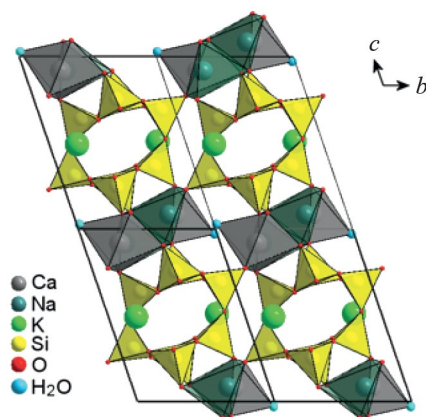


Fig. 6. A fragment of the crystal structure of calcinaksite, projected along the a axis of its triclinic lattice. Structural data taken from (Aksenov et al., 2014)

Рис. 6. Фрагмент структуры кальцинаксита в проекции вдоль оси a триклинной решетки. Данные о структуре взяты из (Aksenov et al., 2014)

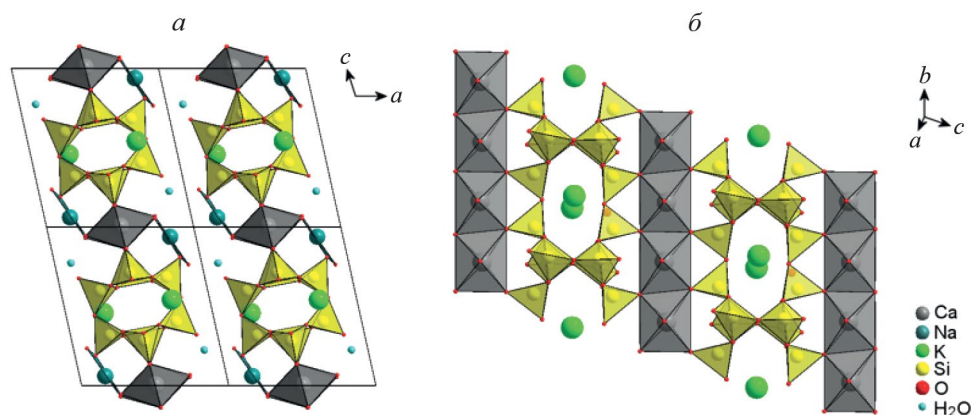


Fig. 7. (a) A fragment of the NHTS structure in projection along the $[010]$ axis (a); a layer of Si tetrahedra and Ca octahedra (b).

Рис. 7. (a) Фрагмент структуры водного трубчатого силиката в проекции вдоль оси $[010]$ (a); слой из Si-тетраэдров и Ca-октаэдров (b).

analysis and was not refined due to the correlation between the site occupancy and the refined parameter of atomic displacements.

As can be easily seen from Table 4, the imbalance between the total negative charge of the O^{2-} and OH^- anions and the positive charge of the Si^{4+} , Ca^{2+} , K^+ and Na^+ cations is +3 per unit cell. This imbalance can be eliminated by assuming that the Ow1, Ow2, and Ow3 positions are occupied equally by water molecules and OH^- anionic groups, i. e., they contain a total of three water molecules and three OH^- groups. The final, charge-balanced formula is $\text{NaK}_2\text{Ca}_2 [\text{Si}_2\text{O}_4(\text{OH})]_4 (\text{OH})_3 \cdot 5\text{H}_2\text{O}$ ($Z = 1$).

Thus, in terms of its major components (Na, K, Ca, Si, H_2O), stoichiometry (excluding water), crystal structure, IR spectrum, and occurrence, NHTS is similar to calcinaksite, being

its highly hydrous analogue. Based these features, one can assume that NHTS is a product of calcinaksite hydrolysis under hydrothermal conditions. The formation of calcinaksite and NHTS, instead of zeolites common in hydrothermal associations in basalt xenoliths, was apparently facilitated by low alumina activity. The low alumina activity in the postmagmatic hydrothermal solutions of Graulai is indirectly indicated by the widespread occurrence of aluminum-free ettringite-group minerals belonging to the hielscherite–thaumasite series, $\text{Ca}_3\text{Si}(\text{SO}_4)(\text{SO}_3, \text{CO}_3)(\text{OH})_6 \cdot 11\text{--}12\text{H}_2\text{O}$ (Pekov et al., 2012), instead of ettringite, $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 27\text{H}_2\text{O}$, which is common in hydrothermal associations hosted by the Eifel basalts at other localities of this region.

Although the water content of NHTS could not be determined directly due to unidentified impurities of hydrous Na, K, Ca-silicates, the presence of approximately five H_2O molecules per formula unit was confirmed by the superior Gladstone–Dale compatibility. As follows from Table 4, the NHTS unit cell with a volume of $711.3(1) \text{ \AA}^3$ contains eight Si tetrahedra, similar to calcinaksite with a unit-cell volume of $495.4(3) \text{ \AA}^3$ (Aksenov et al., 2014). The excess volume of NHTS (compared to calcinaksite) is approximately one-third of the total unit cell volume. The additional water molecules form rather strong hydrogen bonds and absorb IR radiation in the range of $3000\text{--}3400 \text{ cm}^{-1}$ (Fig. 3).

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Новый природный трубчатый силикат $K_2NaCa_2[Si_2O_4(OH)]_4(OH)_3 \cdot 5H_2O$ из палеовулканического региона Айфель (Германия)

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Аннотация. Новый природный водный трубчатый силикат (НВТС) обнаружен в ксенолите высококремнистой породы из щелочного базальта в базальтовом карьере Грауляй близ города Хиллесхайм, Айфель, Германия. Химический состав минерала (мас. %, электронно-зондовые данные, содержание H_2O рассчитано по дефициту суммы анализа): Na_2O 4.10, K_2O 8.64, CaO 12.74, FeO 0.12, SrO 0.08, BaO 0.10, Al_2O_3 0.05, SiO_2 51.56, H_2O 22.62, сумма 100.00. Упрощенная, сбалансированная по заряду формула, полученная с учетом структурных данных, имеет вид $K_2NaCa_2[Si_2O_4(OH)]_4(OH)_3 \cdot 5H_2O$ ($Z = 1$). Ассоциирующие минералы: фторапофилит-(Na), кварц, кальцит, клинопироксен и неидентифицированные Na, K, Ca-силикаты. НВТС встречается в виде агрегатов уплощенных длиннопризматических кристаллов, имеющих размеры до $0.02 \times 0.09 \times 1.5$ мм, в полостях, а также в виде изогнутых волокнистых кристаллов, вросших в агрегаты неидентифицированных водных Na, K, Ca-силикатов. Минерал обладает совершенной спайностью по (101). НВТС белый, с шелковистым блеском. Вычисленная плотность составляет $2.174 \text{ г} \cdot \text{см}^{-3}$. НВТС триклинный, кристаллизуется в пространственной группе $P-1$, параметры элементарной ячейки: $a = 10.2995(4)$, $b = 7.0156(2)$, $c = 11.2824(3) \text{ Å}$, $\alpha = 108.114(7)$, $\beta = 94.990(3)$, $\gamma = 109.912(1)^\circ$, $V = 711.3(1) \text{ Å}^3$, и двойникуется поворотом на 180° вокруг оси b .

Кристаллическая структура НВТС основана на силикатных трубках $\text{Si}_4\text{O}_8(\text{OH})_2$, соединенных октаэдрами $\text{CaO}_4(\text{H}_2\text{O})_2$, имеющими общие ребра. Наиболее интенсивные линии порошковой дифрактограммы [d , Å (I , %) (hkl)]: 9.46 (100) (101), 3.51 (81) (–240, 020, –303), 2.907 (90) (–222, –411, 015, –123) and 2.817 (62) (222, 123). НВТС оптически двуосный (–); $N_p = 1.503(2)$, $N_m = 1.505(2)$, $N_g = 1.506(2)$; $2V = 60(10)^\circ$. Изученный минерал химически и структурно (а также по ИК-спектру) близок к кальцинакситу $\text{KNa}[\text{Ca}(\text{H}_2\text{O})](\text{Si}_4\text{O}_{10})$ и, возможно, является продуктом его гидролиза и гидратации в гидротермальных условиях.

Ключевые слова: водный трубчатый силикат, кальцинаксит, кристаллическая структура, ИК-спектроскопия, базальт, ксенолит, Грауляй, Айфель

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