

CHEMISTRY

Pyatenkoite-(Y) $\text{Na}_5\text{YTiSi}_6\text{O}_{18} \cdot 6\text{H}_2\text{O}$, a New Mineral of the Hilairite Group: Crystal Structure

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A new mineral, rare-earth sodium titanosilicate, in the form of colorless transparent rhombohedral crystals 0.3–0.5 mm in size, was discovered by A.P. Khomyakov [1] in the Lovozero alkalic massif (Kola peninsula). It was found in hydrothermally altered pegmatite in association with albite, natrolite, tetranatrolite, aegirine, neptunite, and fluorite. The mineral was called pyatenkoite¹ after Yu.A. Pyatenko, a well-known Russian scientist and expert in the mineral crystal chemistry.

The IR spectra of this mineral in general resemble the spectra of hilairite $\text{Na}_2\text{ZrSi}_3\text{O}_9 \cdot 3\text{H}_2\text{O}$ [2], sazykinaite $\text{Na}_5\text{YZrSi}_6\text{O}_{18} \cdot 6\text{H}_2\text{O}$ [3], and komkovite $\text{BaZrSi}_3\text{O}_9 \cdot 3\text{H}_2\text{O}$ [4]. In X-ray diffraction powder patterns, pyatenkoite also resembles the aforementioned hilairite-group minerals, above all, sazykinaite. By microprobe [1], the bulk composition of pyatenkoite is $(\text{Na}_{4.7}\text{K}_{0.03})_{\Sigma 4.73}(\text{Y}_{0.5}\text{Dy}_{0.11}\text{Gd}_{0.08}, \text{X}_{0.23})_{\Sigma 0.92}(\text{Ti}_{0.86}\text{Nb}_{0.17}\text{Zr}_{0.03})_{\Sigma 1.06}\text{Si}_{6.03}\text{O}_{18} \cdot 6\text{H}_2\text{O}$, where X is Sm, Er, Nd, Eu, Tb, Ce, Ho, Yb, La, Tm, and Th. The idealized formula of pyatenkoite $\text{Na}_5\text{YTiSi}_6\text{O}_{18} \cdot 6\text{H}_2\text{O}$ can be deduced from (1) the doubled hilairite formula $\text{Na}_4\text{Zr}_2\text{Si}_6\text{O}_{18} \cdot 6\text{H}_2\text{O}$ by replacing one zirconium atom with yttrium with the charge compensation $\text{Y}^{3+} + \text{Na}^+ = \text{Zr}^{4+}$, and the second, with titanium; and (2) sazykinaite $\text{Na}_5\text{YZrSi}_6\text{O}_{18} \cdot 6\text{H}_2\text{O}$ by replacing zirconium with titanium. As in sazykinaite, a considerable part of yttrium in pyatenkoite is replaced by heavy lanthanides, with the lanthanide abundance showing a well-defined maximum for middle-series rare-earths (Dy, Gd).

Intensity data for X-ray crystallography were collected in a reciprocal-space hemisphere from an equant crystal $0.07 \times 0.07 \times 0.07$ mm (Enraf-Nonius automated diffractometer, MoK_α radiation, graphite monochromator, 886 reflections with $I > 2\sigma(I)$, $\sin \theta/\lambda \leq 0.7$, 329 independent reflections with $|F| > 3\sigma(F)$, $R_{\text{merge}} =$

4.3%). The rhombohedral (hexagonal) unit cell parameters were measured and refined on the same diffractometer: $a = 10.696(5)$ Å, $c = 15.728(6)$ Å, $V = 1558(2)$ Å³, space group $R\bar{3}2$, $Z = 3$, $\rho_m = 2.68(5)$ cm³, $\rho_x = 2.70$ g/cm³. All calculations were performed with the AREN program package [5].

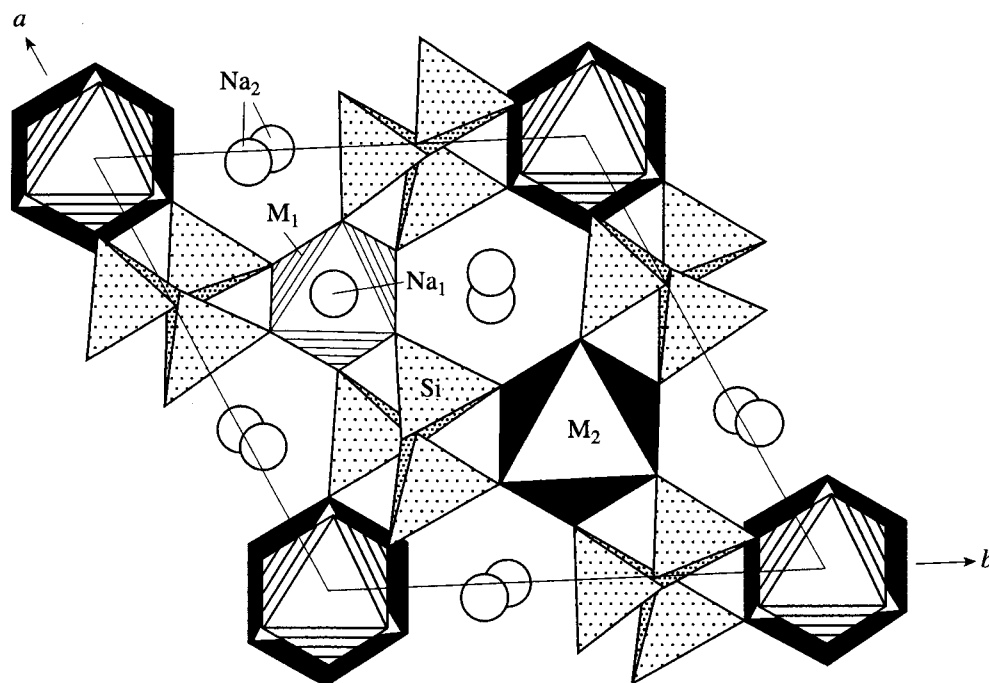
Assuming that the new mineral is isostructural to sazykinaite, we used the structure parameters of the latter as the initial approximation, with Ti and Y located at M_1 and M_2 sites, respectively. The anisotropic least-squares refinement converged to $R = 5.6\%$. Correction for absorption applied using the DIFABS program [6] gave $R = 4.8\%$. The thermal parameters being low for M_1 sites and nearly zero for M_2 made it necessary to account for the occurrence of isomorphous impurities at octahedral sites. The use of mixed scattering f -curves in refinement reduced the residual to $R = 3.9\%$ and gave normal atomic thermal parameters. The Na_2 atom also possessed a high thermal parameter (>4 Å²), which suggested the occurrence of a vacancy. The refined value (0.93) of the Na_2 site occupancy supported this

Table 1. Atomic coordinates and equivalent thermal parameters in the pyatenkoite structure

Atom	x/a	y/b	z/c	$B_{\text{eq}}, \text{\AA}^2$
Si	0.4228(3)	0.4073(3)	0.2476(1)	0.69(6)
M_1	0	0	0	0.78(6)
M_2	0.3333	0.6667	0.1663	1.01(4)
Na_1	0	0	0.1933(5)	2.2(2)
Na_2	0.365(1)	0	0.5	3.1(2)
O_1	0.092(1)	0.168(1)	0.0749(4)	1.2(1)
O_2	0.103(1)	0.211(1)	0.5720(4)	1.3(1)
O_3	0.657(1)	0	0	1.0(2)
O_4	0.641(1)	0	0.5	1.8(2)
H_2O	0.503(1)	0.144(1)	0.0589(5)	1.8(2)
H_1	0.53	0.43	0.04	2.0
H_2	0.48	0.68	0	2.0

Note: $M_1 = (\text{Ti}_{0.8}\text{Nb}_{0.2})$, $M_2 = (\text{Y}_{0.5}\text{Dy}_{0.3}\text{Gd}_{0.2})$.

¹ The name was approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association.



Pyatenkoite structure in (001) projection.

suggestion, in a good agreement with the chemical analyses. Anisotropic refinement converged to $R_{hkl} = 3.66\%$. The difference synthesis showed two peaks whose positions were close to those of hydrogen atoms in the sazykinaite structure. However, attempts to refine

hydrogen positions resulted in the distorted geometry of the hydrogen bond, and the coordinates of hydrogen atoms were not refined.

The coordinates of basis atomic and equivalent thermal parameters are listed in Table 1; bond lengths and angles (including hydrogen bonds) are compiled in Table 2.

The crystal-chemical formula of pyatenkoite, $\text{Na}_2(\text{Na}_{2.75}\text{K}_{0.05})[(\text{Y}_{0.5}\text{Dy}_{0.3}\text{Gd}_{0.2})(\text{Ti}_{0.8}\text{Nb}_{0.2})(\text{Si}_3\text{O}_9)_2] \cdot 6\text{H}_2\text{O}$, points to the occurrence of two independent positions for alkali cations and two different M octahedra. The square brackets isolate a mixed framework, which consists of screwed chains $[\text{Si}_3\text{O}_9]$ running along the c axis, with tetrahedra sharing corners with Y and Ti octahedra. The framework is penetrated by wide channels running along Si chains and voids occupied by alkali cations and water molecules. The cation distribution on M positions correlates with the optimum local bond-valence balance calculated according to Brown [7] with allowance made for isomorphous substitution (Table 3).

Comparison of pyatenkoite, alkali titanosilicate, with sazykinaite, its zirconium analogue, proves that these minerals are isostructural. Both minerals belong to the hilairite structural type [2], along with komkovite and calciophilairite $\text{CaZrSi}_3\text{O}_9 \cdot 3\text{H}_2\text{O}$ [8]. Pyatenkoite and sazykinaite differ from their analogues in that, first of all, they contain two sites instead of one with $\text{Zr}-\text{O} = 2.00\text{--}2.10 \text{ \AA}$ for color centers: a larger, yttrium site ($\text{Y}-\text{O} = 2.26 \text{ \AA}$) and a smaller, titanium-zirconium site ($\text{Ti}-\text{O} = 1.95$, $\text{Zr}-\text{O} = 2.08 \text{ \AA}$). This is responsible for a sizable increase in the parameter a and molar vol-

Table 2. Bond lengths (Å) and angles (degree) in the pyatenkoite structure

Si tetrahedron		M octahedra	
Si-O ₂	1.589(9)	M ₁ -O ₁	1.954(7) × 6
O ₁	1.622(9)	O-O	<2.784>
O ₄	1.628(5)	M ₂ -O ₂	2.256(7) × 6
O ₃	1.652(5)	O-O	<3.123>
	<1.623>		
Na polyhedra			
Na ₁ -H ₂ O	2.291(9) × 3	Na ₂ -H ₂ O	2.330(9) × 2
O ₁	2.428(9) × 3	O ₂	2.650(9) × 2
	<2.359>	O ₁	2.787(5) × 2
		O ₄	2.952(9)
			<2.641>
H-bonds			
H ₂ O-H ₁	1.08	H ₁ -O ₃	1.84
H ₂	1.07	H ₂ -O ₂	1.72
		∠H ₂ O-H ₁ -O ₃	170
		∠H ₂ O-H ₂ -O ₂	150
		H ₁ -H ₂	1.55
		∠H ₁ -H ₂	92

Table 3. Local bond-valence balance on anions in the pyatenkoite structure

Atom	Si	M ₁	M ₂	Na ₁	Na ₂	H ₁	H ₂	V _i	$ \Delta _i$
O ₁	1.02	0.72		0.18	0.07			1.99	0.01
O ₂	1.11		0.53		0.09		0.16	1.89	0.11
O ₃	0.92×2					0.16		2.00	0
O ₄	0.98×2				0.04			2.00	0
H ₂ O				0.27	0.23			0.50	—

Note: $D = 1.6\%$, $|\Delta|_{\max} = 5.5\%$.

Table 4. Crystal data for hilairite-group minerals

Mineral	a , Å	c , Å	V , Å ³	Site composition	
				M ₁	M ₂
Sazykinaite	10.825(5)	15.809(4)	1604	Zr _{0.7} Ti _{0.2} Nb _{0.1}	Y _{0.8} TR _{0.2}
Pyatenkoite	10.696(5)	15.728(6)	1558	Ti _{0.8} Nb _{0.2}	Y _{0.5} TR _{0.5}
Hilairite	10.556(1)	15.855(2)	1530	Zr	Zr
Komkovite	10.52(1)	15.72(1)	1507	Zr	Zr
Calciohilairite	10.435×2	16.002	1509×4	Zr	Zr

Table 5. Angles (deg) O–Si–O and Si–O–Si in the chain radical $[\text{Si}_3\text{O}_9]$ in hilairite-group minerals

Angle	Mineral			
	pyatenkoite	sazykinaite	hilairite	komkovite
O ₁ –Si–O ₂	113.5	113.9	113.6	111.8
O ₃	108.6	109.4	109.5	92.6
O ₄	110.3	108.1	108.3	74.0
O ₂ –Si–O ₃	106.8	106.8	107.5	105.4
O ₄	110.1	111.4	109.3	141.5
O ₃ –Si–O ₄	107.3	107.1	108.5	112.5
Si–O ₃ –Si	132.5	135.6	136.9	130.8
Si–O ₄ –Si	137.7	135.4	134.0	140.6

ume of the rare-earth representatives of the family (Table 4).

Pyatenkoite is a hydrothermal mineral that forms at late stages of formation of hyperagpaitic permatites and hydrothermalites upon crystallization of residual silicate–saline fluids abnormally enriched in alkalis, volatiles, and rare elements [10]. One consequence of these processes is extensive fractionation of rare earths to yttrium and heavy lanthanide minerals in final crystallization products. The fact that pyatenkoite and sazykinaite, rare-earth minerals formed under different

geochemical conditions of the Lovozero and Khibin massifs, respectively, bear great similarity emphasizes the important role of the crystal-chemical factor in rare-earth fractionation. Pyatenkoite and sazykinaite show higher alkali abundances than the ones in zirconium analogues ($\text{Na} : \text{M} = 2.5$ against 2), with the Na₂ site occupancy in their structures being maximum.

The complete isomorphous substitution of Ti (pyatenkoite) for Zr (hilairite structure) makes the new mineral the end, titanium member of the hilairite family. The limited miscibility between Ti and Zr, which is

well known for mineralogists [9], explains the fact that only a few zirconium minerals are known to have titanium analogues. The discovery of pyatenkoite increases the number of isostructural Ti and Zr silicates of the general formula $A_2B[Si_3O_9] \cdot nH_2O$ ($A = Zr, Ti, Y, Ln$; $B = Na, Ca, Ba$), in which the great variability of population at octahedral positions of the framework and cations of various size occupying voids occurs within the hilairite structure type and space group $R32$. The apparent crystal-chemical reason for this structure type to be stable is the plasticity of screwed chains $[Si_3O_9]$, which were first detected in hilairite. Distortion of Si tetrahedra and their turn with respect to each other (Table 5) prove the high ability of the metasilicate $[Si_3O_9]$ to adopt framework polyhedra of various size. The greatest distortion of the chain radical is observed in the komkovite structure (when the Na octahedron is replaced by the Ba dodecatope): the repetition period of the chain even changes from three to six.

The identified chemical and structural features of pyatenkoite suggest that the number of mineral species of the hilairite family be increased.

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