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Crystal Structure of a New Mineral Turkestanite: A Calcium Analogue of Steacyite

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Abstract—The crystal structure of a new mineral turkestanite $Th(Ca,Na)_2(K_{1-z}\square_z)[Si_8O_{20}]$, $z = 0.47$ (Dzhelisu massif, Alayskiy range, Tien Shan)—a calcium analogue of steacyite—determined by the Rietveld method (ADP-2 diffractometer; λCuK_α; Ni filter; $8.00° < 2\theta < 140.00°$; 2θ step, 0.02°; count time per step, 10 s; 850 Bragg reflections). All calculations are performed with the WYRIET program (version 3.3) in space group $P4/mcc$. The unit-cell parameters are $a = 7.5792(1)$ and $c = 14.7042(2)$ Å, and $V = 844.68(1)$ Å^3. The structure of turkestanite is refined in the anisotropic–isotropic approximation (the Pearson function) to $R_p = 3.16$, $R_{wp} = 4.04$, $R_B = 2.18$, $R_F = 1.90$, $s = 1.41$, $DWD = 1.10$, and $\sigma_x = 1.839$. The turkestanite sample contains thorite $ThSiO_4$ as a second phase; quantitative analyses show that the thorite content is 1.34 wt %. Turkestanite is the third mineral (along with steacyite and iraqite) that contains a discrete $[Si_8O_{20}]$ radical, which consists of a pair of four-membered rings formed by Si–O-tetrahedra. The predominance of Ca^{2+} in the B position in distinction to Na^+ in steacyite $Th(Na,Ca)_2(K_{1-z}\square_z)[Si_8O_{20}]$ ($z = 0.40$) makes possible distinguishing turkestanite as an original mineral species.

INTRODUCTION

On September 4, 1996, turkestanite $Th(Ca,Na)_2(K_{1-z}\square_z)[Si_8O_{20}]$ ($z = 0.47$) was approved as a new mineral species by the Comission on New Minerals and Mineral Names of the International Mineralogical Association.

Turkestanite is the third mineral, along with steacyite [1–3] and iraqite [4], that contains a discrete $[Si_8O_{20}]$ radical, which consists of a pair of four-membered rings formed of Si–O tetrahedra. A general crystal chemical formula of the three minerals is $AB_2C[Si_8O_{20}]$, where A = Th or RE, B = Ca or Na, and C = K. The predominance of Ca^{2+} in the B position in distinction to Na^+ in steacyite $Th(Na,Ca)_2(K_{1-z}\square_z)[Si_8O_{20}]$ ($z = 0.40$) makes possible distinguishing turkestanite as an original mineral species. In iraqite, rare earths prevail in the A position, and a suffix corresponding to the dominant rare earth is assigned to the mineral—iraqite-(La). The structure of iraqite-(La) was not studied. The crystal structure of steacyite (under the name of "ekanite") was studied in [2]: sp. gr. $P4/mcc$; $a = 7.58(1)$ and $c = 14.77(2)$ Å; and $z = 2$. As late as 1982, steacyite found its present name [3]. Ekanite $ThCa_2Si_8O_{20}$ [5, 6] crystallizes in the tetragonal system similar to steacyite, turkestanite, and iraqite-(La). The unit-cell parameters of ekanite [$a = 7.483(3)$ and $c = 14.893(3)$ Å] are close to those of the three above minerals; however, the space group $I422$ is defined by another Si–O radical, namely, by the $[Si_8O_{20}]$ layers.

In 1965, the $Th(Ca,Na)_2(K_{1-z}\square_z)[Si_8O_{20}]$ mineral from Central Asia was described in [7]. However, this mineral was not approved formally as a new mineral species. The crystal structure under the name ekanite $ThK(Ca,Na)_2[Si_8O_{20}]$ was described in [8]: $a = 7.58$ and $c = 14.82$ Å; sp. gr. $P4/mcc$; and $R = 9.8\%$. In [3], the authors suggested that steacyite and its Ca analogue form an isomorphic series [7, 8].

EXPERIMENTAL

Sample description. Turkestanite was first discovered in the course of investigations of alkali complexes from the Dzhelisu and Dara-i-Pioz massifs of Turkestano-Alay. A specimen from the exocontact zone of the Dzhelisu massif was used for structure investigations. The Dzhelisu massif is formed of albatized nepheline syenites cutting through Upper-Carboniferous sandy-schistous rocks. Turkestanite forms metacrystals 2–50 mm in size, which are composed of the {100} and {101} simple forms. Crystals of turkestanite contain numerous inclusions of country rocks and thorite; the outer zones of crystals are characterized by a smaller content of inclusions. The mineral is colored brown; the hues are caused by different inclusions. Thin sections of the mineral are colorless. Turkestanite is optically negative and uniaxial. The extinction is direct, and the elongation is negative. The Mohs hardness is 5.5–6. The IR spectrum of turkestanite is similar to the spectra of cyclosilicates. It contains intense absorption bands at 449, 591, 1040, and 1097 cm^{-1} and

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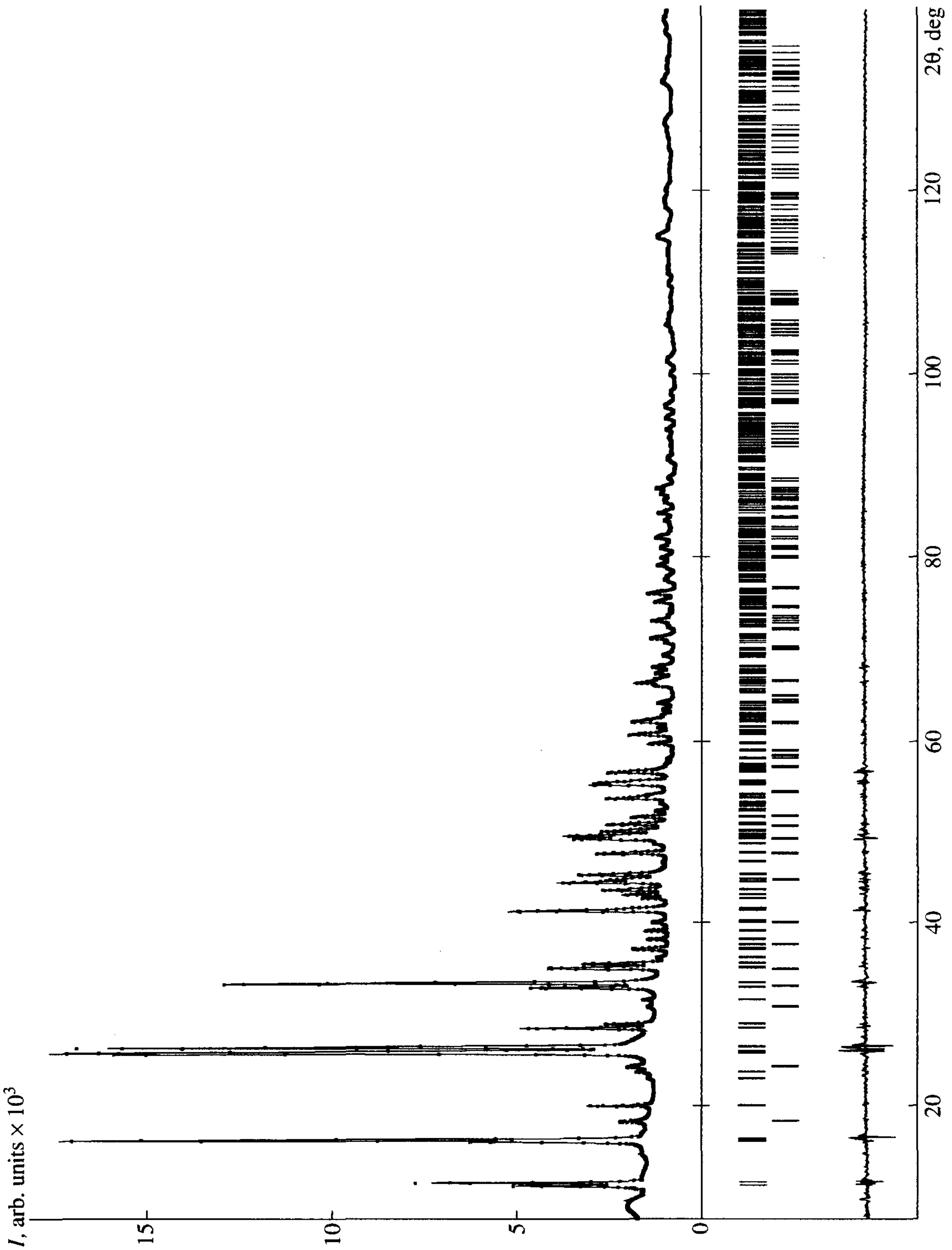

Fig. 1. Experimental (points) and calculated (solid line) X-ray diffraction patterns of turkestanite and thorite.

Table 1. Parameters of data-collection and structure-refinement by the Rietveld method

Parameter	Turkestanite	Thorite
Unit-cell parameters		
a, Å	7.5792(1)	7.1760(1)
c, Å	14.7042(2)	6.2888(1)
V_0, Å^3	844.68(1)	323.84(1)
No. of formula units, z	2	4
Space group	$P4/mcc$	$I4_1/amd$
2θ range, deg	8–140	8–140
Asymmetry, 2θ, deg	40	40
No. of Bragg reflections	850	182
No. of parameters in the refinement	61	20
R_p	3.16	3.16
R_{wp}	4.04	4.04
R_{exp}	2.87	2.87
R_B	2.18	6.24
R_F	1.90	4.75
s*	1.41	1.41
DWD**	1.10	1.10
σ_x***	1.839	1.839

* $s = R_{wp}/R_{exp}$, where R_{exp} is the expected value of R_{wp}.

** DWD is the Durbin–Watson statistics [11].

*** σ_x is a multiplier for calculated standard deviations [12].

Table 2. Atomic coordinates and thermal parameters (Å^2) in the structure of turkestanite

Position	Parameter	Value
A	x	0
	y	0
	z	0.25
	B_{iso}	0.85(2)
	β_{11}	0.0035(4)
	β_{22}	0.0035(4)
	β_{33}	0.0028(2)
	β_{12}	0
	β_{13}	0
	β_{23}	0
B	x	0
	y	0.5
	z	0.25
	B_{iso}	0.7(1)
	β_{11}	0.0028(9)
	β_{22}	0.0028(9)
	β_{33}	0.0019(6)
	β_{12}	0
	β_{13}	0
	β_{23}	0
C	x	0
	y	0
	z	0
	B_{iso}	1.8(4)
	β_{11}	0.026(4)
	β_{22}	0.026(4)
	β_{33}	0.002(1)
	β_{12}	0
	β_{13}	0
	β_{23}	0
Si	x	0.2597(9)
	y	0.3358(6)
	z	0.1073(6)
	B_{iso}	2.8(2)
	β_{11}	0.008(1)
	β_{22}	0.007(1)
	β_{33}	0.0059(6)
	β_{12}	−0.001(1)
	β_{13}	−0.0000(6)
	β_{23}	0.0004(6)
O(1)	x	0.229(2)
	y	0.310(2)
	z	0
	B_{iso}	3.3(4)
O(2)	x	0.454(1)
	y	0.261(1)
	z	0.1337(6)
	B_{iso}	2.6(2)
O(3)	x	0.111(1)
	y	0.250(1)
	z	0.1574(6)
	B_{iso}	2.6(2)

a broad band near 3460 cm^{-1} associated with the presence of water in the mineral.

The electron microprobe analysis carried out by A.I. Tsepin (Cameca SX-45; voltage, 20 kV; current, 25 mA; the reference samples: diopside for Si, Ca, and Fe; orthoclase for K; UO_2 for U; and ThO_2 for Th) showed the following composition of turkestanite from Dzhelisu (Kyrgyzstan) (wt %): SiO_2, 49.80; Al_2O_3, 1.11; Fe_2O_3, 0.04; ThO_2, 30.76; UO_2, not found; PbO, 0.40; BaO, 0.40; CaO, 8.29; Na_2O, 1.75; and $\Sigma = 95.21$. It is possible that the thorium content is overestimated, because of the presence of very fine ingrowths of thorite. After the substraction of 1.5% thorite, the formula was recalculated to $Th_{1.06}(Ca_{1.40}Na_{0.49})_{1.89}(K_{0.53}\square_{0.47})_{1.00}[(Si_{7.80}Al_{0.20})_{8.00} \times O_{19.93}(OH)_{0.07}] \cdot nH_2O$; $\rho_{exp} = 2.95(5)$ g/cm^3.

A monofraction of turkestanite for the structural study was obtained by magnetic separation, centrifugal separation in mixtures of bromoform and methylene iodide, and flotation methods. Nonetheless, the obtained fraction contained near 1.5% of the thorite admixture against all our efforts to remove it.

Refinement of the crystal structure of turkestanite by the Rietveld method. The X-ray diffraction pattern of a two-phase powder sample that contained turkestanite with an admixture of thorite $ThSiO_4$ was obtained on an ADP-2 automated diffractometer (λCuK_α, Ni filter) with 2θ scan at 0.02° intervals and an exposure time of 10 s. All the calculations were performed with the WYRIET program (version 3.3) [9]. The turkestanite structure was refined in space group $P4/mcc$. The atomic coordinates of steacyite [2] were taken as the starting points of the refinement. The Pearson function at 6FWHM, where FWHM is the full width at half-maximum, was chosen for the description of peak shapes. The scattering factors for ions were applied. Occupancy factors were refined, provided that the *A* position was populated by the Th^{4+} ions, the *B* position was divided between the Ca^{2+} and Na^+ ions, and the *C* position was occupied by the K^+ ions.

The atomic coordinates of thorite were taken from [10]. A quantitative analysis of the mixture revealed an admixture of thorite to the extent of 1.34 wt %.

RESULTS AND DISCUSSION

The experimental (points) and calculated (solid line) X-ray diffraction patterns of turkestanite are shown in Fig. 1.

The data-collection and structure-refinement parameters, including the unit-cell parameters for turkestanite and thorite, are summarized in Table 1. Atomic coordinates and isotropic and anisotropic thermal parameters in the turkestanite structure are listed in Table 2. Selected interatomic distances and bond angles in the turkestanite structure are given in Table 3.

The unit-cell parameters of turkestanite [a = 7.5792(1) and c = 14.7042(2) Å, V = 844.68(1) $Å^3$ (Table 1)] agree well with the parameters of steacyite {a = 7.58(1) and c = 14.77(2) Å [2]} and iraqite {a = 7.61(1) and c = 14.77(2) Å [4]}.

The refinement of the *A*-, *B*-, and *C*-site occupancies resulted in the following compositions: $A = Th_{1.00}$; $B = Ca_{0.70}Na_{0.25}\square_{0.05}$; and $C = K_{0.53}\square_{0.47}$. In steacyite, according to [2], the vacancies are observed in all three positions: *A*, 9%; *B*, 7%; and *C*, 38%. The X-ray structure investigation of turkestanite leads to the following formula: $Th(Ca,Na)_2(K_{1-z}\square_z)[Si_8O_{20}]$, ($z$ = 0.47), sp. gr. $P4/mcc$, z = 2, and ρ_{calc} = 3.01 g/cm^3. The observed density was underestimated as compared to the calculated density, because the sample used for density measurement contained albite ingrowths and water.

The Si atoms are surrounded tetrahedrally by oxygen atoms at 1.643–1.469 Å distances (the mean Si–O distance is 1.58 Å). This mean distance is uncommon for a Si tetrahedron and results from the contribution of a very short Si–O(3) bond [1.469(6) Å]. Three other distances to the bridging oxygen atoms in the tetrahedron vary between 1.643 and 1.606 Å. The abnormally short Si–O(3) distance is apparently a consequence of the poor quality of the powder sample, which complicated the procedure of structural refinement. The presence of Th is responsible for the metamict properties of the sample. Nonstoichiometric water entrapped in large cavities of the structure and other admixtures severely complicate the analysis of the diffraction pattern of turkestanite. Nonetheless, all other interatomic distances are within normal values. In steacyite, the Si–O(3) distance (1.57 Å) is also the shortest in the Si tetrahedron [2], which is explained by the fact that the O(3) oxygen atom is situated at the nonbridging vertex of the tetrahedron. Probably, the O(3) ligand of the silicon atom in turkestanite can be represented by not only oxygen atoms but also hydroxyl groups, similar to steacyite [2], in which this position was represented as $[O_{0.88}(OH)_{0.12}]$. According to the chemical-analysis data, the structure contains some quantity of water. Its largest part is not the water of crystallization, but it is situated in the large cavities of the turkestanite structure.

Table 3. Selected interatomic distances (Å) and bond angles (deg) in turkestanite

Distances and angles	Value
A–O(3) × 8	2.527(5)
B–O(2) × 4	2.637(5)
O(3) × 4	2.435(5)
Average	2.536
C–O(1) × 4	2.923(8)
O(3) × 8	3.145(5)
Average	3.071
Si–O(1)	1.606(5)
O(2)	1.622(6)
O(2')	1.643(6)
O(3)	1.469(6)
Average	1.585
O(1)–Si–O(2)	108.8(4)
O(1)–Si–O(2')	110.5(4)
O(1)–Si–O(3)	109.5(4)
O(2)–Si–O(2')	106.3(3)
O(2)–Si–O(3)	115.7(3)
O(2')–Si–O(3)	106.0(3)
Average	109.5
Si–O(1)–Si'	158.3(3)
Si–O(2)–Si'	145.6(3)

The O–Si–O and Si–O–Si bond angles (Table 3) are very close to those in steacyite.

The thorium atoms at the *A* position and the calcium and sodium atoms at the *B* position exhibit eightfold coordination, and the potassium atoms at the *C* position have twelve oxygen ligands (Table 3). The O(3) atom is involved in the coordination of the atoms at the *B* and *C* positions. The *B*–O(3) interatomic distances in the structures of turkestanite and steacyite are virtually identical, whereas the Th–O(3) bonds in turkestanite (2.527 Å) are longer than those in steacyite (2.41 Å).

In the turkestanite structure, the Si tetrahedra are linked into double-level four-membered $[Si_8O_{20}]$ rings related by the (001) mirror plane. The *B* = Ca and Na atoms are located among the discrete Si–O radicals

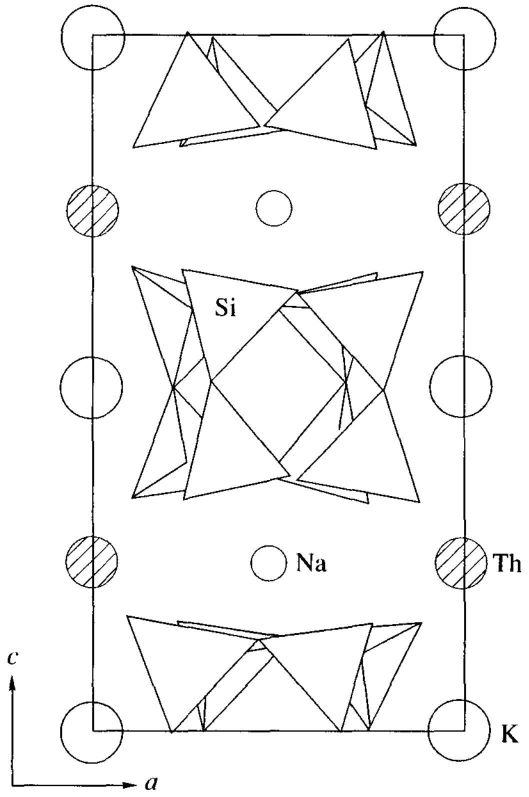

Fig. 2. Crystal structure of turkestanite.

along the c-axis (Fig. 2). The Th and K atoms alternate in the large channels running along the c-axis. These atoms occupy special sites; therefore, they are characterized by small thermal parameters.

CONCLUSION

Turkestanite $Th(Ca,Na)_2(K_{1-z}\square_z)[Si_8O_{20}]$, $z = 0.47$, is the third mineral species that contains the discrete $[Si_8O_{20}]$ radical, which consists of double four-membered rings formed of Si–O tetrahedra. The predominance of Ca^{2+} at position B, in distinction to Na^+ in steacyite $Th(Na,Ca)_2(K_{1-z}\square_z)[Si_8O_{20}]$ (z = 0.40), makes possible distinguishing turkestanite as an original mineral species.

The discovery of turkestanite confirmed the hypothesis advanced in [3] on the existence of the

$$Th(Ca,Na)_2(K_{1-z}\square_z)[Si_8O_{20}]$$
$$- Th(Na,Ca)_2(K_{1-z}\square_z)[Si_8O_{20}]$$

isomorphic series.

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