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STRUCTURE OF INORGANIC COMPOUNDS

$Na_3Tb_3[Si_6O_{18}] \cdot H_2O$, a Synthetic Analogue of Microporous Mineral Gerenite

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Abstract—Crystals of a new silicate, $Na_3Tb_3[Si_6O_{18}] \cdot H_2O$, space group $P\bar{1}$, are obtained under hydrothermal conditions. The formula of the compound is determined in the course of structure solution. The silicate is a synthetic analogue of the gerenite mineral $(Ca_{1.21}Na_{0.57})(Y_{2.24}Dy_{0.68})Si_6O_{18} \cdot 2H_2O$, whose structure contains six-membered rings formed by SiO_4 tetrahedra. The $[Si_6O_{18}]$ rings are connected by TbO_6 octahedra into a mixed microporous framework with voids filled by Na atoms and water molecules. The new silicate differs from gerenite by the occupation of the Ca position by Na atoms and population of the pores sandwiched between six-membered rings. By virtue of conditions of hydrothermal synthesis in the absence of Ca and excess of Na in the system, an additional Na position appears in the void. It is populated statistically, and in gerenite it was occupied by water molecules only. In the new structure, the position of water is split into two statistically populated positions. The inclusion of Na atoms in additional positions in framework pores and their high thermal vibrations are indicative of ion-exchange properties of the structure. Possible paths of ion exchange are discussed.

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INTRODUCTION

A wide spectrum of chemical and physical properties of silicates, as well as a diversity and complexity of their structural motifs, determine the great interest in this class of compounds. The number of structural types of rare earth silicates approaches 50 [1]. Compounds of this class were found in nature and obtained synthetically. They exhibit a large variety of anionic silicon–oxygen radicals, from ortho groups to frameworks. High thermal stability and mechanical strength make them promising materials. Many of the crystals of rare earth silicates possess semiconducting, ion-conducting, catalytic, magnetic, laser, nonlinear optical, or luminescent properties. Compounds $Na_5\mathit{REE}Si_4O_{12}$ (*REE* are rare earth elements) and $Ag_5HoSi_4O_{12}$ [2], $Na_3NdSi_6O_{15} \cdot 2H_2O$ [3], and two modifications of $K_3NdSi_6O_{15}$ [4, 5] form ion conducting crystals.

The primary diagnostics of the new $Na_3Tb_3[Si_6O_{18}] \cdot H_2O$ (**I**) silicate showed that it is a synthetic analogue of the gerenite mineral, whose structure was determined for the $(Ca_{1.21}Na_{0.57})(Y_{2.24}Dy_{0.68})Si_6O_{18} \cdot 2H_2O$ (**II**) composition [6]. It belongs to the class of ring silicates containing the $[Si_6O_{18}]$ soro radical. In nature, this mineral is formed in pegmatite–aplite lenses of alkaline granite complexes, where the conditions are close to those used for the preparation of new silicate **I**. In [6] silicate **II** is compared with the kainosite $Ca_2(Y,Ce)_2(SiO_3)_4CO_3 \cdot H_2O$ and leifite $Na_6Be_2Al_2Si_{16}O_{39}(OH)_2 \cdot 1.5H_2O$ minerals.

Aside from gerenite, the following ring rare earth silicates are known: $Na_3Y[Si_6O_{15}]$ contains double three-membered rings [7], $Na_6Eu_3Si_6O_{18}$ contains six-membered rings [8], $K_4Lu_2[Si_8O_{20}](OH)_2$ contains eight-membered rings [9], and $Na_{15}Dy_3[Si_{12}O_{36}]$ contains corrugated twelve-membered rings [10].

In this work the results of hydrothermal synthesis, a study of the crystal structure of new silicate $Na_3Tb_3[Si_6O_{18}] \cdot H_2O$ (**I**), and a comparative crystal-chemical analysis between the structures of **I** and the gerenite mineral (**II**) are reported.

EXPERIMENTAL

Synthesis and properties of crystals. Crystals $Na_3Tb_3[Si_6O_{18}] \cdot H_2O$ (**I**) were obtained under hydrothermal conditions. The ratio of liquid and solid phases was 1 : 5. In the solid phase of the system, the ratio of oxides was $Tb_2O_3 : Na_2O : SiO_2 : B_2O_3 = 1 : 1 : 1 : 1$. The synthesis was conducted at $T = 270°C$ and $P \sim 70$ atm in standard autoclaves 5–6 cm^3 in volume protected with a fluoroplastic coating. The lower temperature was limited by the kinetics of hydrothermal reactions, and the upper temperature was limited by the potentialities of the apparatus. The filling factor of

Table 1. Crystal data, details of data collection, and results of structure refinement for $Na_3Tb_3[Si_6O_{18}] \cdot H_2O$ (**I**)

Chemical formula	$Na_3Tb_3[Si_6O_{18}] \cdot H_2O$
M	1018.27
Crystal system, space group, Z	Triclinic, $P\bar{1}$, 1
a, b, c, Å	5.5074(4), 9.3612(8), 9.7425(8)
α, β, γ, deg	117.3568(13), 96.8612(15), 100.4326(14)
V, Å^3	426.76(6)
D_x, g/cm^3	3.962
Radiation; λ, Å	MoK_α; 0.71073
μ, mm^{-1}	12.894
T, K	120
Crystal size, mm	0.05 × 0.075 × 0.125
Diffractometer	Bruker SMART APEX DUO
Scan mode	ω
θ_{max}, deg	30.622
Limiting indices	$-7 \leqslant h \leqslant 7$, $-13 \leqslant k \leqslant 13$, $-13 \leqslant l \leqslant 13$
Refinement method	Least squares on $F^2(hkl)$
Number of reflections: measured/unique/with $I \geqslant 1.96\,\sigma(I)/R_{int}$	5938/2617/2364/0.0279
Weighting scheme	$1/[\sigma^2(F_o)^2 + (0.0330P)^2 + 1.7016P]$, $P = [\max(F_o)^2 + 2(F_c)^2]/3$
Number of parameters	160
$R_{\rm all}$	0.0330
R_{gt}, R_{wgt}	0.0284, 0.0670
S	1.047
Programs	SHELX
$\Delta\rho_{min}/\Delta\rho_{max}$, e/Å^3	−2.322/1.564

an autoclave was chosen so that pressure remained constant. The duration of the experiments was 18–20 days, which was necessary to complete the reaction, and crystals were washed with water. Aggregates of transparent colorless flattened crystals were found in the experiment. A test for second harmonic generation showed that the crystals are centrosymmetric.

X-ray diffraction study. The parameters of the new phase were determined on an Xcalibur S diffractometer equipped with a CCD detector. The single crystal in the shape of a thin flattened prism chosen for data collection was small in size, rather perfect, and transparent. A triclinic cell was determined; its cell parameters were close to those of the gerenite mineral $(Ca_{1.21}Na_{0.57})(Y_{2.24}Dy_{0.68})Si_6O_{18} \cdot 2H_2O$ (**II**) found in the ICSD database of inorganic compounds [1]. A three-dimensional experimental set of intensities for structure determination was collected at 120 K in the complete sphere of the reciprocal space on a Bruker SMART APEX DUO diffractometer equipped with an area CCD detector and a low-temperature attachment. The data were processed with the APEX2 program [11]. The coordinates in [6] were brought into correspondence with the chosen setting of axes by transformations $x_{\rm I} = z_{\rm II}$, $y_{\rm I} = x_{\rm II}$, $z_{\rm I} = y_{\rm II}$ and used as a starting model. The Tb atom was located at the position of Y atom, Ca was located at the Na position, and the remaining positions coincided. Their refinement resulted in satisfactory estimates and atomic displacement parameters other than high parameters of the O atom of water molecule, which was located at the same structural void as in structure **II**. Two additional peaks, which had no analogues in the gerenite structure, appeared on the difference map of electron density. Both peaks were located at the same void as the water molecule; the height and coordination of the first peak corresponded to the additional Na2 atom. The other peak near the center of inversion corresponded to the Ow atom of water molecule. Because of the short distance between the Ow and Na2 atomic positions, they could be occupied statistically by 0.5 each. The Ow position appeared to be split into two positions, namely, O10w and O11w (Na2–O10w = 1.95 Å, Na2–O10w = 2.16 Å). The occupancies of the O10w and O11w positions were determined in the refinement of the atomic thermal parameters with the ratio of occupancies altering step by step provided that the total site occupancy of water was equal to 0.5. The H atoms were not localized because of the splitting of the Ow position. The positional and anisotropic thermal parameters of atoms were refined by the least-squares procedure with consideration for the anomalous dispersion of Mo radiation using the SHELXL program package [12]. The final formula of the synthetic silicate is $Na_3Tb_3[Si_6O_{18}] \cdot H_2O$. The highest peak and the deepest hole of the residual electron density (Table 1) are located in the vicinity of disordered Na2 and O10w positions in the structural void.

The crystal data, details of data collection, and results of the final refinement of the structure are summarized in Table 1. The atomic coordinates and thermal parameters are listed in Table 2. Selected interatomic distances are given in Table 3. The data on the structure are available in the ICSD database, deposition no. 430502.

RESULTS AND DISCUSSION

Description of the structure. The new silicate $Na_3Tb_3[Si_6O_{18}] \cdot H_2O$ (**I**) is a structural analogue of

Table 2. Coordinates, site occupation factors (s.o.f), and equivalent isotropic parameters of the basis atoms in the structure of $Na_3Tb_3[Si_6O_{18}] \cdot H_2O$ (**I**)

Atom	s.o.f.	*x/a*	*y/b*	*z/c*	$U_{eq.}$, Å^2
Tb1	0.5	0	0.5	0.5	0.0108(1)
Tb2	1.0	0.3155(1)	0.7796(1)	0.3630(1)	0.0056(1)
Na1	1.0	0.1734(4)	0.6149(3)	0.9395(2)	0.0117(4)
Na2	0.5	0.437 (1)	0.9344(8)	0.7891(7)	0.034(1)
Si1	1.0	0.3891(3)	0.3686(2)	0.2513(2)	0.0066(2)
Si2	1.0	0.1081(3)	0.1181(2)	0.3590(2)	0.0057(2)
Si3	1.0	0.7740(3)	0.7590(2)	0.1225(2)	0.0092(3)
O1	1.0	0.9701(7)	0.6729(5)	0.1671(4)	0.0112(7)
O2	1.0	0.3145(7)	0.6135(6)	0.7230(5)	0.0181(9)
O3	1.0	0.3032(8)	0.5330(5)	0.3613(5)	0.0141(8)
O4	1.0	0.9096(9)	0.9595(5)	0.2053(6)	0.028(1)
O5	1.0	0.0446(9)	0.7670(6)	0.5264(5)	0.0221(9)
O6	1.0	0.5055(8)	0.7311(7)	0.1642(5)	0.025(1)
O7	1.0	0.3072(7)	0.0559(5)	0.4382(5)	0.0111(7)
O8	1.0	0.2589(7)	0.3070(5)	0.0687(5)	0.0167(8)
O9	1.0	0.249(1)	0.2226(7)	0.2840(7)	0.037(1)
O10w	0.32	0.336(3)	0.924(2)	0.970(1)	0.018(3)
O11w	0.18	0.152(6)	0.984(3)	0.993(3)	0.027(6)

Table 3. Selected interatomic distances *d* between cations and anions in the structure of $Na_3Tb_3[Si_6O_{18}] \cdot H_2O$ (**I**)

$Tb1O_6$ octahedron		$Si1O_4$ tetrahedron	
Bond	*d*, Å	Bond	*d*, Å
Tb1–O2 × 2	2.272(4)	Si1–O2	1.587(4)
Tb1–O3 × 2	2.333(4)	Si1–O3	1.615(4)
Tb1–O5 × 2	2.355(4)	Si1–O8	1.617(4)
Average	2.320	Si1–O9	1.626(5)
		Average	1.611
$Tb2O_6$ octahedron		$Si2O_4$ tetrahedron	
Bond	*d*, Å	Bond	*d*, Å
Tb2–O6	2.213(4)	Si2–O5	1.600(4)
Tb2–O1	2.225(4)	Si2–O7	1.606(4)
Tb2–O3	2.290(4)	Si2–O9	1.614(5)
Tb2–O5	2.335(4)	Si2–O4	1.618(4)
Tb2–O7	2.353(4)	Average	1.610
Tb2–O7	2.362(4)	$Si3O_4$ tetrahedron	
Average	2.296	Bond	*d*, Å
		Si3–O6	1.588(5)
		Si3–O1	1.590(4)
		Si3–O4	1.640(5)
		Si3–O8	1.645(4)
		Average	1.615

natural mineral gerenite $(Ca,Na)_2(Y,REE)_3Si_6O_{18} \cdot 2H_2O$. According to [6], the formula of the only representative characterized structurally, $(Ca_{1.21}Na_{0.57})(Y_{2.24}Dy_{0.68})Si_6O_{18} \cdot 2H_2O$ (**II**), has a 0.25 deficiency of positive charge. The synthetic silicate maintains main specific structural features of the natural gerenite. In structure **I**, Tb atoms (like Y atoms in structure **II**) are located in two independent positions (Tb1 and Tb2) and coordinated by six oxygen atoms (Table 3) in the shape of octahedra (Fig. 1). Octahedra share edges to form zigzag chains running along the *b* axis. The anionic part of structures **I** and **II** is represented by tetrahedrally coordinated silicon atoms. Three independent SiO_4 tetrahedra share vertices and, together with the tetrahedra related by a center of inversion, form six-membered rings parallel to the *bc* plane (Fig. 1). Sharing terminal vertices with columns of octahedra, they form a three-dimensional structure, which can be described as a mixed framework consisting of two types of polyhedra. Along the *c* axis, layers containing the rings alternate with chains of TbO_6 octahedra (Figs. 1, 2). The silicon–oxygen radicals and chains of $(Y,REEO_6)$ octahedra are identical in the two structures. The mixed frameworks of structures **I** and **II** contain identical voids occupied by Na1 atoms in silicate **I** and (Ca,Na) atoms in silicate **II** (Figs. 1, 3). The Na1 atoms are coordinated by five O atoms located at short Na1–O distances of 2.33–2.62 Å, whereas the O10w molecule from the neighboring ring forms the sixth vertex at a distance of 2.74 Å.

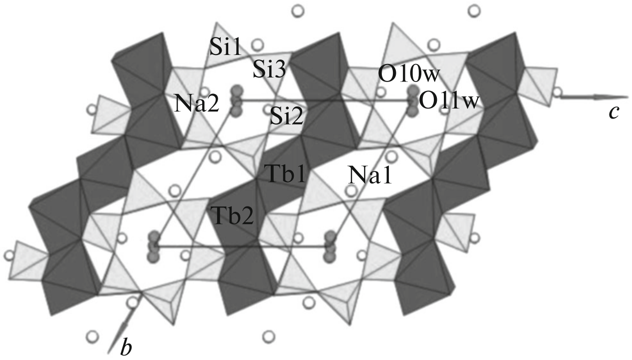

Fig. 1. Projection of crystal structure **I** onto the *bc* plane. SiO_4 tetrahedra and TbO_6 octahedra are shown; open circles indicate Na atoms and shaded circles indicate H_2O molecules.

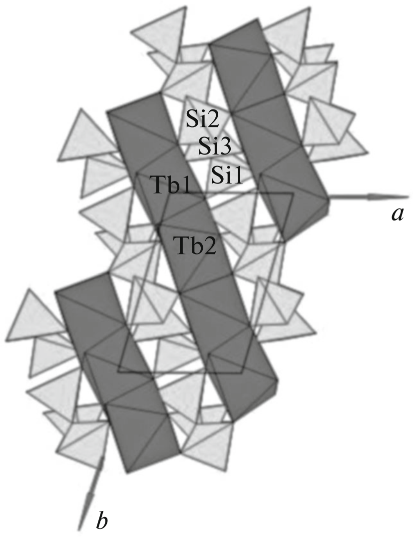

Fig. 2. Projection of crystal structure **I** onto the *ab* plane. SiO_4 tetrahedra and TbO_6 octahedra are shown.

The difference between the structures consists of the population of the voids between the six-membered rings formed by SiO_4 tetrahedra. The structural details of population of voids in the mixed framework were revealed due to the high quality of the diffraction data obtained at a low temperature. In both structures the voids accommodate water molecules; however, in structure **I** this position is split into two positions, O10w and O11w. In structure **I**, the O10w water molecules are located slightly closer to the center of inversion and slightly shifted in the diagonal direction of the *bc* plane, whereas in structure **II** they are slightly closer to the walls of the rings and aligned along the *a* axis (Figs. 1, 3). In structure **I**, the O11w molecules are located in the immediate vicinity of the center of inversion. An additional position Na2 appears in the new structure apart from the difference in the location of water molecules. The Na2 atoms are located in the same void as water molecules but closer to the walls rather than at the center (Fig. 1). The voids are continuous in the *a* direction in structure **I** (in the *c* direction in structure **II**). The Na2 atoms are coordinated by six O atoms at Na2–O distances of 2.30–2.90 Å and two O11w water molecules at distances Na2–O11w = 2.60 and 2.64 Å. Inasmuch as the distances between the Na2 and O10w positions are short (1.95 and 2.16 Å), these positions are occupied statistically (Table 2): if the Na2 position is occupied, the Ow position remains unoccupied and, vice versa, if the Ow position is occupied, the Na2 position is free. It should be stressed that in both structures the Na(Ca) atoms and H_2O molecules are located in the voids between the rings rather than in the plane of the rings (Fig. 4).

CONCLUSIONS

Structures **I** and **II** are microporous framework structures with voids of an effective cross section of ~2.3 Å occupied by cations and water molecules. The population of voids in $Na_3Tb_3[Si_6O_{18}] \cdot H_2O$ is more diverse than in gerenite. Both structures exhibit ion-exchange properties, as is confirmed by the fact that, in the new structure with substantial sodium content, the additional Na2 atom is included in the void unoccupied in gerenite. Thus, the replacement of Ca atoms in the natural compound by larger amount of Na atoms ensures the electrical neutrality of the synthetic

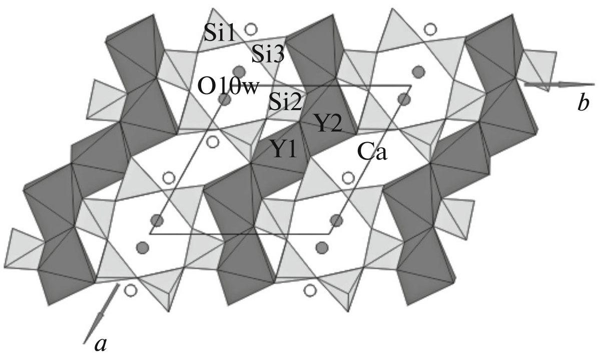

Fig. 3. Projection of the crystal structure of gerenite **II** onto the *ab* plane. SiO_4 tetrahedra and YO_6 octahedra are shown; open circles indicate Ca atoms and shaded circles indicate H_2O molecules.

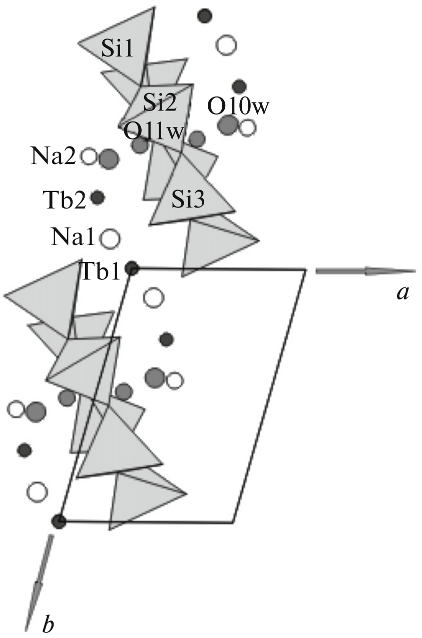

Fig. 4. Projection of a fragment of crystal structure **I** onto the *ab* plane. SiO_4 tetrahedra are shown; small closed circles indicate Tb atoms, open circles indicate Na atoms, and shaded circles indicate H_2O molecules.

analogue. The possible ion exchange in the calcium and sodium varieties can proceed along channels in the direction of the *a* axis: ions migrate through six-membered rings and voids below them, turn to the interring space, and run in an almost perpendicular direction along the *b* axis.

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