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Caryochroite, a Rare Mineral from the Titanosilicate Group: Crystal Structure, Crystal Chemistry, and Thermal Properties

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Abstract—The crystal structure of the rare mineral caryochroite is determined for the first time using X-ray diffractometry and electron microdiffraction data. The new idealized crystal formula of the mineral is

 $[Na(Sr_{0.5}Ca_{0.5})Mg]_3[Fe_8^{3+}Mn(Fe_{0.5}^{2+}\Box_{0.5})]_{10}(Ti_2Si_{12})O_{37}(OH)_{14}(H_2O)_3$. The parameters of the monoclinic unit cell refined by the least square method are *a* 16.550(3), *b* 5.281(2), *c* 24.25(3) Å, β 93.0°, Z = 2, space group P2/n. The crystal structure of caryochroite is a new type of Ti–Si lattice responsible for the large structural channels, which are able to enclose the exchange cations and a high amount of water components (OH groups and H₂O molecules).

Keywords: titanosilicates, caryochroite, crystal structure, thermal analysis **DOI:** 10.1134/S1028334X23600354

INTRODUCTION

Titanosilicates are rare accessory minerals of alkaline rocks and related pegmatites and metasomatites. The synthetic porous titanosilicates exhibit excellent sorption and ion-exchange properties and are used as active and selective heterogeneous catalysts for the production of industrial organic precursors [1]. These thermally and radiation stable materials are able to clean liquid radioactive wastes effectively from longlived nuclides [2]. To simplify the synthesis of the materials with the prescribed properties, it is necessary to study in detail the crystal chemical features of natural compounds.

The crystal structures of titanosilicates, which belong to a large family of heterophyllosilicates, contain three-layered blocks, which are composed of a central octahedral net and Si tetrahedra nets adjacent from top and bottom with incorporated Ti octahedra. In some minerals, the octahedra around Ti are vertexsharing with the formation of complex three-dimensional structures, which are penetrated by channels with OH groups, H_2O molecules, and some additional cations.

Caryochroite

 $(Na,Sr)_{3}(Fe^{3+},Mg)_{10}Ti_{2}Si_{12}O_{37}(H_{2}O,O,OH)_{17},$

which belongs to the titanosilicate group, was approved as a new mineral by the Commission on New Minerals of the International Mineralogical Association in 2005 (IMA 2005-031). The samples for study were collected by P.M. Kartashov in 1987 in dumps of the Umbozero underground mine at Mt. Alluaiv in the northwestern sector of the Lovozero alkaline pluton. It was later established that the mineral originated from Elpiditovy pegmatite, which was exposed by the underground mines. The samples were massive, microporous, compact masses up to $9 \times 6 \times 5$ cm. The mineral was closely associated with elpidite, pyrite, albite, natrolite, and drops of solid bituminous material. The parameters of the monoclinic unit cell of caryochroite are a 16.47, b 5.303, c 24.39 Å, β 93.5°. The suggested formula was $(Na,Sr)_{3}(Fe^{3+},Mg)_{10}[Ti_{2}Si_{12}O_{37}] \cdot (H_{2}O,O,OH)_{17}$, but the structure of the mineral was not solved [3]. Its structure is analogous to that of nafertisite [4]. Both minerals belong to the group of titanolsilicates, which contain micalike three-layered (HOH) structures: a central octahedral net (O) of edge-sharing octahedra with nets of Si-tetrahedra rings adjacent from top and bottom (H), which are connected by single Ti octahedra [5, 6]. In addition to Ti atoms, some minerals also contain Nb and Zr atoms. The channels of the threedimensional structure locally host Na^+ , K^+ , Ba^{2+} , and other cations, OH groups, and H₂O molecules.

The diversity of structures of minerals of the titanosilicate groups depends on a series of factors: the nature of octahedral cations, the configuration and composition of the H-net, and the nature and amount of nonframework cations. Many minerals of this group (\sim 75) are characterized by structures with Si₂O₇

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Fig. 1. Crystal structure of bafertisite (a, general view; b, configuration of H-net) and astrophyllite (c, general view; d, configuration of H-net).

diorthogroups, which are connected by octahedra around Ti, Zr, and/or Nb atoms. The simplest minerals of this groups include bafertisite $Ba_2Fe_4^{2+}Ti_2(Si_2O_7)_2O_2(OH)_2F_2$ 8] and surkhobite (Figs. 1a, 1b) [7, $(Ba,K)_2CaNa(Mn,Fe^{2+},Fe^{3+})_8Ti_4(Si_2O_7)_4O_4(F,OH,O)_6$ [9]. Some minerals of this group have more complex structures because of the incorporation of PO₄ tetrahedra (lomonosovite Na₅Ti₂[Si₂O₇][PO₄]O₂ [10, 11], sobolevite $Na_{13}Ca_2Mn_2Ti_3(Si_2O_7)_2(PO_4)_4O_3F_3$ [12]), triangle groupings (bussenite CO_3 or



Fig. 2. H-net in the structure of nafertisite.

 $Na_2Ba_2Fe^{2+}$ [TiSi₂O₇][CO₃]O(OH)(H₂O)F [13]). The minerals with H-nets of the Ti(Zr,Nb)-Si₂O₇ composition are described in a series of papers [8, 11, 14, 15], which provide the refined structures of some minerals and the relationship between them.



Fig. 3. Morphology and microdiffraction pattern for finedisperse caryochroite samples. TEM image.

hkl

 $\overline{1}01$

101 002

004

 $21\overline{1}$

114, 213, 402

 $21\overline{4}$

305, 214

 $\overline{1}07$ 008

<u>4</u>14, <u>2</u>08, <u>1</u>17

512, 217, 51

020, 109, 018,

513

022, 118

023

 $51\overline{5}$

515

 $028, \overline{5}19$

0.2.12, 726,

5.1.13

531, 531

533, 1.1.15

5	9	2.386	2.380	515
4	4	2.226	2.229, 2.226	$614. \overline{5}17$

1.988

1.590

1.549

1.533

Table 1. Experimental and calculated X-ray powder diff	frac
tion of data carvochroite	

d (calc)

14.00

13.33

12.11

6.054

4.398

3.899, 3.851,

3.849 3.634

3.546, 3.538

3.422

3.027

2.917, 2.892,

2.872

2.703, 2.694,

2.684 2.640, 2.634,

2.626, 2.611

2.579, 2.576

2.509

2.473

1.990, 1.985

1.603, 1.590,

1.584

1.552 1.548

1.533, 1.530

 $d(\exp)$

14.10

13.30

12.10

6.049

4.390

3.895

3.630

3.541

3.399

3.000

2.911

2.689

2.638

2.575

2.507

2.465

I (exp)

20

35

100

5

10

6

4

4

5

10

5

12

12

8

6

5

5

4

4

6

6

I(calc)

16

40

100

8

15

8

4

5

8

13

5

15

11

7

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5

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4

3

Only few minerals are characterized by structures with H-nets of the $Ti(Zr,Nb)_2Si_8O_{26}$ composition. The most abundant natural mineral of this group
includes astrophyllite $K_2NaFe_7^{2+}Ti_2Si_8O_{26}(OH)_4F$, the structure of which was repeatedly refined for samples of various compositions (Figs. 1c, 1d) [16, 17]. The H-net in this structure includes two incomplete tetrahedral rings connected by single Ti octahedra. Another representatives of the minerals of this group include bulgakite
$Li_2(Ca, Na)Fe_7^{2+}Ti_2Si_8O_{26}(OH)_4(F,O)(H_2O)_2$, nalivki- nite $Li_2Na(Fe^{2+}, Mn^{2+})_7Ti_2Si_8O_{27}(OH)_4F$ [18], and

laverovite $K_2NaMn_7Zr_2Si_8O_{26}(OH)_4F$ [19]. In spite of the significantly larger size of the channels relative to the structures of the minerals with Si₂O₇ groups, the minerals with H-nets Ti(Zr,Nb)₂Si₈O₂₆ do not contain the additional radicals PO₄ or CO₃, that explains the

Table 2. Atomic	coordinates in	1 the structure	of carvochroite
	•••••••		01 000 00000000000000000000000000000000

Atoms	x	У	z	Atoms	x	У	Z.
Si1	0.423	0.390	0.885	O 8	0.516	0.413	0.870
Si2	0.169	0.386	0.877	09	0.393	0.145	0.849
Si3	0.020	0.650	0.108	O10	0.392	0.650	0.851
Si4	0.121	0.140	0.100	O11	0.235	0.595	0.839
Si5	0.397	0.662	0.100	O12	0.210	0.145	0.850
Si6	0.302	0.148	0.095	O13	0.070	0.360	0.867
Ti	0.300	0.900	0.838	O14	0.924	0.602	0.883
Fe1	0.097	0.509	-0.008	O15	0.930	0.090	0.874
Fe2	0.300	0.550	-0.013	O16	0.784	0.855	0.876
Fe3	0.200	0.043	-0.018	O17	0.655	0.587	0.886
Fe4	0.402	0.023	-0.012	O18	0.639	0.072	0.878
Fe ²⁺	0.5	0.5	0	O19	0.25	0.800	0.75
Mn	0	0	0	OH1	0.092	0.863	-0.050
A*	0.520	0.840	0.280	OH2	0.496	0.145	0.044
Na	0.25	0.400	0.25	OH3	0.202	0.696	0.026
01	0.400	0.365	-0.052	OH4	0.530	0.450	0.270
O2	0.192	0.402	-0.058	OH5	0.400	0.870	0.760
03	0.010	0.660	0.042	OH6	0.390	0.400	0.250
O4	0.110	0.160	0.034	OH7	0.650	0.295	0.303
05	0.303	0.175	0.029	H_2O1	0.25	0.250	0.75
06	0.400	0.690	0.035	H_2O2	0.660	0.450	0.227
O 7	0.300	0.900	-0.067				

low amount of these minerals: only 15 species of this group have been discovered by the present.

The determination of the crystal structure of rare mineral nafertisite

 $(Na,K)_{3}(Fe^{2+},Fe^{3+}\Box)_{10}[Ti_{2}(Si,Fe^{3+},Al)_{12}O_{37}](O,OH)_{6}$ [4] revealed a new type of H-nets of an idealized composition of $Ti_2Si_{12}O_{37}$ (Fig. 2), which consist of three Si_2O_7 groups connected by single Ti octahedra. Caryochroite, evidently, is the second representative of this mineral group.

This paper describes the crystal structure of caryochroite, in particular, the position of cations, OH groups, and H₂O molecules in the structural channels, proposes its crystal chemical formula, and characterizes the thermal properties.

ANALYTICAL METHODS

The following methods were used to obtain the complex of experimental data: X-ray diffractometry (XRD, a Siemens D-500 powder diffractometer with CuK α radiation and a scanning interval of $20^{\circ} - 70^{\circ} 2\theta$), electron microscopy (a Philips CM12 transmitted electron microscope (TEM) equipped with an EDAX 9800), and thermography (synchronous thermal analysis (STA) on a STA 449 F1 Jupiter Netzsch analyzer with a sampling weight of 40 mg, a rate of survey of 10°C/min, an Ar atmosphere, and a closed corundum crucible). The crystal formula was refined using EDS data (Table 1). The new structural data are determineg by ATOMS and CARINE software, which allows the estimation of interatomic distances in various coordination surroundings of cations and the calculation of the diffraction characteristics (XRD and microdiffraction data).

RESULTS

The XRD pattern of caryochroite is most similar to data provided by Kartashov et al. [3]. Some differences in the experimental values of intensities could be related to the formation of texturated specimens by fine-disperse samples (Table 1).

According to TEM analysis, the caryochroite particles form very fine ribbons (Fig. 3), which prevent a qualitative microdiffraction pattern in contrast to similar platy nafertisite particles. The only microdiffraction pattern shown in the inset in Fig. 3 is a plane of reverse lattice (001)* with all integral indices k, whereas direction [100]* demonstrates the reflexes with indices h = 2n.

The XRD pattern and the microdiffraction pattern refined by the least square method yielded the parameters of the monoclinic unit cell: *a* 16.550(3), *b* 5.281(2), *c* 24.25(3) Å, β 93.0°. The XRD data correspond to the condition of h + l = 2n, i.e., the *B*-centered lattice. The only possible spatial group *B*2/*n* prohibits the presence of two intense reflections $\overline{101}$ and 101 in a low-angle area; therefore, the spatial group *P*12/*n*1 was chosen for caryochroite.

The similar experimental values of intensities and interplane distances, as well as the unit cell parameters, with data published by Kartashov et al. [3] give grounds to use the EDS data, which are also supported by the results of chemical analysis and the Mössbauer spectra, which determined three valent states of Fe [3]. The detailed analysis of the crystal formula from this work

$$(Na_{1.19}Sr_{0.62}Ca_{0.41}Mn_{0.35}K_{0.26})_{2.83}(Fe_{7.98}^{3+}Mg_{1.15}Mn_{0.49}Fe_{0.38}^{2+})_{10}(Ti_{1.87}Fe_{0.13}^{3+})_{2}(Si_{11.74}Al_{0.26})_{12}O_{54.1}OH_{20.4}OH_{20.4}OH_{20.4}OH_{20.4}OH_{20.4}OH_{20.4}OH_{20.4}OH_{20.4}OH_{20.4}OH_{20.4}OH_{20.4}OH_{20.4}OH_{20.4}OH_{20.4}O$$

(molecular weight 1968.970) showed that the given amount of Fe²⁺ cations is only 4.48% of the total Fe amount, whereas, according to the Mössbauer spectra data, this amount is ~7%. Suggesting that the Fe cations positioned together with Ti in this formula are also two valent, the total Fe²⁺ cations increase to 0.51, which is ~6% of the total Fe amount. From the crystal chemical viewpoint, the position of all Fe cations in the octahedral net is more warranted; all Mn atoms similar to Fe both in ionic radius and two/three valent states can also be concentrated in this net. At the same time, the position of Mg atoms in the octahedral net is unwarranted, because Mg in many swelling and mixed-layered clay minerals (e.g., mont-morillonite) occurs in the interlayer space and is a typical exchange cation, whereas caryochroite is characterized by cation-exchange properties [3]. The position of Mg atoms together with Na, Ca, and Sr atoms is thus more warranted in channels of the suggested structure of caryochroite. As a result of this analysis, we suggest a new idealized crystal formula of caryochroite:

$$Fe_{8,0}^{3+}Mn_{1,0}(Fe_{0,5}^{2+}\Box_{0,5})_{10,0}(Ti_{2}Si_{12})O_{37}(OH)_{6}\cdot [Na_{1,0}(Sr_{0,5}Ca_{0,5})Mg_{1,0}]_{3,0}(OH)_{8}(H_{2}O)_{3,0}(OH)_{1,0}(Fe_{0,5}^{2+}\Box_{0,5})_{1,0}(Fe_{0,5}^{2+}\Box_{0,5})_{1,0}(Fe_{0,5}^{2+}\Box_{0,5})_{1,0}(Fe_{0,5})_{1,0}(Fe_{0,5})_{1,0}(Fe_{0,5})_{1,0}(Fe_{0,5})_{1,0}(Fe_{0,5})_{1,0}(Fe_{0,5})_{1,0}(Fe_{0,5})_{1,0}(Fe_{0,5})_{1,0}(Fe_{0,5})_{1,0}(Fe_{0,5})_{1,0}(Fe_{0,5})_{1,0}(Fe_{0,5})_{1,0}(Fe_{0,5})_{1,0}(Fe_{0,5})_{1,0}(Fe_{0,5})_{1,0}(Fe_{0,5})_{1,0}(Fe_{0,5})_{1,0}(Fe_{0,5})_{1,0}(Fe_{0,5})_{1,0}($$

(molecular weight 1957.795), Z = 2, d (calc) of 3.012 fully corresponds to d (exp) of 2.990. Its first part reflects the composition of HOH layers, for which the total positive cation charge +83 is not fully compensated by the charge of the anion part $O_{37}(OH)_6$ (-80). The OH groups necessary for the full compensation of the positive charge of 3 could be positioned in the channels together with the Na⁺, Sr²⁺, Ca²⁺, and Mg²⁺ cations and five OH groups, which compensate for the total positive charge of these cations. As a result, eight OH groups occur in the channels. If three H_2O molecules also occur in the channels, the total H_2O content would be ten molecules (14 OH groups correspond to seven H_2O molecules), which is 9.20 wt % fully corresponding to STA data (9.17 wt %). The above crystal chemical formula would be as follows in the classical view for titanosilicates:

$$[Na(Sr_{0.5}Ca_{0.5})Mg]_{3}[Fe_{8.0}^{3+}Mn(Fe_{0.5}^{2+}\Box_{0.5})]_{10}(Ti_{2}Si_{12})O_{37}(OH)_{14}(H_{2}O)_{3}$$

The coordinates of atoms in the structure of caryochroite are determined in the ATOMS program within the spatial group P2/n, which suggests multiples of the general position xyz of four atoms and mul-

tiples of certain positions in the symmetrical centers and on axis 2 (which follows along the direction [010] at the levels of 0.25, *y*, 0.25 and 0.25, *y*, -0.25) of two atoms. In accordance with this, four octahedral Fe³⁺

cations were located in general positions, whereas the Mn^{2+} and $(Fe_{0.5}^{2+}\Box_{0.5})$ cations were localized in the symmetrical centers. All tetrahedral Si⁴⁺ cations and Ti atoms, as well as O atoms (excluding O19) and OH groups of the HOH layer, occupy general positions, whereas atom O19, which connected two octahedra around Ti atoms, is located on axis 2 (Fig. 4, Table 2).

The Na⁺, Mg²⁺, and statistically distributed $(Sr_{0.5}Ca_{0.5})^{2+}$ cations, eight OH groups, and three H₂O molecules should be positioned in the channels, which follow along short translation *b*. Because within the chosen spatial group there are only two particular positions in the channels (0.25, *y*, 0.25 and 0,25, *y*, -0.25) with multiples of 2, the localization of Na⁺ in a particular position and two-valent cations in the general position is most warranted. Similarly, the OH groups were placed in particular positions (with multi-

Fig. 4. Crystal structure of caryochroite: a, in the projection along axis *b*; b, configuration of the H-net.

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ples of 4) mostly in coordination of nonstructural cations.

During STA, dehydroxilization of caryochroite occurs in three stages upon heating (Fig. 5). The mass loss on thermogravimetric (TG) curves at a temperature of $<130^{\circ}$ C is explained by surface-related water and is ignored in the chemical composition. The OH groups are removed from structural channels in the temperature range of 130–250°C, which is 2.76%. The higher temperatures lead to the removal of OH groups, which occur in the coordination of cations in the channels (6.18%). The OH groups, which are incorporated in the coordination of octahedral cations (0.77%), are removed at the highest temperatures, which results in the full decomposition of the structure and formation of the Fe₃O₄, TiO₂, and SiO₂ phases. The exothermal peaks with maxima at 731.9, 766.8, and 809°C on the differential scanning calorimetry curve are related to the recrystallization and formation of these phases. The weight addition on the TG curve (0.35%) indicates the oxidation of newly formed phases and supports their presence.

DISCUSSION

The crystal structure determined for carvochroite (Table 2, Fig. 5) is based on the theoretically calculated XRD data (d (calc), I(calc)), which are in agreement with the experimental data (Table 1). The interatomic distances in the structure match the limits typical of the structures of other silicates. In tetrahedra H-nets, the Si–O distances are within 1.600–1.649 Å and the longest Si-O distances are confined to O atoms included in the coordination of Ti atoms. In the octahedra around Ti atoms, the Ti-O distances in the equatorial plane (with the O-tetrahedra atoms) occur within 2.005-2.027 Å, whereas the distances with O atoms, which are incorporated in the coordination of octahedral cations, and O atoms, which are common for the neighboring two Ti octahedra, these distances are much longer: 2.304 and 2.390 Å, respectively.

In the octahedral net of the HOH layer, the interatomic Fe³⁺–O and Mn²⁺–O distances are within 2.066–2.264 Å and the longest contacts (2.219–2.264 Å) correspond to O atoms, which are also included in Ti coordination. In octahedra occupied by Fe²⁺ cations only for 50%, the Fe–O distances are 2.148–2.159 Å. Due to strong repulsion, the lateral octahedra edges of high-charged cations are much shorter than the basal edges.

The Na⁺ cations located in the structural channels are surrounded by two OH₆ groups at a distance of 2.310 Å, whereas the statistically distributed $(Sr_{0.5}Ca_{0.5})^{2+}$ and Mg²⁺ cations, which occupy the same position, are coordinated by OH₄ and OH₅ groups at distances of 2.081 and 2.274 Å. The H₂O molecules and the OH₇ group are not incorporated in the coordination of nonstructural cations and are con-





Fig. 5. Thermal curves of caryochroite: TG, thermogravimetric; DSC, differential scanning calorimetry; DTG, differential thermogravimetry.

nected with atoms of the OH-net and other OH groups in the channels by weak H bonds.

The three-layered HOH blocks are combined into one structure by only the O19 atom, which connects two neighboring TiO_6 octahedra. Weak interlayer interaction is responsible for the fine-dispersive state of the caryochroite samples and the absence of even very small crystals, whereas structurally similar natural nafertisite occurs as the finest acicular crystals, which allow the qualitative microdiffraction patterns.

CONCLUSIONS

The structures of carvochroite and nafertisite are a new type of HOH layers with distinct and more volumetric H-net of the idealized composition of Ti₂Si₁₂O₃₇ in comparison with previously known titanosilicates. The significant difference of the carvochroite structure is related to the large diameter of the structural channels and numerous water components in them (OH groups and H₂O molecules). These peculiarities are first caused by the presence of highly charged Fe³⁺ cations in the octahedral net. In contrast other Lovozero titanosilicates. to carvochroite is the lowest temperature and probably the latest mineral. Its crystal structure, which is first resolved, is responsible for the large structural channels able to incorporate the exchange cations and abundant water components and demonstrates the unique state of caryochroite and possible synthesis of titanosilicates with sorption properties.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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