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STRUCTURE OF INORGANIC COMPOUNDS

Crystal Structure of New Micalike Titanosilicate—Bussenite, $Na_2Ba_2Fe^{2+}[TiSi_2O_7][CO_3]O(OH)(H_2O)F$

H. Zhou*, R. K. Rastsvetaeva, A. P. Khomyakov***, Z. Ma****, and N. Shi******

** China University of Geosciences, Wuhan, 430074 China*

*** Shubnikov Institute of Crystallography, Russian Academy of Sciences, Leninskiĭ pr. 59, Moscow, 117333 Russia*

e-mail: rast@ns.crys.ras.ru

**** Institute of Mineralogy, Geochemistry, and Crystal Chemistry of Rare Elements, ul. Veresaeva 15, Moscow, 121357 Russia*

***** China University of Geosciences, Beijing, 100083 China*

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Abstract—The crystal structure of mineral bussenite, $Na_2Ba_2Fe[TiSi_2O_7][CO_3]O(OH)(H_2O)F$, found in the Khibiny massif (the Kola Peninsula) has been determined. The parameters of the triclinic unit-cell are a = 5.399(3) Å, b = 7.016(9) Å, c = 16.254(14) Å, α = 102.44(8)°, β = 93.18(6)°, γ = 90.10(7)°, sp. gr. $P\bar{1}$, R = 0.054 for 1418 reflections with $|F| > 2.5\sigma(F)$. The mineral studied belongs to the family of layered titanosilicates, in which, unlike the sulfate- and phosphate-containing representatives of this family, the interlayer spaces are filled with carbonate groups. © *2002 MAIK "Nauka/Interperiodica".*

A peculiar group of natural compounds crystallizing from derivates of nepheline–syenite magmas highly supersaturated with alkaline and volatile components includes hybrid minerals with the structures consisting of alternating blocks of essentially silicate and salt compositions [1, 2]. We studied the crystal structure of the new mineral, bussenite [2–4], the first carbonate-containing representative of this group.

Bussenite was discovered in a sodalite–natrolite–calcite veinlet from the Khibiny alkaline massif (the Kola Peninsula). The mineral occurs as curved yellowish-brown micalike platelets 2–5 cm in length and 0.5 mm in thickness. The mineral is characterized by perfect cleavage along the (001) plane and moderate cleavage along the (110) and (1–10) planes. Both visually and in a microscope, bussenite resembles high-barium lamprophyllite Na(Sr, Ba)(Ti, Fe)Ti$[Si_2O_7]$(O, $OH)_2$ [5]. However, the new mineral differs from the latter by a number of characteristic features. In particular, the IR spectrum of the new mineral has absorption bands at 1410 and 1445 cm^{-1} attributed to vibrations of carbonate groups. The chemical composition of bussenite corresponds (the cation sum is 8; Z = 2) to the empirical formula $(Na_{1.94}K_{0.09})(Ba_{1.25}Sr_{0.44}Ca_{0.19})(Fe^{2+}_{0.63}Mn_{0.44}) \cdot (Ti_{0.97}Nb_{0.05}) \cdot Si_2O_{7.27}(CO_3)_{0.87}(OH)_{2.89}F_{0.98}$.

The investigation of the mineral structure was hindered by the absence of a single crystal suitable for X-ray diffraction analysis. Finally, the collaborative study undertaken by Russian and Chinese researchers was crowned with the first results of the structure investigation of bussenite reported earlier [3]. The X-ray diffraction study performed on an automated single-crystal AFC5R diffractometer demonstrated that the mineral possesses the triclinic structure, which was solved by the Patterson methods and refined within the acentric sp. gr. $P1$ to R = 0.070 by the SHELXL93 program package. Thus, the structural motif of the mineral and its general crystallochemical formula were established. However, the formula contradicted a number of essential details of the chemical analysis.

The subsequent refinement of the structure based on the construction of mixed scattering curves for some cationic positions was performed using the AREN program [6]. This allowed us to remove the above-mentioned inconsistencies and to obtain the adequate crys-

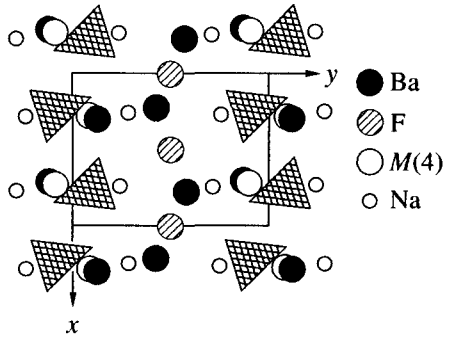

Fig. 1. A bussenite layer having the salt composition projected onto the (001) plane; CO_3 groups are shown by hatched triangles; large cations are indicated by circles.

Table 1. Structural data and details of X-ray diffraction study

Characteristic	Value
Unit-cell parameters, Å, deg	$a = 5.399(3)$, $b = 7.016(9)$, $c = 16.254(14)$, $\alpha = 102.44(8)$, $\beta = 93.18(6)$, $\gamma = 90.10(7)$
Unit-cell volume, Å^3	$V = 600.3$
Sp. gr.; Z	$P\bar{1}$; 1
Density ρ_{exp}, ρ_{cal}, g/cm^3	3.63(2), 3.65
Hardness	4
Radiation; λ, Å	MoK_α; 0.71073
Crystal dimensions, mm	$0.2 \times 0.15 \times 0.1$
Diffractometer	AFC5R
Scan mode	$\omega/2\theta$
$\sin\theta/\lambda$	0.807
Ranges of the indices of measured reflections	$-8 < h < 8$, $-11 < k < 10$, $0 < l < 25$
Total number of reflections	4487
Number of independent reflections	1418 $\|F\| > 2.5\sigma(F)$
R-factor upon anisotropic refinement	0.054
Program for absorption correction	AREN [6]

Table 2. Atomic coordinates, equivalent thermal parameters, multiplicities (Q), and occupancies of the positions (q)

Atom	x/a	y/b	z/c	B_{eq}, Å^2	Q	q
Si(1)	0.1911(7)	0.0583(5)	0.6684(2)	0.76(6)	2	1
Si(2)	0.8083(7)	0.3887(5)	0.3315(2)	0.81(6)	2	1
Ti	0.6951(4)	0.3449(3)	0.6897(1)	0.87(4)	2	1
M(1)	0.0073(5)	0.2513(4)	0.5030(1)	0.65(4)	2	1
M(2)	0.5	0	0.5	0.75(7)	1	1
M(3)	0.5	0.5	0.5	0.53(6)	1	1
M(4)	0.2789(7)	0.0938(6)	0.1870(2)	2.50(6)	2	0.53(2)
Ba(1)	0.2234(2)	0.4246(1)	0.8493(1)	1.80(3)	2	1
Ba(2)	0.2933(3)	0.1222(2)	0.2449(1)	1.56(4)	2	0.47(2)
Na(1)	0.733(4)	0.243(2)	0.9527(8)	3.1(3)	2	0.50(2)
Na(2)	0.251(3)	0.289(2)	0.0461(8)	2.4(2)	2	0.50(2)
C	0.758(6)	0.052(3)	0.106(1)	4.6(4)	2	1
F(1)	0.5	0.5	0	3.7(2)	1	1
F(2)	0	0.5	0	5.7(2)	1	1
O(1)	0.957(2)	0.165(1)	0.7119(6)	1.0(2)	2	1
O(2)	0.045(2)	0.451(2)	0.2870(6)	1.4(2)	2	1
O(3)	0.555(2)	0.450(2)	0.2863(6)	1.4(2)	2	1
O(4)	0.449(2)	0.162(2)	0.7134(6)	1.7(2)	2	1
O(5)	0.800(2)	0.150(2)	0.3044(8)	2.0(2)	2	1
O(6)	0.180(2)	0.032(2)	0.5690(6)	2.2(2)	2	1
O(7)	0.822(2)	0.460(2)	0.4302(6)	2.5(2)	2	1
O(8)	0.677(2)	0.292(2)	0.5809(6)	1.7(2)	2	1
O(9)	0.154(5)	0.097(3)	0.902(1)	9.6(2)	2	1
O(10)	0.889(4)	0.213(2)	0.106(1)	7.9(2)	2	1
O(11)	0.555(4)	0.138(3)	0.095(1)	9.4(2)	2	1
OH	0.338(2)	0.215(2)	0.4314(7)	1.8(2)	2	1
H_2O	0.719(2)	0.417(2)	0.8360(9)	2.7(2)	2	1

Table 3. Characteristics of the coordination polyhedra

Position	Composition, $Z = 1$	Coordination number	Distance K–A, Å	
			range	average
Si(1)	2Si	4	1.58–1.63	1.60
Si(2)	2Si	4	1.57–1.63	1.60
Ti	1.9Ti + 0.1Nb	6	1.72–2.31	1.98
M(1)	1.0Na + 0.55Mn + 0.45Fe	6	2.17–2.28	2.24
M(2)	0.5Fe + 0.4Na + 0.1Mn	6	2.09–2.35	2.22
M(3)	0.5Na + 0.4Fe + 0.1Mn	6	2.11–2.33	2.22
M(4)	0.64Sr + 0.42Ca	7	2.23–3.02	2.82
Ba(1)	1.6Ba + 0.4K	11	2.57–3.21	2.80
Ba(2)	0.94Ba	9	2.61–3.21	2.81
Na(1)	1.0Na	7	2.22–3.01	2.57
Na(2)	1.0Na	6	2.16–2.49	2.32
C	2C	3	1.13–1.33	1.22

tallochemical formula of bussenite (Z = 1): $\{Na_2(Ba_{2.54}Sr_{0.64}Ca_{0.42}K_{0.40})[CO_3]_2F_2\}\{Na_{1.90}Fe_{1.35}Mn_{0.75}\cdot (OH)_2[(Ti_{1.9}Nb_{0.1})(Si_2O_7)_2]O_2 \cdot (H_2O)_2\}$. In this formula, the compositions of the salt and titanosilicate blocks are given in braces. The main characteristics of the crystal and the details of the X-ray diffraction study are listed in Table 1. The atomic coordinates corresponding to the final value R = 0.054 (the absorption was ignored) for the centrosymmetric structure are listed in Table 2. The main characteristics of polyhedra are presented in Table 3.

The refinement within the acentric space group resulted in the correlation between the thermal parameters of the atoms related by an inversion center and resulted in a slightly lower R factor and revealed no ordering in the sites characterized by mixed compositions.

As can be seen from Figs. 1, 2, and 3, large Ba cations occupy two positions. One of these positions, is also filled with K atoms. The distance between the Ba(2) position and the M(4) (Sr,Ca)-position is 0.917(4) Å. The Na atoms also occupy two positions with 50% occupancy. The possible distribution of the Mn atoms over three octahedral positions, M(1)–M(3), corresponds to the average cationic radii in these positions. The F^{1-} ions occupy the inversion centers in the interlayer space. The O, F, OH, and H_2O were distributed over fluorine and oxygen positions based on the calculated local balance of valence strengths at the anions. The water molecule participates in the distorted octahedral coordination of the Ti atom. The distance from the Ti atom to this water molecule equals 2.31 Å, whereas the distance of this Ti atom to the O atom at opposite vertex is shortened (1.72 Å). Such a distortion of the Ti-octahedron allows one to consider it as a pseudopentagonal pyramid and, thus, to relate this mineral to lamprophyllite [5] and monoclinic astrophyllite [7]. In the latter two minerals, Ti atoms have the coordination number five.

Bussenite belongs to the family of titanosilicate micas [8] or, according to the nomenclature proposed in [9], to heterophyllotitanosilicates. The structures of these minerals consist of triple layers responsible for the constant values of the a- and b-parameters of the

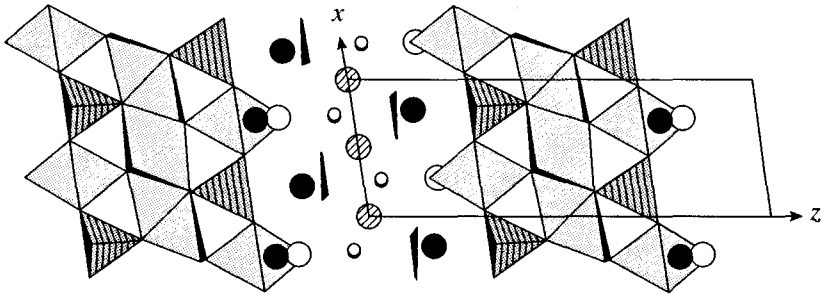

Fig. 2. Bussenite structure projected onto the (010) plane; Si_2O_7-diortho groups are hatched with solid lines; CO_3 groups are represented by black triangles; cations are indicated by circles (for description, see Fig. 1).

unit cell. The middle layer in the bussenite structure consists of the close-packed (Na,Fe,Mn)-octahedra; the side layers are composed by Ti-octahedra and $[Si_2O_7]$-diortho groups. The latter groups have the standard Si–O bond lengths, and the Si(1)–O(5)–Si(2) angle characterizing rotation of tetrahedra equals 149.3(8)°. The character of filling of the space between the triple layers, which determines the *c*-parameter of the unit cell, in the minerals of this group is essentially different. Comparing the formulas of bussenite and heterophyllotitanosilicates such as lomonosovite $\{2NaPO \cdot Na_2\}\{Na_2Ti_4Si_4O_{18}\}$ [10] and innelite $\{2BaSO_4(Ba, K)_2\}\{(Na, Ca)_3Ti_3Si_4O_{18}$ [11], we see that compositions of the interlayer considerably differ (the first fragment enclosed in braces). The $[CO_3]^{2-}$ group found in bussenite is the new specific component of this fragment.

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