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Crystal Structure of Calcioburbankite and the Characteristic Features of the Burbankite Structure Type

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Abstract—The crystal structure of calcioburbankite $(Na,Ca)_3(Ca,RE,Sr,Ba)_3(CO_3)_5$ found in carbonatites from Vuoriyarvi (North Kareliya) was solved by the Rietveld method. The experimental data were collected on an ADP-2 diffractometer (λCuK_α radiation; Ni filter; $16.00° < 2\theta < 130.00°$; the number of $(\alpha_1 + \alpha_2)$ reflections was 455). All the calculations were performed within the sp. gr. $P6_3mc$; $a = 10.4974(1)$ Å, $c = 6.4309(1)$ Å, $V = 613.72(1)$ Å^3; $R_{wp} = 2.49\%$. The structure was refined with the use of the anisotropic thermal parameters for the (Na,Ca) and (Sr,Ba,Ce) cations. The comparison of the crystal structures of all of the known hexagonal representatives of the burbankite family demonstrates that the burbankite structure type (sp. gr. $P6_3mc$) is stable, irrespectively of the occupancy of the ten-vertex polyhedra predominantly with Ca, Sr, or Ba cations and the occupancies of the positions in the eight-vertex polyhedra. *© 2001 MAIK "Nauka/Interperiodica".*

INTRODUCTION

Calcioburbankite $(Na,Ca)_3(Ca,RE,Sr,Ba)_3(CO_3)_5$ belongs to the burbankite family comprising hexagonal and pseudohexagonal monoclinic carbonates described by the general formula $A_{3-4}B_{2-3}(CO_3)_5$, where A = Na, Ca, or □ and B = Sr, Ba, RE, or Ca (or, sometimes, Na). In calcioburbankite, the position B is predominantly occupied by calcium. This mineral was discovered in 1995 in alkaline hydrothermolites from Saint-Élier (Quebec, Canada) [1]. The structure of the mineral has not been studied as yet.

Calcioburbankite found in carbonatites from the Vuoriyarvi alkaline ultrabasic massif (North Kareliya) was characterized mineralogically in 1999 [2]. In this study, we determined the crystal structure of the mineral by the Rietveld method.

EXPERIMENTAL

The mineral under study originates from calcite carbonatites and occurs in associations with dolomite, phlogopite, apatite, sulfides, and some other minerals. Calcioburbankite exists in the form of massive granular greenish-yellow aggregates. Under hydrothermal conditions, calcioburbankite is unstable and is readily replaced by calcite, ancylite-(Ce), barite, strontianite, and other mineral aggregates.

The cationic composition of calcioburbankite (Table 1) was studied by X-ray spectral analysis by the analyst Ya.A. Pakhomovskiĭ on a Cameca MS 46 instrument at the Institute of Geology of the Kol'skiĭ Research Center of the Russian Academy of Sciences, Apatity.

The X-ray spectrum of a powdered sample was obtained on an ADP-2 diffractometer (λCuK_α radiation; Ni filter; $16.00° < 2\theta < 130.00°$; 2θ scanning technique; 0.02° per scan step; the exposure time 15–20 s; the number of $(\alpha_1 + \alpha_2)$ reflections 455). All the computations were performed by the WYRIET program (version 3.3) [3] within the sp. gr. $P6_3mc$. We used as the starting model the crystal structure of burbankite found in hydrothermolites from the Kukisvumchorr mountain (the Khibiny massif, the Kola Peninsula) [4]. The ionic scattering curves were used. The peak profiles were approximated by the Pearson VII function with 6FWHM. The asymmetry was refined for $2\theta < 40°$. The refinement was carried out by adding gradually the parameters to be refined with the continuous automatic modeling of the background until the moment when the R factors attained the constant values. The isotropic refinement converged to the R_{wp} factor = 2.56%.

Some characteristics of the data collection and the results of the calcioburbankite structure refinement with the anisotropic (the A and B cations) and isotropic (the oxygen and carbon atoms) thermal parameters are listed in Table 2. The experimental (solid line) and calculated (dots) X-ray spectra of the mineral are shown in the figure. The atomic coordinates, the isotropic ther-

Table 1. Unit-cell parameters and the cationic compositions of structurally studied minerals of the burbankite family

Characteristic	Calcioburbankite	Burbankite (low-rare-earth)	Burbankite	Burbankite	Burbankite	Khanneshite	Remondite-(Ce)	Petersenite-(Ce)
Sp. gr.	$P6_3mc$	$P6_3mc$	$P6_3mc$	$P6_3mc$	$P6_3mc$	$P6_3mc$	$P2_1$	$P2_1$
a_0, Å	10.4974(1)	10.5263(1)	10.5313(1)	10.52(4)	10.512(2)	10.5790(1)	10.412(4)	20.872(4)
b_0, Å	10.4974(1)	10.5263(1)	10.5313(1)	10.52(4)	10.512(2)	10.5790(1)	10.414(4)	10.601(2)
c_0, Å	6.4309(1)	6.5392(1)	6.4829(1)	6.51(2)	6.492(2)	6.5446(1)	6.291(3)	6.367(1)
β, deg	120	120	120	120	120	120	119.80(5)	120.50(1)*
V_0, Å^3	613.72(1)	627.49(1)	622.68(1)	–	621.3	634.31(1)	591.9	1213.9(4)
Z	2	2	2	2	2	2	2	4
Cationic composition, wt %								
Na_2O	13.27	8.51	10.61	11.44	8.34	11.86	17.16	17.38
CaO	10.80	10.04	6.96	10.86	11.47	5.37	10.54	1.32
SrO	8.44	36.28	33.73	12.86	25.08	9.04	3.98	1.70
BaO	11.36	9.91	7.92	11.62	11.47	22.99	–	0.32
Y_2O_3	–	0.48	0.57		<0.03	–	0.24	–
La_2O_3	6.17	1.32	2.94	–	3.37	4.07	11.60	14.49
Ce_2O_3	10.86	0.44	5.74	–	5.39	10.46	14.99	23.66
Pr_2O_3	0.58	–	0.45	–	0.46	1.01	1.49	2.00
Nd_2O_3	2.56	–	1.36	–	1.26	3.60	3.34	5.82
Sm_2O_3	–	–	–	–	0.14	–	0.50	0.60
$\Sigma(RE_2O_3)$	(20.17)	(1.76)	(10.49)	15.12	(11.08)	(19.14)	(32.394)	(46.57)
Total	64.04	66.98	70.28	64.96**	67.47***	68.40	64.314****	67.29
References	Present study	Belovitskaya *et al.*, 2000 [4]	Belovitskaya *et al.*, 2000 [4]	Voronkov and Shumyatskaya, 1968 [6, 10]	Effenberger *et al.*, 1985 [5]	Belovitskaya *et al.* (in press)	Ginderow, 1989 [7, 10]	Grice *et al.*, 1994 [8]

Note: * In the original study, b_0 and c_0 are interchanged. The analysis showed additionally (wt %): ** K_2O, 0.99; MgO, 0.35; Al_2O_3, 1.05; Fe_2O_3, 0.48; SiO_2, 0.19; *** Gd_2O_3, 0.41; Tb_2O_3, 0.05; **** Eu_2O_3, 0.09; Gd_2O_3, 0.24; Dy_2O_3, 0.07; Ho_2O_3, 0.01; Er_2O_3, 0.03; Yb_2O_3, 0.03; Lu_2O_3, 0.004.

Table 2. Characteristics of the refinement of the crystal structure of calcioburbankite by the Rietveld method

Characteristic	Value	Characteristic	Value
Sp. gr.	$P6_3mc$	R_{exp}	6.92
2θ scanning range, deg	16.00–130.00	R_B	3.35
Number of reflections	455	R_F	2.98
Number of parameters in the refinement	54	s*	0.36
R_p	1.88	DWD**	1.33
R_{wp}	2.49	σ_x^{***}	1.384

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

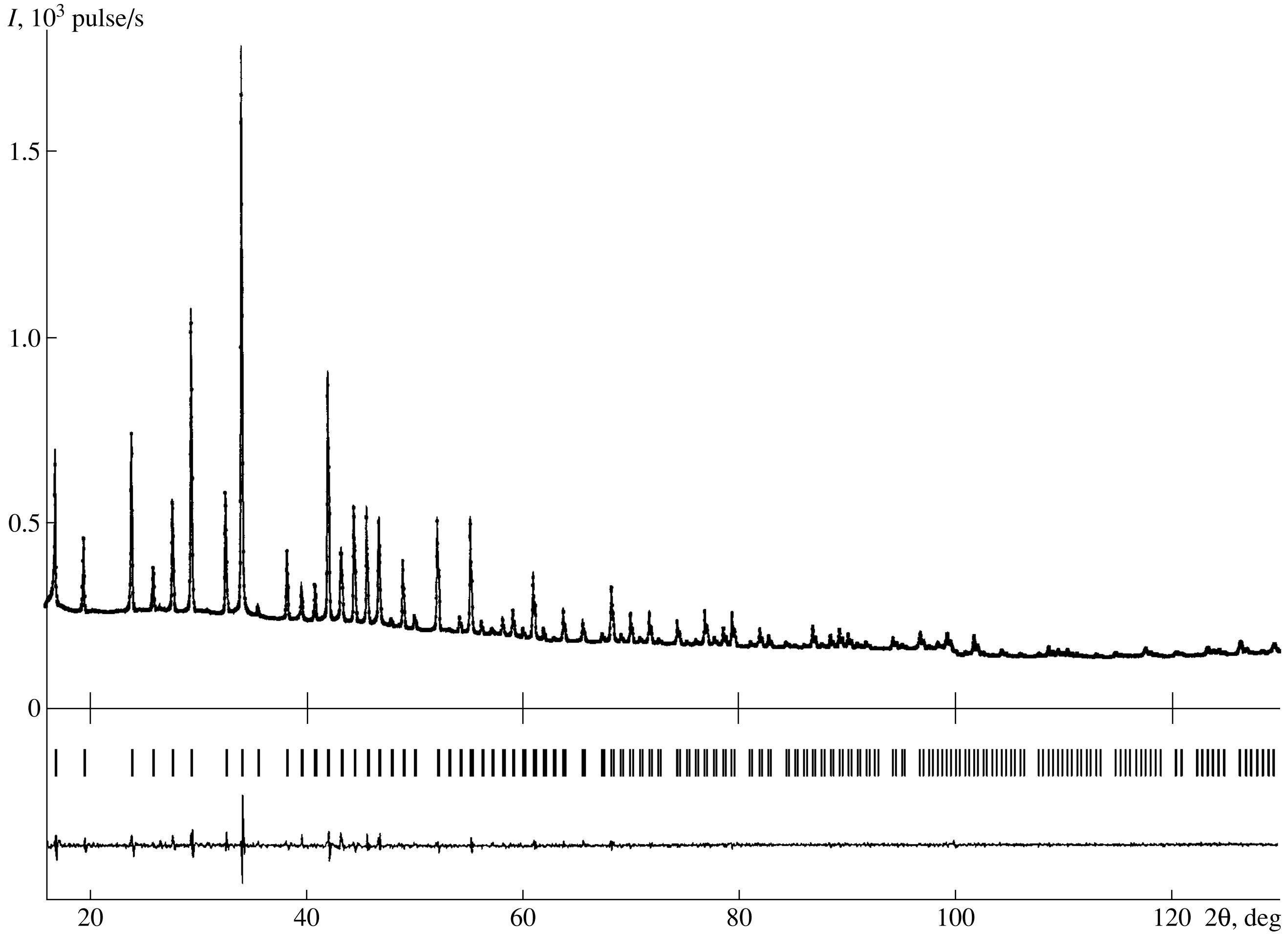
** The Durbin–Watson statistics [11].

*** The multiplier for calculations of standard deviations [12].

mal parameters, and the occupancies of the positions in the calcioburbankite structure are listed in Table 3.

RESULTS AND DISCUSSION

Similar to the burbankite structure [5, 6], the crystal structure of calcioburbankite contains two independent cationic positions in the centers of eight- and ten-vertex polyhedra (*A* and *B*, respectively) formed by oxygen atoms and three types of triangular carbonate groups denoted as C(1), C(2), and C(3) having different orientations. The average distances in the polyhedra are as follows: *A*–O is 2.51 Å; *B*–O is 2.67 Å; and C(1)–O, C(2)–O, and C(3)–O are 1.23, 1.36, and 1.28 Å, respec-



Experimental (solid line) and calculated (dots) X-ray spectra of calcioburbankite.

Table 3. Structural and thermal parameters (Å^2) and occupancies of positions in the structure of calcioburbankite

Atom	Characteristic	Value	Atom	Characteristic	Value
A	x	0.5241(6)	C(2)	z	0.88(1)
	y	0.4759(6)		B_j	1(1)
	z	0.317(2)	C(3)	x	0.3333
	B_j	1.4(2)		y	0.6667
	q (Na)	2.22(2)		z	0.49(2)
	q (Ca)	0.48(1)		B_j	2(1)
	q (*RE*)*	0.09(1)	O(1)	x	0.376(1)
B	x	0.8406(1)		y	0.088(2)
	y	0.1594(1)		z	0.633(2)
	z	0		B_j	1.1(4)
	B_j	1.01(9)	O(2)	x	0.926(1)
	q (*RE* + Ba)*	1.17(1)		y	0.074(1)
	q (Ca)	0.94(1)		z	0.344(4)
	q (Sr)	0.54(1)		B_j	1.8(6)
	q (Na)	0.43(1)	O(3)	x	0.4037(8)
				y	0.5963(8)
C(1)	x	0.797(2)		z	0.476(7)
	y	0.203(2)		B_j	0.5(4)
	z	0.55(1)	O(4)	x	0.776(1)
	B_j	5(2)		y	0.224(1)
C(2)	x	0		z	0.359(5)
	y	0		B_j	1.8(6)

* All *RE* were refined with the use of the *f* curve of cerium.

tively. In calcioburbankite, the ten-vertex polyhedra are occupied predominantly by Ca. This is reflected in both unit-cell parameters of calcioburbankite (whose values are lower than those of burbankite). The *B* position is occupied by Ca, Sr, *RE*, and Ba and a small amount of Na. The incorporation of Na atoms into the ten-vertex polyhedra is typical of remondite, which is a monoclinic representative of the burbankite family [7]. However, unlike the positions in burbankite and khanneshite, the *A* position in the calcioburbankite structure, is occupied not only by Na and Ca, but also by a small amount of *RE* (Table 3). The presence of lanthanides in the *A* position in the minerals of this structure type is observed for the first time. The refinement of the structure based on the standard model containing only Na and Ca atoms in the eight-vertex polyhedra resulted in the unreasonable thermal parameters for these cations. The calcioburbankite formula established by the X-ray diffraction analysis is $(Na_{2.23}Ca_{0.49}RE_{0.09})_{2.81}(Ca_{0.95}RE_{0.69}Sr_{0.55}Ba_{0.50}Na_{0.44})_{3.13}(CO_3)_5$ and somewhat differs from the formula $(Na_{2.87}Ca_{0.16})_{3.03}(Ca_{1.14}Sr_{0.55}Ba_{0.50}Ce_{0.44}La_{0.25}Nd_{0.10} \times Pr_{0.02})_{3.00}(CO_3)_5$ determined by the electron probe analysis. Most likely, this difference can be attributed to the variations in the composition of the specimen under study. Our and other well-known results demonstrate that the intraphase inhomogeneity is typical of the minerals of the burbankite group.

Minerals of the burbankite family crystallize in three structure types—burbankite (sp. gr. $P6_3mc$), remondite (sp. gr. $P2_1$; the unit cell is close to that of burbankite but with the angle γ being slightly different from 120°), and petersenite (sp. gr. $P2_1$ with the unit-cell parameter a_0 twice exceeding that of remondite) (Table 1). The crystal chemistry of the monoclinic representatives of this family has well been studied [7, 8], whereas the structures of the hexagonal representatives has been considered only in two articles [5, 6] devoted to burbankite with the *B* position occupied simultaneously by *RE*, Ca, and Sr. We noticed that the powder X-ray diffraction patterns of burbankites of various compositions essentially differ from one another [4], which gives the impetus to their systematic study. We compared burbankite with the typical composition with low-rare-earth burbankite [4], khanneshite (a barium analog of burbankite), and calcioburbankite. All these minerals appear to be isostructural and differ only in the nature of the divalent cations (Sr, Ba, or Ca) occupying mainly the *B* position. Therefore, the burbankite structure type is very stable and is retained as long as the *B* position is occupied mainly by divalent cations of different sizes. This structure type persists over a wide range of the RE^{3+}/M^{2+} ratios from the terminal member $(Na_2,Ca)(Sr,Ca,Ba)_3(CO_3)_5$ [4], which is virtually free of rare-earth elements, to, at least, calcioburbankite of the composition $(Na_{2.2}Ca_{0.5}RE_{0.1})_{2.8}$ $(Ca_{1.0}RE_{0.7}Sr_{0.6}Ba_{0.5}Na_{0.4})_{3.2}(CO_3)_{5.1}$ with the highest content of rare-earth elements in all the structurally studied hexagonal representatives of this family. Only the presence of *RE* (in a type-forming amount) and, correspondingly, filling of the position *A* only with Na lowers the symmetry down to monoclinic because of the deviation of the angle γ from 120° [7]. The fact that the *A* position in the eight-vertex polyhedron is partial vacant (which was found by Effenberger *et al.* [5]), which was confirmed in our study [4], cannot prevent the formation of the burbankite structure type either.

Thus, the crystal structures of all the known hexagonal representatives of the burbankite family have been studied. These minerals form a continuous isomorphous series. In this respect, the burbankite structure type can be considered as unique, because all the Ca-, Sr-, and Ba-dominant phases are not only isostructural (the examples of this isostructurality are well known, (aragonite–strontianite–witherite), but also exhibit the complete isomorphous miscibility. Even in minerals, whose structures contain large cavities (zeolites and pyrochlores) and where divalent cations are present in type-forming amounts, no ratio of the type Ca : Sr : Ba ≈ 1 : 1 : 1 was ever observed. Analysis of the known data demonstrates that the minerals containing simultaneously considerable amounts of Ba and Ca are characterized by their ordered distribution over different structural positions (double Ba,Ca-carbonates, wenkite, etc.). A substantial accumulation of Sr in calcium minerals or of Ba in strontium minerals often leads to the change of the structure type (the apatite group and olgite). The only exception is made by the hexagonal members of the burbankite family.

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