Crystal structure of a new bradleyite-group mineral Na$_3$Sr[PO$_4$](CO$_3$)

E. V. Sokolova and A. P. Khomyakov

M. V. Lomonosov State University, Moscow

(Submitted December 2, 1991)

A new Na, Sr-carbophosphate was discovered by A. P. Khomyakov in the Khibinskii alkaline massif. The microprobe data analysis and x-ray diffraction spectra of the mineral allowed us to assign the chemical formula Na$_3$Sr[PO$_4$](CO$_3$) to the mineral and to propose that it belongs to the bradleyite-group structural family comprising bradleyite Na$_3$Mg[PO$_4$](CO$_3$) (Ref. 1) itself, sidorenkite Na$_3$Mn[PO$_4$](CO$_3$) (Ref. 2), and bonshtedtite Na$_3$Fe[PO$_4$](CO$_3$) (Ref. 3). Of the three minerals the sidorenkite and bonshtedtite had been studied with regard to their structure; however, the close similarity of the infrared spectra, optical properties, and x-ray diffraction spectra for all three minerals allows us to conclude that they are fully isostructural.[3] The distinctiveness of the new mineral's optical properties and the considerable difference in the size of its double-valent cations indicate that the mineral may be structurally different from the other three.

The parameters of the monoclinic unit cell were determined with the automatic diffractometer P$\bar{1}$ Sinteks using 11 reflections for angles $10 \leq \theta \leq 27°$, and are given by $a = 9.817(3)$, $b = 5.279(1)$, $c = 6.707(2)$ Å, and $\gamma = 89.98(3)°$. The intensities of 474 independent nonzero ($I \geq 1.96\sigma I$) reflections were measured with the same diffractometer using a crystal with linear dimensions $0.1 \times 0.125 \times 0.150$ mm by the $2\theta{:}\theta$ method, and scanning at the rate of 3–12° per minute (MoK_α, s in$\theta/\lambda \leq 0.880$Å^{-1}). The conversion of measured intensities into the structural amplitude moduli, disregarding the absorption ($\mu r_{max} = 1.37$), and all subsequent calculations were performed using the INEXTL code.[4] The analysis of regular extinctions for the measured intensity set indicated that two space groups may exist: $P2_1/m$ and $P2_1$. The interpretation of the mineral's structure was accomplished using the Patterson method initially for the space group $P2_1/m$. The presence of short interatomic anion–anion distances forced us to lower the symmetry, so that structural studies were continued for the space group $P2_1$. The refinement of all structural models for the crystal of incorrect form, taking into account absorption correction and using the DIFABS software code in the full-matrix anisotrop-
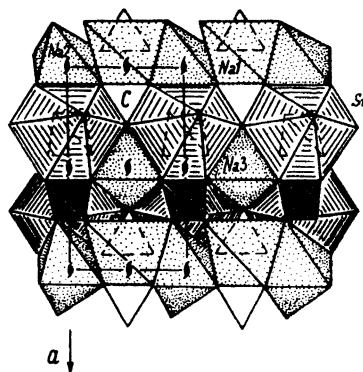

FIG. 1. Projection of the Na$_3$Sr[PO$_4$](CO$_3$) structure onto the (001) plane.

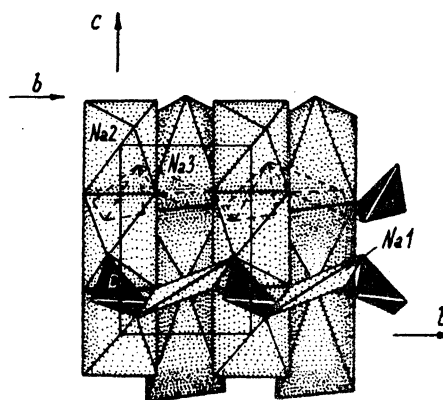
FIG. 2. Projection of a fragment of the Na$_3$Sr[PO$_4$](CO$_3$) structure onto the (100) plane. The figure shows the linking of several types of Na polyhedra.

ic approximation, led to $R_{hkl} = 0.040$, $R_w = 0.039$, and $s = 1.51$. The coordinates of basis atoms and interatomic distances for the Na, Sr-carbophosphate structure are given in Tables I and II. As assumed, the structural formula for the new

TABLE I. Coordinates and Equivalent Thermal Corrections (Å)^2 of the Basis Atoms

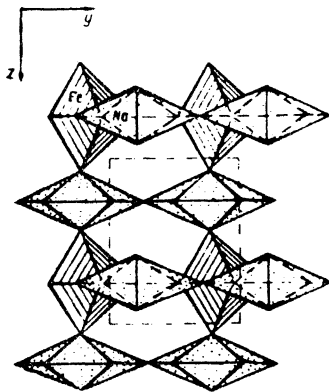| Atom	x/a	y/b	z/c	B_{equ}
Sr	0,6764 (2)	−0,0003 (3)	0,25	1,10 (3)
P	0,3305 (5)	−0,0001 (8)	0,254 (2)	0,58 (7)
Na 1	0,1584 (9)	0,498 (1)	0,236 (4)	3,4 (3)
Na 2	0,006 (2)	−0,006 (6)	0,006 (3)	3,3 (2)
Na 3	0,4658 (7)	0,501 (2)	0,456 (1)	1,3 (2)
C	0,154 (2)	0,508 (3)	0,773 (0)	3,1 (7)
O1	0,705 (1)	0,493 (2)	0,270 (4)	1,8 (3)
O2	0,915 (1)	0,290 (2)	0,246 (7)	3,9 (5)
O3	0,235 (1)	0,143 (3)	0,105 (2)	1,9 (4)
O4	0,427 (1)	0,805 (2)	0,156 (2)	2,2 (4)
O5	0,917 (1)	0,711 (2)	0,255 (7)	4,2 (5)
O6	0,426 (1)	0,197 (2)	0,153 (2)	1,5 (3)
O7	0,762 (1)	0,137 (2)	0,911 (2)	1,2 (3)

FIG. 3. Projection of a fragment of the bonshtedtite structure onto the (100) plane. The figure shows the linking of Na octahedra across a low-density Na layer.

mineral is $Na_3Sr[PO_4](CO_3)$ (space group $P2_1$, $Z = 2$, ρ_{calc} = 3.18 gm/cm³, ρ_{exp} = 3.05 gm/cm³. The lower value of ρ_{exp} is due to crystal imperfections of the mineral, which typically has a large number of voids and fissures.

Next we considered the cation polyhedra inside the structure of the new mineral. Strontium atoms are surrounded by eight oxygen ligands at a distance of 2.54 Å to 2.67 Å and

by two other oxygen atoms 3.05 and 3.06 Å away from the Sr atom. Na1 atoms are tetrahedrally and Na2 and Na3 octahedrally surrounded by oxygen atoms, respectively. The interatomic distances in the P-tetrahedron agree closely with published values. The C atom is slightly displaced from the center of the triangle toward the O2 atom; i.e., from the edge O2-O5 = 2.22 Å that it shares with the Na1 tetrahedron. Correspondingly, in the Na1 tetrahedron we have d(Na1−O2, O5) > d(Na1−O3, O7). As a result of an analogous cation−cation interaction in the sidorenkite and bonshtedtite structures between the Mn^{2+} (Fe^{2+}) ions (coordination number = 6) and Cr^{4+} ions (coordination number = 3), there are also displacements from the common oxygen edge.

In the crystal synthesis of the discussed mineral, two types of massive layers parallel to the (100) direction may be distinguished (Fig. 1). The first layer, which is located on the $x \approx 0.08$ plane along the a axis, is formed by different types of Na polyhedra. The structure exhibits ribbons which are formed from Na2 octahedra joined along common edges (Fig. 2) and which extend along the c axis of the mineral's elementary unit cell; there ribbons are connected into a layer by discrete Na1 tetrahedra. The joining of Na1 and Na2 polyhedra also takes place at common edges d(O2−O3) = 3.19 and d(O5−O7) = 3.23 Å. In the structure of the bradleyite-group minerals, an Na layer which is comprised of only octahedra that are linked along the b axis, as shown in Fig. 3, may be identified.

The second layer of the Na, Sr-carbophosphate, consists of different types of polyhedra. The layer is based on a mixed $\{Na[PO_4](CO_3)\}^{4-}$ anion lattice comprised of Na3 octahedron columns, which are oriented along the 2_{1z} axis and which are rigidly linked along triangular faces (O1−O4−

TABLE II. Interatomic Distances (Å)

Sr-eight-vertex figure			Na1-tetrahedra	
Sr − 01	2,69(1)		Na1 − 02	2,50(1)
01'	2,62(1)		03	2,19(2)
02	2,67(1)		05	2,49(1)
03	2,62(1)		07	2,37(2)
04	2,59(1)		Mean	2,39
05	2,68(1)		$(0-0)_{av}$	3,61
06	2,61(1)			
07	2,52(1)			
Mean	2,63			
$(0-0)_{av}$	3.30			

Na2-octahedra			Na3-octahedra	
Na2 − 02	2,40(4)		Na3 − 01	2,53(2)
02'	2,41(4)		01'	2,63(3)
03	2.34(3)		04	2,60(2)
05	2,39(4)		04'	2,32(2)
05'	2,40(4)		06	2,61(2)
07	2,45(3)		06'	2,30(2)
Mean	2.40		Mean	2,50
$(0-0)_{av}$	3,33		$(0-0)_{av}$	3,54

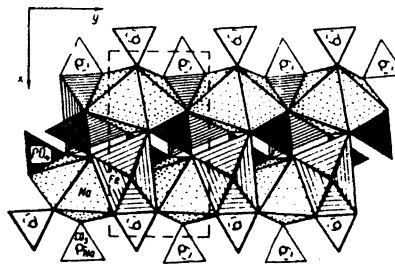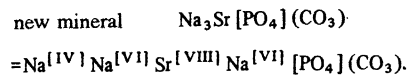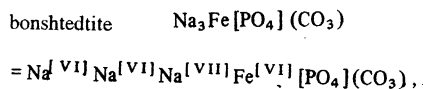| P-tetrahedra			C-triangle	
P − 03	1,53(2)		C− 01	1,29(2)
04	1,51(2)		02	1,25(2)
06	1,52(1)		05	1,33(2)
07	1,54(2)			
Mean	1,53		Mean	1,29
$(0-0)_{av}$	2,40		$(0-0)_{av}$	2,23

FIG. 4. Projection of a fragment of the bonshtedtite structure−the dense layer comprising seven-cornered Na polyhedra and Fe octahedra−onto the (001) plane.

TABLE III. Crystallometric Characteristics of Bradleyite-Group Minerals

Mineral	a, Å	b, Å	c, Å	γ	Space group
Sidorenkite Na₃Mn[PO₄](CO₃)	8,997(4)	5,163(2)	6,741(2)	90,16°	$P2_1/m$
Bradleyite Na₃Mg[PO₄](CO₃)	8,841(7)	5,117(6)	6,620(6)	90,42	$P2_1/m$
Bonshtedtite Na₃Fe[PO₄](CO₃)	8,8955(7)	5,149(3)	6,629(2)	90,45	$P2_1/m$
new mineral Na₃Sr[PO₄](CO₃)	9,187(3)	5,279(1)	6,707(2)	89,98(3)	$P2_1$

E. V. Sokolova and A. P. Khomyakov

O6), and of separate [PO$_4$] and (CO$_3$) anion radicals. Different types of polyhedra are joined at their vertices. The {Mn[PO$_4$](CO$_3$)}$^{3-}$ lattice may be identified in the sidorenkite. However, despite the similarity in their formulas, the sidorenkite structure is different. The Mn octahedra are separate (as are the Fe octahedra in bonshtedtite) and are connected to each other only with P tetrahedra, but the (CO$_3$) radicals link with Mn(Fe) polyhedra along common edges (Fig. 4). Large eight-cornered Sr polyhedra, which are connected at their vertices to form a chain along the b axis, border the central lattice at planes ~ 0.25 and 0.75 along the c axis, and the CO$_3$ triangles have two common ribs with Sr polyhedra: $d(O1-O2) = 2.21$ Å and $d(O1-O5) = 2.26$ Å.

The deciphering of the structure of the new natural carbophosphate serves as a graphic illustration of the key role of large cations in the formation of crystal structures. The parameters of the investigated crystal are insignificantly larger than the parameters of similar bradleyite-group minerals (Table III). The structural types of the bradleyite and of the investigated mineral are different. The large Sr atom ($r_{Sr}[VIII] = 1.25$ Å; Ref. 5) cannot serve as a replacement for the "color" cations Mn^{2+} (Fe^{2+}) ($r_{Mn}[VI] = 0.67$ Å, $r_{Fe}[VII] = 0.61$ Å), and is structurally closer to Na$^+$ ($r_{Na}[VIII] = 1.13$ Å). The structural formulas of the minerals may be compared as follows (here, bonshtedtite serves as a representative of the bradleyite-group minerals):

bonshtedtite   Na$_3$Fe[PO$_4$] (CO$_3$)

= Na$^{[VI]}$Na$^{[VI]}$Na$^{[VIII]}$Fe$^{[VI]}$[PO$_4$](CO$_3$),

new mineral   Na$_3$Sr [PO$_4$] (CO$_3$)

= Na$^{[IV]}$Na$^{[VI]}$Sr$^{[VIII]}$Na$^{[VI]}$[PO$_4$](CO$_3$).

The exchange of Na$^+$ for Sr^{2+}, with a parallel substitution of Fe^{2+} for Na$^+$, leads to a complete structural-type rearrangement of bradleyite into the Na, Sr carbophosphate structure, regardless of their similar parameters and a formal analogy between the two. A general characteristic of all the investigated minerals (Table III) is the unusual edge-linkage of the (CO$_3$) radicals with cationic polyhedra, i.e., the couplings with all three edges of the C triangle.

[1] J. J. Fakey, *U. S. Geol. Surv. Prof. Paper*, No. **405**, 1 (1962).

[2] T. A. Kurova, N. G. Shumyatskaya, A. A. Voronkov, and Yu. A. Pyatenko, *Mineral. Zh.* **2**, 65 (1980).

[3] Chin Tkhi Le Tkhy, T. N. Nabezhina, E. A. Pobedimskaya, and A. P. Khomyakov, *ibid.* **6**, 79 (1984).

[4] R. G. Gerr, A. I. Yanovskii, and Yu. T. Struchkov, *Kristallografiya* **28**, 1029 (1983) [*Sov. Phys. Crystallogr.* **28**, 609 (1983)].

[5] R. D. Shannon and C. T. Prewitt, *Acta Crystallogr.* **B25**, 925 (1969).

Translated by F. S.