THE CRYSTAL STRUCTURE OF NACAPHITE, Na₂Ca(PO₄)F: A RE-INVESTIGATION

Sergey V. Krivovichev[§]

Department of Crystallography, St. Petersburg State University, University Emb. 7/9, St. Petersburg 199034, Russia

Victor N. Yakovenchuk, Gregory Yu. Ivanyuk and Yakov A. Pakhomovsky

Geological Institute, Kola Science Center, Russian Academy of Sciences, Apatity 184209, Russia

Thomas Armbruster

Laboratorium für chemische und mineralogische Kristallographie, Universität Bern, CH–3102 Bern, Switzerland

Ekaterina A. Selivanova

Geological Institute, Kola Science Center, Russian Academy of Sciences, Apatity 184209, Russia

Abstract

The crystal structure of nacaphite, $Na_2Ca(PO_4)F$, has been re-investigated using an untwinned crystal from a late-stage hydrothermal vein within ijolite–urtite of the Khibiny alkaline massif, Kola Peninsula, Russia. In contrast to previous findings, which identified nacaphite as a pseudo-orthorhombic triclinic mineral, we have shown that nacaphite is monoclinic, $P2_1/c$, a 13.3185(14), b 7.0964(8), c 10.6490(11) Å, β 113.526(1)°, V 922.81(17) Å^3, $Z = 8$. The structure has been solved by direct methods and refined to R_1 0.034 for 1376 unique observed reflections. It contains two Ca and four Na positions. The Ca1 site is coordinated by two F$^-$ and five O^{2-} anions with Ca^{2+}–φ distances in the range of 2.32–2.57 Å. The Ca2 cation has six closest anions (two F$^-$ and four O^{2-}) with Ca^{2+}–φ bond lengths of 2.29–2.37 Å, and an additional remote O7 anion at 3.049 Å. All Na$^+$ cations are octahedrally coordinated by four O^{2-} and two F$^-$ anions each. The Ca^{2+} and Na^{2+} cations form cation arrangements parallel to the (100) plane and separated by F$^-$ anions and PO$_4^{3-}$ tetrahedra. The F$^-$ ions are coordinated by four Na$^+$ and two Ca^{2+} cations. The $(FNa_4Ca_2)^{7+}$ octahedra share faces to produce $[FNa_2Ca]^{3-}$ chains parallel to c. The overall topology of the structure is in agreement with the previous studies of the structure. However, there are two essential differences in schemes of order and local geometry of coordination: (1) the Ca^{2+} and Na$^+$ cations are completely ordered, and the respective sites are fully occupied; (2) the Ca^{2+} cations have seven-fold coordination of two different types, whereas Na$^+$ cations are octahedrally coordinated. The results of the new crystal-structure refinement of nacaphite are in agreement with the powder X-ray-diffraction pattern of this mineral.

Keywords: nacaphite, crystal structure, twinning, Kola Peninsula, Russia.

Sommaire

Nous avons ré-examiné la structure cristalline de la nacaphite, $Na_2Ca(PO_4)F$, en utilisant un monocristal non maclé provenant d'une veine hydrothermale tardive recoupant ijolite et urtite dans le massif alcalin de Khibiny, péninsule de Kola, en Russie. Contrairement aux résultats antérieurs, que la nacaphite est un minéral pseudo-orthorhombique triclinique, nous démontrons qu'il s'agit d'un minéral monoclinique, $P2_1/c$, a 13.3185(14), b 7.0964(8), c 10.6490(11) Å, β 113.526(1)°, V 922.81(17) Å^3, $Z = 8$. Nous en avons résolu la structure par méthodes directes, et nous l'avons affiné jusqu'à un résidu R_1 de 0.034 en utilisant 1376 réflexions observées uniques. La structure contient deux positions de Ca et quatre positions de Na. Le site Ca1 est entouré de deux anions F$^-$ et cinq anions O^{2-}, les distances Ca^{2+}–φ étant comprises entre 2.32 et 2.57 Å. Le cation Ca2 possède une coordinence octaédrique, avec deux anions F$^-$ et quatre anions O^{2-}, les distances Ca^{2+}–φ étant comprises entre 2.29 et 2.37 Å, sauf pour un anion O7 plus distant à 3.049 Å. Tous les cations Na$^+$ possèdent une coordinence octaédrique, chacun entouré de quatre anions O^{2-} et deux anions F$^-$. Les cations Ca^{2+} et Na$^+$ sont agencés parallèles à (100), ces plans étant séparés par les anions F$^-$ et les tétraèdres PO$_4^{3-}$. Les ions F$^-$ sont coordonnés par quatre cations Na$^+$ et deux cations Ca^{2+}. Les octaèdres $(FNa_4Ca_2)^{7+}$ partagent des faces pour produire des chaînes $[FNa_2Ca]^{3-}$ parallèles à c. La topologie globale de la structure concorde avec celle déduite dans les études antérieures. Toutefois, il demeure deux différences essentielles, impliquant les schémas de mise en ordre et de géométrie locale des polyèdres de coordination: (1) les cations Ca^{2+} et Na$^+$ sont complètement ordonnés, et leurs

---

[§] *E-mail address*: skrivovi@mail.ru

sites respectifs sont remplis; (2) les cations Ca^{2+} possèdent deux types de coordinence sept, tandis que les cations Na^+ possèdent une coordinence octaédrique. Les résultats de ce nouvel affinement de la nacaphite concordent avec le spectre de diffraction X prélevé sur poudre.

(Traduit par la Rédaction)

Mots-clés: nacaphite, structure cristalline, macle, péninsule de Kola, Russie.

INTRODUCTION

Nacaphite, $Na_2Ca(PO_4)F$, was first described by Khomyakov *et al.* (1980) as small inclusions up to 0.1 mm in diameter in thermonatrite associated with villiaumite, fluorapatite, aegirine, and barytolamprophyllite in arfvedsonite–nepheline–microcline veins within ijolite–urtite at Mt. Rasvumchorr, Khibiny massif, Kola Peninsula. Its empirical and simplified chemical formulas were established as $Na_{1.99}(Ca_{0.94}Sr_{0.01} Mn_{0.01})P_{1.00}O_{3.97}F_{0.97}$ and $Na_2Ca(PO_4)F$, respectively. The mineral was initially described as orthorhombic, with possible space-groups *Cmma* or *C2ma*, *a* 10.644(2), *b* 24.423(60), *c* 7.098(2) Å. The structure of nacaphite was reported by Sokolova *et al.* (1989) in the space group *C*1, *a* 10.656(4), *b* 24.4430(60), *c* 7.102(2) Å, α 89.99(2), β 90.01(2), γ 90.01(2)° (note that the deviations of the angles from 90° do not exceed 0.01°). The structure model was refined to *R* = 0.098 and consists of 72 atom positions, 64 of which are only partially occupied. As was later pointed out by Sokolova & Hawthorne (2001), "…the refinement was very unstable". However, the structure solution was sufficient to establish major topological aspects of the structure and to describe it as a member of the seidozerite–nacaphite polysomatic series (Egorov-Tismenko & Sokolova 1990, Sokolova 1998, Christiansen *et al.* 1999, Ferraris *et al.* 2004).

The structure of nacaphite was re-investigated by Sokolova & Hawthorne (2001). In the first stage, the large *C*-centered triclinic unit cell was established with dimensions *a* 10.6464(4), *b* 24.4206(9), *c* 7.0961(2) Å, α 90.002(1), β 89.998(1), γ 89.965(1)°. The refinement in the space group *C*1 resulted in R_1 = 0.073. At this stage, it was decided that the crystal is twinned, with both the *a* and *b* unit-cell parameters halved so that the cell is transformed into primitive triclinic (again, pseudo-orthorhombic) cell with dimensions *a* 5.3232(2), *b* 12.2103(4), *c* 7.0961(2) Å, α 90.002(1), β 89.998(1), γ 89.965(1)°. Within this cell, the structure was solved in the space group $P\bar{1}$ and refined to R_1 = 0.056. The structure model that they proposed contains one fully occupied Na site and five sites statistically occupied by both Ca and Na. The topology of the structure is the same as previously established by Sokolova *et al.* (1989). However, the structure model with the halved *a* and *b* parameters was in disagreement with the powder X-ray-diffraction pattern of nacaphite, which contains several lines with *h* = 2*n* + 1 and *k* = 2*n* + 1. The pres-

ence of these lines strongly suggests that both *a* and *b* parameters are doubled, as suggested by Khomyakov *et al.* (1980) in the initial description.

During our investigation of late-stage hydrothermal assemblages of Khibiny alkaline massif (Yakovenchuk *et al.* 2005), we found large untwinned crystals of nacaphite up to 2 cm long and 3 mm in diameter that allow us to re-investigate crystal structure of this mineral. The results of this study are reported herein.

EXPERIMENTAL

The crystal used for this study originates from a hydrothermal nepheline – microcline – aegirine vein within ijolite–urtite at Mt. Rasvumchorr. Nacaphite occurs here as elongate-prismatic pseudohexagonal crystals in interstices of nepheline, potassic-arfvedsonite, microcline and eudialyte, in association with sodalite, kalsilite, pectolite, lamprophyllite, lomonosovite, ershovite, loparite-(Ce), djerfisherite and some unidentified phases. The chemical composition and powder-diffraction data of nacaphite are similar to the data reported by Khomyakov *et al.* (1980). The composition of nacaphite (Table 1) was determined by wavelength-dispersion spectroscopy using a Cameca MS–46

TABLE 1. THE CHEMICAL COMPOSITION OF NACAPHITE

	1*	2*	3*	4**
Na_2O wt.%	28.50	29.49	28.59	31.44
K_2O				0.10
CaO	27.81	27.92	28.18	26.66
SrO	0.59	0.62	0.57	0.55
MgO	0.17	0.10	0.12	
MnO	0.30	0.22	0.23	0.39
FeO	0.04	0.06	0.06	
P_2O_5	33.75	34.07	34.92	36.00
F	8.55	8.28	8.13	9.32
Total	99.71	100.76	100.80	104.46
Na *apfu****	1.93	1.98	1.88	1.99
Ca	1.04	1.04	1.02	0.94
Sr	0.01	0.01	0.01	0.01
Mg	0.01	0.01	0.01	
Mn	0.01	0.01	0.01	0.01
P	1.00	1.00	1.00	1.00
O	4.06	4.11	4.06	3.97
F	0.95	0.91	0.87	0.97

* Results of electron-microprobe analyses, this work.
** Results of a wet-chemical analysis, Khomyakov *et al.* (1980).
*** Calculated values on the basis of P ≈ 1 atom per formula unit (*apfu*).

electron microprobe operating at 20 kV and 1 nA with a beam diameter of ~2 μm. It is important to note that the samples for chemical analysis were prepared using kerosene to prevent the loss of fluorine. The optical properties were measured in immersion liquids and were found to be different from those reported previously: biaxial (+), α 1.536(2), β 1.528(2), γ 1.524(5), $2V_{meas}$ 65 ± 5° (our data) and biaxial (–), α 1.508, β 1.515, γ 1.520, $2V_{meas}$ 80° (Khomyakov *et al.* 1980). The compatibility constants (Mandarino 1981) calculated using our data and data obtained by Khomyakov *et al.* (1980) are –0.010 (superior) and 0.018 (superior), respectively. At present, we are unable to explain the obvious differences in the optical constants and are inclined to assign them to the effects of polysynthetic twinning, which is commonly observed in nacaphite crystals (see below).

The crystal selected was mounted on a Bruker three-circle CCD-based X-ray diffractometer operated at 50 kV and 40 mA. More than a hemisphere of three-dimensional data was collected using monochromatic MoKα X-radiation, with frame widths of 0.3° in ω, and with 10 s counting times for each frame. The cell was first determined as being orthorhombic *C*-centered (*a* 10.650, *b* 24.425, *c* 7.097 Å, α 89.99, β 90.00, γ 90.04°), in complete agreement with the large cell reported previously by Khomyakov *et al.* (1980), Sokolova *et al.* (1989), and Sokolova & Hawthorne (2001). However, the reflection statistics indicate a strong preference for the monoclinic primitive subcell, which can be obtained from the initial cell by the transfomation matrix [100/00$\overline{1}$/½½0] and has dimensions *a* 10.650, *b* 7.097, *c* 13.319 Å, α 90.00, β 113.53, γ 90.00°. In particular, the R_{int} = 0.053 value for this unit cell is significantly better than for the *C*-centered supercell (R_{int} = 0.144). The unit-cell parameters of the primitive cell were refined with 827 reflections using least-squares techniques (Table 2). The intensity data were reduced and corrected for Lorentz, polarization, and background effects using the Bruker program SAINT. A semi-empirical absorption-correction was made using 1507 intense reflections. The crystal was modeled as an ellipsoid, which lowered the R_{int} from 0.053 to 0.024.

The Bruker SHELXTL Version 5 system of programs was used for the determination and refinement of the crystal structure. The structure solution in the primitive monoclinic cell proceeded smoothly. Systematic absences and reflection statistics were found to be consistent with the space group $P2_1/c$. The structure was solved by direct methods. The final model included the positional parameters and anisotropic displacement parameters for all atoms, and a weighting scheme of the structure factors. The final refinement converged to an agreement index (R_1) of 0.034, calculated for 1376 unique observed ($|Fo| \geq 4\sigma_F$) reflections. The final coordinates and anisotropic displacement parameters are given in Table 3, and selected interatomic distances are listed in Table 4. Calculated and observed

structure-factors are available from the Depository of Unpublished Data, MAC web site [document Nacaphite CM45_915].

RESULTS

Nacaphite contains two Ca and four Na positions. The Ca1 site is coordinated by two F⁻ and five O^{2-} anions with individual Ca^{2+}–φ distances in the range of 2.32–2.57 Å (φ = F⁻, O^{2-}). The Ca2 cation has six closest anions (two F⁻ and four O^{2-}), with the Ca^{2+}–φ bond lengths in the range 2.29–2.37 Å, and an additional remote O7 anion at 3.049 Å. All Na⁺ cations are octahedrally coordinated by four O^{2-} and two F⁻ anions each. The configurations of two symmetrically independent PO_4^{3-} tetrahedra are typical for the structures of phosphate minerals (Huminicki & Hawthorne 2002).

Bond-valence sums for the cation and anion positions have been calculated using bond-valence parameters given by Brese & O'Keeffe (1991). They are listed in Table 5 and are in agreement with the formal valences of the atoms.

The structure of nacaphite is shown in Figure 1. The Ca^{2+} and Na⁺ cations form cation arrangements parallel to the (100) plane and separated by F⁻ anions and PO_4^{3-} tetrahedra (Fig. 1a). A projection of the structure along the *c* axis (Fig. 1b) reveals that the triangular faces of the phosphate tetrahedra are oriented perpendicular to the [001] direction. It is of interest that the F⁻ ions have a rather higher coordination number and are coordinated by four Na⁺ and two Ca^{2+} cations each. The $(FNa_4Ca_2)^{7+}$ octahedra share faces to produce $[FNa_2Ca]^{3-}$ chains parallel to the *c* axis (Fig. 1c).

DISCUSSION

The results of the structure refinement of nacaphite reported here are in disagreement with the structure models previously suggested by Sokolova *et al.* (1989) and Sokolova & Hawthorne (2001). The symmetry of nacaphite turns out to be monoclinic. However, the monoclinic primitive cell has a pseudo-orthorhombic *C*-

TABLE 2. CRYSTALLOGRAPHIC DATA AND REFINEMENT PARAMETERS FOR NACAPHITE

a (Å)	13.3185(14)	D_{calc} (g/cm³)	2.880
b (Å)	7.0964(8)	Crystal size (mm)	0.36 × 0.32 × 0.12
c (Å)	10.6490(11)	Radiation	MoKα
β (°)	113.5260(10)	Total reflections	4338
V (Å³)	922.81(17)	Unique reflections	1865
Space group	$P2_1/c$	Unique $|F_o| \geq 4\sigma_F$	1376
F_{000}	784	R_1	0.034
μ (cm⁻¹)	1.832	wR_2	0.098
Z	8	S	1.089

Note: $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where P = $(F_o^2 + 2F_c^2)$/3; S = $\{\Sigma[w(F_o^2 - F_c^2)] / (n - p)\}^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

TABLE 3. COORDINATES AND DISPLACEMENT PARAMETERS OF ATOMS IN NACAPHITE

Atom	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ca1	-0.33098(7)	0.0120(1)	-0.30111(8)	0.0129(2)	0.0133(4)	0.0127(5)	0.0127(4)	-0.0006(3)	0.0054(3)	-0.0002(3)
Ca2	-0.17252(7)	0.4948(1)	-0.45051(8)	0.0154(2)	0.0151(5)	0.0138(5)	0.0162(4)	-0.0004(3)	0.0049(3)	-0.0005(4)
Na1	-0.33061(14)	0.4821(2)	-0.26287(16)	0.0190(4)	0.0210(9)	0.0168(9)	0.0200(8)	0.0010(7)	0.0090(7)	0.0016(8)
Na2	-0.41221(13)	0.2283(2)	-0.08763(16)	0.0190(4)	0.0168(10)	0.0209(10)	0.0196(9)	-0.0036(7)	0.0076(7)	0.0010(7)
Na3	-0.08990(13)	0.2536(2)	-0.17631(16)	0.0191(4)	0.0168(10)	0.0205(11)	0.0204(9)	0.0025(7)	0.0079(7)	0.0000(7)
Na4	-0.16432(13)	0.0242(2)	-0.45586(17)	0.0207(4)	0.0161(9)	0.0159(9)	0.0314(9)	0.0013(8)	0.0110(8)	-0.0013(8)
P1	-0.41350(9)	0.74075(15)	-0.05929(10)	0.0116(3)	0.0110(6)	0.0117(6)	0.0124(5)	0.0012(4)	0.0049(4)	-0.0002(4)
P2	-0.08406(9)	0.75538(15)	-0.14455(10)	0.0119(3)	0.0116(6)	0.0121(6)	0.0123(5)	-0.0006(4)	0.0051(4)	-0.0005(4)
O1	-0.3551(2)	0.5515(4)	-0.0487(3)	0.0189(7)	0.020(2)	0.016(2)	0.022(2)	-0.005(1)	0.009(1)	0.002(1)
O2	-0.5311(2)	0.7324(4)	-0.1673(3)	0.0195(7)	0.015(2)	0.020(2)	0.021(2)	0.000(1)	0.005(1)	-0.003(1)
O3	-0.3505(2)	0.9003(4)	-0.0954(3)	0.0189(7)	0.019(2)	0.020(2)	0.018(2)	0.003(1)	0.007(1)	-0.004(1)
O4	-0.4136(2)	0.7758(4)	0.0842(3)	0.0171(7)	0.019(2)	0.018(2)	0.015(1)	0.002(1)	0.007(1)	0.004(1)
O5	-0.0843(2)	0.7512(4)	0.0008(3)	0.0209(7)	0.023(2)	0.027(2)	0.015(1)	-0.001(1)	0.010(1)	-0.002(1)
O6	0.0346(2)	0.7676(4)	-0.1320(3)	0.0197(7)	0.015(2)	0.021(2)	0.024(2)	0.001(1)	0.009(1)	0.001(1)
O7	-0.1471(2)	0.9318(4)	-0.2184(3)	0.0238(8)	0.016(2)	0.021(2)	0.034(2)	0.008(1)	0.009(1)	0.004(1)
O8	-0.1404(2)	0.5782(4)	-0.2235(3)	0.0216(7)	0.020(2)	0.020(2)	0.024(2)	-0.007(1)	0.007(1)	-0.003(1)
F1	-0.26280(19)	0.2691(3)	-0.3790(2)	0.0189(6)	0.020(1)	0.022(1)	0.017(1)	0.003(1)	0.009(1)	-0.002(1)
F2	-0.24193(19)	0.2271(3)	-0.1201(2)	0.0173(6)	0.020(1)	0.015(1)	0.016(1)	-0.002(1)	0.007(1)	-0.0002(10)

TABLE 4. SELECTED BOND-LENGTHS (Å)
IN THE STRUCTURE OF NACAPHITE

Ca1-O7	2.318(3)	Ca2-F2	2.295(2)
Ca1-O2	2.332(3)	Ca2-F1	2.307(2)
Ca1-F1	2.333(2)	Ca2-O5	2.320(3)
Ca1-F2	2.372(2)	Ca2-O6	2.336(3)
Ca1-O4	2.408(3)	Ca2-O8	2.356(3)
Ca1-O3	2.439(3)	Ca2-O3	2.373(3)
Ca1-O1	2.566(3)	Ca2-O7	3.049(3)
<Ca1-φ*>	2.395	<Ca2-φ>	2.434
Na1-O4	2.321(3)	Na2-F1	2.317(3)
Na1-F1	2.349(3)	Na2-O4	2.335(3)
Na1-F2	2.355(3)	Na2-O1	2.400(3)
Na1-O2	2.448(3)	Na2-O2	2.411(3)
Na1-O1	2.478(3)	Na2-F2	2.427(3)
Na1-O8	2.492(3)	Na2-O3	2.481(3)
<Na1-φ>	2.407	<Na2-φ>	2.395
Na3-O5	2.327(3)	Na4-O6	2.356(3)
Na3-F2	2.337(3)	Na4-O5	2.358(3)
Na3-O7	2.392(4)	Na4-O1	2.391(3)
Na3-O8	2.396(3)	Na4-F2	2.408(3)
Na3-O6	2.433(3)	Na4-F1	2.504(3)
Na3-F1	2.451(3)	Na4-O7	2.532(3)
<Na3-φ>	2.389	<Na4-φ>	2.425
P1-O2	1.530(3)	P2-O8	1.532(3)
P1-O1	1.534(3)	P2-O6	1.535(3)
P1-O3	1.547(3)	P2-O7	1.538(3)
P1-O4	1.549(3)	P2-O5	1.549(3)
<P1-O>	1.540	<P2-O>	1.539

* φ = O, F.

centered supercell, as was initially assigned to nacaphite by Khomyakov *et al.* (1980). The very existence of such a supercell commonly results in a pseudomerohedral twinning according to the matrix $[100/0\bar{1}0/\bar{1}0\bar{1}]$ and has been observed in structures of minerals (Krivovichev *et al.* 2003, Krivovichev & Armbruster 2004). However, in our case, the crystal used for the study is untwinned, reducing the problems in structure solution and refinement. We suggest that it is pseudomerohedral twinning that has led to the different unit-cell parameters and symmetry of nacaphite reported by Sokolova *et al.* (1989) and Sokolova & Hawthorne (2001).

As has been mentioned above, the overall topology of the structure of nacaphite is in agreement with the results of previous investigations of the structure. However, there are two essential differences in patterns of order and local geometry of coordination:

1. In contrast to previous studies, the Ca^{2+} and Na^+ cations are completely ordered, and the respective sites are fully occupied.

2. The Ca^{2+} cations have sevenfold coordination of two different types, whereas Na^+ cations are octahedrally coordinated. In contrast, Sokolova & Hawthorne (2001) reported sixfold coordinations for all Ca- and Na-occupied sites.

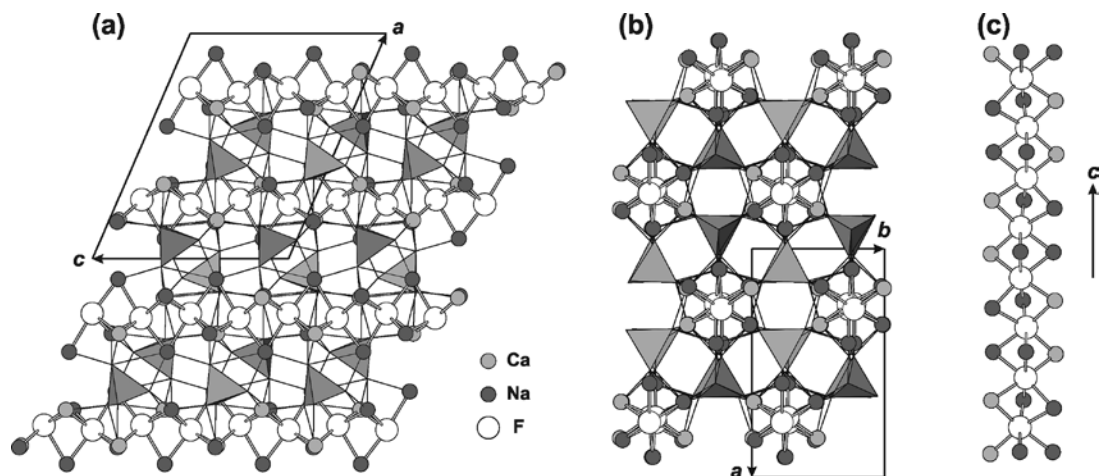Finally, we point out that the results of crystal-structure refinement of nacaphite reported here are in

FIG. 1. The crystal structure of nacaphite projected along the b (a) and c (b) axes, and the chain of the face-sharing F-centered octahedra (c).

TABLE 5. BOND-VALENCE ANALYSIS (*vu*) FOR NACAPHITE

	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)	O(7)	O(8)	F(1)	F(2)	Σ
Ca(1)	0.20	0.37	0.28	0.30			0.39		0.27	0.24	2.05
Ca(2)			0.33		0.39	0.37	0.05	0.35	0.28	0.29	2.07
Na(1)	0.16	0.17		0.24				0.15	0.16	0.16	1.05
Na(2)	0.20	0.19	0.16	0.24					0.18	0.13	1.09
Na(3)					0.24	0.18	0.20	0.20	0.12	0.17	1.11
Na(4)	0.20				0.22	0.22	0.14		0.11	0.14	1.03
P(1)	1.21	1.22	1.17	1.16							4.76
P(2)					1.16	1.21	1.20	1.21			4.78
Σ	1.97	1.95	1.94	1.94	2.01	1.98	1.98	1.91	1.12	1.13	

agreement with the powder X-ray-diffraction pattern of this mineral (PDF 33–1222), whereas structure models provided by Sokolova *et al*. (1989) and Sokolova & Hawthorne (2001) completely ignore diffraction maxima with $h = 2n + 1$ and $k = 2n + 1$, responsible for the doubling the a and b parameters.

REFERENCES

BRESE, N.E. & O'KEEFFE, M. (1991): Bond-valence parameters for solids. *Acta Crystallogr*. **B47**, 192-197.

CHRISTIANSEN, C.C., MAKOVICKY, E. & JOHNSEN, O. (1999): Homology and typism in heterophyllosilicates: an alternate approach. *Neues Jahrb. Mineral., Abh.* **175**, 153-189.

EGOROV-TISMENKO, YU.K. & SOKOLOVA, E.V. (1990): The homologous series seidozerite–nacaphite. *Mineral. Zh.* **12**(4), 40-49 (in Russ.).

FERRARIS, G., MAKOVICKY, E. & MERLINO, S. (2004): *Crystallography of Modular Materials*. Oxford University Press, Oxford, U.K.

HUMINICKI, D.M.C. & HAWTHORNE, F.C. (2002): The crystal chemistry of the phosphate minerals. *In* Phosphates: Geo-

chemical, Geobiological, and Materials Importance (M.L. Kohn, J. Rakovan & J.M. Hughes, eds.). *Rev. Mineral. Geochem.* **48**, 123-253.

KHOMYAKOV, A.P., KAZAKOVA, M.E. & PUSHCHAROVSKII, D.YU. (1980): Nacaphite $Na_2Ca(PO_4)F$ – a new mineral. *Zap. Vses. Mineral. Obshchest.* **109**, 50-52 (in Russ.).

KRIVOVICHEV, S.V. & ARMBRUSTER, T. (2004): The crystal structure of jonesite, $Ba_2(K,Na)[Ti_2(Si_5Al)O_{18}(H_2O)](H_2O)_n$: a first example of titanosilicate with porous double layers. *Am. Mineral.* **89**, 314-318.

KRIVOVICHEV, S.V., YAKOVENCHUK, V.N., BURNS, P.C., PAKHOMOVSKY, YA.A. & MENSHIKOV YU.P. (2003): Cafetite, $Ca[Ti_2O_5](H_2O)$: crystal structure and revision of chemical formula. *Am. Mineral.* **88**, 424-429.

MANDARINO, J.A. (1981): The Gladstone–Dale relationship. IV. The compatibility concept and its application. *Can. Mineral.* **19**, 441-450.

SOKOLOVA, E.V. (1998): The polysomatic series seidozerite–nacaphite. *Zap. Vser. Mineral. Obshchest.* **127**(2), 111-114 (in Russ.).

SOKOLOVA, E.V., EGOROV-TISMENKO, YU.K. & KHOMYAKOV, A.P. (1989): Crystal structure of nacaphite. *Sov. Phys. Dokl.* **34**, 9-11.

SOKOLOVA, E.V. & HAWTHORNE, F.C. (2001): The crystal chemistry of the $[M_3\phi_{11-14}]$ trimeric structures: from hyperagpaitic complexes to saline lakes. *Can. Mineral.* **39**, 1275-1294.

YAKOVENCHUK, V.N., IVANYUK, G.YU., PAKHOMOVSKY, YA.A. & MEN'SHIKOV, YU.P. (2005): *Khibiny*. Laplandia Minerals, Apatity, Russia.