MODULAR APPROACH IN SOLVING THE CRYSTAL STRUCTURE OF A SYNTHETIC DIMORPH OF NACAPHITE, Na$_2$Ca[PO$_4$]F, FROM POWDER-DIFFRACTION DATA

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ABSTRACT

By comparison with the known structures of nacaphite and arctite, the crystal structure of a synthetic dimorph of nacaphite, (Na$_{0.67}$Ca$_{0.33}$)$_3$PO$_4$F, has been solved using a modular approach. The structure model, refined by Rietveld method on the basis of X-ray powder-diffraction data including minor quantities of villiaumite, fluorite and fluorapatite, consists of a stacking of 15 nacaphite-type 7.1 × 7.1 × 2.7 Å modules (slabs) along the [001] direction of a rhombohedral *R3m* cell with $a = 7.0179(7)$, $c = 40.56(4)$ Å. Nacaphite, on the other hand, is triclinic and is based on the stacking of only four such slabs. The slabs and their links in nacaphite and its synthetic dimorph are quite different in detail; thus the two compounds are polymorphs and not polytypes. The role of nacaphite modules in building minerals of hyperagpaitic rocks is discussed in terms of merotype and plesiotype series. Modular relationships with sulphohalite-type minerals also are discussed.

Keywords: nacaphite dimorph, crystal structure, powder diffraction, polysomatic series.

SOMMAIRE

A la suite d'une comparaison avec les structures connues de la nacaphite et de l'arctite, nous avons résolu la structure cristalline d'un dimorphe synthétique de la nacaphite, (Na$_{0.67}$Ca$_{0.33}$)$_3$PO$_4$F, avec une approche fondée sur la notion de modules. Le modèle structural, affiné par la méthode de Rietveld à partir de données en diffraction X (méthode des poudres) prélevées sur un assemblage comprenant des quantités mineures de villiaumite, fluorite et fluorapatite, montre en empilement de quinze modules de type nacaphite, chacun de dimensions 7.1 × 7.1 × 2.7 Å, le long de [001] d'une maille rhomboédrique *R3m* ayant pour dimensions a 7.0179(7), c 40.56(4) Å. La nacaphite, par ailleurs, est triclinique, et sa structure montre un empilement de quatre de ces modules. L'agencement des atomes dans ces modules et les liaisons intermodulaires diffèrent dans les détails entre nacaphite et son dimorphe. Il semble donc que ces deux structures montrent une relation polymorphique et non polytypique. Nous discutons du rôle de tels modules de nacaphite dans la charpente de minéraux de roches hyperagpaïtiques en termes de séries mérotypiques et plésiotypiques, et aussi des relations modulaires avec les minéraux du groupe de la sulphohalite.

(Traduit par la Rédaction)

Mots-clés: dimorphe de la nacaphite, structure cristalline, diffraction X, méthode des poudres, série polysomatique.

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INTRODUCTION

In the alkaline rocks of the silica-undersaturated Lovozero and Khibina massifs, the main hosts of phosphorus and fluorine are apatite and villiaumite, rarely lomonosovite and (Na,Ca)-fluorophosphates. The economic importance of apatite results from its abundance as a major mineral of apatite–nepheline orebodies. In the Khibina alkaline massif, various (Na,Ca)-fluorophosphates do occur, including arctite, $(Na_5Ca)Ca_6Ba[PO_4]_6F_3$, nefedovite, $Na_5Ca_4[PO_4]_4F$, and nacaphite, $Na_2Ca[PO_4]F$ (Khomyakov et al. 1980, 1981, 1983). These (Na,Ca)-fluorophosphates occur in association with apatite, $Ca_5(PO_4)_3(OH,F,Cl)$, aegirine, $NaFeSi_2O_6$, thermonatrite, $Na_2CO_3 \cdot H_2O$, and villiaumite, NaF, in pegmatites emplaced in the ijolite–urtite units, i.e., in an environment characterized by high concentrations of sodium and fluorine. Arctite, nefedovite, and nacaphite also are of general interest because of their high contents of phosphorus and fluorine, and because they actually replace fluorapatite in the hyperagpaitic rocks.

In order to prove the important role of fluorine and sodium in the processes of formation of apatite and associated (Na,Ca)-fluorophosphate minerals (Dawson & Hill 1998, Khomyakov 1995), experimental studies of the cocrystallization of these minerals in the system Ca–Na–PO_4–F were performed by Kirova et al. (1987) using melts. These authors established the fields of crystallization of fluorapatite, CaF_2, NaF, Na_3PO_4, and Na_2CaPO_4F. The phase Na_2CaPO_4F crystallizes from the phosphate–fluoride melt in the range 770–940°C as hexahedral lamellae and represents the compound richest in Na and F among the known (Na,Ca)-fluorophosphates. On addition of Sr or Ba to the system, synthetic Na_2CaPO_4F accommodates up to 5.7 wt.% of SrO and 2.0 wt.% BaO; on the basis of X-ray, chemical, and optical data, and infrared spectra, Kirova et al. (1987) proposed it to be the synthetic equivalent of nacaphite.

In this paper, we present the results of the crystal-structure determination of the compound Na_2CaPO_4F obtained by Kirova et al. (1987) and show that it is a dimorph of nacaphite.

EXPERIMENTAL

Four samples of the synthetic Na_2CaPO_4F prepared by Kirova et al. (1987) were analyzed with a JEOL-733 electron microprobe operated at 10 kV and 50 nA (Institute of Mineral Resources, Moscow); nacaphite from Kola Peninsula was used as a standard. Selected grains from sample #2825 chosen for the present X-ray-diffraction investigation yield practically the ideal composition; on the whole, however, the powder patterns show the presence of other phases that presumably occur as micro-inclusions in the grains (see below).

About twenty grains, which optically seem to be single crystals, were tested by the Laue method; they

showed slightly split spots typical of twins. X-ray-diffraction data were collected on a CAD–4 Enraf–Nonius diffractometer ($MoK\alpha$ radiation, Department of Inorganic Chemistry, Moscow State University) from the best of the tested crystals (dimensions 0.20 × 0.22 × 0.18 mm). On the basis of 25 reflections with $15 < 2\theta < 20°$, the following hexagonal cell has been obtained: a 7.029(1), c 40.54(1) Å, space group $R3m$ or $R\bar{3}m$. Attempts to solve the crystal structure by direct methods failed, presumably because the crystals are affected by some kind of polysynthetic twinning. As a result, we decided to use the Rietveld method.

Powder-diffraction data were collected on a focusing STOE–STADIP diffractometer, equipped with a curved Ge (111) primary monochromator ($MoK\alpha_1$ radiation, $\lambda = 0.70926$ Å; Institute für Kristallographie, Universität München) with a minimum full-width at half-maximum (FWHM) of 0.08°, according to the procedure described by Wölfel (1981). The sample was contained in a quartz capillary rotated around its axis to minimize preferred orientation. Diffracted intensities were collected in a stepwise overlapping mode by a linear position-sensitive detector with about 5° acceptance angle and 0.02° channel (Wölfel 1983); the yield was of 2250 data points in the range $5 < 2\theta < 49°$. Table 1 contains the pertinent details.

STRUCTURE MODEL

After failing a direct solution of the crystal structure, a model of the structure was obtained using concepts of the modular crystallography (Merlino 1997), as exemplified by the classical case of biopyriboles (Thompson 1978). These concepts can profitably be used to predict

TABLE 1. CRYSTAL DATA, DETAILS OF THE RIETVELD PROFILE REFINEMENT OF THE SYNTHETIC DIMORPH OF NACAPHITE AND ASSOCIATED VILLIAUMITE, FLUORITE AND FLUORAPATITE

	Nacaphite dimorph	Villiaumite	Fluorite	Fluor-apatite
a (Å)	7.0179(7)	4.6325(1)	5.4620(1)	9.3661(3)
c (Å)	40.56(4)			6.8892(2)
V_0 (Å³)	1730.21(1)	99.41(1)	162.95(1)	523.38(1)
Z	15	4	4	2
Space group	$R3m$	$Fm\bar{3}m$	$Fm\bar{3}m$	$P6_3/m$
Bragg reflections	560	15	19	511
Refined parameters	76	7	7	8
R_P*	0.027	0.027	0.027	0.027
R_{wp}	0.038	0.038	0.038	0.038
R_{exp}	0.018	0.018	0.018	0.018
R_B	0.036	0.013	0.015	0.169
R_F	0.038	0.011	0.014	0.087
Proportion (wt%)	72.5(4)	15.9(1)	8.11(7)	3.4(1)

*R-indexes: R_P = R-pattern; R_{wp} = R-weighted pattern; R_{exp} = expected value of R_{wp}; R_B = R-Bragg factor; R_F = R-structure factor.

structural models by comparing features of known structures, e.g., chemical composition and unit-cell parameters, with those of new compounds. The method is particularly applicable to silicates, for which modern structural classifications have been derived (Liebau 1985, Lima-de-Faria 1994). The principal problem is the identification of basic structural modules that are common between the known and unknown structures. Modules must be evaluated more on the basis of the topology of polyhedral connectivity than on strict compositional and coordination criteria (Ferraris 1997). To obtain a starting model for the synthetic dimorph of nacaphite, the following features of nacaphite and arctite attracted our attention.

Nacaphite, $Na_2Ca[PO_4]F$, is triclinic, metrically pseudo-orthorhombic, with a 10.654(4), b 24.443(6), c 7.102(2) Å, α 89.99(2), β 90.01(2), γ 90.01(2)°, $C1$, $Z = 16$ (Sokolova et al. 1989); a metrically pseudo-hexagonal cell also is present with $a' = c$ 7.102 and $c' \approx 4a$ 39.96 Å. Infinite triple chains of Na- and M-polyhedra [M = (Na,Ca)] occur along [100], with 7- and 6-fold coordination, and are connected into a framework by PO_4 tetrahedra. However, for the present purposes, it is more useful to describe the structure of nacaphite in terms of two types ($N1$ and $N2$) of (100) slabs (Figs. 1a, b). For each type of slab, a block with dimensions 7.1 × 7.1 × 2.7 (thickness) Å can usefully be singled out for the subsequent discussion. The two types of blocks contain both Na- and M-bearing polyhedra, together with PO_4 tetrahedra oriented up and down; they show pseudohexagonal symmetry and differ from each other only in the orientation of the polyhedra. For each type of slab, four blocks fill the bc net of the cell, and the stacking of four alternating $N1$ and $N2$ slabs along [100] corresponds to an a dimension of 10.654 Å.

Arctite, $(Na_5Ca)Ca_6Ba(PO_4)_6F_3$, is rhombohedral with a 7.094(1), c 41.32(1) Å, $R\bar{3}m$, and $Z = 3$ (Sokolova et al. 1984). In its structure, 12-coordinated Ba and 7-coordinated Ca- and M-cations are grouped in triple columns along [001] and are connected by PO_4 tetrahedra to form a framework. The structure of arctite can be described in terms of three types ($A1$, $A2$ and $A3$) of (001) slabs built from blocks with dimensions 7.1 × 7.1 × 2.7 Å, as in nacaphite. These slabs contain Ba polyhedra ($A1$), Ca polyhedra ($A2$) and M polyhedra ($A3$), respectively; the difference between slabs $A2$ and $A3$ is mainly in the chemical contents (Figs. 2a–c). The independent sequence $A1A2A3$ is stacked according to symmetry elements along [001] according to a 15-slab structure corresponding to a dimension of c 41.32 Å.

The topologies of the slabs $N1$, $N2$, $A2$ and $A3$ (Figs. 1, 2) are comparable, at least if details of the coordination number of Na and Ca cations and the orientation of the PO_4 tetrahedra are disregarded. Therefore, for the purpose of building a structural model of the dimorph of nacaphite, an ideal slab L of polyhedra with 7-coordinated M was considered ($M = \frac{2}{3}Na + \frac{1}{3}Ca$, according to electron-microprobe data). This L slab was substituted

for each of the 15 slabs of the arctite structure according to two possible space-groups: $R3m$ and $R\bar{3}m$. The two models differ in the way the 15 slabs are stacked; the structure is polar in space group $R3m$ (all the tetrahedra point in the same direction along [001]), and nonpolar in $R\bar{3}m$.

STRUCTURE REFINEMENT

The Rietveld refinement of the two models $R3m$ (25 independent atoms) and $R\bar{3}m$ (15 independent atoms) was carried out with the Wyriet 3.3 program (Schneider 1989). The refinement was complicated by the presence of additional phases which, on the basis of the products of synthesis obtained by Kirova et al. (1987), were identified as synthetic villiaumite, NaF, fluorite, CaF_2, and fluorapatite, $Ca_5(PO_4)_3F$, and included in the refinement. For these additional phases, only profile parameters, cell parameters, and scale factors were refined. The Pearson VII function was chosen to describe the reflection profiles by means of six full-widths-at-half-maximum (FWHM). Graphical modeling of the background was used; asymmetry was refined for reflections with $2\theta < 40°$. According to the refinement, the L slab was differentiated into $ND1$ and $ND2$ slabs (see below). Refinement of site occupancies confirmed the ratio Na:Ca = 2:1 for all sites, in agreement with the chemical data. Whereas the values of interatomic distances, isotropic temperature-factors, and estimated standard deviations were not reasonable in the space group $R\bar{3}m$, the refinement in space group $R3m$ successfully converged (Table 1). Because of correlations, also due to local pseudocentrosymmetry of cations in a definite slab, simultaneous refinement of all 76 parameters, 60 of them being structural parameters, could not be performed. Final results are characterized by a value of $s = R_{wp}/R_{exp}$ (goodness of fit) of 2.14, and a Durbin–Watson d-statistic (DWD) (Hill & Flack 1987) of 0.51.

Even allowing for a factor $\sigma_x = 2.015$ for statistical reasons (Bérar & Lelann 1991), estimated standard deviations, as obtained from the refinement, are too optimistic, considering the block strategy of the refinement and the impurities in the sample. Consequently, the successful refinement of the profile (Table 1) is considered more a satisfactory test of the structure model than an accurate estimate of the refined parameters, and bond lengths are reported with two decimal figures only.

RESULTS AND DISCUSSION

The structure

The values of cell parameters of the nacaphite dimorph refined from powder data (Table 1), and used throughout this paper, are very close to those derived from single-crystal data (see above). According to the crystal-structure refinement, the chemical formula of the dimorph is $(Na_{2/3}Ca_{1/3})_3[PO_4]F$ (D_{calc} 2.88 g/cm³; D_{meas}
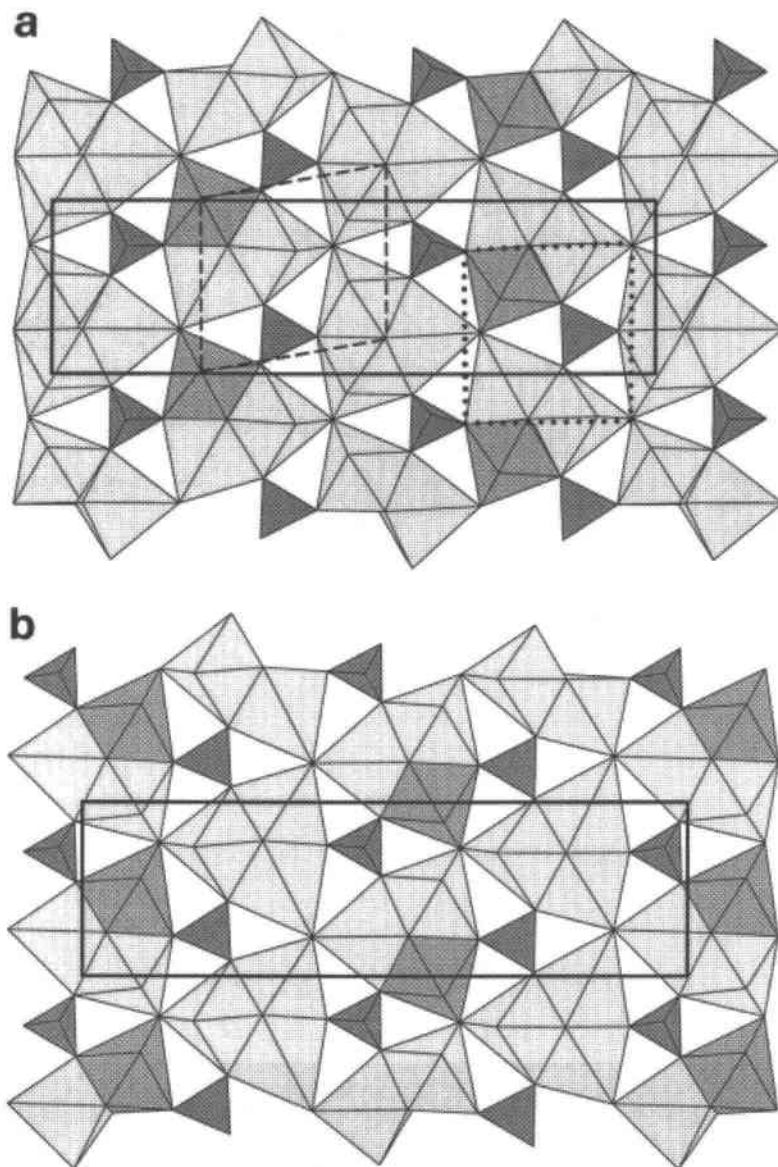
FIG. 1. (100) slabs *N*1 (a) at $x \approx 0$ and *N*2 (b) at $x \approx 0.25$ in the crystal structure of nacaphite. Polyhedra containing 7- and 6-fold-coordinated Na–Ca polyhedra are dark and light grey, respectively. Blocks $7.1 \times 7.1 \times 2.7$ Å and $7.1 \times 5.3 \times 6$ Å are indicated by dashed and dotted lines, respectively; the *bc* net of the cell is shown by a solid line (*b* horizontal).

2.87 g/cm^3; $Z = 15$). In the structure, all atoms are in special positions (Table 2). The *M* atom (Na$_{2/3}$Ca$_{1/3}$) occupies five independent sites on the *m* plane with coordination numbers 6 (*M*1, *M*3, *M*4, *M*5) and 7 (*M*2). Each *M* cation has four (five for *M*2) oxygen and two fluorine ligands, with distances *M*–O in the range 2.23–2.74 Å, and *M*–F in the range 2.19–2.65 Å (Table 3).

The five independent P atoms are in 3*a* positions, with 3*m* symmetry, and the wide range of P–O bonds (1.46–1.61 Å) reflects the problems with the refinement as discussed above.

The crystal structure of the dimorph of nacaphite (Fig. 3) consists of a polar stacking of two types of slabs (*ND*1 and *ND*2) according to a 15-slab sequence along
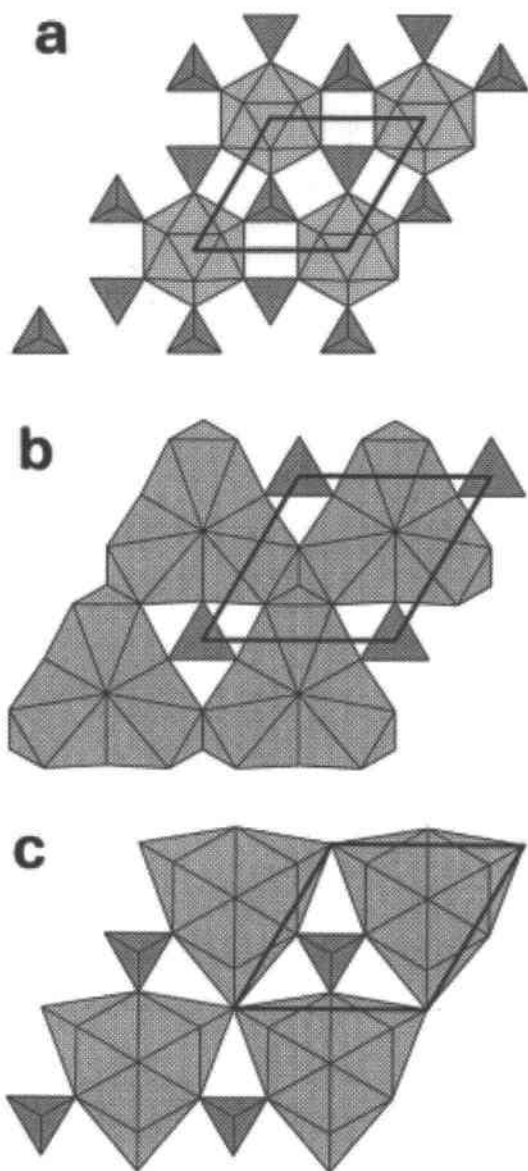
FIG. 2. Types of (001) slabs in the crystal structure of arctite: A1 with 12-coordinated Ba (a) at $z \approx 0$; A2 with 7-coordinated Ca (b) at $z \approx 0.07$; A3 with 7-coordinated M = Na–Ca (c) at $z \approx 0.13$.

TABLE 2. FRACTIONAL COORDINATES AND ISOTROPIC TEMPERATURE-FACTORS B (Å^2) FOR THE DIMORPH OF NACAPHITE

Atom*	Site	x	y	z	B
M(1)	9b	0.171	−0.171	0.270	1.5
M(2)	9b	0.170	−0.170	0.131	1.5
M(3)	9b	0.162	−0.162	0.400	1.5
M(4)	9b	0.158	−0.158	0.536	1.5
M(5)	9b	0.160	−0.160	0.673	1.5
P(1)	3a	0	0	0.195	1.2
P(2)	3a	0	0	0.938	1.2
P(3)	3a	0	0	0.327	1.1
P(4)	3a	0	0	0.805	1.2
P(5)	3a	0	0	0.069	1.1
O(1)	3a	0	0	0.159	2.0
O(2)	3a	0	0	0.289	1.0
O(3)	3a	0	0	0.031	2.1
O(4)	3a	0	0	0.767	3.9
O(5)	3a	0	0	0.900	2.2
O(6)	9b	0.116	−0.116	0.215	1.2
O(7)	9b	0.541	−0.541	0.274	1.3
O(8)	9b	0.543	−0.543	0.139	1.8
O(9)	9b	0.119	−0.119	0.345	1.2
O(10)	9b	0.882	−0.882	0.083	2.0
F(1)	3a	0	0	0.423	1.4
F(2)	3a	0	0	0.569	1.2
F(3)	3a	0	0	0.647	2.2
F(4)	3a	0	0	0.704	1.4
F(5)	3a	0	0	0.495	1.4

* M: ⅔Na + ⅓Ca; for estimated standard deviations, see text.

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) FOR THE DIMORPH OF NACAPHITE

M(1) – O(2)	2.23*	M(5) – O(3)	2.33
M(1) – O(6)	2.30	M(5) – O(7)	2.74
M(1) – O(7)	2.30 × 2	M(5) – O(9)	2.36 × 2
M(1) – F(2)	2.40	M(5) – F(3)	2.22
M(1) – F(3)	2.65	M(5) – F(4)	2.31
<M(1) – (O,F)>	2.37	<M(5) – (O,F)>	2.38
M(2) – O(1)	2.37	P(1) – O(1)	1.46
M(2) – O(8)	2.35 × 2	P(1) – O(6)	1.63 × 3
M(2) – O(10)	2.65 × 2	<P(1) – O>	1.59
M(2) – F(1)	2.59		
M(2) – F(5)	2.35	P(2) – O(5)	1.53
<M(2) – (O,F)>	2.48	P(2) – O(7)	1.53 × 3
		<P(2) – O>	1.53
M(3) – O(4)	2.50		
M(3) – O(9)	2.27	P(3) – O(2)	1.55
M(3) – O(10)	2.49 × 2	P(3) – O(9)	1.61 × 3
M(3) – F(1)	2.19	<P(3) – O>	1.60
M(3) – F(4)	2.39		
<M(3) – (O,F)>	2.39	P(4) – O(4)	1.54
		P(4) – O(8)	1.50 × 3
M(4) – O(5)	2.47	<P(4) – O>	1.51
M(4) – O(6)	2.42 × 2		
M(4) – O(8)	2.63	P(5) – O(3)	1.54
M(4) – F(2)	2.35	P(5) – O(10)	1.56 × 3
M(1) – F(5)	2.54	<P(5) – O>	1.55
<M(4) – (O,F)>	2.47		

* For estimated standard deviations, see text.

[001], which corresponds to $c = 40.56$ Å. In addition to the PO_4 tetrahedra, which are all oriented in the same direction along [001], $ND1$ and $ND2$ (Figs. 4a, b) contain polyhedra containing 6-coordinated and 7-coordinated M ions, respectively. With reference to the labels of the M polyhedra, the independent stacking is $M(2)M(4)M(1)M(5)M(3)$. Within each stack of five
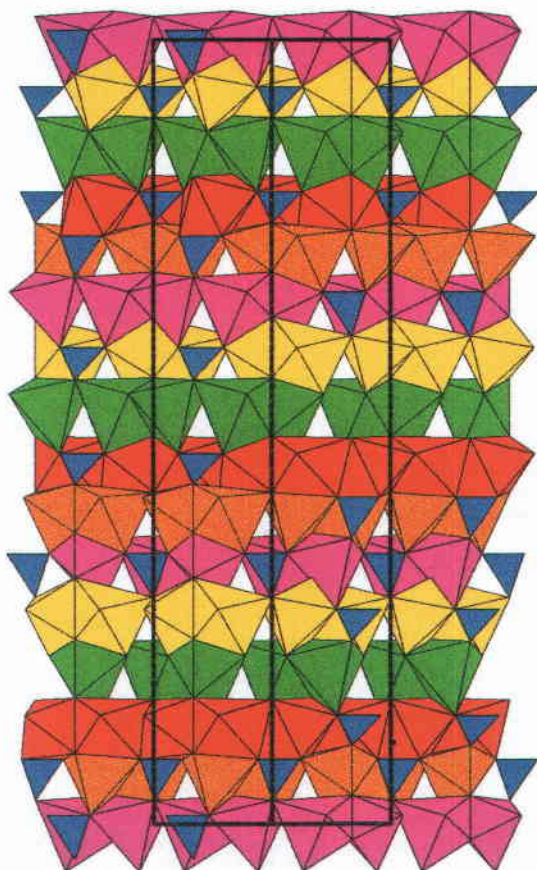
FIG. 3. Perspective view of the crystal structure of the synthetic dimorph of nacaphite seen along [110]. Colors of the M polyhedra are red, green, yellow, magenta and orange within the independent stack $M(2)M(4)M(1)M(5)M(3)$, in that order (see text). The PO$_4$ tetrahedra are shown in blue.

has been shown to include at least 18 minerals (Egorov-Tismenko 1998, Ferraris *et al.* 1997, Sokolova 1996). It constitutes an example of a merotype series (Ferraris 1997), *i.e.*, a series in which one module is variable (Makovicky 1997). The minerals of this series are characterized by a fixed seidozerite module, whereas the contents of the variable module can range from H$_2$O only to a full nacaphite block; cell parameters of about 7.1 and 5.5 Å, which properly match both modules, are typical of the series. In order to build the seidozerite–nacaphite series, the (100) nacaphite slabs have been cut in blocks of about $7.1 \times 5.3 \times 6$ Å with pseudo-orthorhombic symmetry (Egorov-Tismenko & Sokolova 1990). This block corresponds to a $c \times a/2 \times b/4$ module of the nacaphite structure. Its relationship with the block $7.1 \times 7.1 \times 2.7$ Å used for building the structure of the dimorph of nacaphite is shown in Figure 1a.

Nacaphite, arctite, and the synthetic dimorph of nacaphite can be considered members of a new merotype series, which is characterized by a fixed 7.1 $\times$ 7.1 $\times$ 2.7 Å nacaphite module plus a Ba-bearing module in arctite. The topology of this nacaphite module, but with a different chemistry, also occurs in
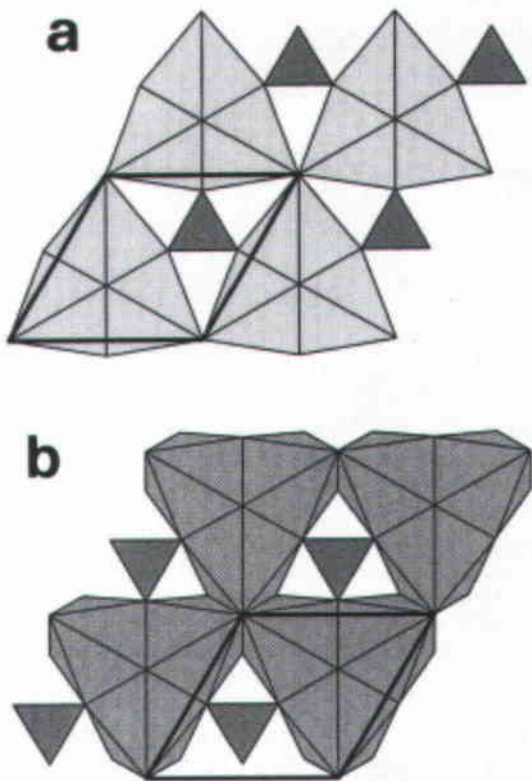

FIG. 4. (001) slabs $ND1$ (a) of Na–Ca octahedra at $z \approx 0$ and $ND2$ (b) of Na–Ca polyhedra with the cation in 7-fold coordination at $z \approx 0.13$. Key of shading as in Figure 1.

slabs, triple columns of M polyhedra are found along [001], compared to the infinite triple chains of nacaphite along [100]. These columns are connected into a framework by the PO$_4$ tetrahedra. The breakup of the infinite chains in nacaphite into columns in the dimorph is related with the R symmetry operation of the space group $R3m$. The main difference between N (nacaphite) and ND slabs (dimorph) is the orientation of the tetrahedra: all tetrahedra have the same polarity in ND, and two opposite polarities within each N slab. Mainly because of that, nacaphite and its dimorph are not polytypes, but really polymorphs.

Modular relationships

The {seidozerite, Na$_2$(Na,Mn,Ti)$_4$[(Na,Ti,Zr)$_2$O$_2$Si$_4$O$_{14}$]F$_2$} – nacaphite series (seidozerite derivatives)

sulphohalite, $Na_6(SO_4)_2(F,Cl)_2$, and the related minerals schairerite, $Na_{21}(SO_4)_7F_6Cl$, and kogarkoite, $Na_3(SO_4)F$, where SO_4 tetrahedra play the role of the PO_4 tetrahedra in the nacaphite-related minerals (Egorov-Tismenko *et al.* 1984). If the coordination numbers of the cations and the orientation of the tetrahedra are taken into account, the group of minerals discussed here should be considered a plesiotype series according to the definition of Makovicky (1997); in fact, the fundamental blocks that they have in common differ in detail from one member to another.

CONCLUSIONS

Dimorphism, favored by the wide range of temperatures of crystallization occurring in the hyperagpaitic rocks of the Kola Peninsula, accounts for the impressively large number of species reported in these rocks, together with other factors, such as isomorphous substitutions, presence of fluids oversaturated with alkalis and volatiles, and high fractionation both in the magmatic and pegmatitic stage (Khomyakov 1995). Natisite (tetragonal) and paranatisite (orthorhombic) $Na_2(TiO)SiO_4$, umbite (orthorhombic) and kostylevite (monoclinic) $K_2ZrSi_3O_9{\cdot}H_2O$, catapleiite (hexagonal) and gaidonnayite (orthorhombic) $Na_2ZrSi_3O_9{\cdot}2H_2O$ are well-known cases of polymorphic pairs (Khomyakov 1995). Nacaphite is triclinic and (partially) ordered, and its synthetic dimorph has a higher symmetry and shows Ca–Na disorder; therefore, nacaphite can be regarded as the low-temperature phase. Nacaphite occurs at Mt. Rasvumchorr, Khibina alkaline massif, both as a primary phase and as a pseudomorph after apatite. The synthetic dimorph of nacaphite described in this paper presumably represents the high-temperature disordered polymorph; it has not been reported in nature, but its occurrence may be expected both as a precursor of nacaphite, for thermodynamic reasons, and, on a crystallographic basis, as an epitactic intergrowth with arctite.

The presence of the nacaphite module, even as blocks of different size, in several minerals of the hyperagpaitic rocks, is connected with the key role played by alkalis in the genesis of these minerals. As already discussed for the seidozerite module (Ferraris *et al.* 1997) and other polysomatic modules (Ferraris 1997), the widespread occurrence of nacaphite modules in different hyperalkaline phases can be regarded as evidence of the high stability of the related structural topologies.

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