

Hydrothermal Synthesis and Crystal Structure of a New Sodium Yttrium Fluoride Phosphate NaYFPO₄

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Received June 14, 2000; in revised form October 12, 2000; accepted October 27, 2000

The new compound NaYFPO₄ has been synthesized by the hydrothermal method ($T = 200^\circ\text{C}$, $p = 20$ bar, $\tau = 300$ h). It crystallizes in the monoclinic system (space group $C2/m$ (No. 12)) with the unit cell parameters $a = 8.944(2)$ Å, $b = 6.930(1)$ Å, $c = 6.469(1)$ Å, $\beta = 106.11(3)^\circ$, $Z = 4$. Its structure has been determined from single-crystal X-ray diffraction data and refined to a conventional $R_1 = 0.0244$ ($wR_2 = 0.0629$) for 358 reflections, with $F_o > 4\sigma(F_o)$. The new fluoride phosphate NaYFPO₄ has an original structure with its own structure type. The YO₆F₂ polyhedral form infinite chains along [010] by sharing two oxygen atoms, which is the unique crystallographic feature of this fluoride phosphated compound. The chains are further linked by the fluorine edges of the YO₆F₂ polyhedra in such a way that, within each chain, the polyhedra alternately have common fluorine atoms with the neighboring chains to their left and right. © 2001

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Key Words: fluoride phosphate; yttrium; sodium; single-crystal X-ray diffraction; IR spectroscopy; second harmonic generation.

1. INTRODUCTION

At present there is great interest in synthesizing new complex phosphates because of their potential applications as luminophores, molecular sieves, and ionic conductors or their catalytic properties. During a study dealing with a new family of $\text{Li}_x\text{RY}_{1-x}(\text{PO}_4)_{1-x}\text{F}_{4x}$ ($R = \text{Gd-Lu, Y}$) structure, closely related to zircon (1), it has been established that Li^+ ions may occupy a site with a tetrahedral environment, whereas the charge balance may be achieved by simultaneous substitution of F^- for O^{2-} ions.

In some other fluoride phosphates of the aforementioned structures, such as $M'M\text{PO}_4\text{F}$ ($M' = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Rb}^+$; $M = \text{Al}^{3+}, \text{Cr}^{3+}, \text{Fe}^{3+}, \text{Sb}^{3+}$) (2–9), the F^- ions belong to the octahedra surrounding the bivalent or trivalent cations. Along with it, they participate in the coordination of phos-

phorus, as is the case in $\text{CoPO}_3\text{F} \cdot 3\text{H}_2\text{O}$ (10), where PO_3F tetrahedra have been evidenced.

In this work we describe the synthesis and crystal structure of NaYFPO₄ and compare its structure with other natural and synthetic fluoride phosphate compounds.

2. EXPERIMENTAL

2.1. Preparation

The NaYFPO₄ compound was prepared by a hydrothermal reaction ($T = 473$ K, $p = 20$ bar, 300 h) in a Teflon-lined stainless-steel autoclave, starting reagents from Y_2O_3 , $\text{NH}_4\text{H}_2\text{PO}_4$, NaF ($\text{Na}^+ : \text{P}^{5+}$ and $\text{Na}^+ : \text{Y}^{3+}$ starting molar ratios are 2.67 and 3.0, respectively), and H_2O . The synthesis of this compound was performed at 473 K. After a slow cooling at 10 K/h to 313 K, the crystalline products were filtered, washed with distilled water and acetone, and finally dried in air at room temperature. A transparent crystal was selected and its structure was determined by single-crystal X-ray diffraction. An X-ray powder pattern of the bulk product indicated that it contained a small amount of unknown phase and all other reflections in the pattern were in excellent agreement with those calculated from single-crystal data.

2.2. Thermogravimetric Analysis (TGA)

The thermogravimetric analysis (DTA, TG, DTG) of sodium yttrium fluoride phosphate was performed using an OD-103 derivatograph. The sample was heated from 300 to 1273 K at 10 K/min in air and then cooled back.

2.3. IR Spectroscopy

Infrared spectrum was collected on a Nicolet Magna-750 Fourier spectrometer in the range of 400–4000 cm^{-1} . The analysis of spectrum was carried out in the area of PO_4^{3-} and OH^- group oscillations (Table 1).

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TABLE 1
The IR Spectrum of NaYFPO₄ in the Area of the PO₄³⁻ Groups Oscillations

Assignments	NaYFPO ₄
ν_{2E}	420 w; 465 w
ν_{4F2}	559 m; 583 sh; 632 m
ν_{1A}	998 s
ν_{3F2}	890 sh; 963 s; 1031 s; 1078 s; 1181 sh
PO ₄ ³⁻ -site symmetry	C _{2v}
PO ₄ ³⁻ -factor group	C _{2h}

Note. Abbreviations used: w, weak; m, medium; s, strong; sh, shoulder.

2.4. Single-Crystal X-ray Diffraction

Single crystals were selected under a polarizing microscope and the quality of them was then checked by Laue photographs. Data were collected on a Nonius CAD4 diffractometer at the room temperature.

Unit cell parameters and orientation matrix were determined by a least-squares fit of 24 reflections in the range $14 < \theta < 17$. Axial oscillation photographs were taken to check the cell parameters and symmetry properties. Of the 894 reflections collected, 358 unique reflections were considered [$F_o > 4\sigma(F_o)$] after Lorentz and polarization corrections. A semiempirical absorption correction was applied based on several ψ -scans. Systematic-absence conditions were consistent with noncentrosymmetric (*C2* (No. 5), *Cm* (No. 8)) and centrosymmetric (*C2/m* (No. 12)) space groups. The space group *C2/m* was used for the crystallographic analysis. Both Na and Y atomic positions were easily localized using direct methods. Then, eight anionic positions with approximately the same electron density were deduced from subsequent least-squares cycles and Fourier synthesis. Refinement of NaYFPO₄ structure showed that if all suggested anion positions are refined as oxygen atom positions, one of the oxygen atoms has an abnormally low atomic displacement parameter. The position of that atom was estimated successfully by single-crystal X-ray diffraction data and by bond valence sum calculations (11) as the fluorine atom position. Final anisotropic atomic refinement converged to $R_1 = 0.0244$ ($wR_2 = 0.0629$) for 358 reflections with $F_o > 4\sigma(F_o)$ (Table 2). Final atomic coordinates and equivalent isotropic atomic displacement parameters are given in Table 3. Selected interatomic distances and angles are listed in Table 4. Neutral atom scattering factors (12) and anomalous scattering terms for the atoms were included. Structure solution and refinement were performed using the SHELXS-97 and SHELXL-97 programs (13, 14).

2.5. Second Harmonic Generation (SHG)

The second harmonic generation response of NaYFPO₄ powder was measured in the reflection mode. A Q-switch

pulsed Nd:YAG laser operating at 1064 nm with a 6.25-Hz repetition rate and a 12-ns pulse width was used as radiation source. The average power incident on the reflector was 0.5 MW. Powdered crystalline SiO₂ was used as a standard sample.

3. RESULTS AND DISCUSSION

3.1. Physical Measurements

According to the thermal analysis data, sodium yttrium fluoride phosphate is stable up to 1120 K. Above this temperature it undergoes congruent melting.

The IR spectrum for NaYFPO₄ shows bands in the 800–1200 cm⁻¹ region associated with Y–O and P–O resonances and does not contain any band between 3000 and 3500 cm⁻¹ corresponding to the OH stretching.

The second harmonic generation measurement provides a highly sensitive and definitive test of symmetry center absence in crystalline materials. The NaYFPO₄ sample gave a negative SHG signal, indicating that the structure does have a symmetry center.

TABLE 2
Crystallographic Data and Data Collection Parameters for NaYFPO₄

Chemical formula	NaYFPO ₄
F_w (g)	225.86
Symmetry	Monoclinic
Space group	<i>C2/m</i> (No. 12)
Unit cell parameters	
a (Å)	8.944(2)
b (Å)	6.930(1)
c (Å)	6.469(1)
β (°)	106.11(3)
V (Å ³)	385.2(2)
Z	4
D , calc. (g cm ⁻³)	3.895
Data collection temperature (K)	293
Crystal size (mm)	0.30 × 0.15 × 0.12
Radiation	MoK α ($\lambda = 0.71073$ Å)
μ (MoK α) (mm ⁻¹)	15.58
Scan mode	$\omega - \theta$
Recording range θ (°)	2–26
$F(000)$	424.0
Index range	$-11 \leq h \leq 11, 0 \leq k \leq 8, 0 \leq l \leq 7$
No. of measured reflections	894
No. of independent reflections	453 ($R_{int} = 0.032$)
No. of reflections with $F_o > 4\sigma(F_o)$	358
Number of variables	45
Weighting scheme	$\omega = 1/[\sigma^2(F_o^2) + (0.0239P)^2]$ where $P = (\text{Max}(F_o^2, 0) + 2F_o^2)/3$
R_1	0.0244
wR_2	0.0629
G.O.F.	$s = 1.030$
$(\Delta\rho)_{\text{max,min}}/e \text{ \AA}^{-3}$	0.61, -0.77

TABLE 3
Atomic Positions and Equivalent Isotropic (U_{eq} , Å²) Atomic Displacement Parameters for NaYFPO₄

Atoms	Wyckoff positions	x/a	y/b	z/c	U_{eq}
Y	4i	0.71714(7)	0	0.11749(8)	0.0051(2)
Na	4h	$\frac{1}{2}$	0.2054(4)	$\frac{1}{2}$	0.0218(7)
P	4i	0.1535(2)	0	0.2760(2)	0.0051(3)
F	4i	0.4823(4)	0	0.1898(5)	0.0108(8)
O(1)	8j	0.6953(3)	0.6743(5)	0.1562(4)	0.0095(7)
O(2)	4i	0.7455(6)	0	0.4920(7)	0.0120(10)
O(3)	4i	0.9809(5)	0	0.2699(7)	0.0110(10)

3.2. Description of the Structure

Figure 1 presents a perspective view of the three-dimensional network of the crystal structure of NaYFPO₄ fluoride phosphate. A yttrium atom anchors the [YO₆F₂] polyhedron. The two F⁻ anions occur in a *cis*-arrangement. As usually encountered, shorter distances ⟨Y–F⟩ (2.273–2.275 Å) can be noticed in comparison with ⟨Y–O⟩ (2.285–2.445 Å) distances (Table 4). The fluorine distribution in yttrium and sodium polyhedra proposed for NaYFPO₄ is supported by various evidence and also confirmed by the accurate refinement noted above. A precedent is set by NaAlPO₄F (3), where the fluoride ions occupy only the interoctahedral sites. Bond valence sum (BVS) calculations support the location of F⁻ ions in the yttrium fluoride phosphate as modeled here. For NaYFPO₄, the BVS value

of 0.998, is in excellent accordance with the expected value of 1.00 for F⁻, when considering Y–F and Na–F interactions (Table 5). Assuming an oxide ion to occupy the same site, the BVS value of 1.64 is obtained, which is substantially below the expected value of 2.00 for O²⁻. The [YO₆F₂] polyhedra share two *cis*-oxygen atoms, thus forming infinite chains running along [010], as is shown in Fig. 2. These chains represent the main crystallographic feature of the structure of NaYFPO₄. The chains are further linked by the fluorine edges of the [YO₆F₂] polyhedra in such a way that within each chain, the polyhedra have common fluorine atoms with the neighboring chains to their right and left, alternately (Fig. 3). By such a linkage, a layer of [YO₆F₂] polyhedra forms in the *ab* plane. Finally, the PO₄³⁻ tetrahedra share all common oxygen vertices with the [YO₆F₂] polyhedra to form the three-dimensional polyhedral network, already shown in Fig. 3. As a consequence, neither of the anions remains terminal.

The 3D polyhedral network has channels spreading along [100], in which the Na⁺ cations reside surrounded by eight oxygen atoms of four PO₄³⁻ tetrahedra and two fluorine atoms of two different [YO₆F₂] polyhedra (Fig. 4).

It is interesting to compare the structure NaYFPO₄ with earlier obtained structural information on the compounds of similar structure and composition.

A different topology of the layers has been found in NaSbPO₄F·1.5H₂O (9). In this compound, Sb³⁺ adopts the fivefold coordination, like Ti⁴⁺ in Na₂TiSiO₅, but the layer is increased because the tetragonal pyramids are stacked on both sides by the tetrahedra.

TABLE 4
Interatomic Distances (Å) and Angles (°) in NaYFPO₄ Structure

Y	Y polyhedron CN 8							
	F'	F''	O(1)'	O(1)''	O(3)	O(3)	O(1)'''	O(1)''''
F'	2.273(4)	2.562(7)	3.264(4)	3.264(4)	4.378(6)	4.315(5)	2.790(4)	2.790(4)
F''	68.6(1)	2.275(4)	3.001(4)	3.001(4)	4.345(6)	2.610(6)	4.286(5)	4.286(5)
O(1)'	91.48(8)	82.28(7)	2.285(3)	4.514(6)	3.334(4)	3.078(4)	4.260(3)	2.691(6)
O(1)''	91.48(8)	82.28(7)	162.0(1)	2.285(3)	3.334(4)	3.078(4)	2.691(6)	4.260(3)
O(3)	147.3(1)	144.2(1)	93.54(8)	93.54(8)	2.291(5)	2.859(6)	3.022(5)	3.022(5)
O(2)	137.0(1)	68.4(1)	82.87(7)	82.87(7)	75.76(2)	2.365(4)	4.533(5)	4.533(5)
O(1)'''	72.4(1)	130.4(1)	69.2(1)	128.44(9)	79.2(1)	141.0(1)	2.445(3)	2.416(6)
O(1)''''	72.4(1)	130.4(1)	128.44(9)	69.2(1)	79.2(1)	141.0(1)	59.2(1)	2.445(3)
⟨Y _{VIII} –O, F⟩ = 2.33 Å, $d_{\text{Shannon}} = 2.38$ Å								
P	P tetrahedron				Na polyhedron CN 10			
	O(2)	O(3)	O(1)'	O(1)''	Na–F × 2		2.429(3)	
O(2)	1.522(5)	2.503(6)	2.500(5)	2.500(6)	–O(3) × 2		2.505(4)	
O(3)	110.1(3)	1.533(5)	2.542(4)	2.542(4)	–O(2) × 2		2.630(4)	
O(1)'	109.7(2)	111.8(2)	1.536(5)	2.416(6)	–O(1)' × 2		3.009(3)	
O(1)''	109.7(2)	111.8(2)	103.7 (3)	1.536(5)	–O(1)'' × 2		3.047(4)	
⟨P–O⟩ = 1.53 Å, $d_{\text{Shannon}} = 1.52$ Å								
⟨Na _X –O, F⟩ = 2.72 Å, $d_{\text{Shannon}} = 2.70$ Å								

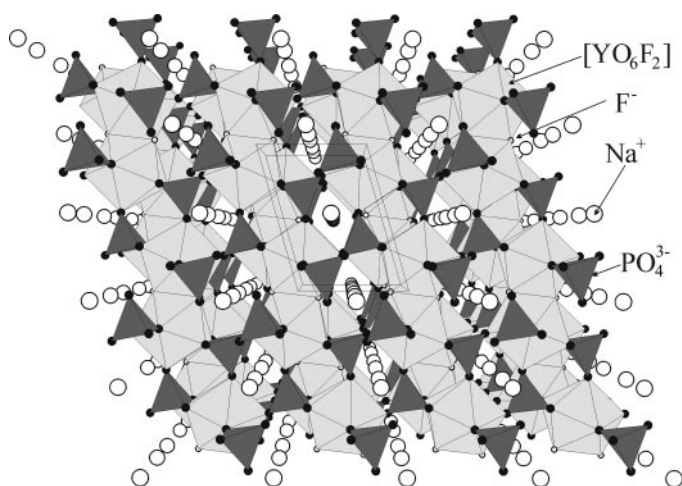


FIG. 1. A perspective view along the b axis of the NaYFPO₄ three-dimensional network.

The structural transformation caused by the isotopic replacement of similar in size acidic (Si^{4+} and P^{5+}) atoms gives rise to homologous series of titanite, CaTiO(SiO₄) (15), to which the minerals lacroixite NaAlPO₄F (3) and durangite NaAlAsO₄F (16) belong. Their anionic frameworks are composed of infinite chains of vertex-shared TiO₆ or AlO₆ octahedra, further linked by chains of AO₄ tetrahedra ($A = \text{P}, \text{Si}, \text{or As}$). Another type of structure transformation, caused by the necessity of anionic adaptation to dimensional variations ($\text{Na}^+ \rightarrow \text{Li}^+$) in the cationic sublattice, is accompanied by the unit cell symmetry being lowered to triclinic in the minerals isotypic with ambligonite LiAlPO₄F. As a rule, this process in nature goes in the opposite direction, and the genesis of lacroixite NaAlPO₄F is usually associated with Na metasomatism of a

TABLE 5
Bond Valence Analysis (11) of NaYFPO₄

Atoms	Na	Y	P	$\sum s$	Charge
F	0.131	0.369	—	0.998	1
O(1)	0.038	0.481	1.202	2.067	2
O(1)'	0.038	0.481	1.202	2.067	2
O(2)	0.106	0.387	1.248	1.848	2
O(3)	0.149	0.473	1.212	1.982	2
$\sum s$	0.952	3.180	4.863		
Charge	1	3	5		

Note. The results refer to the equation $s = \exp[(R_0 - d)/0.37]$ with $R_0 = 2.014, 1.904, 1.800, 1.677,$ and 1.604 for $\text{Y}^{3+}-\text{O}, \text{Y}^{3+}-\text{F}^-, \text{Na}^+-\text{O}, \text{Na}^+-\text{F}^-,$ and $\text{P}^{5+}-\text{O}$, respectively.

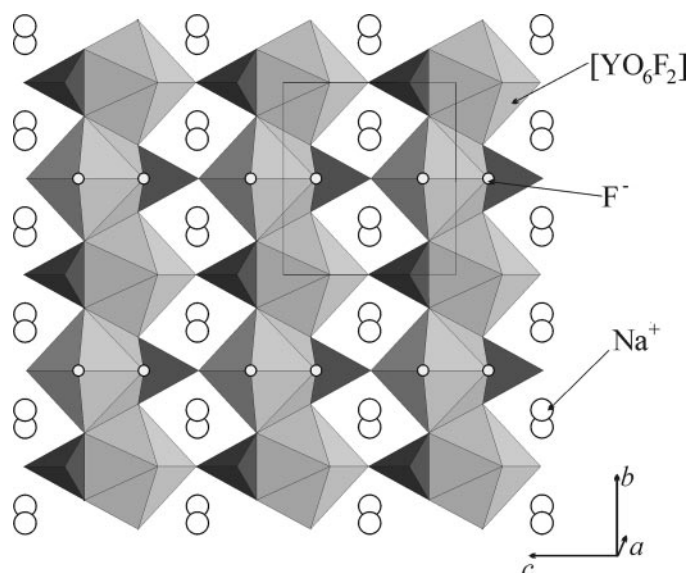


FIG. 2. The $[\text{YO}_6\text{F}_2]$ polyhedra forming infinite chains along $[010]$. The PO_4^{3-} tetrahedra are also shown.

series of minerals: ambligonite, LiAlPO₄F, montebrasite, LiAlPO₄(OH). It is shown in (17) that in a course of Na–Li substitutions in primary phosphates, that nonisostructural minerals lacroixite, NaAlPO₄F, and LiAlPO₄(OH) can form during the decomposition of a solid solution (Li,Na)AlPO₄(OH, F).

Yet another structure type, known as KTP owing to the first investigated crystal structure of KTiOPO₄, is realized

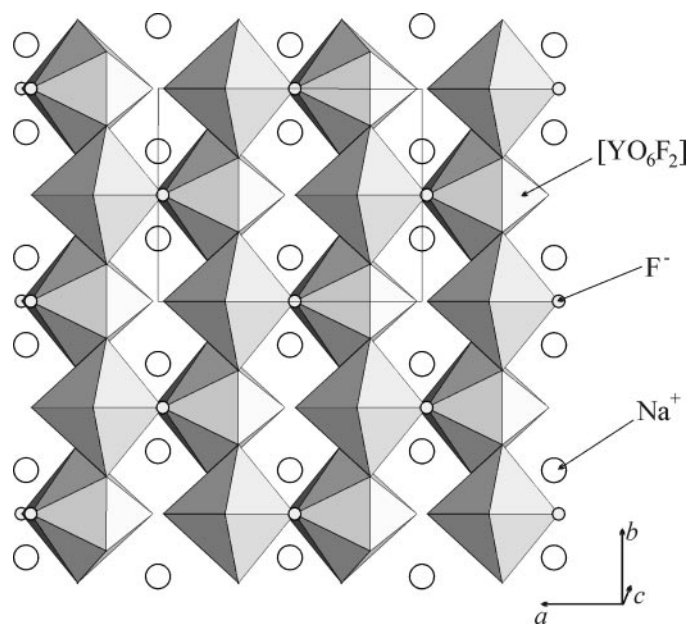


FIG. 3. Projection of NaYFPO₄ structure almost along the c axis. The layer of yttrium polyhedra in plane (ab) is shown.

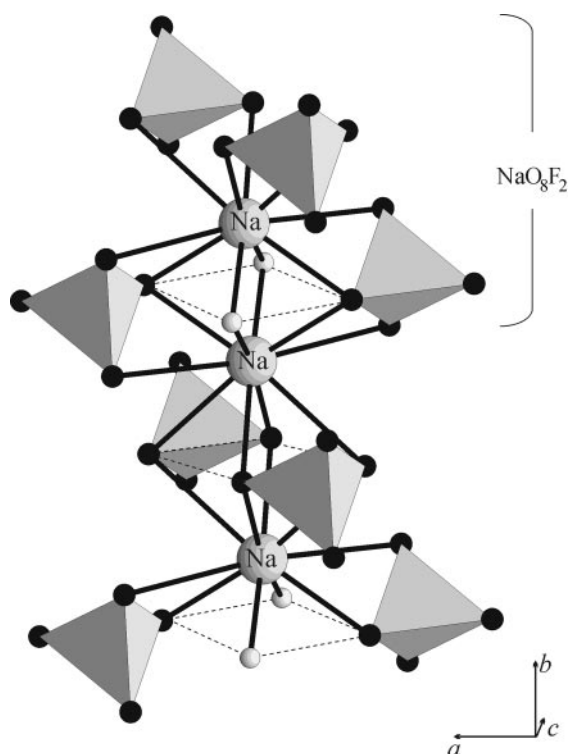


FIG. 4. The coordination of Na^+ in NaYFPO_4 structure [small open circles, F; small black circles, O].

in oxy- and fluoride phosphates MRPO_4X ($R = 3\text{- or }4\text{-valent elements, } X = \text{O}^{2-}, \text{F}^-$), when M is a large univalent cation, K^+ , Rb^+ , Ag^+ , Tl^+ , or NH_4^+ (18). The principal difference of frameworks of a KTP type structure is a motif of the octahedra arrangement. Now, they share not only *trans*- (as in the previous structure groups), but also *cis*-vertices to form zigzag chains.

We believe that it is worthwhile to compare the crystal structure of the title compound with the structures of the fluoride phosphates with the general formula $\text{M}_2\text{PO}_4\text{F}$ ($\text{M}^{2+} = \text{Fe}^{2+}, \text{Cu}^{2+}, \text{Cd}^{2+}, \text{Mn}^{2+}, \text{Mg}^{2+}$). It is easy to show that the formal "replacement" $\text{M}^{2+} + \text{R}^{3+} \rightarrow 2\text{M}^{2+}$ will make their compositions congruent. However, the structures of the divalent derivatives differ from the structure of NaYFPO_4 . The $\text{Fe}_2\text{PO}_4\text{F}$ structure can be described as consisting of nonintersecting chains of Fe_2O_{10} bioctahedra, running mutually perpendicular in two directions (19). Thus obtained framework is consolidated by PO_4 tetrahedra, sharing all their four corners with Fe octahedra.

The structure of wagnerite, $\text{Mg}_2\text{PO}_4\text{F}$ (20), a member of the triplite ($\text{Mn}_2\text{PO}_4\text{F}$) group (21), is characterized by the

doubling of the c parameter. As a consequence, the number of independent Mg atoms is increased to 8, and one-half of polyhedra is described as trigonal bipyramids (C.N. (Mg) = 5) and the second half as MgO_6 octahedra. The F atom in wagnerite bridges only for three metal atoms and not four as in $\text{Fe}_2\text{PO}_4\text{F}$.

To conclude, the new fluoride phosphate NaYFPO_4 has an original structure with its own structure type. The structure exhibits no analogy with the structures of other fluoride- or oxy-containing phosphates (or silicates). It is expected that other compounds of general formula NaRFPO_4 ($R = \text{rare earth elements}$) belong to the same structure type.

ACKNOWLEDGMENT

This work was supported by the Russian Foundation for Basic Research (No. 98-03-32-688).

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