

The Glaserite-like Structure of Double Sodium and Iron Phosphate $\text{Na}_3\text{Fe}(\text{PO}_4)_2$

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The double sodium and iron phosphate $\text{Na}_3\text{Fe}(\text{PO}_4)_2$ was synthesized and studied by the XRD method, the second harmonic generation technique, and Mössbauer and IR spectroscopy. The compound crystallizes into a monoclinic system (space group $C2/c$) with unit cell parameters $a = 9.0736(2)$ Å, $b = 5.0344(1)$ Å, $c = 13.8732(3)$ Å, $\beta = 91.435(2)^\circ$ and is found to be related to the $\text{K}_3\text{Na}(\text{SO}_4)_2$ structure type. The crystal structure was determined by Rietveld analysis ($R_{\text{wp}} = 5.86$, $R_1 = 2.03$). Iron cations occupy the M (Na) position while sodium cations occupy the X (K) and Y (K) positions of the glaserite-like structure. Mössbauer spectroscopy shows the presence of high-spin Fe^{3+} in octahedral coordination. © 2001 Academic Press

Key Words: phosphates; iron; sodium; X-ray diffraction; rietveld; IR spectroscopy; Mössbauer spectroscopy.

INTRODUCTION

The double phosphates of sodium and trivalent metals $\text{Na}_3R(\text{AO}_4)_2$, ($A = \text{P, V, As}$; $R = \text{Y, Bi, In}$, rare earth elements) (1–9) have been studied and characterized by different methods. These phosphates and vanadates have been extensively studied as luminescent materials. Most of these compounds crystallize into a $\beta\text{-K}_2\text{SO}_4$ -like structure (1–6, 9), with eight varieties of crystal lattice for $\text{Na}_3R(\text{AO}_4)_2$ being distinguished (10).

In the $\text{Na}_3\text{PO}_4\text{-FePO}_4$ system two compounds are formed: $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ (11) and $\text{Na}_3\text{Fe}(\text{PO}_4)_2$ (12). The first compound congruently melts at 940°C , and the second compound uncongruently melts at 790°C (12). $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ crystallizes into two polymorphous modifications with NASICON-like structure (11, 13, 14). Despite the interest in the $\text{Na}_3\text{PO}_4\text{-FePO}_4$ system, the structure of double iron and sodium phosphate with the composition of $\text{Na}_3\text{Fe}(\text{PO}_4)_2$ has not been studied yet. This paper describes

the preparation, characterization, and crystal structure of the double phosphate $\text{Na}_3\text{Fe}(\text{PO}_4)_2$.

EXPERIMENTAL

Synthesis

The sodium and iron double phosphate $\text{Na}_3\text{Fe}(\text{PO}_4)_2$ was synthesized by the solid state method from stoichiometric mixtures of FePO_4 , $(\text{NH}_4)_2\text{HPO}_4$, and Na_2CO_3 at $740\text{--}760^\circ\text{C}$ for 120–140 hours in air. FePO_4 was prepared by heating a stoichiometric ratio of Fe_2O_3 and $(\text{NH}_4)_2\text{HPO}_4$ at $880\text{--}900^\circ\text{C}$. The end of the reaction was tested by X-ray diffraction.

Characterization

Powder diffraction data for indexing X-ray patterns and structure refinement of $\text{Na}_3\text{Fe}(\text{PO}_4)_2$ were obtained at room temperature in Bragg–Brentano geometry using a RIGAKU D/max RC powder diffractometer equipped with a scintillation detector ($\text{CuK}\alpha$ radiation, $\lambda = 1.5418$ Å, 12 kW rotating generator, Be window, Ni filter). The data were collected over the range $10\text{--}100^\circ$ (2θ) with a step of 0.02° .

Analysis of the reflex positions in the X-ray pattern of $\text{Na}_3\text{Fe}(\text{PO}_4)_2$ (Table 1) has shown that this compound is isotypic with monoclinic distorted $\text{K}_3\text{Na}(\text{CrO}_4)_2$ (15). The indexing of the X-ray pattern of $\text{Na}_3\text{Fe}(\text{PO}_4)_2$ was carried out in a monoclinic system, space group $C2/c$, $a = 9.079(1)$ Å, $b = 5.037(1)$ Å, $c = 13.889(1)$ Å; $\beta = 91.43(1)^\circ$; the corresponding figures of merit are $M_{20} = 20.2$, and $F_{30} = 32.7$ (0.0148, 62).

The second harmonic generation (SHG) response of the powder $\text{Na}_3\text{Fe}(\text{PO}_4)_2$ sample was measured in the reflection mode (16). The absence of noticeable signal of SHG leads to the choice of the centric space group $C2/c$.

Mössbauer spectroscopy experiments were performed in transmission geometry at room temperature using a

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TABLE 1
Indexing of the X-Ray Pattern of $\text{Na}_3\text{Fe}(\text{PO}_4)_2$

$2\Theta_{\text{exp}}$	I/I_0	hkl	$d_{\text{exp}} (\text{\AA})$	$d_{\text{calc}} (\text{\AA})$	$2\Theta_{\text{exp}}$	I/I_0	hkl	$d_{\text{exp}} (\text{\AA})$	$d_{\text{calc}} (\text{\AA})$
12.735	100	002	6.95	6.94	48.480	14	404	1.8777	1.8780
19.545	2	200	4.54	4.54	48.689	22	-224	1.8701	1.8697
20.127	4	110	4.412	4.404	49.266	15	224	1.8495	1.8494
23.662	33	202	3.760	3.756	50.219	2	-117	1.8167	1.8168
23.782	49	-112	3.741	3.740	50.715	2	117	1.8001	1.8004
25.659	12	004	3.472	3.471	52.391	2	-316	1.7463	1.7453
27.787	2	-113	3.211	3.210	52.772	20	008	1.7346	1.7356
28.128	5	113	3.172	3.171	53.406	1	225	1.7155	1.7154
32.050	26	-204	2.7925	2.7909	53.762	1	026	1.7050	1.7040
32.650	72	-114	2.7426	2.7424	54.277	1	511	1.6900	1.6902
32.861	22	204	2.7255	2.7246	54.445	1	420	1.6852	1.6858
33.023	18	114	2.7125	2.7103	55.810	9	512		1.6494
34.563	76	310	2.5950	2.5935			-422	1.6472	1.6452
35.613	20	020	2.5209	2.5185	56.165	5	131	1.6376	1.6385
38.099	29	-115	2.3619	2.3619	56.755	1	-118	1.6220	1.6214
38.925	1	006	2.3137	2.3141	57.304	14	118	1.6078	1.6081
39.497	1	-313	2.2815	2.2834	57.879	1	-423	1.5931	1.5935
39.702	1	400	2.2702	2.2691	58.151	1	226	1.5863	1.5857
40.208	2	313	2.2428	2.2422	59.299	4	027	1.5583	1.5583
40.802	2	023	2.2115	2.2122	59.782	4	-514	1.5469	1.5468
41.433	6	-221	2.1793	2.1790	60.613	9	-424	1.5277	1.5276
41.600	5	221	2.1709	2.1708	61.044	12	514	1.5179	1.5183
42.176	1	402	2.1426	2.1411	61.307	5	600	1.5120	1.5127
42.942	3	-222	2.1061	2.1064	61.616	3	424	1.5052	1.5055
43.409	1	-206	2.0845	2.0827	62.154	11	-134	1.4934	1.4935
43.999	4	-116	2.0579	2.0588	62.426	6	134	1.4876	1.4883
44.390	5	206	2.0407	2.0411	63.338	7	330	1.4683	1.4681
45.397	2	-223	1.9978	1.9979	63.906	17	-318	1.4567	1.4569
45.845	6	223	1.9793	1.9792	64.740	1	-332	1.4399	1.4398
47.305	3	-404	1.9215	1.9214	65.316	20	028		1.4291
							318	1.4286	1.4284

constant acceleration Mössbauer spectrometer coupled with a 1024 multichannel analyzer. A $^{57}\text{Co}/\text{Rh}$ γ -ray source was used. The velocity scale was calibrated relative to $\alpha\text{-Fe}_2\text{O}_3$. Each chemical shift value (δ) given hereafter is referred to $\alpha\text{-Fe}$. Experimental data were resolved into symmetric doublets with Lorentzian lineshapes using an iterative least-squares fit program.

The room-temperature Mössbauer spectrum of $\text{Na}_3\text{Fe}(\text{PO}_4)_2$ is shown in Fig. 1. The spectrum indicates the presence of a symmetrical doublet with $CS = 0.42$ mm/s (chemical shift), $QS = 0.50$ mm/s (quadrupole splitting), and $\text{FWHM} = 0.31$ mm/s (full width at half-maximum). The CS value characterizes high-spin Fe^{3+} in an octahedral environment.

The IR spectrum was recorded on a Nicolet Magna-750 Fourier spectrometer in the range $400\text{--}4000\text{ cm}^{-1}$. The IR spectrum of $\text{Na}_3\text{Fe}(\text{PO}_4)_2$ is shown in Fig. 2. The analysis of the spectrum was carried out in the area of PO_4^{3-} group oscillations. IR spectroscopy data have proved the existence of only one type of PO_4^{3-} tetrahedra in the structure. The IR spectrum corresponds with the site symmetry of PO_4^{3-}

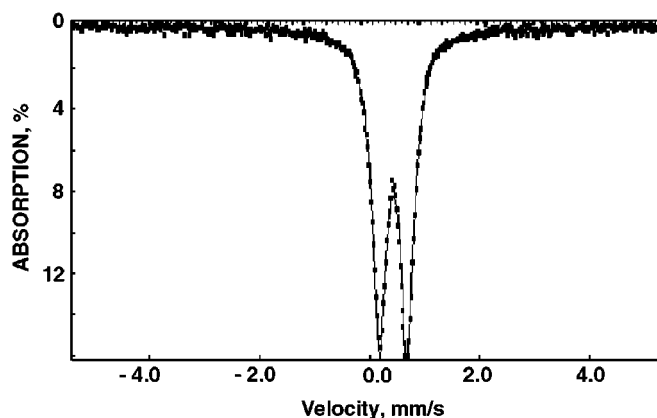


FIG. 1. Mössbauer spectrum of $\text{Na}_3\text{Fe}(\text{PO}_4)_2$ at room temperature.

groups and with the expected modes for the C_{2h} factor group. The IR spectra of $\text{Na}_3\text{Fe}(\text{PO}_4)_2$ and α - and β - $\text{Na}_3\text{In}(\text{PO}_4)_2$ (9) are different from each other which indirectly indicates that iron and indium compounds belong to different structural types.

Structure Determination

The atomic coordinates of the $\text{K}_3\text{Na}(\text{CrO}_4)_2$ (15) structure were used as initial positional parameters for the refinement of crystal structure, which was carried out by the Rietveld method (17) using the RIETAN-94 program (18, 19). The background was refined with a fifth-order polynomial. The peak profile was refined by a modified pseudo-Voigt function. The occupancy factors for iron and sodium positions were allowed to refine but they did not deviate significantly from full occupation.

After refinement a good agreement between observed and calculated patterns was achieved (Fig. 3). Reasonable values

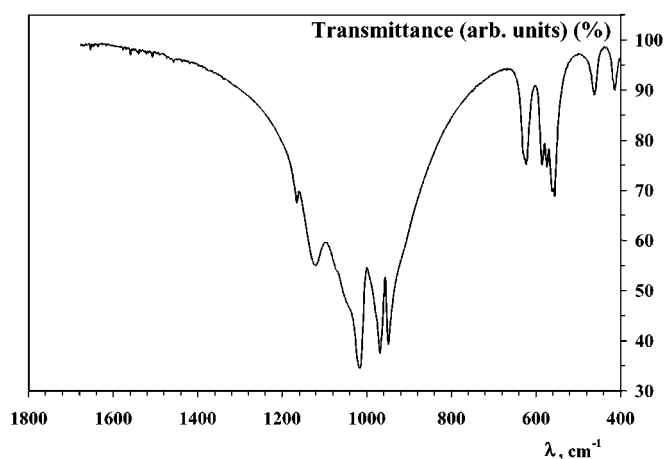


FIG. 2. IR spectrum of $\text{Na}_3\text{Fe}(\text{PO}_4)_2$.

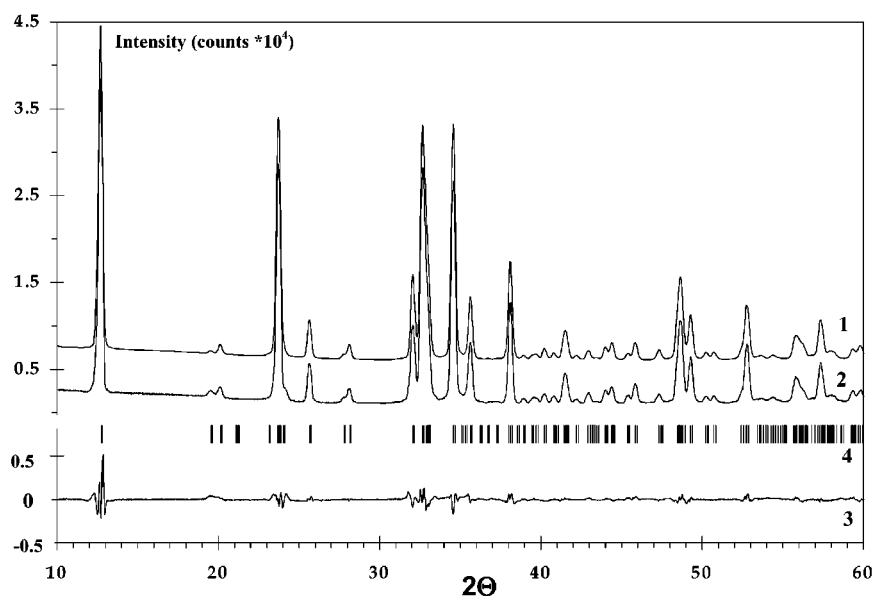


FIG. 3. Portion of the Rietveld refinement profiles for Na₃Fe(PO₄)₂: (1) calculated, (2) observed, (3) difference X-ray powder diffraction patterns, and (4) Bragg reflections. The calculated pattern is shifted 5000 counts from the observed pattern.

of isotropic temperature parameters for all atoms were obtained. The details of data collection are given in Table 2. The final atomic parameters and interatomic distances and angles are presented in Table 3 and Table 4, respectively.

The Fourier maps of electronic density distribution were calculated using the GSAS program (20). The final plots of the observed electron density maps did not show residual peaks. The electron density on the different Fourier map ($\Delta\rho_{\text{exp}}(xyz)$) was within $\pm 0.7e^{-}\text{\AA}^{-3}$.

3. RESULTS AND DISCUSSION

The comparison of Na₃Fe(PO₄)₂, K₃Na(CrO₄)₂ (15), and K₃Na(SO₄)₂ (21) structures reveals that the double iron and sodium phosphate crystallizes into a glaserite-like

TABLE 2
Crystallographic Data, Recording Conditions, and Refinement Results of Double Phosphate Na₃Fe(PO₄)₂

2θ range (°)	10–100	Unit cell parameters:	
Step scan increment (2θ)	0.02	<i>a</i> (Å)	9.0736(2)
Space group	C2/c	<i>b</i> (Å)	5.0344(1)
<i>Z</i>	4	<i>c</i> (Å)	13.8732(3)
<i>I</i> _{max}	38,416	β (°)	91.435(2)
Number of reflections	320	<i>V</i> (Å ³)	633.54(3)
Preferred orientation (<i>hkl</i>)	(001)	Reliable factors ^a	
Murch–Dollase function coefficient	0.82	<i>R</i> _{WP} , <i>R</i> _P	5.86, 4.20
		<i>R</i> _I , <i>R</i> _F	2.03, 1.40
		<i>S</i>	2.86

^a Defined as in (18).

TABLE 3
Fractional Atomic Coordinates and Thermal Parameters

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{iso}
Na(1)	4e	0	0.0435(9)	0.25	2.8(1)
Na(2)	8f	0.1703(4)	0.5399(7)	0.1319(2)	2.6(1)
Fe	4a	0	0	0	2.0(1)
P	8f	0.1680(3)	0.5191(5)	0.3875(1)	2.2(1)
O(1)	8f	0.1641(6)	0.3884(8)	0.2904(3)	2.4(1)
O(2)	8f	0.1099(6)	0.326(1)	0.4738(2)	2.2(1)
O(3)	8f	0.0730(5)	0.7875(8)	0.3848(3)	0.9(1)
O(4)	8f	0.3359(6)	0.5920(9)	0.4148(2)	1.7(1)

(K₃Na(SO₄)₂, space group $P\bar{3}m1$ (21)) structure. The Na₃Fe(PO₄)₂ crystal lattice can be obtained out of a glaserite unit cell by the following transformation: $a = 2a_g + b_g$; $b = b_g$; $c = 2c_g$, where *a*, *b*, *c* and *a_g*, *b_g*, *c_g* are vectors of Na₃Fe(PO₄)₂ and K₃Na(SO₄)₂, respectively. The basic frame K₃Na(SO₄)₂ in Na₃Fe(PO₄)₂ remains the same despite of the PO₄³⁻ tetrahedron rotation (Fig. 4).

In the 3-D framework of K₃Na(SO₄)₂, cations occupy three types of positions with different oxygen sharing: Y^[4+6]O₁₀, X^[6+6]O₁₂, and M^[6]O₆. The Y^[4+6]O₁₀ polyhedron, as in the β -K₂SO₄-like structure (22), is formed by 10 atoms of oxygen: four of them are closer to the Y position than the other six (edges of three tetrahedra). The nearest six oxygen atoms (one out of each tetrahedron) participate in the formation of X^[6+6]O₁₂ and M^[6]O₆ polyhedra. Besides, six remote apical oxygen atoms participate in the formation of X^[6+6]O₁₂ polyhedra. In the glaserite structure Y and

TABLE 4
Interatomic Distances (Å) and Angles (°) in Double Phosphate
 $\text{Na}_3\text{Fe}(\text{PO}_4)_2$

Na(1)–O(1) × 2	2.346(6)	Fe–O(4) × 2	1.934(4)
–O(3) × 2	2.352(5)	–O(2) × 2	1.992(5)
–O(4) × 2	2.771(4)	–O(3) × 2	2.048(4)
⟨Na(1)–O⟩	2.49	⟨Fe–O⟩	1.99
Na(2)–O(1)	2.330(4)	P–O(1)	1.499(4)
–O(4)	2.346(6)	–O(2)	1.539(5)
–O(2)	2.476(4)	–O(3)	1.603(4)
–O(1)′	2.534(6)	–O(4)	1.603(5)
–O(3)	2.541(6)	⟨P–O⟩	1.56
–O(3)′	2.668(6)	O(1)–P–O(2)	109.9(3)
–O(2)′	2.819(7)	O(1)–P–O(3)	110.4(3)
–O(4)′	2.855(6)	O(1)–P–O(4)	108.3(3)
–O(2)″	3.036(7)	O(2)–P–O(3)	110.8(3)
⟨Na(2)–O⟩	2.62	O(2)–P–O(4)	108.7(3)
		O(3)–P–O(4)	108.6(3)

X positions are occupied by potassium cations; sodium cations occupy the *M* position.

In the $\text{Na}_3\text{Fe}(\text{PO}_4)_2$ framework *X* and *Y* positions are occupied by sodium cations: $\text{Na}(1)\text{O}_6$ and $\text{Na}(2)\text{O}_9$ polyhedra, respectively (Fig. 4). The PO_4^{3-} tetrahedra rotation

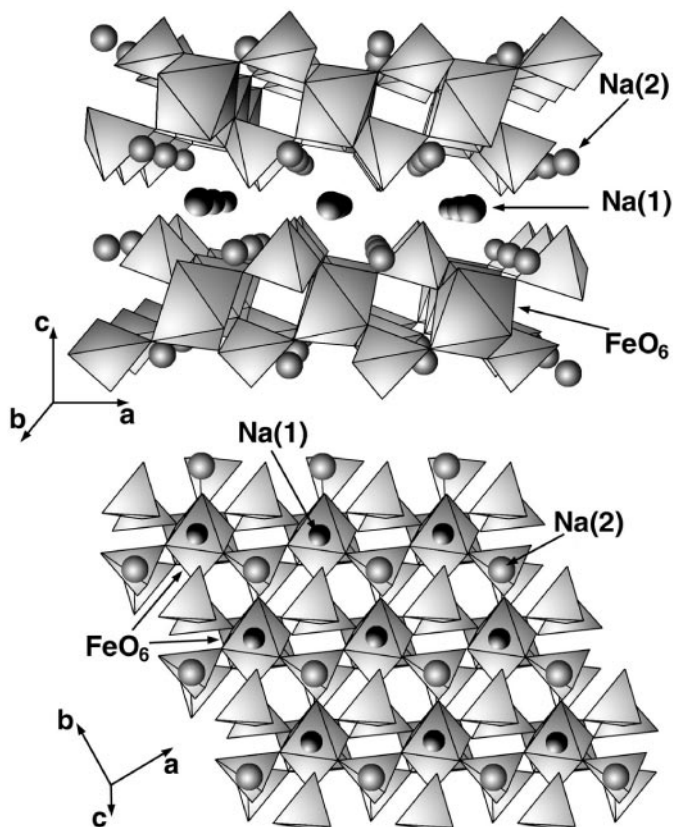


FIG. 4. Projections of $\text{Na}_3\text{Fe}(\text{PO}_4)_2$ structure.

leads to a decrease of the coordination number of sodium cations in *Y* position to 9. Only six oxygen atoms, owing to rotation of PO_4^{3-} tetrahedra and removal of apical oxygen atoms, form the coordination polyhedron of *X* position (Fig. 5).

FeO_6 is a slightly deformed octahedron with Fe–O distances equal to 1.934–2.048 Å. The quadrupole splitting of the doublet in the Mössbauer spectra confirms slight distortion of the FeO_6 octahedra. The $\text{Na}(1)\text{O}_6$ polyhedron is deformed much stronger (distance Na(1)–O is equal to 2.346–2.771 Å). As shown in Fig. 5, $\text{Na}(1)\text{O}_6$ may be considered as a distorted prism.

The PO_4^{3-} tetrahedra rotation and the displacement of sodium cations generate six-membered tunnels (two FeO_6 octahedra and four PO_4^{3-} tetrahedra) along the $[010]$ direction. The Na^+ cations are located in these tunnels and their migration is possible. Each $\text{Na}(1)\text{O}_6$ is connected with six $\text{Na}(2)\text{O}_9$ polyhedra via the common edges O(1)–O(3) or O(3)–O(4): three of them are in a layer above Na(1) and the other three are in a layer below Na(1) (Figs. 4, 5). The coordination environment of $\text{Na}(2)\text{O}_9$ is similar to that of $\text{Na}(1)\text{O}_6$. The distance Na(1)–Na(2) is equal to 3.375–3.41 Å.

The author (23) has analyzed well-known structures of $\text{K}_3\text{Na}(\text{SO}_4)_2$ and $\beta\text{-K}_2\text{SO}_4$ type and proposed to regard the difference between the cation radii in *M* and *X*(*Y*) or *Y* and *X* positions as criteria for stability of these structures. The $\text{K}_3\text{Na}(\text{SO}_4)_2$ -like structures are stable if the difference in cation radii (Δr) in *M* and *X*(*Y*) positions lies in the range $0.59 \leq \Delta r \leq 0.89$ Å (23). When this difference decreases, metastable or $\beta\text{-K}_2\text{SO}_4$ -like structures are formed. In the $\text{Na}_3\text{Fe}(\text{PO}_4)_2$ structure the differences in cation radii (Δr) of sodium ($r_{\text{VI}}(\text{Na}^+) = 1.02$, $r_{\text{IX}}(\text{Na}^+) = 1.32$ Å) in *X*(*Y*) and iron ($r_{\text{VI}}(\text{Fe}^{3+}(\text{HS})) = 0.675$ Å (24)) in the *M* position are

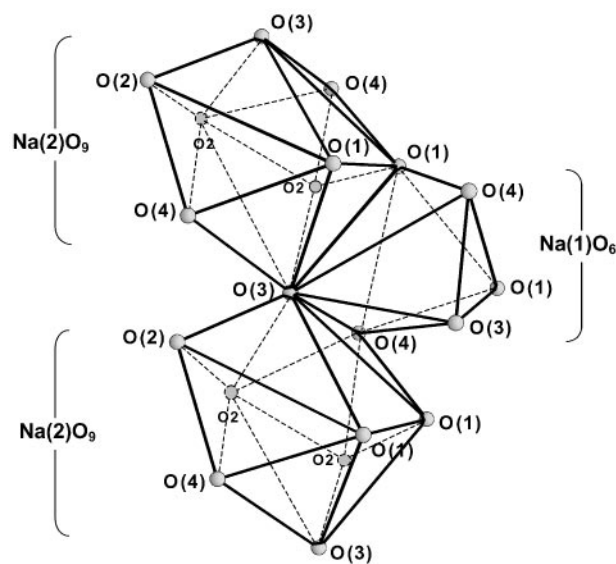


FIG. 5. $\text{Na}(2)\text{O}_9$ and $\text{Na}(1)\text{O}_6$ polyhedra in structure $\text{Na}_3\text{Fe}(\text{PO}_4)_2$.

0.375 and 0.675 Å, respectively. After the Na₃Fe(PO₄)₂ structure was studied it was found that the stability range of glaserite-like structure could be expanded up to $0.375 \leq \Delta r \leq 0.89$ Å.

As was noted the Na₃R(AO₄)₂ (A = P, V, As; R = Y, Bi, In, rare earth elements) compounds crystallize in β-K₂SO₄- or NASICON-like framework (10). It has been defined that Na₃Fe(PO₄)₂ belongs to the K₃Na(SO₄)₂ structure type. This is a new type of crystallization for Na₃R(AO₄)₂ compounds.

Note added in proof. We managed to specify the structure Na₃Fe(PO₉)₂ (25) using powder X-ray data after the paper was accepted for publication.

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