

$\text{Na}_4\text{Fe}^{2+}\text{Fe}^{3+}(\text{PO}_4)_3$, a new synthetic NASICON-type phosphate

Frédéric Hatert

University of Liège, Laboratory of Mineralogy B.18, B-4000 Liège, Belgium
 Correspondence e-mail: fhatert@ulg.ac.be

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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{P}-\text{O}) = 0.008 \text{ \AA}$; R factor = 0.052; wR factor = 0.125; data-to-parameter ratio = 8.4.

This paper reports the crystal structure of tetrasodium diiron tris(phosphate), $\text{Na}_4\text{Fe}^{2+}\text{Fe}^{3+}(\text{PO}_4)_3$, which has been synthesized hydrothermally at 773 K and 0.1 GPa. The crystal structure has been refined in the space group $R\bar{3}c$ and is identical to that of γ -NASICON. The heteropolyhedral framework is based on a regular alternation, in three dimensions, of corner-sharing PO_4 tetrahedra and FeO_6 octahedra, constituting so-called ‘lantern units’ stacked along the c axis. The Na^+ cations are distributed over two crystallographic sites: the six-coordinated Na1 site which lies between two ‘lantern units’, and the eight-coordinated Na2 site which lies at the same z value as the P site.

Related literature

For general background, see: Hatert *et al.* (2006); Hatert & Fransolet (2006); Hatert (2007a,b). For related structures, see: Sljukic *et al.* (1969); Masquelier *et al.* (2000). For bond-valence calculations, see: Brown & Altermatt (1985). For the use of the pressure vessel, see: Tuttle (1949). For the standard used in the chemical analysis, see: Fransolet (1975). For software used to establish the space group, see: Le Page (1987).

Experimental

Crystal data

$\text{Na}_4\text{Fe}_2(\text{PO}_4)_3$
 $M_r = 488.57$
 Trigonal, $R\bar{3}c$
 $a = 8.9543 (9) \text{ \AA}$
 $c = 21.280 (4) \text{ \AA}$
 $V = 1477.6 (4) \text{ \AA}^3$

$Z = 6$
 Mo $K\alpha$ radiation
 $\mu = 3.68 \text{ mm}^{-1}$
 $T = 293 \text{ K}$
 $0.08 \times 0.05 \times 0.03 \text{ mm}$

Data collection

Bruker P4 diffractometer
 Absorption correction: ψ scan (*XSCANS*; Siemens, 1991)
 $T_{\min} = 0.693$, $T_{\max} = 0.896$
 721 measured reflections
 294 independent reflections
 284 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.021$
 3 standard reflections
 every 97 reflections
 intensity decay: 1.9%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.052$
 $wR(F^2) = 0.125$
 $S = 1.40$
 294 reflections
 35 parameters
 $\Delta\rho_{\max} = 1.70 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.97 \text{ e \AA}^{-3}$

Data collection: *XSCANS* (Siemens, 1991); cell refinement: *XSCANS*; data reduction: *SHELXTL-Plus* (Sheldrick, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ATOMS* (Dowty, 1993); software used to prepare material for publication: *SHELXTL-Plus*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: MG2067).

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supporting information

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Na₄Fe²⁺Fe³⁺(PO₄)₃, a new synthetic NASICON-type phosphate

Frédéric Hatert

S1. Comment

In the natural geological environment of granitic pegmatites, Na–Fe–Mn-bearing phosphates play important geochemical and petrological roles. The alluaudite group of minerals, with an idealized chemical composition Na₂(Mn,Fe²⁺)₂Fe³⁺(PO₄)₃, constitutes a good example of primary phosphates which can be used as geothermometer, or to constrain the oxygen fugacity which prevailed in granitic pegmatites (Hatert *et al.*, 2006). In order to better understand the crystallization conditions of iron-rich alluaudites in pegmatites, we decided to investigate the Na–Fe²⁺–Fe³⁺ (+PO₄) ternary system by hydrothermal methods (Hatert & Fransolet, 2006). These experiments produced several new phosphates, which crystallized in the Na-rich part of the system and were investigated by single-crystal X-ray diffraction techniques (Hatert, 2007*a,b*). Starting from the composition Na₄Fe²⁺Fe³⁺(PO₄)₃, the hydrothermal synthesis at 500°C and 0.1 GPa produced large pink crystals; their crystal structure is reported herein.

The crystal structure of the title compound has been refined in space group $R\bar{3}c$ and corresponds to that of centrosymmetric γ -NASICON-type phosphates (Sljukic *et al.*, 1969; Masquelier *et al.*, 2000). The heteropolyhedral framework is based on the regular alternation, in the three dimensions, of corner-sharing PO₄ tetrahedra (P—O = 1.533–1.538 Å) and FeO₆ octahedra (Fe—O = 2.010–2.130 Å; Fig. 1), and shows the stacking, along the *c* direction, of the so-called 'lantern units' (Masquelier *et al.*, 2000). The monovalent Na⁺ cations are distributed over two crystallographic sites: the 6-coordinated Na1 site (Na1—O = 2.402 Å) which lies between two 'lantern units', and the 8-coordinated Na2 site (Na2—O = 2.487–2.990 Å) which lies at the same *z* value as the P atom (Fig. 2).

Bond-valence sums were calculated for each ion using the parameters of Brown & Altermatt (1985). The P1 bond-valence sum is 4.99, and the O-atom bond-valence sums are within the normal acceptable range (1.93–2.10). The bond-valence sums also confirm that the Na1 and Na2 sites are filled by Na (0.98–1.19), and that the Fe1 site contains an equal amount of Fe²⁺ and Fe³⁺ (2.54).

A comparison with the crystal structure of γ -Na₃Fe₂(PO₄)₃ (Masquelier *et al.*, 2000) shows that the two phosphates are isostructural. However, the amount of Na in the title compound reaches 4 atoms per formula unit, and is higher than the Na-content of any other known NASICON-type phosphate. This high Na-content is necessary to maintain charge balance, since the Fe1 site is occupied by 50% Fe²⁺ and 50% Fe³⁺. Na atoms are located on the same positions as in γ -Na₃Fe₂(PO₄)₃, but the two Na1 and Na2 sites are completely filled by Na atoms in the title compound, whereas their occupancy factors are 0.85 (3) (Na1) and 0.72 (3) (Na2) in γ -Na₃Fe₂(PO₄)₃ (Masquelier *et al.*, 2000).

Masquelier *et al.* (2000) demonstrated that the size of the Na1 cavity is increased as this site is depopulated, and that this increase has a direct influence on the value of the *c* unit-cell parameter. This hypothesis is corroborated by our structural data, which show that a full occupancy of the Na1 site in Na₄Fe²⁺Fe³⁺(PO₄)₃ induces small values for the Na1—O distances and for the *c* parameter (2.402 and 21.280 Å, respectively), while a partial occupancy of this site in γ -Na₃Fe₂(PO₄)₃ induces larger values for these parameters (2.500 and 21.808 Å, respectively; Masquelier *et al.*, 2000). The presence of significant amounts of Fe²⁺ in the Fe1 site of the title compound also induces a significant increase of the Fe1

—O average bond length (2.070 Å), when compared to the Fe1—O bond length reported for γ -Na₃Fe₂(PO₄)₃ (2.002 Å; Masquelier *et al.*, 2000). This increase does not affect the *c* unit-cell parameter, but induces a significant increase of the *a* parameter, from 8.727 Å in γ -Na₃Fe₂(PO₄)₃ (Masquelier *et al.*, 2000), to 8.954 Å in the title compound.

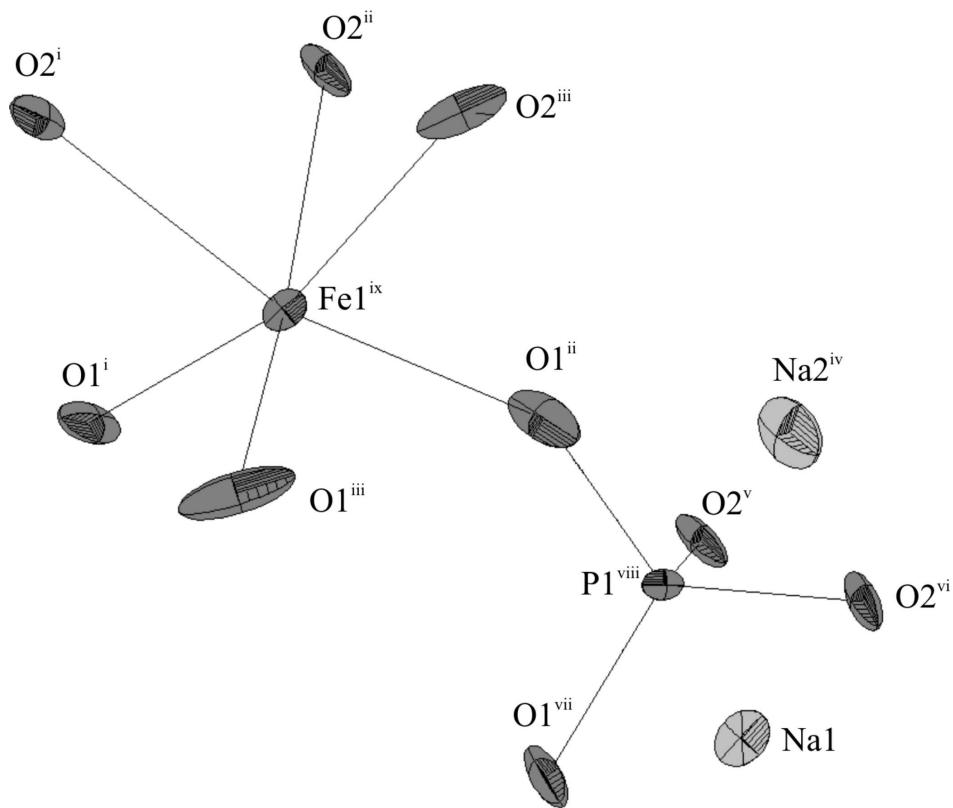
S2. Experimental

The title compound was synthesized under hydrothermal conditions. The starting material was prepared by mixing NaH₂PO₄.H₂O, Na₂HPO₄.2H₂O, FeO and Fe₂O₃ in proportions 2:1:1:1/2. About 25 mg of the homogenized mixture was sealed into a gold tube with an outer diameter of 2 mm and a length of 25 mm, containing 2 mg of distilled water. The gold capsule was then inserted in a Tuttle-type pressure vessel (Tuttle, 1949) and maintained at a temperature of 500°C and a pressure of 0.1 GPa. After 3 d, the sample still in the gold tube in the autoclave, was quenched to room temperature in a stream of cold air. The synthesized phosphates consisted of large pink crystals of the title compound, associated with colourless crystals of maricite, NaFe²⁺(PO₄), and with isometric black crystals of Na₇Fe₄(PO₄)₆.

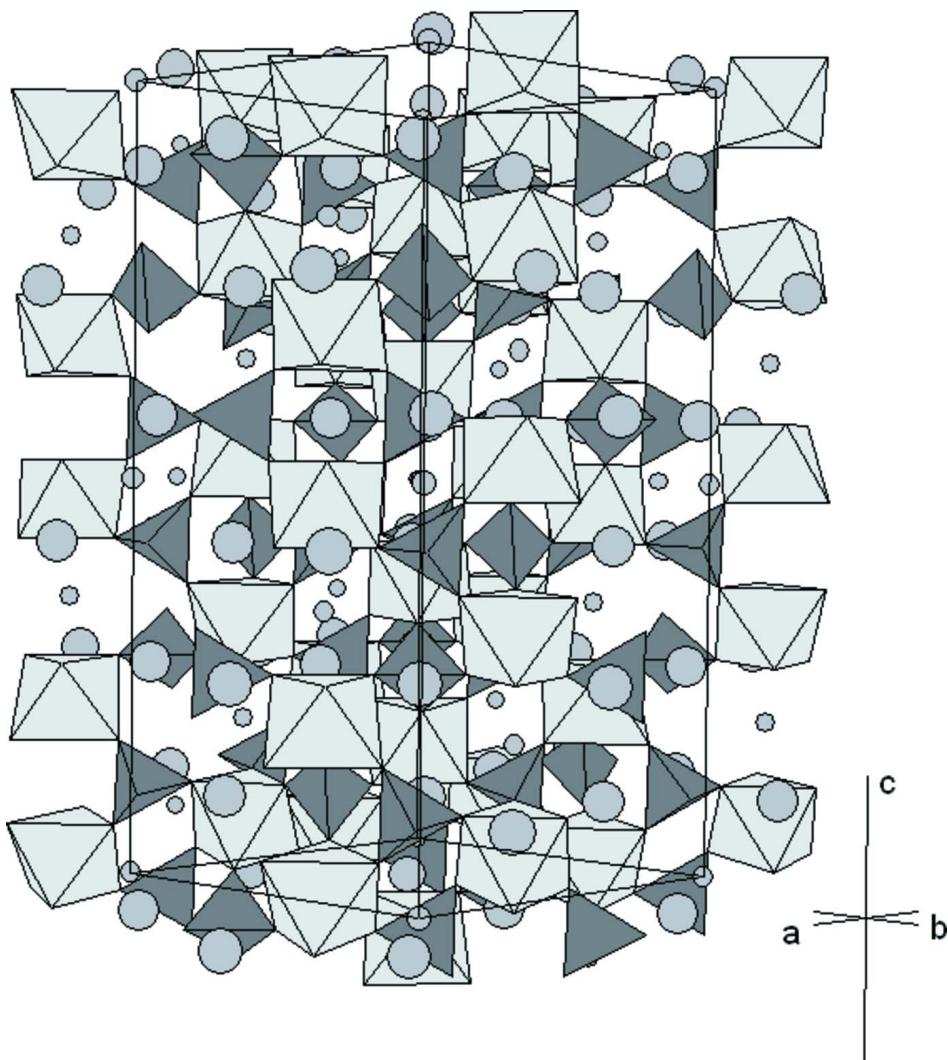
A chemical analysis of the title compound has been performed with a CAMEBAX SX-50 electron microprobe (15 kV acceleration voltage, 20 nA beam current, analyst H.-J. Bernhardt, Ruhr-Universität Bochum, Germany). The standards used were graftonite from Kabira (sample KF16; Fransolet, 1975) (Fe, P), and jadeite (Na). The average of 6 point analyses gives P₂O₅ 42.47, FeO* 16.94, Fe₂O₃* 14.17, Na₂O 24.47, total 98.05 wt. % (* values calculated to maintain charge balance). The chemical composition, calculated on the basis of 3 P, corresponds to Na_{3.96}Fe²⁺_{1.18}Fe³⁺_{0.89}(PO₄)₃.

S3. Refinement

A first refinement in space group *R*3 converged to a satisfactory model with *R*₁ = 0.0328, but a check of these structural data with the program ADDSYM (Le Page, 1987) immediately allowed to identify supplementary symmetry elements, thus confirming the space group *R*³*c*. All atoms were refined anisotropically, and a preliminary refinement of the site occupancy factors of Na1 and Na2 confirmed that these sites were filled with Na atoms only. In the final refinement cycle, the Na1 and Na2 site occupancy factors were consequently constrained to 1.0.

**Figure 1**

Fragment of the $\text{Na}_4\text{Fe}^{2+}\text{Fe}^{3+}(\text{PO}_4)_3$ structure (50% displacement ellipsoids) showing the bonding environments of the Fe and P cations. [Symmetry codes: (i) $2/3 + x - y, 1/3 - y, 1/3 - z$; (ii) $2/3 - x, 1/3 - x + y, 1/3 - z$; (iii) $2/3 + y, 1/3 + x, 1/3 - z$; (iv) $x, -y - 1/3, z$; (v) $x, x - y, 1/6 - z$; (vi) $1/3 + y, 2/3 - x + y, 1/6 - z$; (vii) $2/3 - y, 1/3 + x - y, z - 1/6$; (viii) $-y, -x, z$; (ix) $x + 2/3, y + 1/3, 1/3 - z$.]

**Figure 2**

Polyhedral view of the $\text{Na}_4\text{Fe}^{2+}\text{Fe}^{3+}(\text{PO}_4)_3$ structure. FeO_6 octahedra are shown with light shading, PO_4 tetrahedra with dark shading, $\text{Na}1$ as small circles, and $\text{Na}2$ as large circles.

Tetrasodium diiron tris(phosphate)

Crystal data


 $M_r = 488.57$

 Trigonal, $R\bar{3}c$

Hall symbol: -R 3 2 "c"

 $a = 8.9543 (9) \text{ \AA}$
 $c = 21.280 (4) \text{ \AA}$
 $V = 1477.6 (4) \text{ \AA}^3$
 $Z = 6$
 $F(000) = 1422$
 $D_x = 3.294 \text{ Mg m}^{-3}$

 Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 35 reflections

 $\theta = 5.9\text{--}12.6^\circ$
 $\mu = 3.68 \text{ mm}^{-1}$
 $T = 293 \text{ K}$

Isometric crystal, pink

 $0.08 \times 0.05 \times 0.03 \text{ mm}$

Data collection

Bruker P4
diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
 ω scans
Absorption correction: ψ scan
(*XSCANS*; Siemens, 1991)
 $T_{\min} = 0.693$, $T_{\max} = 0.896$
721 measured reflections

294 independent reflections
284 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.021$
 $\theta_{\max} = 25.0^\circ$, $\theta_{\min} = 3.3^\circ$
 $h = -10 \rightarrow 1$
 $k = -1 \rightarrow 10$
 $l = -25 \rightarrow 1$
3 standard reflections every 97 reflections
intensity decay: 1.9%

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.052$
 $wR(F^2) = 0.125$
 $S = 1.40$
294 reflections
35 parameters
0 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
 $w = 1/[\sigma^2(F_o^2) + (0.0415P)^2 + 5P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 1.70 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.97 \text{ e } \text{\AA}^{-3}$
Extinction correction: *SHELXL97* (Sheldrick, 2008), $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0027 (6)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Fe1	0.0000	0.0000	0.14926 (9)	0.0082 (8)
P1	-0.3333	-0.3672 (3)	0.0833	0.0080 (9)
Na1	0.0000	0.0000	0.0000	0.0129 (17)
Na2	-0.3333	-0.0278 (7)	0.0833	0.0262 (13)
O1	0.1950 (8)	0.2066 (9)	0.1913 (3)	0.0213 (15)
O2	0.1869 (8)	0.0152 (7)	0.0838 (3)	0.0135 (14)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Fe1	0.0070 (8)	0.0070 (8)	0.0105 (11)	0.0035 (4)	0.000	0.000
P1	0.0041 (15)	0.0109 (12)	0.0065 (14)	0.0021 (7)	0.0000 (10)	0.0000 (5)
Na1	0.009 (2)	0.009 (2)	0.020 (4)	0.0047 (12)	0.000	0.000
Na2	0.013 (3)	0.029 (2)	0.031 (3)	0.0065 (13)	-0.001 (2)	-0.0005 (11)
O1	0.015 (3)	0.032 (4)	0.013 (3)	0.008 (3)	-0.006 (2)	-0.008 (3)
O2	0.012 (3)	0.019 (3)	0.012 (3)	0.010 (3)	-0.004 (2)	-0.006 (2)

Geometric parameters (\AA , ^\circ)

Fe1—O1	2.010 (6)	Na1—O2 ^{vii}	2.402 (5)
Fe1—O1 ⁱ	2.010 (6)	Na1—O2 ⁱ	2.402 (5)
Fe1—O1 ⁱⁱ	2.010 (6)	Na1—O2 ⁱⁱ	2.402 (5)
Fe1—O2 ⁱ	2.130 (6)	Na1—O2 ^{viii}	2.402 (5)
Fe1—O2	2.130 (6)	Na2—O2 ⁱ	2.487 (8)
Fe1—O2 ⁱⁱ	2.130 (6)	Na2—O2 ^v	2.487 (8)
P1—O1 ⁱⁱⁱ	1.533 (6)	Na2—O2 ⁱⁱ	2.493 (6)
P1—O1 ^{iv}	1.533 (6)	Na2—O2 ^{ix}	2.493 (6)
P1—O2 ⁱ	1.538 (6)	Na2—O1 ^{ix}	2.534 (6)
P1—O2 ^v	1.538 (6)	Na2—O1 ⁱⁱ	2.534 (6)
Na1—O2 ^{vi}	2.402 (5)	Na2—O1 ^x	2.990 (8)
Na1—O2	2.402 (5)	Na2—O1 ^{xi}	2.990 (8)
O1—Fe1—O1 ⁱ	101.7 (2)	O2—Na1—O2 ^{viii}	109.0 (2)
O1—Fe1—O1 ⁱⁱ	101.7 (2)	O2 ^{vii} —Na1—O2 ^{viii}	71.0 (2)
O1 ⁱ —Fe1—O1 ⁱⁱ	101.7 (2)	O2 ⁱ —Na1—O2 ^{viii}	180.00 (17)
O1—Fe1—O2 ⁱ	165.5 (2)	O2 ⁱⁱ —Na1—O2 ^{viii}	109.0 (2)
O1 ⁱ —Fe1—O2 ⁱ	86.5 (2)	O2 ⁱ —Na2—O2 ^v	60.5 (3)
O1 ⁱⁱ —Fe1—O2 ⁱ	88.1 (2)	O2 ⁱ —Na2—O2 ⁱⁱ	68.1 (3)
O1—Fe1—O2	86.5 (2)	O2 ^v —Na2—O2 ⁱⁱ	128.6 (2)
O1 ⁱ —Fe1—O2	88.1 (2)	O2 ⁱ —Na2—O2 ^{ix}	128.6 (2)
O1 ⁱⁱ —Fe1—O2	165.5 (2)	O2 ^v —Na2—O2 ^{ix}	68.1 (3)
O2 ⁱ —Fe1—O2	81.8 (2)	O2 ⁱⁱ —Na2—O2 ^{ix}	163.3 (4)
O1—Fe1—O2 ⁱⁱ	88.1 (2)	O2 ⁱ —Na2—O1 ^{ix}	93.1 (2)
O1 ⁱ —Fe1—O2 ⁱⁱ	165.5 (2)	O2 ^v —Na2—O1 ^{ix}	70.0 (2)
O1 ⁱⁱ —Fe1—O2 ⁱⁱ	86.5 (2)	O2 ⁱⁱ —Na2—O1 ^{ix}	114.28 (19)
O2 ⁱ —Fe1—O2 ⁱⁱ	81.8 (2)	O2 ^{ix} —Na2—O1 ^{ix}	68.73 (19)
O2—Fe1—O2 ⁱⁱ	81.8 (2)	O2 ⁱ —Na2—O1 ⁱⁱ	70.0 (2)
O1 ⁱⁱⁱ —P1—O1 ^{iv}	109.6 (5)	O2 ^v —Na2—O1 ⁱⁱ	93.1 (2)
O1 ⁱⁱⁱ —P1—O2 ⁱ	106.9 (3)	O2 ⁱⁱ —Na2—O1 ⁱⁱ	68.73 (19)
O1 ^{iv} —P1—O2 ⁱ	112.1 (3)	O2 ^{ix} —Na2—O1 ⁱⁱ	114.28 (19)
O1 ⁱⁱⁱ —P1—O2 ^v	112.1 (3)	O1 ^{ix} —Na2—O1 ⁱⁱ	160.8 (4)
O1 ^{iv} —P1—O2 ^v	106.9 (3)	O2 ⁱ —Na2—O1 ^x	113.49 (19)
O2 ⁱ —P1—O2 ^v	109.2 (5)	O2 ^v —Na2—O1 ^x	154.86 (18)
O2 ^{vi} —Na1—O2	180.0 (3)	O2 ⁱⁱ —Na2—O1 ^x	52.52 (18)
O2 ^{vi} —Na1—O2 ^{vii}	71.0 (2)	O2 ^{ix} —Na2—O1 ^x	112.9 (3)
O2—Na1—O2 ^{vii}	109.0 (2)	O1 ^{ix} —Na2—O1 ^x	86.74 (13)
O2 ^{vi} —Na1—O2 ⁱ	109.0 (2)	O1 ⁱⁱ —Na2—O1 ^x	108.0 (2)
O2—Na1—O2 ⁱ	71.0 (2)	O2 ⁱ —Na2—O1 ^{xi}	154.86 (18)
O2 ^{vii} —Na1—O2 ⁱ	109.0 (2)	O2 ^v —Na2—O1 ^{xi}	113.49 (19)
O2 ^{vi} —Na1—O2 ⁱⁱ	109.0 (2)	O2 ⁱⁱ —Na2—O1 ^{xi}	112.9 (3)
O2—Na1—O2 ⁱⁱ	71.0 (2)	O2 ^{ix} —Na2—O1 ^{xi}	52.52 (18)
O2 ^{vii} —Na1—O2 ⁱⁱ	180.0 (3)	O1 ^{ix} —Na2—O1 ^{xi}	108.0 (2)

O2 ⁱ —Na1—O2 ⁱⁱ	71.0 (2)	O1 ⁱⁱ —Na2—O1 ^{xi}	86.74 (13)
O2 ^{vi} —Na1—O2 ^{viii}	71.0 (2)	O1 ^x —Na2—O1 ^{xi}	82.0 (3)

Symmetry codes: (i) $-x+y, -x, z$; (ii) $-y, x-y, z$; (iii) $-x+y-1/3, y-2/3, z-1/6$; (iv) $x-y-1/3, x-2/3, -z+1/3$; (v) $x-y-2/3, -y-1/3, -z+1/6$; (vi) $-x, -y, -z$; (vii) $y, -x+y, -z$; (viii) $x-y, x, -z$; (ix) $y-2/3, x-1/3, -z+1/6$; (x) $x-1/3, x-y+1/3, z-1/6$; (xi) $-x-1/3, -y+1/3, -z+1/3$.