

The iron phosphate NaBaFe₂(PO₄)₃

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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{Fe}-\text{O}) = 0.005$ Å; disorder in main residue; R factor = 0.025; wR factor = 0.060; data-to-parameter ratio = 9.4.

A new iron phosphate, sodium barium diiron tris(phosphate), NaBaFe₂(PO₄)₃, has been synthesized by the flux method and shown to exhibit the well known langbeinite type structure. The Na, Ba and Fe atoms all lie on threefold axes, while the P and O atoms occupy general positions, one of the O atoms being disordered over two positions, with site occupancy factors of *ca* 0.7 and 0.3. The [Fe₂(PO₄)₃]_∞ framework consists of FeO₆ octahedra sharing all their corners with the PO₄ tetrahedra. The Na⁺ and Ba²⁺ cations are almost equally distributed over two distinct cavities, in which they occupy slightly different positions.

Related literature

For related literature, see: Baur (1974); Moffat (1978); Padhi *et al.* (1997); Shannon (1976). For the structure of langbeinite, see Zemmann & Zemmann (1957); Battle *et al.* (1986, 1988).

Experimental

Crystal data

NaBaFe₂(PO₄)₃
 $M_r = 556.94$
 Cubic, $P2_13$
 $a = 9.796$ (1) Å
 $V = 940.1$ (3) Å³

$Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 7.82$ mm⁻¹
 $T = 293$ (2) K
 $0.1 \times 0.1 \times 0.1$ mm

Data collection

Enraf–Nonius CAD4
 diffractometer
 Absorption correction: ψ scan
 (North *et al.*, 1968)
 $T_{\min} = 0.35$, $T_{\max} = 0.46$
 2114 measured reflections

657 independent reflections
 644 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.082$
 2 standard reflections
 frequency: 120 min
 intensity decay: 1%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.025$
 $wR(F^2) = 0.059$
 $S = 0.92$
 657 reflections
 70 parameters
 4 restraints

$\Delta\rho_{\max} = 0.57$ e Å⁻³
 $\Delta\rho_{\min} = -0.49$ e Å⁻³
 Absolute structure: Flack (1983),
 123 Friedel pairs
 Flack parameter: -0.03 (3)

Table 1

Selected bond angles (°).

O4B ⁱ –Fe2–O1 ⁱⁱ	89.8 (8)	O3–P–O4A	115.1 (3)
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Symmetry codes: (i) z, x, y ; (ii) $-z + \frac{3}{2}, -x + 1, y - \frac{1}{2}$.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BR2076).

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Comment

Iron phosphates are of increasing interest because of their potential applications in various fields ranging from catalysis (Moffat, 1978) to ionic conductivity (Padhi *et al.*, 1997). Moreover, these materials are very attractive in terms of basic research because they exhibit a rich structural chemistry owing to the possible (+2/+3) mixed valence of iron and its tendency to exhibit various coordination polyhedra.

The title compound, sodium barium diiron phosphate NaBaFe₂(PO₄)₃ was isolated during a systematic investigation of the Na₂O–MO–Fe₂O₃–P₂O₅ systems where *M* is a divalent cation. Its structure (Fig. 1) exhibits a three-dimensional [Fe₂(PO₄)₃]_∞ framework built up from corner-sharing FeO₆ octahedra and PO₄ tetrahedra. Each octahedron is linked to six adjacent tetrahedra and reciprocally each tetrahedron is connected to four neighboring octahedra. This framework delimits two sorts of large cavities, statistically occupied by the Na⁺ and Ba²⁺ cations.

The two symmetry distinct FeO₆ octahedra contained in this structure are somewhat distorted as indicated by the Fe—O distances ranging from 1.963 (5) to 1.991 (4) Å. The average <Fe—O> distances of 1.986 Å for Fe(1) and 1.973 Å for Fe(2) are slightly lower than the value 2.03 Å predicted by Shannon for octahedral Fe³⁺ ions (Shannon, 1976).

The PO₄ tetrahedron is strongly distorted with P—O distances scattering from 1.47 (2) to 1.547 (7) Å. Corresponding average value of 1.511 Å agrees with those frequently observed in anhydrous monophosphates (Baur, 1974).

The Na⁺ and Ba²⁺ cations are statistically distributed over two distinct cavities in which they occupy slightly different positions and have partial occupancies of 0.47, 0.53, 0.53 and 0.47 for Na(1), Ba(1), Na(2) and Ba(2), respectively. The environments of these cations (Fig. 2) were determined assuming all cation-oxygen distances are shorter than the shortest to next cationic site. Each of the Na(1), Ba(1) and Ba(2) environments consists of nine O atoms with cation-oxygen distances in the ranges 2.76 (2)–3.04 (2) Å, 2.753 (7)–2.950 (6) Å and 2.722 (5)–3.047 (7) Å for Na(1), Ba(1) and Ba(2), respectively. The Na(2) environment consists of six O atoms with Na—O distances varying from 2.604 (8) and 3.004 (6) Å.

The as-described structure is closely related to the langbeinite-like phosphates KBaM₂(PO₄)₃ (*M* = Fe, Cr) (Battle *et al.*, 1986, 1988). However, it differs by the fact that the atom O4, which occupies a single site in the potassium phosphates, is, in the title compound, statistically occupying two distinct positions, O4A and O4B which exhibit partial occupancies of 0.7 and 0.3, respectively. These different values can be explained by the fact that the O4A site is occupied if it is bonded to Na(1), Ba(1) or Ba(2) whereas the O4B site is occupied if it is bonded to Na(1) or Ba(1).

Experimental

Single crystals of the title compound were grown in a flux of sodium dimolybdate Na₂Mo₂O₇ with an atomic ratio P:Mo = 6:1. A starting mixture of 1.071 g of Na₂CO₃, 1.993 g of BaCO₃, 8.162 g of Fe(NO₃)₃·9H₂O, 4.002 g of (NH₄)₂HPO₄

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and 1.454 g of MoO₃ was dissolved in nitric acid and the obtained solution was evaporated to dryness. The dry residue was transferred into a platinum crucible and then heated up 600°C to decompose H₂O and NH₃. In a second step, the sample was melted for 1 h at 900°C and then cooled down to room temperature with a 10° h⁻¹ rate. The final product, obtained after washing with warm water to dissolve the flux is essentially composed of pink and prismatic shaped crystals. Their qualitative elemental analysis using electron microprobe analysis indicated the presence of Na, Ba, Fe and P and no impurity elements have been detected.

Refinement

The Ba and Fe atoms were located by direct methods and the remaining atoms were found by successive difference Fourier maps. All atomic positions were refined anisotropically.

Figures

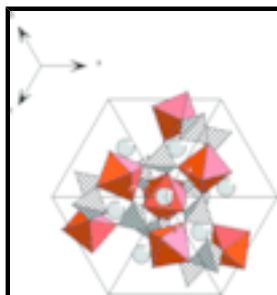


Fig. 1. A projection of the structure along the [111] direction.

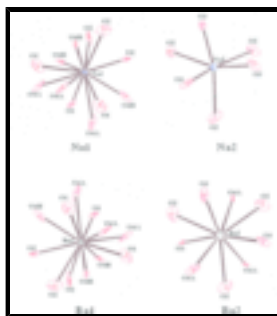


Fig. 2. The environments of the Na and Ba sites showing the anisotropic atomic displacements at the 50% level.

sodium barium diiron tris(phosphate)

Crystal data

NaBaFe₂(PO₄)₃

M_r = 556.94

Cubic, *P*2₁3

Hall symbol: P 2ac 2ab 3

a = 9.796 (1) Å

b = 9.796 (1) Å

c = 9.796 (1) Å

α = 90°

β = 90°

Z = 4

*F*₀₀₀ = 1040

D_x = 3.935 Mg m⁻³

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 9.0–13.0°

μ = 7.82 mm⁻¹

T = 293 (2) K

Prism, pink

$\gamma = 90^\circ$
 $V = 940.1 (3) \text{ \AA}^3$
 $0.1 \times 0.1 \times 0.1 \text{ mm}$

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.082$
Radiation source: fine-focus sealed tube	$\theta_{\text{max}} = 29.9^\circ$
Monochromator: graphite	$\theta_{\text{min}} = 2.9^\circ$
$T = 293(2) \text{ K}$	$h = -1 \rightarrow 13$
$\omega/2\theta$ scans	$k = -1 \rightarrow 13$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$l = -1 \rightarrow 13$
$T_{\text{min}} = 0.35, T_{\text{max}} = 0.46$	2 standard reflections
2114 measured reflections	every 120 min
657 independent reflections	intensity decay: 1%
644 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + 5.7579P]$
$R[F^2 > 2\sigma(F^2)] = 0.025$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.059$	$(\Delta/\sigma)_{\text{max}} = 0.002$
$S = 0.92$	$\Delta\rho_{\text{max}} = 0.57 \text{ e \AA}^{-3}$
657 reflections	$\Delta\rho_{\text{min}} = -0.49 \text{ e \AA}^{-3}$
70 parameters	Extinction correction: SHELXL97 (Sheldrick, 2008), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
4 restraints	Extinction coefficient: 0.0145 (15)
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), with how many Friedel pairs? Flack parameter: $-0.03 (3)$

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.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Na1	0.9427 (12)	0.9427 (12)	0.9427 (12)	0.0144 (3)	0.4738 (16)
Ba1	0.92953 (9)	0.92953 (9)	0.92953 (9)	0.0144 (3)	0.5262 (16)
Na2	0.6862 (8)	0.6862 (8)	0.6862 (8)	0.0232 (4)	0.5262 (16)
Ba2	0.70555 (8)	0.70555 (8)	0.70555 (8)	0.0232 (4)	0.4738 (16)

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Fe1	0.35313 (6)	0.85313 (6)	0.64687 (6)	0.0104 (2)	
Fe2	0.91362 (6)	0.08638 (6)	0.58638 (6)	0.0101 (2)	
P	0.03742 (10)	0.77099 (11)	0.62578 (10)	0.0068 (2)	
O1	0.9926 (5)	0.9134 (4)	0.6562 (7)	0.0461 (14)	
O2	0.9463 (5)	0.6999 (6)	0.5243 (5)	0.0440 (13)	
O3	0.1846 (4)	0.7653 (6)	0.5752 (5)	0.0368 (12)	
O4A	0.0112 (7)	0.6985 (10)	0.7629 (8)	0.0389 (18)	0.701 (4)
O4B	0.0527 (17)	0.672 (2)	0.738 (2)	0.0389 (18)	0.299 (4)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Na1	0.0144 (3)	0.0144 (3)	0.0144 (3)	-0.0019 (3)	-0.0019 (3)	-0.0019 (3)
Ba1	0.0144 (3)	0.0144 (3)	0.0144 (3)	-0.0019 (3)	-0.0019 (3)	-0.0019 (3)
Na2	0.0232 (4)	0.0232 (4)	0.0232 (4)	0.0016 (3)	0.0016 (3)	0.0016 (3)
Ba2	0.0232 (4)	0.0232 (4)	0.0232 (4)	0.0016 (3)	0.0016 (3)	0.0016 (3)
Fe1	0.0104 (2)	0.0104 (2)	0.0104 (2)	0.0001 (2)	-0.0001 (2)	-0.0001 (2)
Fe2	0.0101 (2)	0.0101 (2)	0.0101 (2)	0.0024 (2)	0.0024 (2)	-0.0024 (2)
P	0.0066 (4)	0.0073 (4)	0.0064 (4)	-0.0005 (3)	-0.0028 (3)	0.0010 (3)
O1	0.045 (3)	0.0170 (19)	0.076 (4)	0.0191 (19)	-0.015 (3)	-0.015 (2)
O2	0.029 (2)	0.061 (3)	0.042 (3)	0.003 (2)	-0.025 (2)	-0.031 (2)
O3	0.0120 (16)	0.063 (3)	0.035 (2)	-0.0091 (18)	0.0085 (16)	-0.023 (2)
O4A	0.020 (4)	0.066 (5)	0.031 (3)	0.020 (3)	0.015 (3)	0.040 (3)
O4B	0.020 (4)	0.066 (5)	0.031 (3)	0.020 (3)	0.015 (3)	0.040 (3)

Geometric parameters (\AA , $^\circ$)

Na1—O1 ⁱ	2.864 (12)	Ba2—O3 ^{xiii}	2.772 (5)
Na1—O1	2.864 (12)	Ba2—O3 ^{xiv}	2.772 (5)
Na1—O1 ⁱⁱ	2.864 (12)	Ba2—O2 ⁱⁱ	2.952 (5)
Na1—O4B ⁱⁱⁱ	2.86 (3)	Ba2—O2	2.952 (5)
Na1—O4B ^{iv}	2.86 (3)	Ba2—O2 ⁱ	2.952 (5)
Na1—O4B ^v	2.86 (3)	Ba2—O4A ^{vi}	3.047 (7)
Na1—O4A ^{vi}	3.045 (17)	Ba2—O4A ^{vii}	3.047 (7)
Na1—O4A ^{vii}	3.045 (17)	Ba2—O4A ^{viii}	3.047 (7)
Na1—O4A ^{viii}	3.045 (17)	Fe1—O2 ⁱⁱ	1.979 (4)
Na1—O2 ^{ix}	2.763 (17)	Fe1—O2 ^{xv}	1.979 (4)
Na1—O2 ^x	2.763 (17)	Fe1—O2 ^{xvi}	1.979 (4)
Na1—O2 ^{xi}	2.763 (17)	Fe1—O3 ^{xiii}	1.990 (4)
Ba1—O1 ⁱ	2.753 (7)	Fe1—O3	1.990 (4)
Ba1—O1	2.753 (7)	Fe1—O3 ^{xvii}	1.990 (4)
Ba1—O1 ⁱⁱ	2.753 (7)	Fe1—Ba1 ^{xviii}	3.6878 (19)
Ba1—O4B ⁱⁱⁱ	2.89 (3)	Fe1—Ba2 ^{iv}	3.7867 (6)
Ba1—O4B ^{iv}	2.89 (3)	Fe1—Ba2 ^{xv}	3.7867 (6)
Ba1—O4B ^v	2.89 (3)	Fe2—O4B ^{xix}	1.946 (18)

Ba1—O4A ^{vi}	2.902 (10)	Fe2—O4B ⁱⁱ	1.946 (18)
Ba1—O4A ^{vii}	2.902 (10)	Fe2—O4B ^{xii}	1.946 (18)
Ba1—O4A ^{viii}	2.902 (10)	Fe2—O1 ^{xx}	1.984 (5)
Ba1—O2 ^{ix}	2.950 (6)	Fe2—O1 ^{xxi}	1.984 (5)
Ba1—O2 ^x	2.950 (6)	Fe2—O1 ^{xxii}	1.984 (5)
Ba1—O2 ^{xi}	2.950 (6)	Fe2—O4A ^{xix}	1.982 (7)
Na2—O3 ^{xii}	2.604 (8)	Fe2—O4A ⁱⁱ	1.982 (7)
Na2—O3 ^{xiii}	2.604 (8)	Fe2—O4A ^{xii}	1.982 (7)
Na2—O3 ^{xiv}	2.604 (8)	P—O4B	1.470 (18)
Na2—O2	3.004 (6)	P—O1 ^{xxiii}	1.493 (4)
Na2—O2 ⁱ	3.004 (6)	P—O2 ^{xxiii}	1.506 (4)
Na2—O2 ⁱⁱ	3.004 (6)	P—O3	1.526 (4)
Ba2—O3 ^{xii}	2.772 (5)	P—O4A	1.541 (7)
O1 ⁱ —Na1—O1	94.9 (5)	O2 ^{ix} —Ba1—O2 ^{xi}	55.17 (13)
O1 ⁱ —Na1—O1 ⁱⁱ	94.9 (5)	O2 ^x —Ba1—O2 ^{xi}	55.17 (13)
O1—Na1—O1 ⁱⁱ	94.9 (5)	O3 ^{xii} —Na2—O3 ^{xiii}	100.1 (3)
O1 ⁱ —Na1—O4B ⁱⁱⁱ	58.0 (4)	O3 ^{xii} —Na2—O3 ^{xiv}	100.1 (3)
O1—Na1—O4B ⁱⁱⁱ	79.6 (4)	O3 ^{xiii} —Na2—O3 ^{xiv}	100.1 (3)
O1 ⁱⁱ —Na1—O4B ⁱⁱⁱ	151.3 (7)	O3 ^{xii} —Na2—O2	83.46 (16)
O1 ⁱ —Na1—O4B ^{iv}	151.3 (7)	O3 ^{xiii} —Na2—O2	158.5 (4)
O1—Na1—O4B ^{iv}	58.0 (4)	O3 ^{xiv} —Na2—O2	58.53 (12)
O1 ⁱⁱ —Na1—O4B ^{iv}	79.6 (4)	O3 ^{xii} —Na2—O2 ⁱ	58.53 (12)
O4B ⁱⁱⁱ —Na1—O4B ^{iv}	118.89 (19)	O3 ^{xiii} —Na2—O2 ⁱ	83.46 (16)
O1 ⁱ —Na1—O4B ^v	79.6 (4)	O3 ^{xiv} —Na2—O2 ⁱ	158.5 (4)
O1—Na1—O4B ^v	151.3 (7)	O2—Na2—O2 ⁱ	115.68 (18)
O1 ⁱⁱ —Na1—O4B ^v	58.0 (4)	O3 ^{xii} —Na2—O2 ⁱⁱ	158.5 (4)
O4B ⁱⁱⁱ —Na1—O4B ^v	118.89 (19)	O3 ^{xiii} —Na2—O2 ⁱⁱ	58.53 (12)
O4B ^{iv} —Na1—O4B ^v	118.89 (19)	O3 ^{xiv} —Na2—O2 ⁱⁱ	83.46 (16)
O1 ⁱ —Na1—O4A ^{vi}	46.9 (2)	O2—Na2—O2 ⁱⁱ	115.68 (18)
O1—Na1—O4A ^{vi}	107.0 (6)	O2 ⁱ —Na2—O2 ⁱⁱ	115.68 (18)
O1 ⁱⁱ —Na1—O4A ^{vi}	49.5 (3)	O3 ^{xii} —Ba2—O3 ^{xiii}	92.09 (15)
O1 ⁱ —Na1—O4A ^{vii}	49.5 (3)	O3 ^{xii} —Ba2—O3 ^{xiv}	92.09 (15)
O1—Na1—O4A ^{vii}	46.9 (2)	O3 ^{xiii} —Ba2—O3 ^{xiv}	92.09 (15)
O1 ⁱⁱ —Na1—O4A ^{vii}	107.0 (6)	O3 ^{xii} —Ba2—O2 ⁱⁱ	148.54 (14)
O1 ⁱ —Na1—O4A ^{viii}	107.0 (6)	O3 ^{xiii} —Ba2—O2 ⁱⁱ	57.63 (12)
O1—Na1—O4A ^{viii}	49.5 (3)	O3 ^{xiv} —Ba2—O2 ⁱⁱ	81.64 (14)
O1 ⁱⁱ —Na1—O4A ^{viii}	46.9 (2)	O3 ^{xii} —Ba2—O2	81.64 (14)
O4A ^{vi} —Na1—O4A ^{viii}	81.1 (5)	O3 ^{xiii} —Ba2—O2	148.54 (14)
O4A ^{vii} —Na1—O4A ^{viii}	81.1 (5)	O3 ^{xiv} —Ba2—O2	57.63 (12)
O1 ⁱ —Na1—O2 ^{ix}	97.97 (19)	O2 ⁱⁱ —Ba2—O2	118.95 (3)

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O1—Na1—O2 ^{ix}	104.0 (2)	O3 ^{xii} —Ba2—O2 ⁱ	57.63 (12)
O1 ⁱⁱ —Na1—O2 ^{ix}	156.0 (6)	O3 ^{xiii} —Ba2—O2 ⁱ	81.64 (14)
O4B ^{iv} —Na1—O2 ^{ix}	97.9 (6)	O3 ^{xiv} —Ba2—O2 ⁱ	148.54 (14)
O4B ^v —Na1—O2 ^{ix}	104.6 (6)	O2 ⁱⁱ —Ba2—O2 ⁱ	118.95 (3)
O4A ^{vi} —Na1—O2 ^{ix}	134.2 (2)	O2—Ba2—O2 ⁱ	118.95 (3)
O4A ^{vii} —Na1—O2 ^{ix}	96.81 (16)	O3 ^{xii} —Ba2—O4A ^{vi}	104.95 (16)
O4A ^{viii} —Na1—O2 ^{ix}	144.2 (3)	O3 ^{xiii} —Ba2—O4A ^{vi}	83.7 (2)
O1 ⁱ —Na1—O2 ^x	156.0 (6)	O3 ^{xiv} —Ba2—O4A ^{vi}	162.54 (16)
O1—Na1—O2 ^x	97.97 (19)	O2 ⁱⁱ —Ba2—O4A ^{vi}	81.80 (17)
O1 ⁱⁱ —Na1—O2 ^x	104.0 (2)	O2—Ba2—O4A ^{vi}	127.8 (2)
O4B ⁱⁱⁱ —Na1—O2 ^x	104.6 (6)	O2 ⁱ —Ba2—O4A ^{vi}	47.59 (16)
O4B ^{iv} —Na1—O2 ^x	49.4 (4)	O3 ^{xii} —Ba2—O4A ^{vii}	83.7 (2)
O4B ^v —Na1—O2 ^x	97.9 (6)	O3 ^{xiii} —Ba2—O4A ^{vii}	162.54 (16)
O4A ^{vi} —Na1—O2 ^x	144.2 (3)	O3 ^{xiv} —Ba2—O4A ^{vii}	104.95 (16)
O4A ^{vii} —Na1—O2 ^x	134.2 (2)	O2 ⁱⁱ —Ba2—O4A ^{vii}	127.8 (2)
O4A ^{viii} —Na1—O2 ^x	96.81 (16)	O2—Ba2—O4A ^{vii}	47.59 (16)
O2 ^{ix} —Na1—O2 ^x	59.2 (4)	O2 ⁱ —Ba2—O4A ^{vii}	81.80 (17)
O1 ⁱ —Na1—O2 ^{xi}	104.0 (2)	O4A ^{vi} —Ba2—O4A ^{vii}	81.1 (3)
O1—Na1—O2 ^{xi}	156.0 (6)	O3 ^{xii} —Ba2—O4A ^{viii}	162.54 (17)
O1 ⁱⁱ —Na1—O2 ^{xi}	97.97 (19)	O3 ^{xiii} —Ba2—O4A ^{viii}	104.95 (16)
O4B ⁱⁱⁱ —Na1—O2 ^{xi}	97.9 (6)	O3 ^{xiv} —Ba2—O4A ^{viii}	83.7 (2)
O4B ^{iv} —Na1—O2 ^{xi}	104.6 (6)	O2 ⁱⁱ —Ba2—O4A ^{viii}	47.59 (16)
O4A ^{vi} —Na1—O2 ^{xi}	96.81 (16)	O2—Ba2—O4A ^{viii}	81.80 (17)
O4A ^{vii} —Na1—O2 ^{xi}	144.2 (3)	O2 ⁱ —Ba2—O4A ^{viii}	127.8 (2)
O4A ^{viii} —Na1—O2 ^{xi}	134.2 (2)	O4A ^{vi} —Ba2—O4A ^{viii}	81.1 (3)
O2 ^{ix} —Na1—O2 ^{xi}	59.2 (4)	O4A ^{vii} —Ba2—O4A ^{viii}	81.1 (3)
O2 ^x —Na1—O2 ^{xi}	59.2 (4)	O2 ⁱⁱ —Fe1—O2 ^{xv}	87.3 (2)
O1 ⁱ —Ba1—O1	100.10 (14)	O2 ⁱⁱ —Fe1—O2 ^{xvi}	87.3 (2)
O1 ⁱ —Ba1—O1 ⁱⁱ	100.10 (14)	O2 ^{xv} —Fe1—O2 ^{xvi}	87.3 (2)
O1—Ba1—O1 ⁱⁱ	100.10 (14)	O2 ⁱⁱ —Fe1—O3 ^{xiii}	88.26 (18)
O1 ⁱ —Ba1—O4B ⁱⁱⁱ	58.8 (4)	O2 ^{xv} —Fe1—O3 ^{xiii}	89.2 (2)
O1—Ba1—O4B ⁱⁱⁱ	80.9 (4)	O2 ^{xvi} —Fe1—O3 ^{xiii}	174.5 (2)
O1 ⁱⁱ —Ba1—O4B ⁱⁱⁱ	158.5 (4)	O2 ⁱⁱ —Fe1—O3	174.5 (2)
O1 ⁱ —Ba1—O4B ^{iv}	158.5 (4)	O2 ^{xv} —Fe1—O3	88.26 (18)
O1—Ba1—O4B ^{iv}	58.8 (4)	O2 ^{xvi} —Fe1—O3	89.2 (2)
O1 ⁱⁱ —Ba1—O4B ^{iv}	80.9 (4)	O3 ^{xiii} —Fe1—O3	95.0 (2)
O4B ⁱⁱⁱ —Ba1—O4B ^{iv}	116.8 (2)	O2 ⁱⁱ —Fe1—O3 ^{xvii}	89.2 (2)
O1 ⁱ —Ba1—O4B ^v	80.9 (4)	O2 ^{xv} —Fe1—O3 ^{xvii}	174.5 (2)
O1—Ba1—O4B ^v	158.5 (4)	O2 ^{xvi} —Fe1—O3 ^{xvii}	88.26 (18)
O1 ⁱⁱ —Ba1—O4B ^v	58.8 (4)	O3 ^{xiii} —Fe1—O3 ^{xvii}	95.0 (2)
O4B ⁱⁱⁱ —Ba1—O4B ^v	116.8 (2)	O3—Fe1—O3 ^{xvii}	95.0 (2)

O4B ^{iv} —Ba1—O4B ^v	116.8 (2)	O4B ^{xix} —Fe2—O4B ⁱⁱ	80.8 (9)
O1 ⁱ —Ba1—O4A ^{vi}	49.19 (16)	O4B ^{xix} —Fe2—O4B ^{xii}	80.8 (9)
O1—Ba1—O4A ^{vi}	114.25 (19)	O4B ⁱⁱ —Fe2—O4B ^{xii}	80.8 (9)
O1 ⁱⁱ —Ba1—O4A ^{vi}	51.94 (17)	O4B ^{xix} —Fe2—O1 ^{xx}	169.5 (6)
O1 ⁱ —Ba1—O4A ^{vii}	51.94 (17)	O4B ⁱⁱ —Fe2—O1 ^{xx}	89.8 (8)
O1—Ba1—O4A ^{vii}	49.19 (16)	O4B ^{xii} —Fe2—O1 ^{xx}	93.0 (5)
O1 ⁱⁱ —Ba1—O4A ^{vii}	114.25 (19)	O4B ^{xix} —Fe2—O1 ^{xxi}	93.0 (5)
O1 ⁱ —Ba1—O4A ^{viii}	114.25 (19)	O4B ⁱⁱ —Fe2—O1 ^{xxi}	169.5 (6)
O1—Ba1—O4A ^{viii}	51.94 (17)	O4B ^{xii} —Fe2—O1 ^{xxi}	89.8 (8)
O1 ⁱⁱ —Ba1—O4A ^{viii}	49.19 (16)	O1 ^{xx} —Fe2—O1 ^{xxi}	95.5 (3)
O4A ^{vi} —Ba1—O4A ^{viii}	86.1 (2)	O4B ^{xix} —Fe2—O1 ^{xxii}	89.8 (8)
O4A ^{vii} —Ba1—O4A ^{viii}	86.1 (2)	O4B ⁱⁱ —Fe2—O1 ^{xxii}	93.0 (5)
O1 ⁱ —Ba1—O2 ^{ix}	96.20 (14)	O4B ^{xii} —Fe2—O1 ^{xxii}	169.5 (6)
O1—Ba1—O2 ^{ix}	102.04 (15)	O1 ^{xx} —Fe2—O1 ^{xxii}	95.5 (3)
O1 ⁱⁱ —Ba1—O2 ^{ix}	149.64 (14)	O1 ^{xxi} —Fe2—O1 ^{xxii}	95.5 (3)
O4B ⁱⁱⁱ —Ba1—O2 ^{ix}	47.5 (4)	O1 ^{xx} —Fe2—O4A ^{xix}	168.6 (3)
O4B ^{iv} —Ba1—O2 ^{ix}	93.1 (4)	O1 ^{xxi} —Fe2—O4A ^{xix}	77.4 (3)
O4B ^v —Ba1—O2 ^{ix}	99.2 (4)	O1 ^{xxii} —Fe2—O4A ^{xix}	94.1 (3)
O4A ^{vi} —Ba1—O2 ^{ix}	132.27 (18)	O4B ^{xix} —Fe2—O4A ⁱⁱ	78.2 (6)
O4A ^{vii} —Ba1—O2 ^{ix}	95.97 (17)	O4B ⁱⁱ —Fe2—O4A ⁱⁱ	15.9 (5)
O4A ^{viii} —Ba1—O2 ^{ix}	141.66 (18)	O4B ^{xii} —Fe2—O4A ⁱⁱ	95.9 (8)
O1 ⁱ —Ba1—O2 ^x	149.64 (14)	O1 ^{xx} —Fe2—O4A ⁱⁱ	94.1 (3)
O1—Ba1—O2 ^x	96.20 (14)	O1 ^{xxi} —Fe2—O4A ⁱⁱ	168.6 (3)
O1 ⁱⁱ —Ba1—O2 ^x	102.04 (15)	O1 ^{xxii} —Fe2—O4A ⁱⁱ	77.4 (3)
O4B ⁱⁱⁱ —Ba1—O2 ^x	99.2 (4)	O4A ^{xix} —Fe2—O4A ⁱⁱ	94.0 (3)
O4B ^{iv} —Ba1—O2 ^x	47.5 (4)	O1 ^{xx} —Fe2—O4A ^{xii}	77.4 (3)
O4B ^v —Ba1—O2 ^x	93.1 (4)	O1 ^{xxi} —Fe2—O4A ^{xii}	94.1 (3)
O4A ^{vi} —Ba1—O2 ^x	141.66 (18)	O1 ^{xxii} —Fe2—O4A ^{xii}	168.6 (3)
O4A ^{vii} —Ba1—O2 ^x	132.27 (18)	O4A ^{xix} —Fe2—O4A ^{xii}	94.0 (3)
O4A ^{viii} —Ba1—O2 ^x	95.97 (17)	O4A ⁱⁱ —Fe2—O4A ^{xii}	94.0 (3)
O2 ^{ix} —Ba1—O2 ^x	55.17 (13)	O4B—P—O1 ^{xxiii}	119.9 (10)
O1 ⁱ —Ba1—O2 ^{xi}	102.04 (15)	O4B—P—O2 ^{xxiii}	104.3 (11)
O1—Ba1—O2 ^{xi}	149.64 (14)	O1 ^{xxiii} —P—O2 ^{xxiii}	112.9 (3)
O1 ⁱⁱ —Ba1—O2 ^{xi}	96.20 (14)	O4B—P—O3	97.0 (6)
O4B ⁱⁱⁱ —Ba1—O2 ^{xi}	93.1 (4)	O1 ^{xxiii} —P—O3	112.2 (3)
O4B ^{iv} —Ba1—O2 ^{xi}	99.2 (4)	O2 ^{xxiii} —P—O3	109.2 (3)
O4B ^v —Ba1—O2 ^{xi}	47.5 (4)	O4B—P—O4A	20.6 (6)
O4A ^{vi} —Ba1—O2 ^{xi}	95.97 (16)	O1 ^{xxiii} —P—O4A	102.0 (4)
O4A ^{vii} —Ba1—O2 ^{xi}	141.66 (18)	O2 ^{xxiii} —P—O4A	105.3 (4)
O4A ^{viii} —Ba1—O2 ^{xi}	132.27 (18)	O3—P—O4A	115.1 (3)

supplementary materials

Symmetry codes: (i) y, z, x ; (ii) z, x, y ; (iii) $y+1/2, -z+3/2, -x+1$; (iv) $-x+1, y+1/2, -z+3/2$; (v) $-z+3/2, -x+1, y+1/2$; (vi) $y, z, x+1$; (vii) $x+1, y, z$; (viii) $z, x+1, y$; (ix) $y+1/2, -z+3/2, -x+2$; (x) $-x+2, y+1/2, -z+3/2$; (xi) $-z+3/2, -x+2, y+1/2$; (xii) $-y+3/2, -z+1, x+1/2$; (xiii) $-z+1, x+1/2, -y+3/2$; (xiv) $x+1/2, -y+3/2, -z+1$; (xv) $x-1/2, -y+3/2, -z+1$; (xvi) $-y+1, z+1/2, -x+3/2$; (xvii) $y-1/2, -z+3/2, -x+1$; (xviii) $-x+3/2, -y+2, z-1/2$; (xix) $-x+1, y-1/2, -z+3/2$; (xx) $-z+3/2, -x+1, y-1/2$; (xxi) $-y+2, z-1/2, -x+3/2$; (xxii) $x, y-1, z$; (xxiii) $x-1, y, z$.

Fig. 1

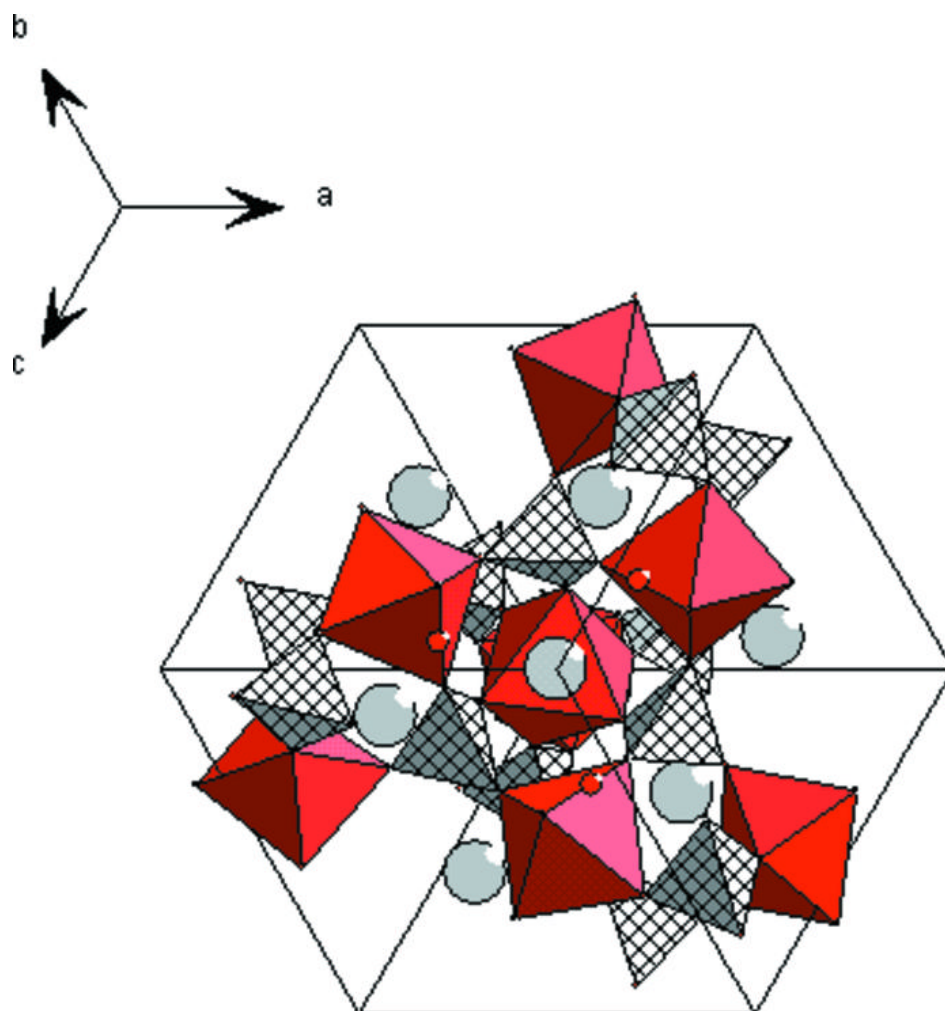


Fig. 2

