

α -Ba₂P₂O₇

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Received 6 October 2010; accepted 25 October 2010

Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{P}-\text{O}) = 0.001$ Å; R factor = 0.021; wR factor = 0.046; data-to-parameter ratio = 69.4.

Single crystals of α -Ba₂P₂O₇, dibarium diphosphate, were obtained by solid-state reaction. The orthorhombic structure is isotypic with α -Sr₂P₂O₇ and is the second polymorph obtained for this composition. The structure is built from two different BaO₉ polyhedra (both with m symmetry), with Ba—O distances in the ranges 2.7585 (10)–3.0850 (6) and 2.5794 (13)–2.9313 (4) Å. These polyhedra are further linked by sharing corners along [010] and either edges or triangular faces perpendicularly to [010] to form the three-dimensional framework. This polyhedral linkage delimits large channels parallel to [010] where the P₂O₇ diphosphate anions are located. These groups (symmetry m) are characterized by a P—O—P angle of 131.52 (9)° and an eclipsed conformation. They are connected to the BaO₉ polyhedra through edges and corners.

Related literature

Besides crystals of the title compound, crystals of the hexagonal polymorph σ -Ba₂P₂O₇ were obtained (ElBelghitti *et al.* 1995). For isotypic structures, see: Hagman *et al.* (1968); Grenier & Masse (1977); Barbier & Echard (1998). For closely related structures, see: Elmarzouki *et al.* (1995). For polymorphism in Ba₂P₂O₇, see: McCauley & Hummel (1968); Mehdi *et al.* (1977); Bian *et al.* (2004); Kokhanovskii (2004). For a review of the crystal chemistry of diphosphates, see: Durif (1995). For applications of alkaline earth diphosphates, see: Pang *et al.* (2009); Peng *et al.* (2010). For an independent refinement of the α -Ba₂P₂O₇ structure based on data from a hydrothermally grown crystal, see: Heyward *et al.* (2010).

Experimental

Crystal data

Ba₂P₂O₇ Orthorhombic, $Pnma$
 $M_r = 448.62$ $a = 9.2875$ (1) Å

$b = 5.6139$ (1) Å
 $c = 13.8064$ (1) Å
 $V = 719.85$ (2) Å³
 $Z = 4$

Mo $K\alpha$ radiation
 $\mu = 11.31$ mm⁻¹
 $T = 296$ K
 $0.26 \times 0.14 \times 0.14$ mm

Data collection

Bruker APEXII CCD diffractometer
 Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
 $T_{\min} = 0.155$, $T_{\max} = 0.205$

18034 measured reflections
 4304 independent reflections
 3726 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.028$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.021$
 $wR(F^2) = 0.046$
 $S = 1.07$
 4304 reflections

62 parameters
 $\Delta\rho_{\text{max}} = 1.59$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.99$ e Å⁻³

Table 1

Selected bond lengths (Å).

Ba1—O3 ⁱ	2.7585 (10)	Ba2—O4 ^{vi}	2.9313 (4)
Ba1—O2 ⁱⁱ	2.7591 (10)	P1—O5	1.5067 (13)
Ba1—O4 ⁱⁱⁱ	2.7978 (13)	P1—O2 ^{vii}	1.5208 (11)
Ba1—O2	2.8392 (10)	P1—O2	1.5208 (11)
Ba1—O5	3.0850 (6)	P1—O1	1.6148 (13)
Ba2—O5 ^{iv}	2.5794 (13)	P2—O4 ^{viii}	1.5175 (13)
Ba2—O3 ⁱⁱ	2.7377 (10)	P2—O3 ^{vii}	1.5236 (11)
Ba2—O2 ⁱⁱⁱ	2.8133 (10)	P2—O3	1.5236 (11)
Ba2—O3 ^v	2.9094 (10)	P2—O1	1.6012 (14)

Symmetry codes: (i) $x + \frac{1}{2}, y, -z + \frac{3}{2}$; (ii) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{3}{2}$; (iii) $-x, -y, -z + 1$; (iv) $-x + \frac{1}{2}, -y, z - \frac{1}{2}$; (v) $-x - \frac{1}{2}, -y, z - \frac{1}{2}$; (vi) $x + \frac{1}{2}, y + 1, -z + \frac{3}{2}$; (vii) $x, -y - \frac{1}{2}, z$; (viii) $x, y, z + 1$.

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINTE* (Bruker, 2008); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1999) and *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

This work was supported by the French–Moroccan integrated action (grant No. MA/05/119 F).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2413).

References

- Barbier, J. & Echard, J. P. (1998). *Acta Cryst.* **C54**, IUC9800070.
 Bian, J., Kim, D. W. & Hong, K. S. (2004). *Jpn. J. Appl. Phys. Part 1*, **43**, 3521–3525.
 Brandenburg, K. (1999). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
 Bruker (2008). *SADABS*, *APEX2* and *SAINTE*. Bruker AXS Inc., Madison, Wisconsin, USA.
 Durif, A. (1995). *Crystal Chemistry of Condensed Phosphates*. New York, London: Plenum Press.
 ElBelghitti, A. A., Elmarzouki, A., Boukhari, A. & Holt, E. M. (1995). *Acta Cryst.* **C51**, 1478–1480.
 Elmarzouki, A., Boukhari, A., Holt, E. M. & Berrada, A. (1995). *J. Alloys Compd.* **227**, 125–130.
 Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
 Grenier, J. C. & Masse, R. (1977). *Bull. Soc. Fr. Miner. Cristallogr.* **92**, 91–92.
 Hagman, L. O., Jansson, I. & Magneli, C. (1968). *Acta Chem. Scand.* **22**, 1419–1429.
 Heyward, C., Mann, M. & Kolis, J. (2010). *Acta Cryst.* **E66**. In the press.
 Kokhanovskii, V. (2004). *Zh. Neorg. Khim.* **49**, 511–517.

McCauley, R. A. & Hummel, F. A. (1968). *Trans. Br. Ceram. Soc.* **67**, 619–628.
Mehdi, S., Raza Hussain, M. & Rama Rao, B. (1977). *Indian J. Chem. Sect. A*, **15**, 820–821.

Pang, R., Li, C., Shi, L. & Su, Q. (2009). *J. Phys. Chem. Solids*, **70**, 303–306.
Peng, M., Sprenger, B., Schmidt, A., Schwefel, H. G. L. & Wondraczek, L. (2010). *Opt. Express*, **18**, 12852–12863.
Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

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Acta Cryst. (2010). E66, i76-i77 [doi:10.1107/S1600536810043539]

α -Ba₂P₂O₇

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Comment

Due to their potential applications as optical materials (Pang *et al.*, 2009, Peng *et al.*, 2010), alkaline earth diphosphates exhibit at the present time a growing interest. Since the optical properties are strongly related to the crystal structure, the study of polymorphism in these materials is worth investigating. Besides the hexagonal form σ -Ba₂P₂O₇ described by ElBelghitti *et al.* (1995), the title compound is the second polymorph for this composition obtained in the form of single-crystals. The orthorhombic title compound α -Ba₂P₂O₇ is isotypic with α -Sr₂P₂O₇ (Hagman *et al.* 1968; Grenier & Masse, 1977; Barbier & Echard, 1998) and closely related to BaPbP₂O₇ (Elmarzouki *et al.*, 1995). The existence of this polymorph has previously been mentioned by Durif (1995) and several other authors (McCauley & Hummel, 1968; Mehdi *et al.*, 1977; Bian *et al.*, 2004; Kokhanovskii, 2004).

The structure of the α -polymorph is built up from two different BaO₉ polyhedra with Ba—O distances ranging from 2.7585 (10) Å to 3.0850 (6) Å and from 2.5794 (13) Å to 2.9313 (4) Å, respectively. Figure 1 displays details of these coordination polyhedra as well as their linkage by corners, edges or triangular faces to form the three-dimensional framework. This polyhedral linkage delimits large channels parallel to [010] where the P₂O₇ diphosphate groups are located (Fig. 2). These groups (symmetry *m*) are characterized by a P—O—P angle of 131.52 (9)° and an eclipsed conformation. They are connected to the BaO₉ polyhedra through edges and corners. Each oxygen atom of the P₂O₇ groups, apart from the O1 bridging oxygen, is bonded to three Ba atoms and one phosphorus atom. During the anisotropic refinement of the displacement parameters of the isotypic α -Sr₂P₂O₇ structure (Barbier & Echard, 1998), the authors observed a very strong anisotropy along the *b* direction for both O5 and O1 atoms located in the (010) mirror plane and interpreted this phenomenon as a possible atomic-scale disorder associated with the local loss of mirror symmetry resulting in a non-centrosymmetric structural arrangement. Such an outstanding feature is still present in our anisotropic structure refinement, although the amplitudes of the atomic displacement parameters are significantly lower, especially for the *U*₂₂ component of the O5 atom. If the strong anisotropy of the O1 atom is perfectly understandable because of its bridging role, that of the O5 atom strongly bonded to two Ba1 atoms at 3.0850 (6) Å, one Ba2 atom at 2.5794 (13) Å and one P1 atom at 1.5067 (13) Å is more surprising. However, due to the relative homogeneity of the values of the isotropic displacement parameters of all oxygen atoms, it does not seem necessary to envisage any atomic-scale disorder for the O5 atom in the present case.

Simultaneous with our refinement, an independent study of the α -Ba₂P₂O₇ structure from a hydrothermally grown crystal was reported by Heyward *et al.* (2010). The results of both refinements in terms of geometric parameters are the same within the threefold standard deviation.

Experimental

Single crystals of the title compound have been obtained during the study of the phase relationships in the ternary system Na₂O—BaO—P₂O₅. They were synthesized in the solid state by reacting Na₂CO₃, BaCO₃ and (NH₄)₂HPO₄ in a platinum crucible. A mixture of these reagents taken in the molar ratio 1: 1: 2 was carefully ground in an agate mortar and successively

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heated at 373 K, 573 K and 773 K for 24 h at each temperature. After a new grinding, the reacting mixture was submitted to a final heat treatment at 973 K for 2 days followed by a slow cooling to room temperature at the rate of 5 K h⁻¹. After an abundant washing of the batch with hot water, single crystals of the title compound could have been extracted.

Refinement

The highest residual peak in the final difference Fourier map was located 0.56 Å from atom Ba1 and the deepest hole was located 0.31 Å from atom Ba2.

Figures

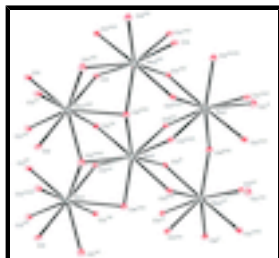


Fig. 1. View of the BaO₉ polyhedra linkage in α -Ba₂P₂O₇. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes: (i) $x + 1/2, y, -z + 3/2$; (ii) $x + 1/2, -y + 1/2, -z + 3/2$; (iii) $-x, -y, -z + 1$; (iv) $x, -y + 1/2, z$; (v) $x, y + 1, z$; (vi) $-x, y + 1/2, -z + 1$; (vii) $-x - 1/2, -y, z - 1/2$; (viii) $-x - 1/2, -y, z + 1/2$; (ix) $-x - 1/2, y + 1/2, z - 1/2$; (x) $x + 1/2, y + 1, -z + 1/2$; (xi) $x + 1/2, y, -z + 1/2$; (xii) $x + 1/2, y + 1, -z + 3/2$; (xiii) $x, -y - 1/2, z$; (xiv) $x, y, z + 1$; (xv) $-x - 1/2, -y, z + 1/2$; (xvi) $x - 1/2, y, -z + 3/2$; (xvii) $x, y, z - 1, -z + 1/2$; (xviii) $x - 1/2, y, -z + 1/2$; (xix) $x - 1/2, y, -z + 1/2$; (xx) $x - 1/2, y, -z + 1/2$; (xxi) $-x + 1/2, -y, z + 1/2$; (xxii) $x, y - 1, z$;

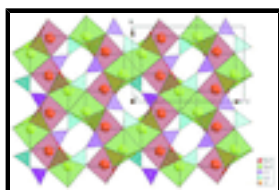


Fig. 2. Projection of the α -Ba₂P₂O₇ structure along [010] showing the connections between the P₂O₇ diphosphate groups and the three-dimensional framework of the BaO₉ polyhedra.

dibarium diphosphate

Crystal data

Ba₂P₂O₇

$M_r = 448.62$

Orthorhombic, *Pnma*

Hall symbol: -P 2ac 2n

$a = 9.2875 (1) \text{ \AA}$

$b = 5.6139 (1) \text{ \AA}$

$c = 13.8064 (1) \text{ \AA}$

$V = 719.85 (2) \text{ \AA}^3$

$Z = 4$

$F(000) = 792$

$D_x = 4.139 \text{ Mg m}^{-3}$

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

Cell parameters from 7790 reflections

$\theta = 3.7\text{--}52.2^\circ$

$\mu = 11.31 \text{ mm}^{-1}$

$T = 296 \text{ K}$

Hexagonal prism, colourless

$0.26 \times 0.14 \times 0.14 \text{ mm}$

Data collection

Bruker APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube
graphite

Detector resolution: $8.3333 \text{ pixels mm}^{-1}$

ω and ϕ scans

4304 independent reflections

3726 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.028$

$\theta_{\text{max}} = 52.4^\circ$, $\theta_{\text{min}} = 4.5^\circ$

$h = -17 \rightarrow 20$

Absorption correction: multi-scan
(*SADABS*; Bruker, 2008) $k = -12 \rightarrow 10$
 $T_{\min} = 0.155$, $T_{\max} = 0.205$ $l = -30 \rightarrow 28$
18034 measured reflections

Refinement

Refinement on F^2 Primary atom site location: structure-invariant direct methods
Least-squares matrix: full Secondary atom site location: difference Fourier map
 $R[F^2 > 2\sigma(F^2)] = 0.021$ $w = 1/[\sigma^2(F_o^2) + (0.0176P)^2 + 0.4317P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $wR(F^2) = 0.046$ $(\Delta/\sigma)_{\max} = 0.004$
 $S = 1.07$ $\Delta\rho_{\max} = 1.59 \text{ e } \text{\AA}^{-3}$
4304 reflections $\Delta\rho_{\min} = -1.99 \text{ e } \text{\AA}^{-3}$
62 parameters Extinction correction: *SHELXL97* (Sheldrick, 2008),
 $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
0 restraints Extinction coefficient: 0.0075 (2)

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>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ba1	0.159652 (9)	0.2500	0.744870 (6)	0.00801 (2)
Ba2	0.138138 (9)	0.2500	0.417071 (6)	0.00841 (2)
P1	-0.04603 (4)	-0.2500	0.81569 (3)	0.00724 (6)
P2	-0.28072 (4)	-0.2500	0.95778 (3)	0.00722 (6)
O1	-0.11642 (14)	-0.2500	0.92264 (9)	0.0129 (2)
O2	-0.09496 (10)	-0.0264 (2)	0.76295 (7)	0.01169 (13)
O3	-0.35537 (10)	-0.0271 (2)	0.91982 (6)	0.01215 (14)
O4	-0.27382 (15)	-0.2500	0.06760 (9)	0.0130 (2)
O5	0.11429 (14)	-0.2500	0.83242 (11)	0.0160 (3)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ba1	0.00795 (3)	0.00736 (4)	0.00873 (3)	0.000	-0.00047 (2)	0.000

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Ba2	0.00856 (3)	0.00891 (4)	0.00776 (3)	0.000	0.00084 (2)	0.000
P1	0.00544 (11)	0.00757 (16)	0.00873 (13)	0.000	0.00010 (9)	0.000
P2	0.00839 (12)	0.00706 (16)	0.00622 (12)	0.000	0.00066 (9)	0.000
O1	0.0088 (4)	0.0198 (7)	0.0100 (4)	0.000	0.0012 (3)	0.000
O2	0.0126 (3)	0.0091 (4)	0.0133 (3)	0.0008 (3)	0.0005 (2)	0.0022 (3)
O3	0.0145 (3)	0.0101 (4)	0.0119 (3)	0.0029 (3)	0.0000 (2)	0.0022 (3)
O4	0.0161 (5)	0.0160 (6)	0.0069 (4)	0.000	0.0003 (3)	0.000
O5	0.0061 (3)	0.0243 (8)	0.0176 (5)	0.000	-0.0008 (3)	0.000

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

Ba1—O3 ⁱ	2.7585 (10)	P1—O2 ^{xiii}	1.5208 (11)
Ba1—O3 ⁱⁱ	2.7585 (10)	P1—O2	1.5208 (11)
Ba1—O2 ⁱⁱ	2.7591 (10)	P1—O1	1.6148 (13)
Ba1—O2 ⁱ	2.7591 (10)	P1—Ba2 ⁱⁱⁱ	3.3255 (4)
Ba1—O4 ⁱⁱⁱ	2.7978 (13)	P2—O4 ^{xiv}	1.5175 (13)
Ba1—O2	2.8392 (10)	P2—O3 ^{xiii}	1.5236 (11)
Ba1—O2 ^{iv}	2.8392 (10)	P2—O3	1.5236 (11)
Ba1—O5 ^v	3.0850 (6)	P2—O1	1.6012 (14)
Ba1—O5	3.0850 (6)	P2—Ba2 ^{xv}	3.3668 (4)
Ba2—O5 ^{vi}	2.5794 (13)	P2—Ba2 ^{xvi}	3.3812 (2)
Ba2—O3 ⁱⁱ	2.7377 (10)	P2—Ba2 ^{xvii}	3.3812 (2)
Ba2—O3 ⁱ	2.7377 (10)	O2—Ba1 ^{xvi}	2.7591 (10)
Ba2—O2 ⁱⁱⁱ	2.8133 (10)	O2—Ba2 ⁱⁱⁱ	2.8133 (10)
Ba2—O2 ^{vii}	2.8133 (10)	O3—Ba2 ^{xvi}	2.7377 (10)
Ba2—O3 ^{viii}	2.9094 (10)	O3—Ba1 ^{xvi}	2.7585 (10)
Ba2—O3 ^{ix}	2.9094 (10)	O3—Ba2 ^{xv}	2.9094 (10)
Ba2—O4 ^x	2.9313 (4)	O4—P2 ^{xviii}	1.5175 (13)
Ba2—O4 ^{xi}	2.9313 (4)	O4—Ba1 ⁱⁱⁱ	2.7978 (13)
Ba2—P1 ⁱⁱⁱ	3.3255 (4)	O4—Ba2 ^{xix}	2.9313 (4)
Ba2—P2 ^{viii}	3.3668 (4)	O4—Ba2 ^{xx}	2.9313 (4)
Ba2—P2 ^{xii}	3.3812 (2)	O5—Ba2 ^{xxi}	2.5794 (13)
P1—O5	1.5067 (13)	O5—Ba1 ^{xxii}	3.0850 (6)
O3 ⁱ —Ba1—O3 ⁱⁱ	68.66 (5)	O3 ⁱⁱ —Ba2—O3 ^{ix}	76.39 (3)
O3 ⁱ —Ba1—O2 ⁱⁱ	109.06 (3)	O3 ⁱ —Ba2—O3 ^{ix}	104.688 (19)
O3 ⁱⁱ —Ba1—O2 ⁱⁱ	72.09 (3)	O2 ⁱⁱⁱ —Ba2—O3 ^{ix}	94.29 (3)
O3 ⁱ —Ba1—O2 ⁱ	72.09 (3)	O2 ^{vii} —Ba2—O3 ^{ix}	71.99 (3)
O3 ⁱⁱ —Ba1—O2 ⁱ	109.06 (3)	O3 ^{viii} —Ba2—O3 ^{ix}	50.95 (4)
O2 ⁱⁱ —Ba1—O2 ⁱ	68.43 (4)	O5 ^{vi} —Ba2—O4 ^x	77.53 (3)
O3 ⁱ —Ba1—O4 ⁱⁱⁱ	141.44 (2)	O3 ⁱⁱ —Ba2—O4 ^x	52.44 (3)
O3 ⁱⁱ —Ba1—O4 ⁱⁱⁱ	141.44 (3)	O3 ⁱ —Ba2—O4 ^x	118.59 (3)
O2 ⁱⁱ —Ba1—O4 ⁱⁱⁱ	73.93 (3)	O2 ⁱⁱⁱ —Ba2—O4 ^x	122.07 (3)

O2 ⁱ —Ba1—O4 ⁱⁱⁱ	73.93 (3)	O2 ^{vii} —Ba2—O4 ^x	71.11 (3)
O3 ⁱ —Ba1—O2	73.87 (3)	O3 ^{viii} —Ba2—O4 ^x	131.51 (3)
O3 ⁱⁱ —Ba1—O2	109.79 (3)	O3 ^{ix} —Ba2—O4 ^x	80.73 (3)
O2 ⁱⁱ —Ba1—O2	177.035 (6)	O5 ^{vi} —Ba2—O4 ^{xi}	77.53 (3)
O2 ⁱ —Ba1—O2	112.59 (4)	O3 ⁱⁱ —Ba2—O4 ^{xi}	118.59 (3)
O4 ⁱⁱⁱ —Ba1—O2	103.55 (3)	O3 ⁱ —Ba2—O4 ^{xi}	52.44 (3)
O3 ⁱ —Ba1—O2 ^{iv}	109.79 (3)	O2 ⁱⁱⁱ —Ba2—O4 ^{xi}	71.11 (3)
O3 ⁱⁱ —Ba1—O2 ^{iv}	73.87 (3)	O2 ^{vii} —Ba2—O4 ^{xi}	122.07 (3)
O2 ⁱⁱ —Ba1—O2 ^{iv}	112.59 (4)	O3 ^{viii} —Ba2—O4 ^{xi}	80.73 (3)
O2 ⁱ —Ba1—O2 ^{iv}	177.035 (6)	O3 ^{ix} —Ba2—O4 ^{xi}	131.51 (3)
O4 ⁱⁱⁱ —Ba1—O2 ^{iv}	103.55 (3)	O4 ^x —Ba2—O4 ^{xi}	146.51 (5)
O2—Ba1—O2 ^{iv}	66.25 (4)	O5—P1—O2 ^{xiii}	111.63 (5)
O3 ⁱ —Ba1—O5 ^v	146.01 (3)	O5—P1—O2	111.63 (5)
O3 ⁱⁱ —Ba1—O5 ^v	78.63 (3)	O2 ^{xiii} —P1—O2	111.29 (8)
O2 ⁱⁱ —Ba1—O5 ^v	67.45 (3)	O5—P1—O1	105.06 (8)
O2 ⁱ —Ba1—O5 ^v	129.77 (3)	O2 ^{xiii} —P1—O1	108.47 (5)
O4 ⁱⁱⁱ —Ba1—O5 ^v	71.89 (3)	O2—P1—O1	108.47 (5)
O2—Ba1—O5 ^v	110.43 (3)	P2—O1—P1	131.52 (9)
O2 ^{iv} —Ba1—O5 ^v	49.81 (3)	P1—O2—Ba1 ^{xvi}	136.86 (5)
O3 ⁱ —Ba1—O5	78.63 (3)	P1—O2—Ba2 ⁱⁱⁱ	95.57 (5)
O3 ⁱⁱ —Ba1—O5	146.01 (3)	Ba1 ^{xvi} —O2—Ba2 ⁱⁱⁱ	95.66 (3)
O2 ⁱⁱ —Ba1—O5	129.77 (3)	P1—O2—Ba1	104.14 (5)
O2 ⁱ —Ba1—O5	67.45 (3)	Ba1 ^{xvi} —O2—Ba1	112.16 (4)
O4 ⁱⁱⁱ —Ba1—O5	71.89 (3)	Ba2 ⁱⁱⁱ —O2—Ba1	106.55 (3)
O2—Ba1—O5	49.81 (3)	P2—O3—Ba2 ^{xvi}	101.17 (4)
O2 ^{iv} —Ba1—O5	110.43 (3)	P2—O3—Ba1 ^{xvi}	136.36 (5)
O5 ^v —Ba1—O5	130.97 (5)	Ba2 ^{xvi} —O3—Ba1 ^{xvi}	111.02 (4)
O5 ^{vi} —Ba2—O3 ⁱⁱ	110.68 (3)	P2—O3—Ba2 ^{xv}	93.55 (5)
O5 ^{vi} —Ba2—O3 ⁱ	110.68 (3)	Ba2 ^{xvi} —O3—Ba2 ^{xv}	103.61 (3)
O3 ⁱⁱ —Ba2—O3 ⁱ	69.25 (4)	Ba1 ^{xvi} —O3—Ba2 ^{xv}	106.11 (3)
O5 ^{vi} —Ba2—O2 ⁱⁱⁱ	74.14 (3)	P2 ^{xviii} —O4—Ba1 ⁱⁱⁱ	160.15 (8)
O3 ⁱⁱ —Ba2—O2 ⁱⁱⁱ	169.56 (3)	P2 ^{xviii} —O4—Ba2 ^{xix}	93.46 (3)
O3 ⁱ —Ba2—O2 ⁱⁱⁱ	118.44 (3)	Ba1 ⁱⁱⁱ —O4—Ba2 ^{xix}	92.23 (3)
O5 ^{vi} —Ba2—O2 ^{vii}	74.14 (3)	P2 ^{xviii} —O4—Ba2 ^{xx}	93.46 (3)
O3 ⁱⁱ —Ba2—O2 ^{vii}	118.44 (3)	Ba1 ⁱⁱⁱ —O4—Ba2 ^{xx}	92.23 (3)
O3 ⁱ —Ba2—O2 ^{vii}	169.56 (3)	Ba2 ^{xix} —O4—Ba2 ^{xx}	146.51 (5)
O2 ⁱⁱⁱ —Ba2—O2 ^{vii}	53.01 (4)	P1—O5—Ba2 ^{xxi}	161.87 (9)
O5 ^{vi} —Ba2—O3 ^{viii}	144.15 (3)	P1—O5—Ba1 ^{xxii}	94.30 (3)
O3 ⁱⁱ —Ba2—O3 ^{viii}	104.688 (19)	Ba2 ^{xxi} —O5—Ba1 ^{xxii}	93.20 (3)
O3 ⁱ —Ba2—O3 ^{viii}	76.39 (3)	P1—O5—Ba1	94.30 (3)
O2 ⁱⁱⁱ —Ba2—O3 ^{viii}	71.99 (3)	Ba2 ^{xxi} —O5—Ba1	93.20 (3)

supplementary materials

O2^{vii}—Ba2—O3^{viii}

94.29 (3)

Ba1^{xxii}—O5—Ba1

130.97 (5)

O5^{vi}—Ba2—O3^{ix}

144.15 (3)

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

Fig. 1

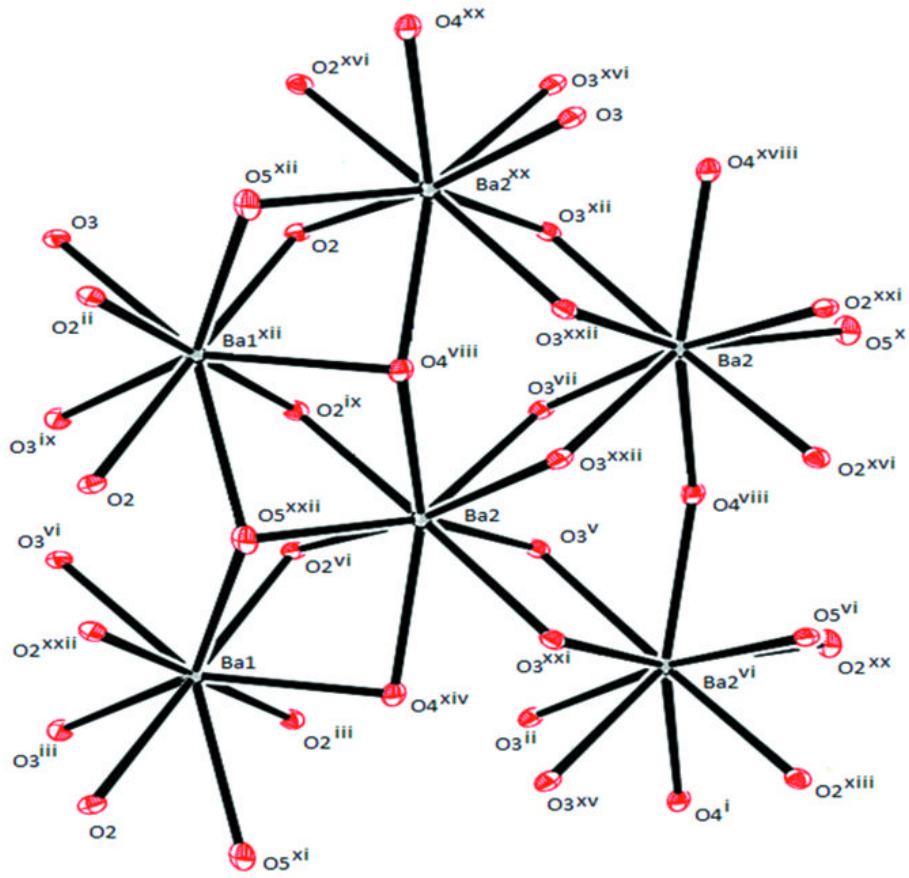


Fig. 2

