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$LaZnB_5O_{10}$, the first lanthanum zinc borate

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Key indicators: single-crystal X-ray study; T = 295 K; mean σ(O–B) = 0.006 Å; R factor = 0.036; wR factor = 0.086; data-to-parameter ratio = 15.0.

Lanthanum zinc pentaborate, $LaZnB_5O_{10}$, was synthesized by flux-supported solid-state reaction. It is a member of the $LnMB_5O_{10}$ (Ln = rare earth ion and M = divalent metal ion) structure type. The crystal shows a three-dimensional structure constructed from two-dimensional $\{[B_5O_{10}]^{5-}\}_n$ layers with the lanthanum (coordination number nine) and zinc (coordination number six) ions filling in the interlayers.

Related literature

For general background to inorganic borates and their applications, see: Thakare *et al.* (2004); Yavetskiy *et al.* (2007); Ye & Chai (1999); Becker (1998). For related structures, see: Bernadette *et al.* (1980); Abdullaev *et al.* (1980); Campa *et al.* (1995). For the bond-valence-sum (BVS) calculation, see: Brese & O'Keeffe (1991).

Experimental

Crystal data

$LaZnB_5O_{10}$
M_r = 418.33
Monoclinic, $P2_1/n$
a = 8.7923 (19) Å
b = 7.629 (2) Å
c = 9.566 (2) Å
β = 92.667 (19)°
V = 641.0 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 10.37 mm^{-1}
T = 295 K
0.10 × 0.08 × 0.06 mm

Data collection

Bruker P4 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.259, T_{max} = 0.347
3122 measured reflections
2318 independent reflections
2174 reflections with $I > 2\sigma(I)$
R_{int} = 0.033
3 standard reflections
every 97 reflections
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.086
S = 1.01
2318 reflections
155 parameters
$\Delta\rho_{max}$ = 3.81 e Å^{-3}
$\Delta\rho_{min}$ = −1.63 e Å^{-3}

Data collection: *XSCANS* (Bruker, 1997); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BR2126).

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supporting information

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S1. Comment

Inorganic borates have long been a focus of research for their wide applications as phosphors, laser materials and nonlinear optical (NLO) materials *etc* (Thakare *et al.*, 2004; Yavetskiy *et al.*, 2007; Ye *et al.*, 1999; Becker *et al.*, 1998). Among these materials, rear-earth borates especially lanthanum or yttrium borates, have been proved to be attractive matrices for lasing materials or rare-earths sensitizer-activator pairs containing phosphors. $LaZnB_5O_{10}$ is a new member of the family of $LnMB_5O_{10}$ (Ln = rear earth ions, *M* = divalent metal ions) (Abdullaev *et al.*, 1980; Bernadette *et al.*, 1980; Campa *et al.*, 1995). The asymmetric unit of $LaZnB_5O_{10}$ contains one unique La ion, one Zn ion, five B atoms and ten oxygen atoms as shown in Fig.1. Three BO_4 tetrahedra and two BO_3 triangles are linked to form a B_5O_{12} double-ring group (Fig.2a), and these B_5O_{12} groups are further connected to form a $[B_5O_{10}]^{5-}{}_n$ layer through sharing BO_4 tetrahedra.

The local coordination geometries of Zn and La atoms in $LaZnB_5O_{10}$ are also shown in Fig.2. As can be observed, the La1 atom is bonded to nine oxygen atoms to form a distorted tetrakaidecahedron. The bond valence sum (BVS) of 3.143 for La^{3+} ions calculated by the Brese & Keeffe (Brese *et al.*, 1991) formalism shows that its valence requirement is satisfied by this coordination. The distorted tetrakaidecahedra here are further connected with each other through sharing edges to form a one-dimensional infinite chain which is arranged between the $[B_5O_{10}]^{5-}{}_n$ layers along *b* axis. The zinc cation adopts a sixfolded coordination to form a distorted octahedron. However, among these Zn—O bonds, Zn1—O1 and Zn1—O4 are significantly longer than the others. This could be probably due to the fact that the O1-O4 edge is shared with a BO_3 group. This reduces the O1-Zn-O4 angle and tends to lengthen the bonds. Two adjacent ZnO_6 octahedra are connected with each other through two bridging oxygen atoms and the zinc atoms are almost embedded in the $[B_5O_{10}]^{5-}{}_n$ layers. Both the zinc and lanthanum atoms link the adjacent $[B_5O_{10}]^{5-}{}_n$ layers to form a three dimensional framework (Fig.3).

S2. Experimental

Single crystals of the title compound were synthesized by flux-supported solid-state reaction. A mixture La_2O_3(99.9%), ZnO(99.0%) and H_3BO_3(99.99%) in the molar ratio of 1:2:14 was ground to a fine powder in a mortar and compressed into a Pt crucible. The mixture was gradually heated to 1273 K. After the mixture melted completely, it was cooled down to 1100 K at a rate of 1 °K/h, followed by cooling to room temperature at 20 °K/h. The title crystals could be obtained from the top section of the solidified melt. While in the bottom of the solidified melt, plate-like crystals were obtained which were confirmed to be LaB_3O_6 through the powder X-ray diffraction (PXRD) method.

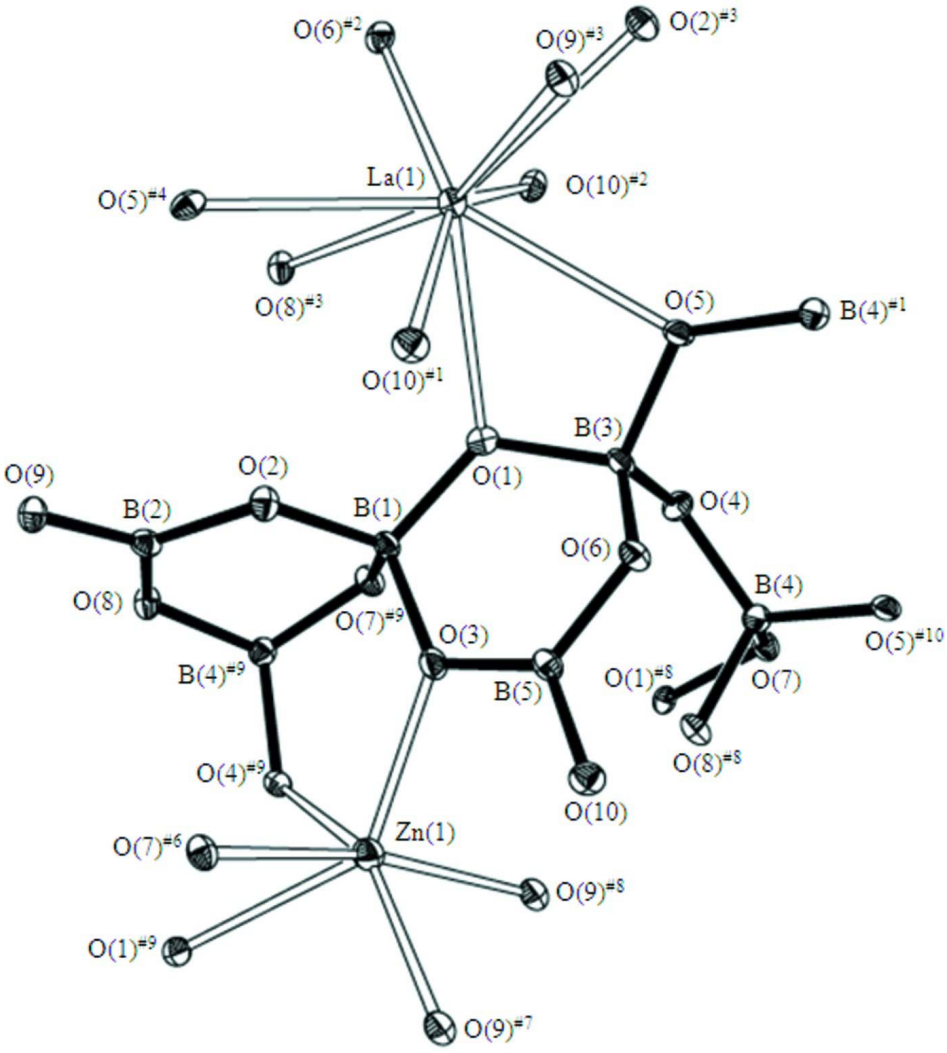

Figure 1

ORTEP drawing of $LaZnB_5O_{10}$ with 35% probability ellipsoids, showing the atomic numbering scheme.

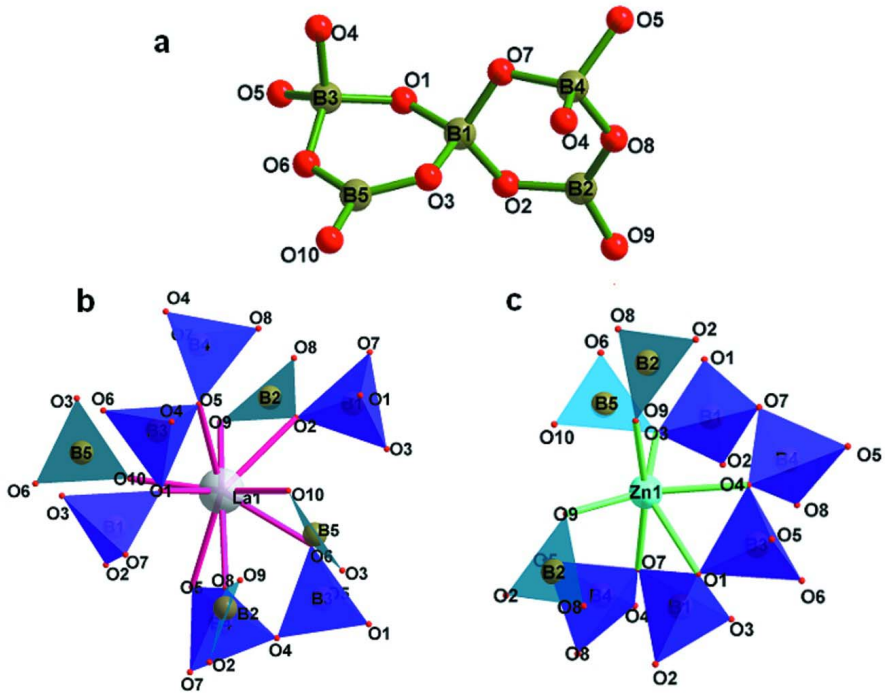

Figure 2

(*a*) The B_5O_{12} double-ring group; (*b*) The coordination environment of the La atom; (*c*) The coordination environment of the Zn atom. The blue polyhedra are the [BO_3] triangles while the purple polyhedra are the [BO_4] tetrahedra in the lower two figures.

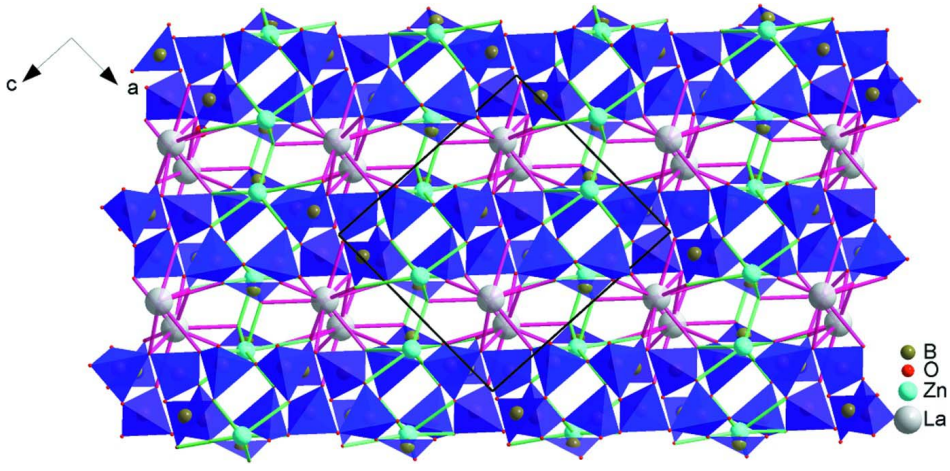

Figure 3

The representation of the three-dimensional $LaZnB_5O_{10}$ structure projected along the [010] direction with the BO_3 triangles and BO_4 tetrahedra. The structure contains the infinite two-dimensional $[B_5O_{10}]^{5-}{}_n$ layers running almost perpendicular to the [101] direction. The La atoms are located in layers, while the Zn atoms are almost embedded in the layers.

Lanthanum zinc pentaborate

Crystal data

$LaZnB_5O_{10}$
$M_r = 418.33$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 8.7923$ (19) Å
$b = 7.629$ (2) Å
$c = 9.566$ (2) Å
$\beta = 92.667$ (19)°
$V = 641.0$ (3) Å^3
$Z = 4$
$F(000) = 768$
$D_x = 4.335$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 36 reflections
$\theta = 5.8$–$12.5°$
$\mu = 10.37$ mm^{-1}
$T = 295$ K
Prism, colorless
0.10 × 0.08 × 0.06 mm

Data collection

Bruker P4 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.259$, $T_{max} = 0.347$
3122 measured reflections
2318 independent reflections
2174 reflections with $I > 2\sigma(I)$
$R_{int} = 0.033$
$\theta_{max} = 32.5°$, $\theta_{min} = 3.1°$
$h = -13 \rightarrow 1$
$k = -1 \rightarrow 11$
$l = -14 \rightarrow 14$
3 standard reflections every 97 reflections
intensity decay: none

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.086$
$S = 1.01$
2318 reflections
155 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
$w = 1/[\sigma^2(F_o^2) + (0.001P)^2 + 14.P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 3.81$ e Å^{-3}
$\Delta\rho_{min} = -1.63$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.133 (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.

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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
La1	0.18084 (3)	0.68446 (4)	0.23425 (3)	0.00861 (13)
Zn1	0.88916 (7)	0.41215 (8)	0.38049 (7)	0.01160 (16)
O1	0.4743 (4)	0.7209 (5)	0.2592 (4)	0.0097 (6)

O2	0.5128 (4)	0.4196 (5)	0.1869 (4)	0.0105 (6)
O3	0.6830 (4)	0.5372 (5)	0.3613 (4)	0.0104 (6)
O4	0.5839 (4)	0.9780 (5)	0.3570 (4)	0.0099 (6)
O5	0.3289 (4)	0.8921 (5)	0.4150 (4)	0.0097 (6)
O6	0.5383 (4)	0.7202 (5)	0.5088 (4)	0.0102 (6)
O7	0.8125 (4)	1.1547 (5)	0.3721 (4)	0.0100 (6)
O8	0.6912 (4)	0.3737 (5)	0.0101 (4)	0.0098 (6)
O9	0.5056 (4)	0.1522 (5)	0.0688 (4)	0.0101 (6)
O10	0.7299 (4)	0.5391 (5)	0.6081 (4)	0.0112 (6)
B1	0.5877 (6)	0.5824 (7)	0.2330 (5)	0.0082 (8)
B2	0.5734 (6)	0.3144 (7)	0.0839 (6)	0.0096 (9)
B3	0.4843 (6)	0.8275 (7)	0.3895 (6)	0.0092 (9)
B4	0.7168 (6)	1.0340 (7)	0.4479 (5)	0.0093 (9)
B5	0.6498 (6)	0.5943 (7)	0.4924 (6)	0.0092 (8)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
La1	0.00934 (16)	0.00822 (17)	0.00831 (16)	0.00018 (8)	0.00087 (9)	0.00037 (8)
Zn1	0.0114 (3)	0.0094 (3)	0.0140 (3)	0.0001 (2)	0.0000 (2)	−0.0002 (2)
O1	0.0091 (14)	0.0105 (15)	0.0095 (14)	−0.0007 (12)	0.0003 (11)	0.0014 (12)
O2	0.0115 (15)	0.0104 (15)	0.0098 (14)	−0.0014 (12)	0.0028 (12)	−0.0009 (12)
O3	0.0126 (15)	0.0104 (15)	0.0083 (14)	0.0029 (12)	0.0006 (11)	−0.0016 (12)
O4	0.0096 (14)	0.0099 (15)	0.0100 (14)	−0.0025 (12)	−0.0002 (11)	0.0007 (12)
O5	0.0073 (14)	0.0135 (16)	0.0085 (14)	0.0028 (12)	0.0008 (11)	−0.0006 (12)
O6	0.0107 (14)	0.0082 (14)	0.0117 (15)	0.0026 (12)	0.0010 (12)	0.0003 (12)
O7	0.0100 (15)	0.0087 (14)	0.0116 (15)	−0.0003 (12)	0.0033 (12)	−0.0006 (12)
O8	0.0108 (15)	0.0085 (15)	0.0103 (14)	−0.0028 (12)	0.0036 (12)	−0.0011 (12)
O9	0.0121 (15)	0.0087 (15)	0.0098 (15)	−0.0018 (12)	0.0018 (12)	−0.0004 (12)
O10	0.0121 (15)	0.0114 (16)	0.0099 (14)	0.0014 (13)	−0.0001 (12)	0.0020 (12)
B1	0.010 (2)	0.007 (2)	0.0076 (19)	0.0018 (16)	0.0003 (16)	0.0002 (16)
B2	0.008 (2)	0.012 (2)	0.009 (2)	0.0015 (17)	0.0019 (16)	−0.0001 (17)
B3	0.009 (2)	0.010 (2)	0.009 (2)	0.0031 (17)	0.0014 (16)	−0.0008 (16)
B4	0.010 (2)	0.010 (2)	0.0080 (19)	0.0003 (17)	0.0009 (16)	0.0005 (16)
B5	0.009 (2)	0.009 (2)	0.010 (2)	0.0006 (16)	0.0027 (16)	0.0002 (17)

Geometric parameters (Å, º)

La1—O10^{i}	2.385 (4)	B2—O2	1.396 (6)
La1—O10^{ii}	2.478 (4)	B1—O2	1.464 (7)
La1—O6^{ii}	2.549 (4)	B5—O3	1.372 (6)
La1—O9^{iii}	2.566 (4)	B1—O3	1.495 (6)
La1—O1	2.595 (4)	B3—O4	1.486 (7)
La1—O2^{iii}	2.608 (4)	B4—O4	1.486 (7)
La1—O5	2.643 (4)	B3—O5	1.484 (6)
La1—O5^{iv}	2.648 (4)	B4—O5^{x}	1.500 (6)
La1—O8^{v}	2.678 (4)	B5—O6	1.387 (6)
Zn1—O3	2.049 (4)	B3—O6	1.466 (7)

Zn1—O7^{vi}	2.077 (4)	B4—O7	1.462 (7)
Zn1—O9^{vii}	2.088 (4)	B1—O7^{ix}	1.472 (6)
Zn1—O9^{viii}	2.099 (4)	B2—O8	1.358 (6)
Zn1—O1^{ix}	2.346 (4)	B4—O8^{viii}	1.511 (7)
Zn1—O4^{ix}	2.350 (4)	B2—O9	1.378 (7)
B1—O1	1.482 (6)	B5—O10	1.351 (6)
B3—O1	1.488 (7)		

O10^{i}—La1—O10^{ii}	148.99 (6)	O7^{vi}—Zn1—O9^{vii}	87.47 (15)
O10^{i}—La1—O6^{ii}	150.84 (13)	O3—Zn1—O9^{viii}	89.60 (15)
O10^{ii}—La1—O6^{ii}	55.60 (12)	O7^{vi}—Zn1—O9^{viii}	166.66 (15)
O10^{i}—La1—O9^{iii}	70.71 (13)	O9^{vii}—Zn1—O9^{viii}	79.20 (16)
O10^{ii}—La1—O9^{iii}	124.81 (12)	O3—Zn1—O1^{ix}	135.44 (14)
O6^{ii}—La1—O9^{iii}	110.05 (12)	O7^{vi}—Zn1—O1^{ix}	64.12 (14)
O10^{i}—La1—O1	73.86 (13)	O9^{vii}—Zn1—O1^{ix}	95.83 (14)
O10^{ii}—La1—O1	76.04 (12)	O9^{viii}—Zn1—O1^{ix}	116.27 (14)
O6^{ii}—La1—O1	119.66 (12)	O3—Zn1—O4^{ix}	86.69 (14)
O9^{iii}—La1—O1	127.52 (12)	O7^{vi}—Zn1—O4^{ix}	102.25 (14)
O10^{i}—La1—O2^{iii}	120.59 (12)	O9^{vii}—Zn1—O4^{ix}	144.77 (14)
O10^{ii}—La1—O2^{iii}	71.71 (12)	O9^{viii}—Zn1—O4^{ix}	88.49 (14)
O6^{ii}—La1—O2^{iii}	75.30 (12)	O1^{ix}—Zn1—O4^{ix}	60.35 (13)
O9^{iii}—La1—O2^{iii}	53.55 (12)	O2—B1—O7^{ix}	112.7 (4)
O1—La1—O2^{iii}	124.01 (12)	O2—B1—O1	111.0 (4)
O10^{i}—La1—O5	82.96 (13)	O7^{ix}—B1—O1	106.0 (4)
O10^{ii}—La1—O5	73.55 (12)	O2—B1—O3	106.2 (4)
O6^{ii}—La1—O5	126.16 (12)	O7^{ix}—B1—O3	108.5 (4)
O9^{iii}—La1—O5	83.62 (12)	O1—B1—O3	112.4 (4)
O1—La1—O5	54.44 (12)	O8—B2—O9	125.6 (5)
O2^{iii}—La1—O5	72.95 (12)	O8—B2—O2	120.1 (5)
O10^{i}—La1—O5^{iv}	74.93 (12)	O9—B2—O2	114.4 (4)
O10^{ii}—La1—O5^{iv}	117.16 (12)	O6—B3—O5	108.9 (4)
O6^{ii}—La1—O5^{iv}	77.42 (12)	O6—B3—O4	115.0 (4)
O9^{iii}—La1—O5^{iv}	108.04 (12)	O5—B3—O4	109.5 (4)
O1—La1—O5^{iv}	98.43 (12)	O6—B3—O1	110.6 (4)
O2^{iii}—La1—O5^{iv}	136.90 (12)	O5—B3—O1	107.5 (4)
O5—La1—O5^{iv}	149.36 (8)	O4—B3—O1	105.1 (4)
O10^{i}—La1—O8^{v}	107.11 (12)	O7—B4—O4	110.2 (4)
O10^{ii}—La1—O8^{v}	68.05 (12)	O7—B4—O5^{x}	112.4 (4)
O6^{ii}—La1—O8^{v}	61.25 (12)	O4—B4—O5^{x}	112.6 (4)
O9^{iii}—La1—O8^{v}	159.02 (12)	O7—B4—O8^{viii}	109.2 (4)
O1—La1—O8^{v}	69.00 (12)	O4—B4—O8^{viii}	108.6 (4)
O2^{iii}—La1—O8^{v}	132.27 (12)	O5^{x}—B4—O8^{viii}	103.5 (4)
O5—La1—O8^{v}	117.15 (11)	O10—B5—O3	121.6 (5)
O5^{iv}—La1—O8^{v}	52.70 (11)	O10—B5—O6	117.9 (4)

O3—Zn1—O7^{vi}	98.79 (16)	O3—B5—O6	120.4 (5)
O3—Zn1—O9^{vii}	125.64 (15)		

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