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The defect scheelite-type lanthanum(III) *ortho*-oxidomolybdate(VI) $La_{0.667}[MoO_4]$

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Key indicators: single-crystal X-ray study; T = 293 K; mean σ(Mo–O) = 0.001 Å; disorder in main residue; R factor = 0.016; wR factor = 0.032; data-to-parameter ratio = 16.2.

In scheelite-type $La_{0.667}[MoO_4]$, one crystallographically unique position with site symmetry $\overline{4}$.. and an occupancy of 2/3 is found for the La^{3+} cation. The cation is surrounded by eight O atoms in the shape of a trigonal dodecahedron. The structure also contains one $[MoO_4]^{2-}$ anion (site symmetry $\overline{4}$..), which is surrounded by eight vertex-attached La^{3+} cations. The polyhedra around the La^{3+} cations are interconnected *via* common edges, building up a three-dimensional network, in the tetrahedral voids of which the Mo^{6+} cations reside.

Related literature

For isotypic $Ln_{0.667}[MoO_4]$ structures with Ln = Ce, Pr, Nd and Sm, see: Schustereit *et al.* (2011). For synthetic details, see: Liu *et al.* (2012).

Experimental

Crystal data

$La_{0.667}[MoO_4]$
M_r = 252.59
Tetragonal, $I4_1/a$
a = 5.3599 (3) Å
c = 11.9425 (7) Å
V = 343.09 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 11.74 mm^{-1}
T = 293 K
0.11 × 0.08 × 0.06 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: numerical (*X-SHAPE*; Stoe & Cie, 1995)
T_{min} = 0.291, T_{max} = 0.480
2577 measured reflections
260 independent reflections
174 reflections with $I > 2\sigma(I)$
R_{int} = 0.046

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.016
$wR(F^2)$ = 0.032
S = 0.98
260 reflections
16 parameters
$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}

Table 1
Selected bond lengths (Å).

La—O^{i}	2.5728 (14)	Mo—O	1.7606 (14)
La—O^{ii}	2.5766 (14)		

Symmetry codes: (i) $y+\frac{1}{4}, -x+\frac{1}{4}, z+\frac{1}{4}$; (ii) $-x+\frac{1}{2}, -y, z+\frac{1}{2}$.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2006); 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: WM2715).

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The defect scheelite-type lanthanum(III) *ortho*-oxidomolybdate(VI) $La_{0.667}[MoO_4]$

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S1. Comment

The title compound crystallizes isotypically with the already known defect scheelite-type lanthanide ortho-oxidomolybdates(VI) with general formula $Ln_{0.667}[MoO_4]$ (*Ln* = Ce, Pr, Nd, and Sm; Schustereit *et al.*, 2011). The crystallographically unique La^{3+} cation at Wyckoff position 4*b* is surrounded by eight oxide anions in the shape of a trigonal dodecahedron (Fig. 1). Besides the lanthanum cation, the structure also contains an isolated and bisphenoidally distorted tetrahedral ortho-oxidomolybdate(VI) unit $[MoO_4]^{2-}$. Its central Mo^{6+} cation at Wyckoff position 4*a* exhibits the same site symmetry ($\bar{4}$..) as the La^{3+} cation. Hence, in order to maintain electroneutrality, the latter shows a statistically under-occupation of 2/3 on its atomic position. The $[MoO_4]^{2-}$ tetrahedra share common vertices with eight $[LaO_8]^{13-}$ dodecahedra to build up the scheelite-type crystal structure (Fig. 2). The cations at the sites 4*a* (La^{3+}) and 4*b* (Mo^{6+}) are thereby arranged in two interpenetrating diamond-like lattices (Schustereit *et al.*, 2011).

S2. Experimental

Colourless, irregular-shaped single crystals of scheelite-type $La_{0.667}[MoO_4]$ were obtained as a by-product in an unsuccessful attempt to synthesize $LaF[MoO_4]$ according to the Pecchini method (Liu *et al.*, 2012). Aqueous solutions with stoichiometric amounts of $La(NO_3)_3$ and $(NH_4)_6Mo_7O_{24}$ (molar ratio 7 : 1) were prepared for each compound and HF was added to the latter (molar ratio HF : $(NH_4)_6Mo_7O_{24}$ = 7 : 1). As chelating agent, citric acid (CA) was dissolved in both solutions with a molar ratio of CA : La^{3+} = 1 : 1 and CA : Mo^{6+} = 2 : 1. The pH value of the La^{3+}-containing solution was adjusted to 3 – 4 with an aqueous ammonia solution as well as the pH value of the CA/HF/$(NH_4)_6Mo_7O_{24}$ mixture, in this case to a value of 7 – 8. The two solutions were combined, stirred, and heated for about 30 minutes to obtain a transparent solution, which was then dried at 473 K for 5 hours. The residual product was thermally treated in air at 1123 K for 12 hours.

S3. Refinement

The site occupation factor of the La^{3+} site was refined freely to a value of 0.6676 (10).

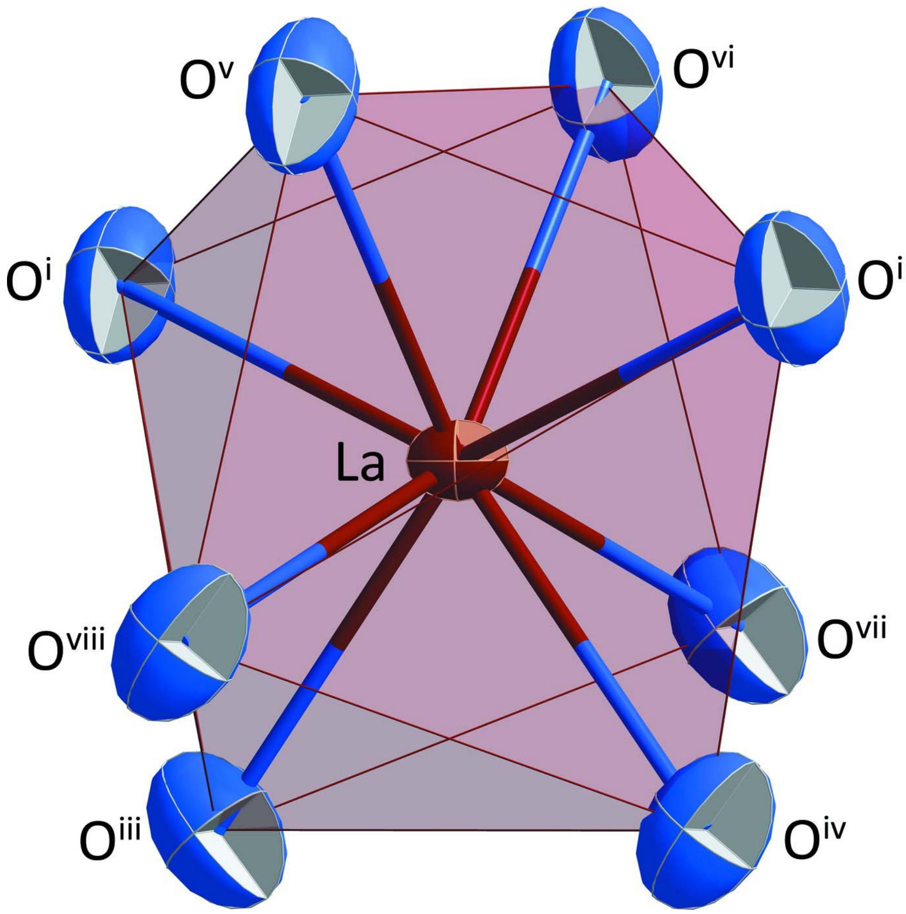

Figure 1

Trigonal dodecahedral oxygen environment of the La^{3+} cation in defect scheelite-type $La_{0.667}[MoO_4]$; ellipsoids are drawn at the 80 % probability level. [Symmetry codes: (i) *x*, *y*, *z*; (ii) –*x*+1/2, –*y*, *z*+1/2; (iii) –*y*+3/4, *x*+1/4, *z*+1/4; (iv) *y*+3/4, –*x*+3/4, *z*+3/4; (v) –*x*, –*y*, –*z*; (vi) *x*+1/2, *y*, –*z*+1/2; (vii) *y*+1/4, –*x*+3/4, –*z*+3/4; (viii) –*y*+1/4, *x*+1/4, –*z*+1/4].

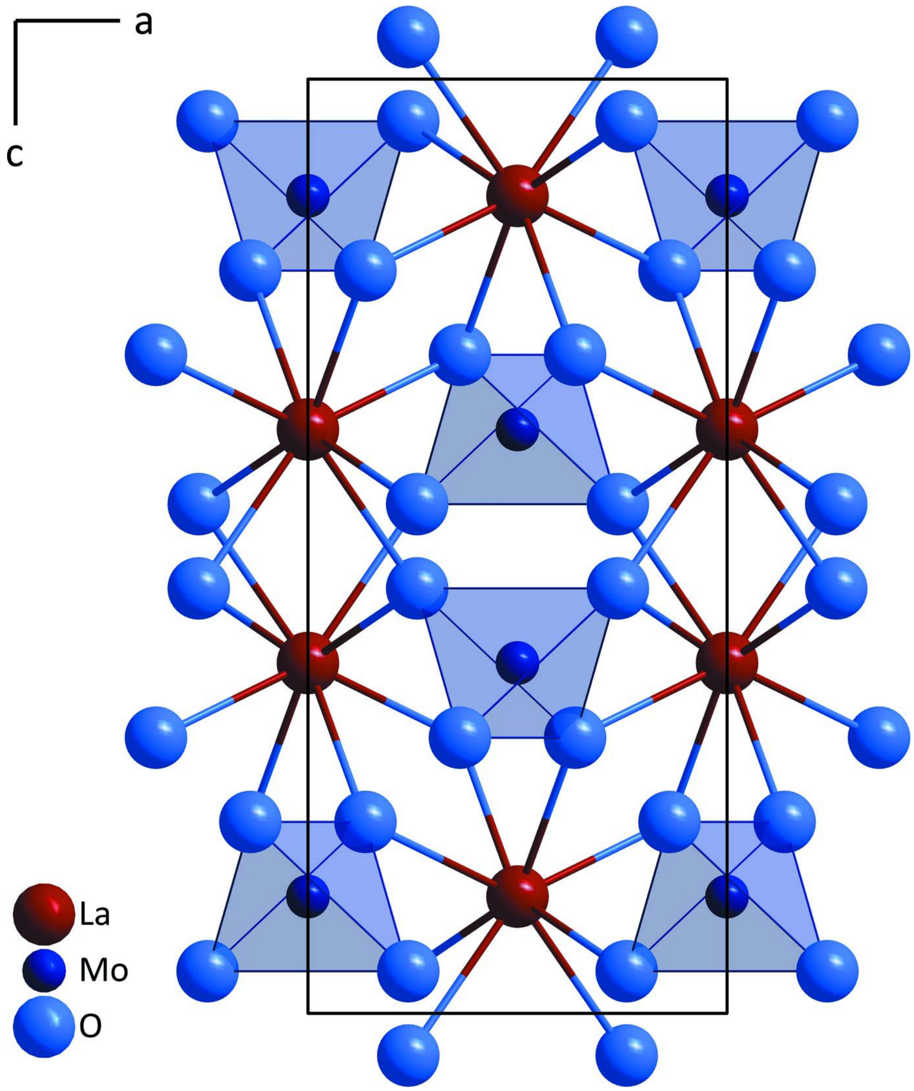

Figure 2

View of the crystal structure of defect scheelite-type $La_{0.667}[MoO_4]$ along [010]; the bisphenoidally distorted tetrahedral ortho-oxidomolybdate(VI) units $[MoO_4]^{2-}$ are given in the polyhedral representation.

Lanthanum(III) *ortho*-tetraoxidomolybdate(VI)

Crystal data

$La_{0.667}[MoO_4]$
M_r = 252.59
Tetragonal, $I4_1/a$
Hall symbol: -I 4ad
a = 5.3599 (3) Å
c = 11.9425 (7) Å
V = 343.09 (3) Å^3
Z = 4
F(000) = 448
D_x = 4.890 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1769 reflections
θ = 0.4–30.5°
μ = 11.74 mm^{-1}
T = 293 K
Irregular, colourless
0.11 × 0.08 × 0.06 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scans
Absorption correction: numerical (*X-SHAPE*; Stoe & Cie, 1995)
T_{min} = 0.291, T_{max} = 0.480
2577 measured reflections
260 independent reflections
174 reflections with $I > 2\sigma(I)$
R_{int} = 0.046
θ_{max} = 30.4°, θ_{min} = 4.2°
$h = -7 \rightarrow 7$
$k = -7 \rightarrow 7$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.016
$wR(F^2)$ = 0.032
S = 0.98
260 reflections
16 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
$w = 1/[\sigma^2(F_o^2) + (0.0079P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0082 (5)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 > 2sigma(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}	Occ. (<1)
La	0.0000	0.2500	0.6250	0.01492 (18)	0.6676 (10)
Mo	0.0000	0.2500	0.1250	0.01706 (15)	
O	0.1374 (3)	0.0106 (2)	0.20490 (13)	0.0313 (5)	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
La	0.0171 (2)	0.0171 (2)	0.0107 (2)	0.000	0.000	0.000
Mo	0.01534 (18)	0.01534 (18)	0.0205 (2)	0.000	0.000	0.000
O	0.0209 (8)	0.0329 (9)	0.0403 (9)	0.0048 (6)	0.0031 (9)	0.0105 (7)

Geometric parameters (Å, º)

La—O^{i}	2.5728 (14)	La—La^{x}	4.0120 (2)
La—O^{ii}	2.5728 (14)	La—La^{xi}	4.0120 (2)
La—O^{iii}	2.5728 (14)	La—La^{iv}	4.0120 (2)
La—O^{iv}	2.5728 (14)	Mo—O^{xii}	1.7605 (14)

La—O^{v}	2.5766 (14)	Mo—O^{xiii}	1.7605 (14)
La—O^{vi}	2.5766 (14)	Mo—O^{xiv}	1.7605 (14)
La—O^{vii}	2.5766 (14)	Mo—O	1.7606 (14)
La—O^{viii}	2.5766 (14)	O—La^{iv}	2.5728 (14)
La—La^{ix}	4.0120 (2)	O—La^{xv}	2.5766 (14)
O^{i}—La—O^{ii}	128.57 (4)	O^{iii}—La—La^{x}	161.84 (3)
O^{i}—La—O^{iii}	75.70 (7)	O^{iv}—La—La^{x}	66.64 (3)
O^{ii}—La—O^{iii}	128.57 (4)	O^{v}—La—La^{x}	103.20 (4)
O^{i}—La—O^{iv}	128.57 (4)	O^{vi}—La—La^{x}	38.79 (3)
O^{ii}—La—O^{iv}	75.70 (7)	O^{vii}—La—La^{x}	129.62 (3)
O^{iii}—La—O^{iv}	128.57 (4)	O^{viii}—La—La^{x}	85.04 (3)
O^{i}—La—O^{v}	148.98 (6)	La^{ix}—La—La^{x}	123.628 (3)
O^{ii}—La—O^{v}	68.24 (3)	O^{i}—La—La^{xi}	161.84 (3)
O^{iii}—La—O^{v}	74.21 (2)	O^{ii}—La—La^{xi}	66.64 (3)
O^{iv}—La—O^{v}	77.64 (5)	O^{iii}—La—La^{xi}	103.00 (3)
O^{i}—La—O^{vi}	74.21 (2)	O^{iv}—La—La^{xi}	38.85 (3)
O^{ii}—La—O^{vi}	77.64 (5)	O^{v}—La—La^{xi}	38.79 (3)
O^{iii}—La—O^{vi}	148.98 (6)	O^{vi}—La—La^{xi}	103.20 (4)
O^{iv}—La—O^{vi}	68.24 (3)	O^{vii}—La—La^{xi}	85.04 (3)
O^{v}—La—O^{vi}	136.53 (7)	O^{viii}—La—La^{xi}	129.62 (3)
O^{i}—La—O^{vii}	77.64 (5)	La^{ix}—La—La^{xi}	123.628 (3)
O^{ii}—La—O^{vii}	148.98 (6)	La^{x}—La—La^{xi}	83.823 (4)
O^{iii}—La—O^{vii}	68.24 (3)	O^{i}—La—La^{iv}	38.85 (3)
O^{iv}—La—O^{vii}	74.20 (2)	O^{ii}—La—La^{iv}	161.84 (3)
O^{v}—La—O^{vii}	97.88 (2)	O^{iii}—La—La^{iv}	66.64 (3)
O^{vi}—La—O^{vii}	97.88 (2)	O^{iv}—La—La^{iv}	103.00 (3)
O^{i}—La—O^{viii}	68.24 (3)	O^{v}—La—La^{iv}	129.62 (3)
O^{ii}—La—O^{viii}	74.20 (2)	O^{vi}—La—La^{iv}	85.04 (3)
O^{iii}—La—O^{viii}	77.64 (5)	O^{vii}—La—La^{iv}	38.79 (3)
O^{iv}—La—O^{viii}	148.98 (6)	O^{viii}—La—La^{iv}	103.20 (4)
O^{v}—La—O^{viii}	97.88 (2)	La^{ix}—La—La^{iv}	83.823 (4)
O^{vi}—La—O^{viii}	97.88 (2)	La^{x}—La—La^{iv}	123.628 (3)
O^{vii}—La—O^{viii}	136.53 (7)	La^{xi}—La—La^{iv}	123.628 (3)
O^{i}—La—La^{ix}	66.64 (3)	O^{xii}—Mo—O^{xiii}	107.08 (5)
O^{ii}—La—La^{ix}	103.00 (3)	O^{xii}—Mo—O^{xiv}	114.36 (10)
O^{iii}—La—La^{ix}	38.85 (3)	O^{xiii}—Mo—O^{xiv}	107.08 (5)
O^{iv}—La—La^{ix}	161.84 (3)	O^{xii}—Mo—O	107.08 (5)
O^{v}—La—La^{ix}	85.04 (3)	O^{xiii}—Mo—O	114.36 (10)
O^{vi}—La—La^{ix}	129.62 (3)	O^{xiv}—Mo—O	107.08 (5)
O^{vii}—La—La^{ix}	103.20 (4)	Mo—O—La^{iv}	134.75 (7)
O^{viii}—La—La^{ix}	38.79 (3)	Mo—O—La^{xv}	120.66 (7)
O^{i}—La—La^{x}	103.00 (3)	La^{iv}—O—La^{xv}	102.36 (5)
O^{ii}—La—La^{x}	38.85 (3)		

Symmetry codes: (i) *y*+1/4, −*x*+1/4, *z*+1/4; (ii) *x*, *y*+1/2, −*z*+1; (iii) −*y*−1/4, *x*+1/4, *z*+1/4; (iv) −*x*, −*y*, −*z*+1; (v) *x*−1/2, *y*+1/2, *z*+1/2; (vi) −*x*+1/2, −*y*, *z*+1/2; (vii) −*y*−1/4, *x*−1/4, −*z*+3/4; (viii) *y*+1/4, −*x*+3/4, −*z*+3/4; (ix) −*x*, −*y*+1, −*z*+1; (x) −*x*+1/2, −*y*+1/2, −*z*+3/2; (xi) −*x*−1/2, −*y*+1/2, −*z*+3/2; (xii) *y*−1/4, −*x*+1/4, −*z*+1/4; (xiii) −*x*, −*y*+1/2, *z*; (xiv) −*y*+1/4, *x*+1/4, −*z*+1/4; (xv) *x*+1/2, *y*−1/2, *z*−1/2.