

Redetermination of terbium scandate, revealing a defect-type perovskite derivative

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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{Sc}-\text{O}) = 0.002$ Å; disorder in main residue; R factor = 0.024; wR factor = 0.047; data-to-parameter ratio = 11.4.

The crystal structure of terbium(III) scandate(III), with ideal formula TbScO_3 , has been reported previously on the basis of powder diffraction data [Liferovich & Mitchell (2004). *J. Solid State Chem.* **177**, 2188–2197]. The current data were obtained from single crystals grown by the Czochralski method and show an improvement in the precision of the geometric parameters. Moreover, inductively coupled plasma optical emission spectrometry studies resulted in a nonstoichiometric composition of the title compound. Site-occupancy refinements based on diffraction data support the idea of a Tb deficiency on the A site (inducing O defects on the O2 position). The crystallochemical formula of the investigated sample thus may be written as $A_{(\square_{0.04}\text{Tb}_{0.96})}^B\text{ScO}_{2.94}$. In the title compound, Tb occupies the eightfold-coordinated sites (site symmetry m) and Sc the centres of corner-sharing $[\text{ScO}_6]$ octahedra (site symmetry $\bar{1}$). The mean bond lengths and site distortions fit well into the data of the remaining lanthanoid scandates in the series from DyScO_3 to NdScO_3 . A linear structural evolution with the size of the lanthanoid from DyScO_3 to NdScO_3 can be predicted.

Related literature

Rietveld refinements on powders of LnScO_3 with $\text{Ln} = \text{La}^{3+}$ – Ho^{3+} were reported by Liferovich & Mitchell (2004). The crystal structures of the Dy, Gd, Sm and Nd members, refined from single-crystal diffraction data, have been recently provided by Veličkov *et al.* (2007). Geometrical parameters have been calculated by means of atomic coordinates following the concept of Zhao *et al.* (1993). A more detailed description of the growth procedure of the Ln scandates is given by Uecker *et al.* (2006). For the applications of Ln scandates, see: Choi *et al.* (2004); Haeni *et al.* (2004).

Experimental

Crystal data

$\text{Tb}_{0.96}\text{ScO}_{2.94}$	$V = 247.07$ (6) Å ³
$M_r = 244.56$	$Z = 4$
Orthorhombic, $Pnma$	Mo $K\alpha$ radiation
$a = 5.7233$ (8) Å	$\mu = 29.58$ mm ⁻¹
$b = 7.9147$ (12) Å	$T = 298$ (2) K
$c = 5.4543$ (7) Å	$0.14 \times 0.12 \times 0.02$ mm

Data collection

Stoe IPDS-II diffractometer	2143 measured reflections
Absorption correction: analytical (Alcock, 1970)	353 independent reflections
$T_{\min} = 0.088$, $T_{\max} = 0.278$	328 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.065$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.024$	31 parameters
$wR(F^2) = 0.047$	1 restraint
$S = 1.20$	$\Delta\rho_{\max} = 2.15$ e Å ⁻³
353 reflections	$\Delta\rho_{\min} = -1.12$ e Å ⁻³

Table 1

Selected bond lengths (Å).

Tb1–O1 ⁱ	2.241 (5)	Tb1–O2 ^v	2.837 (4)
Tb1–O2 ⁱⁱ	2.277 (4)	Sc2–O2 ⁱⁱ	2.088 (3)
Tb1–O1 ⁱⁱⁱ	2.334 (5)	Sc2–O2 ^{vi}	2.095 (4)
Tb1–O2 ^{iv}	2.586 (4)	Sc2–O1 ^{vii}	2.1141 (19)

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

Data collection: *X-AREA* (Stoe & Cie, 2006); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2006); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXS97* (Sheldrick, 2008); molecular graphics: *ATOMS* (Dowty, 2004); 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: WM2190).

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supporting information

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S1. Comment

The lanthanoid scandates, LnScO_3 , with $\text{Ln} = \text{La}^{3+}$ to Ho^{3+} are known to adopt an orthorhombic derivative of the perovskite structure. Their lattice dimensions are suitable to use them as substrates for the epitaxial growth of strain engineered BaTiO_3 and SrTiO_3 films (Choi *et al.*, 2004; Haeni *et al.*, 2004).

Liferovich & Mitchell (2004) studied the crystal structure of lanthanoid scandates, including TbScO_3 , by Rietveld analysis from powder diffraction data. Crystallographic data of DyScO_3 , GdScO_3 , SmScO_3 and NdScO_3 obtained from single crystals were recently reported by Veličkov *et al.* (2007). However, in the literature there are disagreements concerning some structural characteristics and their dependence on the Ln-substitution: Veličkov *et al.* (2007) assumed linear trends, whereas Liferovich & Mitchell (2004) observed no obvious continuous evolution. Especially the TbScO_3 and EuScO_3 compounds seemed to exhibit an anomalous behaviour in the latter study. The present paper provides first results on TbScO_3 , redetermined from single-crystal data. Investigations on EuScO_3 are in preparation.

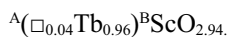
The orthorhombic distorted perovskite structure of TbScO_3 (Fig. 1) is confirmed from our refinements. Whereas the lattice parameters for TbScO_3 compare well with the data of Liferovich & Mitchell (2004), the atomic coordinates show deviations of up to 0.008 in the fractional atomic coordinates, resulting in slightly different geometrical parameters. The A-site is occupied by Tb and has an average bond length in an eightfold coordination of $^{\text{[8]}}\langle\text{A—O}\rangle = 2.499 \text{ \AA}$ with a polyhedral bond length distortion of $^{\text{A}}\Delta_8 = 8.78 \times 10^{-3}$ ($\Delta_n = 1/n \sum \{(r_i - r)/r\}^2$). The B-site shows bond lengths typical for octahedrally coordinated scandium ($\langle\text{B—O}\rangle = 2.101 \text{ \AA}$) and is rather distorted with $^{\text{B}}\Delta_6 = 0.025 \times 10^{-3}$ and a bond angle variance of $\delta = 3.23^\circ$. The tilting of the corner sharing octahedra calculated after Zhao *et al.* (1993) are $\theta = 20.64^\circ$ in $[110]$ and $\varnothing = 12.97^\circ$ in $[001]$ directions. From our data we can establish linear trends for the crystallochemical parameters from DyScO_3 to NdScO_3 in dependence on the Ln-substitution. Consequently, an anomalous behaviour of TbScO_3 in Ln-scandate series could not be confirmed.

S2. Experimental

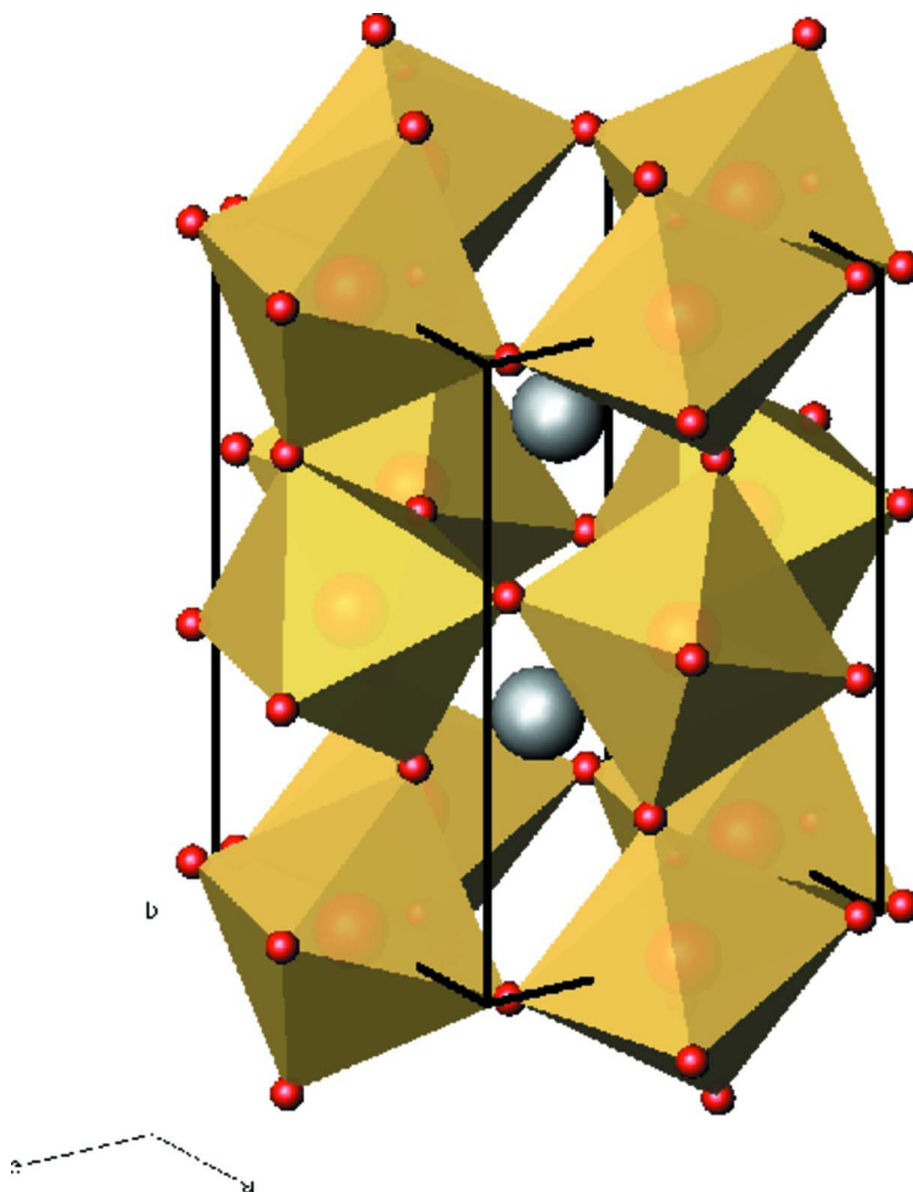
TbScO_3 was grown as a bulk crystal ($\varnothing = 20 \text{ mm}$) from a melt by conventional Czochralski technique with an automatic diameter control. The starting materials Tb_2O_3 and Sc_2O_3 (Alfa Aesar) with 99.99% purity were dried, mixed in a stoichiometric ratio, sintered and pressed to pellets easing the melting procedure. An iridium crucible (40 x 40 mm) was used as melt container combined with an iridium afterheater both RF-heated with a 25 kW mf generator. The crystal was withdrawn with a pulling rate of 1 mm/h under flowing nitrogen atmosphere. The grown crystal was colourless, so that a valence state of Tb^{3+} can be assumed. A part of the single-crystal material was crushed and irregular fragments were screened using a polarizing light microscope to find a sample of good optical quality for diffraction experiments.

S3. Refinement

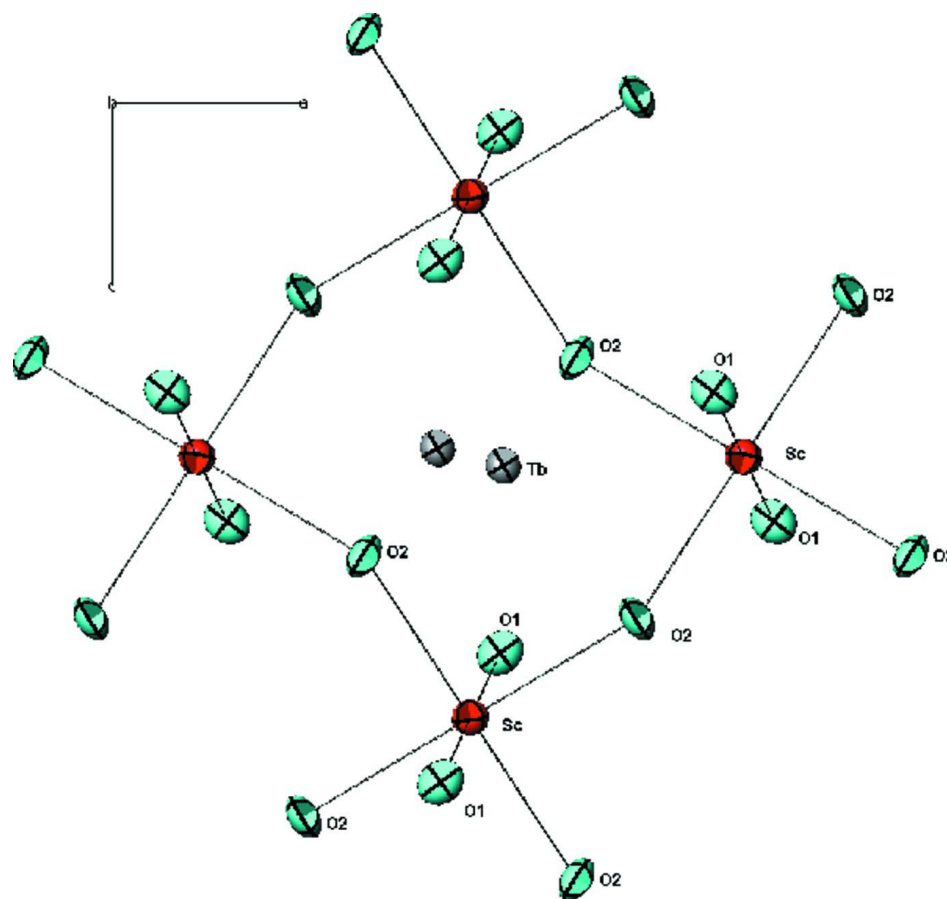
The ICP OES (inductively coupled plasma optical emission spectrometry) investigation of this sample resulted in a composition of $\text{Tb}_2\text{O}_3 = 48.79 \text{ mol}\%$ and $\text{Sc}_2\text{O}_3 = 51.21 \text{ mol}\%$, indicating a non-stoichiometric chemical composition. Site occupancy refinements based on diffraction data support the idea of the Tb-deficiency on the A-site coupled with O-defects on the O2-position. The calculated chemical compositions provided by structure refinement agree very well with the data of the ICP OES study. The crystallochemical formula of the investigated sample may thus be written as



The highest peak and deepest hole are located 0.59 and 1.42 Å from Tb1. Site occupation refinements indicated deviations from full occupancy on the Tb1 and the O2 sites. For the final refinement cycle a constraint ensuring charge neutrality was included. In contrast to the previous powder refinement, performed with the setting *Pbnm* of space group no. 62, the standard setting in *Pnma* was used for the present redetermination.

**Figure 1**

The orthorhombic perovskite structure of TbScO₃ characterized by a tilted corner sharing ScO₆ framework and the 8-fold coordinated Tb sites. The ScO₆ octahedra are brownish and translucent, the Tb atoms are grey and the O atoms are red.

**Figure 2**

Projection of the TbScO_3 structure along $[010]$, showing the Tb atoms and the Sc coordination with displacement ellipsoids at the 80% probability level.

terbium(III) scandate(III)

Crystal data

$\text{Tb}_{0.96}\text{ScO}_{2.94}$

$M_r = 244.56$

Orthorhombic, *Pnma*

Hall symbol: $-P\ 2ac\ 2n$

$a = 5.7233\ (8)\ \text{\AA}$

$b = 7.9147\ (12)\ \text{\AA}$

$c = 5.4543\ (7)\ \text{\AA}$

$V = 247.07\ (6)\ \text{\AA}^3$

$Z = 4$

$F(000) = 427$

$D_x = 6.55\ \text{Mg m}^{-3}$

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

Cell parameters from 1947 reflections

$\theta = 2.6\text{--}29.1^\circ$

$\mu = 29.58\ \text{mm}^{-1}$

$T = 298\ \text{K}$

Plate, colourless

$0.14 \times 0.12 \times 0.02\ \text{mm}$

Data collection

Stoe IPDS-II
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: $6.67\ \text{pixels mm}^{-1}$

ω scans

Absorption correction: analytical
(Alcock, 1970)

$T_{\min} = 0.088$, $T_{\max} = 0.278$

2143 measured reflections

353 independent reflections

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

$R_{\text{int}} = 0.065$

$\theta_{\max} = 29.1^\circ$, $\theta_{\min} = 4.5^\circ$
 $h = -7 \rightarrow 7$

$k = -9 \rightarrow 10$
 $l = -7 \rightarrow 7$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.024$
 $wR(F^2) = 0.047$
 $S = 1.20$
 353 reflections
 31 parameters
 1 restraint
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 $w = 1/[\sigma^2(F_o^2) + (0.0165P)^2 + 1.3905P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.015$
 $\Delta\rho_{\max} = 2.15 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -1.12 \text{ e } \text{\AA}^{-3}$
 Extinction correction: *SHELXS97* (Sheldrick,
 2008), $F_c^* = kFc[1 + 0.001x \text{Fc}^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.158 (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>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Tb1	0.06029 (6)	0.25	0.01672 (6)	0.0087 (2)	0.9591 (13)
Sc2	0	0	0.5	0.0082 (3)	
O1	0.4455 (10)	0.25	0.8761 (9)	0.0114 (10)	
O2	0.1946 (7)	0.9357 (5)	0.8100 (6)	0.0108 (8)	0.9693 (10)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Tb1	0.0074 (3)	0.0106 (3)	0.0080 (2)	0	0.00053 (12)	0
Sc2	0.0085 (6)	0.0085 (7)	0.0075 (5)	-0.0003 (7)	-0.0002 (4)	0.0002 (4)
O1	0.013 (3)	0.010 (2)	0.012 (2)	0	0.0018 (19)	0
O2	0.0078 (19)	0.014 (2)	0.0111 (15)	-0.0024 (14)	-0.0037 (13)	0.0025 (13)

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

Tb1—O1 ⁱ	2.241 (5)	Sc2—O2 ⁱⁱ	2.088 (3)
Tb1—O2 ⁱⁱ	2.277 (4)	Sc2—O2 ^{xii}	2.088 (3)
Tb1—O2 ⁱⁱⁱ	2.277 (4)	Sc2—O2 ^{xiii}	2.095 (4)
Tb1—O1 ^{iv}	2.334 (5)	Sc2—O2 ^{vi}	2.095 (4)
Tb1—O2 ^v	2.586 (4)	Sc2—O1 ^{xiv}	2.1141 (19)
Tb1—O2 ^{vi}	2.586 (4)	Sc2—O1 ^x	2.1141 (18)
Tb1—O2 ^{vii}	2.837 (4)	Sc2—Tb1 ^{xv}	3.2026 (4)
Tb1—O2 ^{viii}	2.837 (4)	Sc2—Tb1 ⁱ	3.2026 (4)

Tb1—Sc2 ^{ix}	3.2026 (4)	Sc2—Tb1 ^{xvi}	3.3140 (4)
Tb1—Sc2 ^x	3.2026 (4)	Sc2—Tb1 ^{xvii}	3.4608 (4)
Tb1—Sc2 ^{xi}	3.3140 (4)	Sc2—Tb1 ^{xviii}	3.4608 (4)
Tb1—Sc2	3.3140 (4)		
O1 ⁱ —Tb1—O2 ⁱⁱ	102.07 (14)	O2 ^{xii} —Sc2—O2 ^{xiii}	89.16 (7)
O1 ⁱ —Tb1—O2 ⁱⁱⁱ	102.07 (14)	O2 ⁱⁱ —Sc2—O2 ^{vi}	89.16 (7)
O2 ⁱⁱ —Tb1—O2 ⁱⁱⁱ	80.4 (2)	O2 ^{xii} —Sc2—O2 ^{vi}	90.84 (7)
O1 ⁱ —Tb1—O1 ^{iv}	87.86 (12)	O2 ^{xiii} —Sc2—O2 ^{vi}	180
O2 ⁱⁱ —Tb1—O1 ^{iv}	137.88 (11)	O2 ⁱⁱ —Sc2—O1 ^{xiv}	87.26 (17)
O2 ⁱⁱⁱ —Tb1—O1 ^{iv}	137.88 (11)	O2 ^{xii} —Sc2—O1 ^{xiv}	92.74 (17)
O1 ⁱ —Tb1—O2 ^v	138.63 (11)	O2 ^{xiii} —Sc2—O1 ^{xiv}	86.91 (18)
O2 ⁱⁱ —Tb1—O2 ^v	117.25 (8)	O2 ^{vi} —Sc2—O1 ^{xiv}	93.09 (18)
O2 ⁱⁱⁱ —Tb1—O2 ^v	73.97 (9)	O2 ⁱⁱ —Sc2—O1 ^x	92.74 (17)
O1 ^{iv} —Tb1—O2 ^v	72.00 (13)	O2 ^{xii} —Sc2—O1 ^x	87.26 (17)
O1 ⁱ —Tb1—O2 ^{vi}	138.63 (11)	O2 ^{xiii} —Sc2—O1 ^x	93.09 (18)
O2 ⁱⁱ —Tb1—O2 ^{vi}	73.97 (9)	O2 ^{vi} —Sc2—O1 ^x	86.91 (18)
O2 ⁱⁱⁱ —Tb1—O2 ^{vi}	117.25 (8)	O1 ^{xiv} —Sc2—O1 ^x	180
O1 ^{iv} —Tb1—O2 ^{vi}	72.00 (13)	Sc2 ^{xix} —O1—Sc2 ^{xv}	138.8 (3)
O2 ^v —Tb1—O2 ^{vi}	69.28 (17)	Sc2 ^{xix} —O1—Tb1 ^{xx}	105.22 (14)
O1 ⁱ —Tb1—O2 ^{vii}	72.51 (9)	Sc2 ^{xv} —O1—Tb1 ^{xx}	105.22 (14)
O2 ⁱⁱ —Tb1—O2 ^{vii}	76.86 (13)	Sc2 ^{xix} —O1—Tb1 ^{xviii}	91.96 (15)
O2 ⁱⁱⁱ —Tb1—O2 ^{vii}	154.79 (10)	Sc2 ^{xv} —O1—Tb1 ^{xviii}	91.96 (15)
O1 ^{iv} —Tb1—O2 ^{vii}	67.26 (9)	Tb1 ^{xx} —O1—Tb1 ^{xviii}	126.2 (2)
O2 ^v —Tb1—O2 ^{vii}	126.67 (6)	Sc2 ^{xxi} —O2—Sc2 ^{xxii}	141.9 (2)
O2 ^{vi} —Tb1—O2 ^{vii}	66.45 (5)	Sc2 ^{xxi} —O2—Tb1 ⁱⁱ	98.72 (15)
O1 ⁱ —Tb1—O2 ^{viii}	72.51 (9)	Sc2 ^{xxii} —O2—Tb1 ⁱⁱ	119.09 (16)
O2 ⁱⁱ —Tb1—O2 ^{viii}	154.79 (10)	Sc2 ^{xxi} —O2—Tb1 ^{xxii}	85.81 (12)
O2 ⁱⁱⁱ —Tb1—O2 ^{viii}	76.86 (13)	Sc2 ^{xxii} —O2—Tb1 ^{xxii}	89.52 (13)
O1 ^{iv} —Tb1—O2 ^{viii}	67.26 (9)	Tb1 ⁱⁱ —O2—Tb1 ^{xxii}	103.74 (15)
O2 ^v —Tb1—O2 ^{viii}	66.45 (5)	Sc2 ^{xxi} —O2—Tb1 ^{xxiii}	87.91 (13)
O2 ^{vi} —Tb1—O2 ^{viii}	126.67 (6)	Sc2 ^{xxii} —O2—Tb1 ^{xxiii}	79.43 (12)
O2 ^{vii} —Tb1—O2 ^{viii}	122.50 (15)	Tb1 ⁱⁱ —O2—Tb1 ^{xxiii}	103.14 (13)
O2 ⁱⁱ —Sc2—O2 ^{xii}	180	Tb1 ^{xxii} —O2—Tb1 ^{xxiii}	153.02 (16)
O2 ⁱⁱ —Sc2—O2 ^{xiii}	90.84 (7)		

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