Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

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

Boža Veličkov,[a]* Volker Kahlenberg,[b] Rainer Bertram[a] and Reinhard Uecker[a]

[a]Leibniz-Institute for Crystal Growth, Max-Born-Strasse 2, 12489 Berlin, Germany, and [b]University of Innsbruck, Institute of Mineralogy and Petrography, Innrain 52, 6020 Innsbruck, Austria
Correspondence e-mail: velickov@ikz-berlin.de

Received 14 August 2008; accepted 14 October 2008

Key indicators: single-crystal X-ray study; T = 298 K; mean σ(Sc–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 $^{A}(\square_{0.04}Tb_{0.96})^{B}ScO_{2.94}$. In the title compound, Tb occupies the eightfold-coordinated sites (site symmetry m) and Sc the centres of corner-sharing $[ScO_6]$ octahedra (site symmetry $\overline{1}$). 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

Rietvelt refinements on powders of $LnScO_3$ with Ln = 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

$Tb_{0.96}ScO_{2.94}$
M_r = 244.56
Orthorhombic, *Pnma*
a = 5.7233 (8) Å
b = 7.9147 (12) Å
c = 5.4543 (7) Å
V = 247.07 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 29.58 mm^{-1}
T = 298 (2) K
0.14 × 0.12 × 0.02 mm

Data collection

Stoe IPDS-II diffractometer
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_{int} = 0.065

Refinement

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

The authors thank M. Bernhagen for technical support in carrying out the growth experiments.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2190).

References

Alcock, N. W. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, p. 271. Copenhagen: Munksgaard.
Choi, K. J., Biegalski, M., Li, Y. L., Sharan, A., Schubert, J., Uecker, R., Reiche, P., Chen, L.-Q., Gopalan, V., Schlom, D. G. & Eom, C. B. (2004). *Science*, **306**, 1005–1009.
Dowty, E. (2004). *ATOMS for Windows*. Shape Software, Kingsport, Tennessee, USA.
Haeni, J. H., Irvin, P., Chang, W., Uecker, R., Reiche, P., Li, Y. L., Choudhury, S., Hawley, M. E., Craigo, B., Tagantsev, A. K., Pan, X. Q., Streiffer, S. K., Chen, L. Q., Kichoefer, S., Levy, J. & Schlom, D. G. (2004). *Nature (London)*, **430**, 758–761.
Liferovich, R. P. & Mitchell, R. H. (2004). *J. Solid State Chem.* **177**, 2188–2197.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Stoe & Cie (2006). *X-AREA and X-RED32*. Stoe & Cie, Darmstadt, Germany.
Uecker, R., Wilke, H., Schlom, D. G., Veličkov, B., Reiche, P., Polity, A., Bernhagen, M. & Rossberg, M. (2006). *J. Cryst. Growth*, **295**, 84–91.
Veličkov, B., Kahlenberg, V., Bertram, R. & Bernhagen, M. (2007). *Z. Kristallogr.* **222**, 466–473.
Zhao, Y., Weidner, D. J., Parise, J. B. & Cox, D. E. (1993). *Phys. Earth Planet. Inter.* **76**, 1-16.

supporting information

Acta Cryst. (2008). E**64**, i79   [doi:10.1107/S1600536808033394]

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

Boža Veličkov, Volker Kahlenberg, Rainer Bertram and Reinhard Uecker

S1. Comment

The lanthanoid scandates, $LnScO_3$, with Ln = 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 continious 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 $^{[8]}\langle A—O\rangle = 2.499$ Å with a polyhedral bond length distortion of $^{A}\Delta_8 = 8.78\times10^{-3}$ ($\Delta_n=1/n\Sigma\{(r_i-r)/r\}^2$). The B-site shows bond lengths typical for octahedrally coordinated scandium ($\langle B—O\rangle = 2.101$ Å) and is rather distorted with $^{B}\Delta_6 = 0.025\times10^{-3}$ and a bond angle variance of $\delta = 3.23°$. The tilting of the corner sharing octahedra calculated after Zhao *et al.* (1993) are $\theta = 20.64°$ in [110] and Ø = 12.97° 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 (Ø = 20 mm) from a melt by conventional Czochralski technique with an automatic diameter control. The starting materials Tb_4O_7 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 compostion of Tb_2O_3 = 48.79 mol% and Sc_2O_3 = 51.21 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 $^{A}(\square_{0.04}Tb_{0.96})^{B}ScO_{2.94.}$

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.

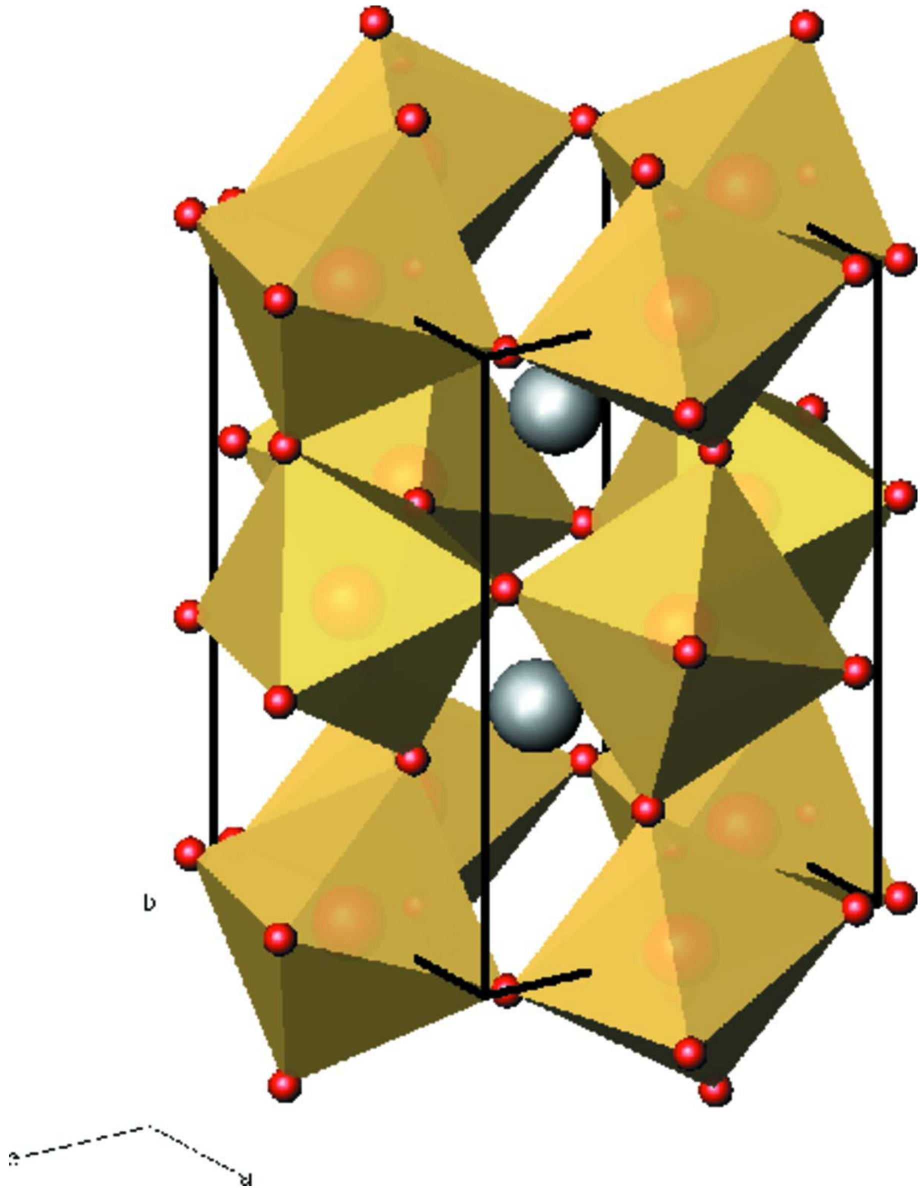

Figure 1

The orthorhombic perovskite structure of $TbScO_3$ characterized by a tilted corner sharing ScO_6 framework and the 8-fold coordinated Tb sites. The ScO_6 octahedra are brownish and translucent, the Tb atoms are grey and the O atoms are red.

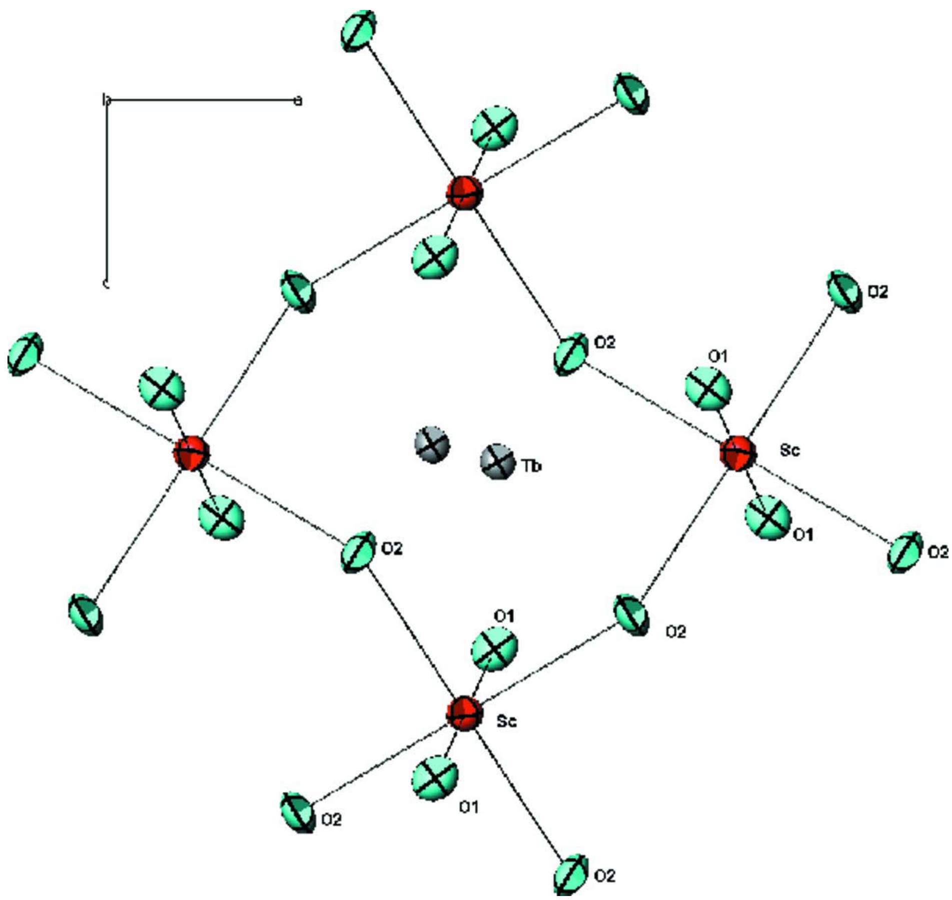

Figure 2

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

$Tb_{0.96}ScO_{2.94}$
M_r = 244.56
Orthorhombic, *Pnma*
Hall symbol: -P 2ac 2n
a = 5.7233 (8) Å
b = 7.9147 (12) Å
c = 5.4543 (7) Å
V = 247.07 (6) Å^3
Z = 4
F(000) = 427
D_x = 6.55 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1947 reflections
θ = 2.6–29.1°
μ = 29.58 mm^{-1}
T = 298 K
Plate, colourless
0.14 × 0.12 × 0.02 mm

Data collection

Stoe IPDS-II
diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 6.67 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_{int} = 0.065

θ_{max} = 29.1°, θ_{min} = 4.5°
h = −7→7
k = −9→10
l = −7→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 e Å^{-3}
$\Delta\rho_{min}$ = −1.12 e Å^{-3}
Extinction correction: *SHELXS97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
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 (Å²)

	x	y	z	U_{iso}*/U_{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 (Å²)

	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 (Å, º)

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.