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Crystal structure of $Ti_8Bi_9O_{0.25}$ containing interstitial oxygen atoms

Hisanori Yamane* and Keita Hiraka

Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai, 980-8577, Japan. *Correspondence e-mail: hisanori.yamane.a1@tohoku.ac.jp

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Single crystals of $Ti_8Bi_9O_{0.25}$, titanium bismuth oxide (8/9/0.25), were obtained from a sample prepared by heating a mixture of Ti, TiO_2 and Bi powders in an Ar atmosphere. Single-crystal X-ray analysis revealed that the introduction of O atoms into the structure of Ti_8Bi_9 retains the space-group type $P4/nmm$. The oxygen site is located within a Ti_4 tetrahedron (point group symmetry $\bar{4}m2$) that is vacant in the Ti_8Bi_9 crystal structure. The occupancy of this site is 0.25 (4), and the O—Ti distance is 1.8824 (11) Å.

1. Chemical context

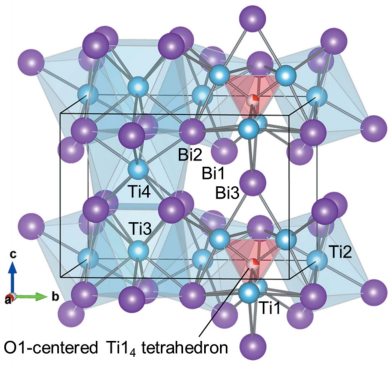
The crystal structure of Ti_8Bi_9, having the tetragonal space group $P4/nmm$, a = 10.277 (1) Å, c = 7.375 (1) Å, Z = 2, was determined by Richter and Jeitschko (1997). This compound was identified in Ti–Bi binary phase diagrams (Okamoto, 2010, 2015), and was also confirmed by powder X-ray diffraction (PXRD) in a study of the Ti–Bi phase diagram (Maruyama *et al.*, 2013). Recently, the use of a Bi flux has enabled single-crystal growth of a new polymorph of TiO (ε-phase; Amano *et al.*, 2016) and some new suboxides: $Ti_8(Sn_xBi_{1-x})O_7$, $Ti_{11.17}(Sn_{0.85}Bi_{0.15})_3O_{10}$ and $Ti_{12-\delta}Ga_xBi_{3-x}O_{10}$ (Amano & Yamane, 2017; Yamane & Amano, 2017). While exploring new suboxides containing Ti using a Bi flux, we also found the title compound, $Ti_8Bi_9O_{0.25}$ where interstitial O sites are partly occupied.

In the present communication, details of single-crystal growth of $Ti_8Bi_9O_{0.25}$ and its comparison with the crystal structure of Ti_8Bi_9 (Richter & Jeitschko, 1997) are reported.

2. Structural commentary

Reflections from a single crystal of $Ti_8Bi_9O_{0.25}$ could be indexed with a primitive tetragonal cell similar to that of the oxygen-free compound Ti_8Bi_9 (Richter & Jeitschko, 1997). The differences in the lengths of the a and c axes and in the cell volume from those of Ti_8Bi_9 were +1.0%, −0.09% and +0.74%, respectively. The reflection conditions observed for the new compound were the same as for Ti_8Bi_9, revealing space group $P4/nmm$.

The crystal structure and atomic arrangement for $Ti_8Bi_9O_{0.25}$ are depicted in Figs. 1 and 2, respectively. In the crystal structure of Ti_8Bi_9 (Richter & Jeitschko, 1997), the Ti2 site is in a trigonal antiprism (point group symmetry. .2/m) made up from Bi atoms with Bi—Ti distances of 2.848 (1) and 2.931 (1) Å (Table 1). The Ti3 and Ti4 sites are situated in square antiprisms in which the Bi—Ti distances range from 2.937 (5) to 3.144 (6) Å. The Ti3- and Ti4-centered $Bi1_4Bi2_4$



O1-centered $Ti1_4$ tetrahedron

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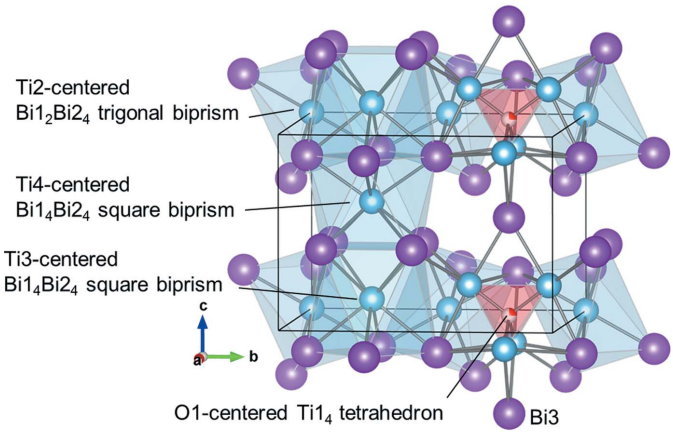

Figure 1
Crystal structure of $Ti_8Bi_9O_{0.25}$ drawn with Ti- and O-centered Bi polyhedra. The red part of the O1 sphere in the $Ti1_4$ tetrahedron shows the occupancy.

square antiprisms both exhibit point group symmetry 4*mm* and are arranged along the *c* axis by sharing the square planes. The Bi1Bi2$_2$ triangle plane is shared by the Ti2-centered Bi1$_2$Bi2$_4$ trigonal antiprism and the Ti3-centered Bi1$_4$Bi2$_4$ square antiprism. In the crystal structure of Ti_8Bi_9, only the Ti1 site forms a Ti polyhedron. The Ti1—Ti1 distances of the $Ti1_4$ tetrahedron are 2.934 (6) and 3.074 (3) Å. In addition to the three Ti1 sites, each Ti1 site is surrounded by six Bi atoms at distances of 2.945 (4)–3.074 (5) Å, and by two Ti2 sites at a distance of 3.017 (2) Å. The O atom of $Ti_8Bi_9O_{0.25}$ is located in the $Ti1_4$ tetrahedron at a site with symmetry $\overline{4}m2$ and with a site occupancy of 0.25 (4). The partial occupation by the O atoms changes the Ti1—Ti1 distances in the tetrahedron to

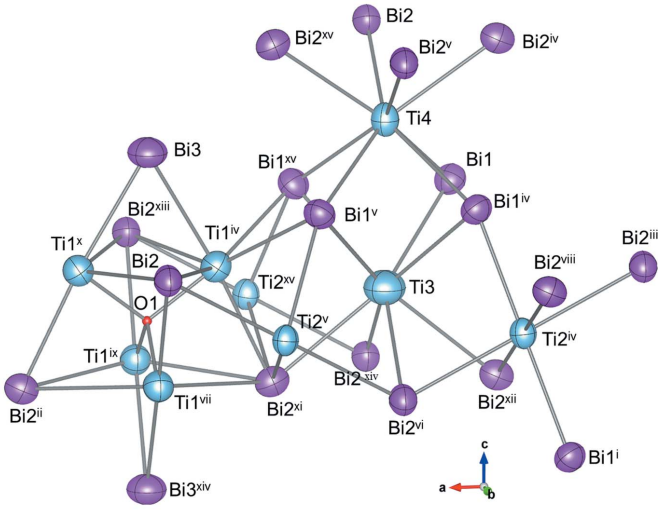

Figure 2
Atomic arrangement around Ti and Bi atoms in the structure of $Ti_8Bi_9O_{0.25}$. Displacement ellipsoids are drawn at the 99% probability level. [Symmetry codes: (i) $-y, -x+\frac{1}{2}, -z$; (ii) $y+1, -x+\frac{1}{2}, z-1$; (iii) $-x+\frac{1}{2}, -y+\frac{1}{2}, z-1$; (iv) $y, -x+\frac{1}{2}, z$; (v) $-x+\frac{1}{2}, -y+\frac{1}{2}, z$; (vi) $-x+\frac{1}{2}, -y+\frac{1}{2}, z-1$; (vii) $-x+1, -y+1, -z$; (viii) $-y, x+\frac{1}{2}, -z+1$; (ix) $x+\frac{1}{2}, y-\frac{1}{2}, -z$; (x) $-y+\frac{3}{2}, x, z$; (xi) $-y+\frac{1}{2}, x, z-1$; (xii) $y, -x+\frac{1}{2}, z-1$; (xiii) $x+\frac{1}{2}, y-\frac{1}{2}, -z+1$; (xiv) $x, y, z-1$; (xv) $-y+\frac{1}{2}, x, z$.]

Table 1
Selected interatomic distances (Å) for Ti_8Bi_9 (Richter & Jeitschko, 1997) and $Ti_8Bi_9O_{0.25}$ (this study).

	Ti_8Bi_9	$Ti_8Bi_9O_{0.25}$
Ti1—Ti1	2.934 (6)	2.992 (2)
Ti1—Ti1	3.074 (3) × 2	3.1142 (19) × 2
Ti1—Ti2	3.017 (2) × 2	3.0228 (6) × 2
Ti1—Bi1	2.971 (4) × 2	2.9610 (9) × 2
Ti1—Bi2	2.848 (1)	2.8305 (11)
Ti1—Bi2	3.074 (5) × 2	3.1175 (6) × 2
Ti1—Bi3	2.945 (4)	2.9491 (11)
Ti2—Bi1	2.848 (1) × 2	2.8488 (2) × 2
Ti2—Bi2	2.931 (1) × 4	2.94278 (11) × 4
Ti3—Bi1	3.122 (6) × 4	3.1227 (16) × 4
Ti3—Bi2	3.144 (6) × 4	3.1434 (16) × 4
Ti4—Bi1	2.937 (5) × 4	2.9398 (13) × 4
Ti4—Bi2	2.985 (5) × 4	2.9771 (13) × 4
O1—Ti1		1.8824 (11) × 4

2.992 (2) and 3.1142 (19) Å, representing increases of 1.9% and 1.3%, respectively. The Ti1—Bi2 distance is also increased by 1.4%, although the changes in the Ti3—Bi and Ti4—Bi distances are both less than 0.4%.

The O1—Ti1 distance of 1.8824 (11) Å is intermediate between the sums of ionic radii for Ti^{3+} and O^{2-} (1.91 Å) and Ti^{2+}—O^{2-} (1.845 Å), based on ionic radii of 0.67 and 0.605 Å for Ti^{3+} and Ti^{2+}, respectively, in sixfold coordination, and an O^{2-} radius of 1.24 Å in fourfold coordination (Shannon, 1976). The bond-valence sums (BVSs) calculated for the O1 site in the $Ti1_4$ tetrahedron using bond-valence parameters (R_0) for Ti^{4+} (1.815 Å), Ti^{3+} (1.815 Å) and Ti^{2+} (1.734 Å) and B = 0.37 (Brese & O'Keeffe, 1991; Amano & Yamane, 2017) are 3.33, 3.12 and 2.68 valence units (v.u.), respectively. All of these values are considerably greater than the expected valence value of 2 for an O atom, which may suggest that the O1 site is not fully occupied, or that bond-valence parameters for titanium in lower oxidation states (and/or tetrahedral coordination) need revision. Complete occupation of O atoms in tetrahedral sites surrounded by Ti atoms has been reported for the crystal structures of $Ti_{12-\delta}Ga_xBi_{3-x}O_{10}$. In these structures, the Ti—O distances range from 1.957 (3) to 2.291 (3) Å, all of which exceed the value of 1.8824 (11) Å for O1—Ti1 in $Ti_8Bi_9O_{0.25}$. The BVSs calculated for the O sites in $Ti_{12-\delta}Ga_xBi_{3-x}O_{10}$ using the parameters for Ti^{3+} and Ti^{2+} were found to be in the ranges 2.18–2.21 and 1.87–1.89 v.u., respectively (Amano & Yamane, 2017).

3. Synthesis and crystallization

A sample containing the title compound was prepared by combining 0.85 mmol Ti powder (99.99%, Mitsuwa Chemical Co., Ltd), 0.125 mol TiO_2 powder (rutile, 99.99%, Rare Metallic Co., Ltd) and 1.5 mmol Bi powder (99.999%, Mitsuwa Chemical Co., Ltd) in an agate mortar and subsequent pressing into a pellet (Ø 6 mm) under atmospheric conditions. The pellet was placed in a Ta boat that was then transferred into a stainless-steel tube and sealed with a cap in an Ar-filled glove box (MBRAUN; O_2 and H_2O < 1 ppm). The sealed stainless-steel tube was heated to 1073 K at a rate of

approximately 400 K h^{-1}, maintained at this temperature for 10 h, and subsequently cooled to 723 K at a rate of 10 K h^{-1}. Below 723 K, the sample was cooled to room temperature by shutting off the electric power to the heater of the furnace. The resulting sample was crushed and single-crystal fragments of $Ti_8Bi_9O_{0.25}$ were extracted. A single crystal for XRD analysis was sealed in a glass capillary. The crushed sample was also analyzed by electron probe microanalysis (EPMA, JEOL, JXA-8200). Only Bi, Ti and O were found in the bulk. The O concentration was greater than the expected values, indicating that some oxidation had occurred while transferring the specimens to the EPMA instrument. In addition to fragments with a Ti:Bi atomic ratio of approximately 8:9, some Bi-rich (>85%) portions and fragments with a Ti:Bi ratio of approximately 3:2 were also identified.

4. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The diffraction data of $Ti_8Bi_9O_{0.25}$ were initially analyzed using the Ti_8Bi_9 model (Richter & Jeitschko, 1997), and a residual electron density of 8.4 e $Å^{-3}$ was observed at (3/4, 1/4, 0), which corresponds to the 2*a* site in the $Ti1_4$ tetrahedron. The O-atom occupancy of this site was refined to be 0.25 (4), resulting in a decrease in $R[F^2 > 2\sigma(F^2)]$ from 0.045 to 0.020. For this site an isotropic atomic displacement parameter was considered.

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Table 2
Experimental details.

Crystal data	
Chemical formula	$Ti_8Bi_9O_{0.25}$
M_r	2267.94
Crystal system, space group	Tetragonal, *P*4/*nmm*
Temperature (K)	301
a, *c* (Å)	10.3198 (2), 7.3684 (1)
V (Å^3)	784.72 (3)
Z	2
Radiation type	Mo *Kα*
μ (mm^{-1})	104.26
Crystal size (mm)	0.10 × 0.08 × 0.06
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Numerical (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.011, 0.075
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	14767, 1101, 1079
R_{int}	0.059
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.833
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.020, 0.044, 1.36
No. of reflections	1101
No. of parameters	34
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.55, −1.61

Computer programs: *APEX3* and *SAINT* (Bruker, 2015), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *VESTA* (Momma & Izumi, 2011) and *publCIF* (Westrip, 2010).

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supporting information

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Crystal structure of $Ti_8Bi_9O_{0.25}$ containing interstitial oxygen atoms

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Computing details

Data collection: *APEX3* (Bruker, 2015); cell refinement: *SAINT* (Bruker, 2015); data reduction: *SAINT* (Bruker, 2015); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *VESTA* (Momma & Izumi, 2011); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Titanium bismuth oxide (8/9/0.25)

Crystal data

$Ti_8Bi_9O_{0.25}$
M_r = 2267.94
Tetragonal, *P*4/*nmm*
a = 10.3198 (2) Å
c = 7.3684 (1) Å
V = 784.72 (3) Å^3
Z = 2
F(000) = 1850
D_x = 9.598 Mg m^{-3}
Mo *Kα* radiation, λ = 0.71073 Å
Cell parameters from 9927 reflections
θ = 2.8–36.3°
μ = 104.26 mm^{-1}
T = 301 K
Granule, black
0.10 × 0.08 × 0.06 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: micro focus sealed tube
Detector resolution: 7.4074 pixels mm^{-1}
ω– and φ–scans
Absorption correction: numerical (*SADABS*; Krause *et al.*, 2015)
T_{min} = 0.011, T_{max} = 0.075
14767 measured reflections
1101 independent reflections
1079 reflections with $I > 2\sigma(I)$
R_{int} = 0.059
θ_{max} = 36.3°, θ_{min} = 2.8°
h = −17→17
k = −16→17
l = −11→12

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.020
$wR(F^2)$ = 0.044
S = 1.36
1101 reflections
34 parameters
0 restraints
$w = 1/[\sigma^2(F_o^2) + 5.5451P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.55 e Å^{-3}
$\Delta\rho_{min}$ = −1.61 e Å^{-3}
Extinction correction: SHELXL2014 (Sheldrick, 2015b), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.00132 (8)

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Ti1	0.2500	0.60505 (11)	0.15508 (15)	0.00985 (18)	
Ti2	0.0000	0.0000	0.0000	0.0082 (2)	
Ti3	0.2500	0.2500	0.0782 (3)	0.0161 (4)	
Ti4	0.2500	0.2500	0.5769 (3)	0.0094 (3)	
Bi1	0.08500 (2)	0.08500 (2)	0.34804 (3)	0.00996 (6)	
Bi2	0.2500	0.01379 (2)	0.80886 (3)	0.00990 (6)	
Bi3	0.7500	0.2500	0.5000	0.01392 (9)	
O1	0.7500	0.2500	0.0000	0.001 (6)*	0.25 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ti1	0.0095 (4)	0.0098 (4)	0.0102 (4)	0.000	0.000	−0.0005 (3)
Ti2	0.0073 (3)	0.0073 (3)	0.0099 (6)	0.0006 (4)	0.0002 (3)	0.0002 (3)
Ti3	0.0180 (6)	0.0180 (6)	0.0122 (9)	0.000	0.000	0.000
Ti4	0.0081 (5)	0.0081 (5)	0.0119 (8)	0.000	0.000	0.000
Bi1	0.01015 (7)	0.01015 (7)	0.00956 (10)	−0.00054 (6)	−0.00099 (4)	−0.00099 (4)
Bi2	0.00785 (9)	0.01194 (10)	0.00990 (10)	0.000	0.000	0.00110 (6)
Bi3	0.01626 (13)	0.01626 (13)	0.00924 (17)	0.000	0.000	0.000

Geometric parameters (Å, º)

Ti1—O1^{i}	1.8824 (11)	Ti4—Bi1^{v}	2.9398 (13)
Ti1—Bi2^{ii}	2.8305 (11)	Ti4—Bi1	2.9399 (13)
Ti1—Bi3^{iii}	2.9491 (11)	Ti4—Bi2^{xviii}	2.9771 (13)
Ti1—Bi1^{iv}	2.9610 (9)	Ti4—Bi2^{v}	2.9771 (13)
Ti1—Bi1^{v}	2.9610 (9)	Ti4—Bi2^{iv}	2.9771 (13)
Ti1—Ti1^{vi}	2.992 (2)	Ti4—Bi2	2.9771 (13)
Ti1—Ti2^{iv}	3.0228 (6)	Bi1—Ti1^{xviii}	2.9610 (9)
Ti1—Ti2^{v}	3.0227 (6)	Bi1—Ti1^{v}	2.9610 (9)
Ti1—Ti1^{vii}	3.1142 (19)	Bi1—Bi1^{xiv}	3.3423 (4)
Ti1—Ti1^{viii}	3.1142 (19)	Bi1—Bi1^{iv}	3.4054 (3)
Ti1—Bi2^{ix}	3.1175 (6)	Bi1—Bi1^{xviii}	3.4054 (3)
Ti1—Bi2^{x}	3.1175 (6)	Bi2—Ti1^{xx}	2.8305 (11)
Ti2—Bi1	2.8488 (2)	Bi2—Ti2^{xxi}	2.9428 (1)
Ti2—Bi1^{xi}	2.8488 (2)	Bi2—Ti2^{xxii}	2.9428 (1)
Ti2—Bi2^{xii}	2.9428 (1)	Bi2—Ti1^{xxiii}	3.1175 (6)
Ti2—Bi2^{xiii}	2.9428 (1)	Bi2—Ti1^{xxiv}	3.1175 (6)
Ti2—Bi2^{xiv}	2.9428 (1)	Bi2—Ti3^{xxii}	3.1434 (16)

Ti2—Bi2^{xv}	2.9428 (1)	Bi2—Bi2^{xviii}	3.4474 (3)
Ti2—Ti1^{xvi}	3.0228 (6)	Bi2—Bi2^{iv}	3.4474 (3)
Ti2—Ti1^{v}	3.0228 (6)	Bi2—Bi3^{xxv}	3.5482 (2)
Ti2—Ti1^{xvii}	3.0228 (6)	Bi3—Ti1^{iv}	2.9491 (11)
Ti2—Ti1^{xviii}	3.0228 (6)	Bi3—Ti1^{iii}	2.9491 (11)
Ti3—Bi1^{v}	3.1227 (16)	Bi3—Ti1^{xxvi}	2.9491 (11)
Ti3—Bi1^{iv}	3.1227 (16)	Bi3—Ti1^{xxvii}	2.9491 (11)
Ti3—Bi1^{xviii}	3.1227 (16)	Bi3—Bi2^{xxviii}	3.5482 (2)
Ti3—Bi1	3.1228 (16)	Bi3—Bi2^{xxv}	3.5482 (2)
Ti3—Bi2^{xiii}	3.1434 (16)	Bi3—Bi2^{xxix}	3.5482 (2)
Ti3—Bi2^{xv}	3.1434 (16)	Bi3—Bi2^{xviii}	3.5482 (2)
Ti3—Bi2^{ii}	3.1434 (16)	O1—Ti1^{xxvii}	1.8824 (11)
Ti3—Bi2^{xix}	3.1434 (16)	O1—Ti1^{xxx}	1.8824 (11)
Ti4—Bi1^{iv}	2.9398 (13)	O1—Ti1^{iv}	1.8824 (11)
Ti4—Bi1^{xviii}	2.9398 (13)	O1—Ti1^{i}	1.8824 (11)

O1^{i}—Ti1—Bi2^{ii}	78.30 (4)	Bi2^{xv}—Ti3—Bi2^{xix}	66.51 (4)
O1^{i}—Ti1—Bi3^{iii}	96.90 (4)	Bi2^{ii}—Ti3—Bi2^{xix}	66.51 (4)
Bi2^{ii}—Ti1—Bi3^{iii}	175.19 (4)	Bi1^{iv}—Ti4—Bi1^{xviii}	109.99 (7)
O1^{i}—Ti1—Bi1^{iv}	144.872 (13)	Bi1^{iv}—Ti4—Bi1^{v}	70.79 (4)
Bi2^{ii}—Ti1—Bi1^{iv}	98.38 (3)	Bi1^{xviii}—Ti4—Bi1^{v}	70.79 (4)
Bi3^{iii}—Ti1—Bi1^{iv}	85.54 (3)	Bi1^{iv}—Ti4—Bi1	70.79 (4)
O1^{i}—Ti1—Bi1^{v}	144.872 (13)	Bi1^{xviii}—Ti4—Bi1	70.79 (4)
Bi2^{ii}—Ti1—Bi1^{v}	98.38 (3)	Bi1^{v}—Ti4—Bi1	109.99 (7)
Bi3^{iii}—Ti1—Bi1^{v}	85.54 (3)	Bi1^{iv}—Ti4—Bi2^{xviii}	143.472 (1)
Bi1^{iv}—Ti1—Bi1^{v}	70.21 (3)	Bi1^{xviii}—Ti4—Bi2^{xviii}	81.667 (5)
O1^{i}—Ti1—Ti1^{vi}	37.37 (3)	Bi1^{v}—Ti4—Bi2^{xviii}	81.667 (5)
Bi2^{ii}—Ti1—Ti1^{vi}	115.67 (2)	Bi1—Ti4—Bi2^{xviii}	143.471 (2)
Bi3^{iii}—Ti1—Ti1^{vi}	59.52 (2)	Bi1^{iv}—Ti4—Bi2^{v}	81.667 (5)
Bi1^{iv}—Ti1—Ti1^{vi}	131.482 (19)	Bi1^{xviii}—Ti4—Bi2^{v}	143.472 (1)
Bi1^{v}—Ti1—Ti1^{vi}	131.482 (19)	Bi1^{v}—Ti4—Bi2^{v}	81.667 (5)
O1^{i}—Ti1—Ti2^{iv}	93.18 (3)	Bi1—Ti4—Bi2^{v}	143.471 (1)
Bi2^{ii}—Ti1—Ti2^{iv}	60.259 (18)	Bi2^{xviii}—Ti4—Bi2^{v}	70.76 (4)
Bi3^{iii}—Ti1—Ti2^{iv}	120.510 (18)	Bi1^{iv}—Ti4—Bi2^{iv}	81.667 (5)
Bi1^{iv}—Ti1—Ti2^{iv}	56.850 (12)	Bi1^{xviii}—Ti4—Bi2^{iv}	143.472 (1)
Bi1^{v}—Ti1—Ti2^{iv}	115.77 (3)	Bi1^{v}—Ti4—Bi2^{iv}	143.472 (1)
Ti1^{vi}—Ti1—Ti2^{iv}	111.02 (2)	Bi1—Ti4—Bi2^{iv}	81.667 (5)
O1^{i}—Ti1—Ti2^{v}	93.18 (3)	Bi2^{xviii}—Ti4—Bi2^{iv}	109.93 (7)
Bi2^{ii}—Ti1—Ti2^{v}	60.259 (18)	Bi2^{v}—Ti4—Bi2^{iv}	70.76 (4)
Bi3^{iii}—Ti1—Ti2^{v}	120.510 (18)	Bi1^{iv}—Ti4—Bi2	143.472 (1)
Bi1^{iv}—Ti1—Ti2^{v}	115.77 (3)	Bi1^{xviii}—Ti4—Bi2	81.668 (5)
Bi1^{v}—Ti1—Ti2^{v}	56.850 (12)	Bi1^{v}—Ti4—Bi2	143.472 (2)
Ti1^{vi}—Ti1—Ti2^{v}	111.02 (2)	Bi1—Ti4—Bi2	81.667 (5)
Ti2^{iv}—Ti1—Ti2^{v}	117.19 (4)	Bi2^{xviii}—Ti4—Bi2	70.76 (4)
O1^{i}—Ti1—Ti1^{vii}	34.188 (17)	Bi2^{v}—Ti4—Bi2	109.93 (7)
Bi2^{ii}—Ti1—Ti1^{vii}	63.05 (3)	Bi2^{iv}—Ti4—Bi2	70.76 (4)
Bi3^{iii}—Ti1—Ti1^{vii}	112.88 (4)	Ti2—Bi1—Ti4	150.82 (4)
Bi1^{iv}—Ti1—Ti1^{vii}	113.225 (13)	Ti2—Bi1—Ti1^{xviii}	62.668 (16)

Bi1^{v}—Ti1—Ti1^{vii}	161.22 (5)	Ti4—Bi1—Ti1^{xviii}	109.028 (19)
Ti1^{vi}—Ti1—Ti1^{vii}	61.29 (2)	Ti2—Bi1—Ti1^{v}	62.668 (16)
Ti2^{iv}—Ti1—Ti1^{vii}	58.99 (2)	Ti4—Bi1—Ti1^{v}	109.028 (19)
Ti2^{v}—Ti1—Ti1^{vii}	107.75 (4)	Ti1^{xviii}—Bi1—Ti1^{v}	122.09 (4)
O1^{i}—Ti1—Ti1^{viii}	34.188 (17)	Ti2—Bi1—Ti3	76.27 (4)
Bi2^{ii}—Ti1—Ti1^{viii}	63.05 (3)	Ti4—Bi1—Ti3	74.55 (5)
Bi3^{iii}—Ti1—Ti1^{viii}	112.88 (4)	Ti1^{xviii}—Bi1—Ti3	75.04 (2)
Bi1^{iv}—Ti1—Ti1^{viii}	161.22 (5)	Ti1^{v}—Bi1—Ti3	75.04 (2)
Bi1^{v}—Ti1—Ti1^{viii}	113.225 (13)	Ti2—Bi1—Bi1^{xiv}	106.253 (10)
Ti1^{vi}—Ti1—Ti1^{viii}	61.29 (2)	Ti4—Bi1—Bi1^{xiv}	102.93 (4)
Ti2^{iv}—Ti1—Ti1^{viii}	107.75 (4)	Ti1^{xviii}—Bi1—Bi1^{xiv}	106.02 (2)
Ti2^{v}—Ti1—Ti1^{viii}	58.99 (2)	Ti1^{v}—Bi1—Bi1^{xiv}	106.02 (2)
Ti1^{vii}—Ti1—Ti1^{viii}	57.42 (4)	Ti3—Bi1—Bi1^{xiv}	177.48 (4)
O1^{i}—Ti1—Bi2^{ix}	70.76 (2)	Ti2—Bi1—Bi1^{iv}	107.934 (3)
Bi2^{ii}—Ti1—Bi2^{ix}	106.54 (2)	Ti4—Bi1—Bi1^{iv}	54.606 (18)
Bi3^{iii}—Ti1—Bi2^{ix}	71.53 (2)	Ti1^{xviii}—Bi1—Bi1^{iv}	54.897 (13)
Bi1^{iv}—Ti1—Bi2^{ix}	141.17 (3)	Ti1^{v}—Bi1—Bi1^{iv}	131.480 (19)
Bi1^{v}—Ti1—Bi2^{ix}	76.984 (10)	Ti3—Bi1—Bi1^{iv}	56.957 (19)
Ti1^{vi}—Ti1—Bi2^{ix}	61.325 (18)	Bi1^{xiv}—Bi1—Bi1^{iv}	121.663 (4)
Ti2^{iv}—Ti1—Bi2^{ix}	161.73 (4)	Ti2—Bi1—Bi1^{xviii}	107.934 (3)
Ti2^{v}—Ti1—Bi2^{ix}	57.249 (4)	Ti4—Bi1—Bi1^{xviii}	54.606 (18)
Ti1^{vii}—Ti1—Bi2^{ix}	104.57 (2)	Ti1^{xviii}—Bi1—Bi1^{xviii}	131.480 (19)
Ti1^{viii}—Ti1—Bi2^{ix}	54.03 (3)	Ti1^{v}—Bi1—Bi1^{xviii}	54.897 (13)
O1^{i}—Ti1—Bi2^{x}	70.76 (2)	Ti3—Bi1—Bi1^{xviii}	56.957 (19)
Bi2^{ii}—Ti1—Bi2^{x}	106.54 (2)	Bi1^{xiv}—Bi1—Bi1^{xviii}	121.663 (4)
Bi3^{iii}—Ti1—Bi2^{x}	71.53 (2)	Bi1^{iv}—Bi1—Bi1^{xviii}	90.0
Bi1^{iv}—Ti1—Bi2^{x}	76.984 (10)	Ti1^{xx}—Bi2—Ti2^{xxi}	63.110 (6)
Bi1^{v}—Ti1—Bi2^{x}	141.17 (3)	Ti1^{xx}—Bi2—Ti2^{xxii}	63.110 (6)
Ti1^{vi}—Ti1—Bi2^{x}	61.325 (18)	Ti2^{xxi}—Bi2—Ti2^{xxii}	122.496 (7)
Ti2^{iv}—Ti1—Bi2^{x}	57.249 (5)	Ti1^{xx}—Bi2—Ti4	150.71 (4)
Ti2^{v}—Ti1—Bi2^{x}	161.73 (4)	Ti2^{xxi}—Bi2—Ti4	108.320 (15)
Ti1^{vii}—Ti1—Bi2^{x}	54.03 (3)	Ti2^{xxii}—Bi2—Ti4	108.320 (14)
Ti1^{viii}—Ti1—Bi2^{x}	104.57 (2)	Ti1^{xx}—Bi2—Ti1^{xxiii}	62.93 (4)
Bi2^{ix}—Ti1—Bi2^{x}	121.67 (4)	Ti2^{xxi}—Bi2—Ti1^{xxiii}	109.73 (2)
Bi1—Ti2—Bi1^{xi}	180.0	Ti2^{xxii}—Bi2—Ti1^{xxiii}	59.756 (18)
Bi1—Ti2—Bi2^{xii}	81.606 (5)	Ti4—Bi2—Ti1^{xxiii}	139.81 (3)
Bi1^{xi}—Ti2—Bi2^{xii}	98.393 (5)	Ti1^{xx}—Bi2—Ti1^{xxiv}	62.93 (4)
Bi1—Ti2—Bi2^{xiii}	98.394 (5)	Ti2^{xxi}—Bi2—Ti1^{xxiv}	59.756 (18)
Bi1^{xi}—Ti2—Bi2^{xiii}	81.607 (5)	Ti2^{xxii}—Bi2—Ti1^{xxiv}	109.73 (2)
Bi2^{xii}—Ti2—Bi2^{xiii}	180.0	Ti4—Bi2—Ti1^{xxiv}	139.81 (3)
Bi1—Ti2—Bi2^{xiv}	81.606 (5)	Ti1^{xxiii}—Bi2—Ti1^{xxiv}	57.35 (4)
Bi1^{xi}—Ti2—Bi2^{xiv}	98.393 (5)	Ti1^{xx}—Bi2—Ti3^{xxii}	76.52 (4)
Bi2^{xii}—Ti2—Bi2^{xiv}	71.710 (9)	Ti2^{xxi}—Bi2—Ti3^{xxii}	74.653 (16)
Bi2^{xiii}—Ti2—Bi2^{xiv}	108.290 (9)	Ti2^{xxii}—Bi2—Ti3^{xxii}	74.653 (16)
Bi1—Ti2—Bi2^{xv}	98.394 (5)	Ti4—Bi2—Ti3^{xxii}	74.19 (5)
Bi1^{xi}—Ti2—Bi2^{xv}	81.607 (5)	Ti1^{xxiii}—Bi2—Ti3^{xxii}	128.56 (3)
Bi2^{xii}—Ti2—Bi2^{xv}	108.290 (9)	Ti1^{xxiv}—Bi2—Ti3^{xxii}	128.56 (3)
Bi2^{xiii}—Ti2—Bi2^{xv}	71.710 (9)	Ti1^{xx}—Bi2—Bi2^{xviii}	107.841 (15)

Bi2^{xiv}—Ti2—Bi2^{xv}	180.0	Ti2^{xxi}—Bi2—Bi2^{xviii}	54.145 (4)
Bi1—Ti2—Ti1^{xvi}	119.52 (2)	Ti2^{xxii}—Bi2—Bi2^{xviii}	130.853 (4)
Bi1^{xi}—Ti2—Ti1^{xvi}	60.48 (2)	Ti4—Bi2—Bi2^{xviii}	54.621 (18)
Bi2^{xii}—Ti2—Ti1^{xvi}	117.005 (19)	Ti1^{xxiii}—Bi2—Bi2^{xviii}	163.087 (18)
Bi2^{xiii}—Ti2—Ti1^{xvi}	62.995 (19)	Ti1^{xxiv}—Bi2—Bi2^{xviii}	106.151 (18)
Bi2^{xiv}—Ti2—Ti1^{xvi}	56.632 (18)	Ti3^{xxii}—Bi2—Bi2^{xviii}	56.746 (19)
Bi2^{xv}—Ti2—Ti1^{xvi}	123.369 (18)	Ti1^{xx}—Bi2—Bi2^{iv}	107.841 (15)
Bi1—Ti2—Ti1^{v}	60.48 (2)	Ti2^{xxi}—Bi2—Bi2^{iv}	130.853 (4)
Bi1^{xi}—Ti2—Ti1^{v}	119.52 (2)	Ti2^{xxii}—Bi2—Bi2^{iv}	54.145 (4)
Bi2^{xii}—Ti2—Ti1^{v}	62.995 (19)	Ti4—Bi2—Bi2^{iv}	54.621 (18)
Bi2^{xiii}—Ti2—Ti1^{v}	117.005 (19)	Ti1^{xxiii}—Bi2—Bi2^{iv}	106.151 (18)
Bi2^{xiv}—Ti2—Ti1^{v}	123.369 (18)	Ti1^{xxiv}—Bi2—Bi2^{iv}	163.087 (18)
Bi2^{xv}—Ti2—Ti1^{v}	56.632 (18)	Ti3^{xxii}—Bi2—Bi2^{iv}	56.746 (19)
Ti1^{xvi}—Ti2—Ti1^{v}	180.00 (4)	Bi2^{xviii}—Bi2—Bi2^{iv}	90.0
Bi1—Ti2—Ti1^{xvii}	119.52 (2)	Ti1^{xx}—Bi2—Bi3^{xxv}	104.22 (2)
Bi1^{xi}—Ti2—Ti1^{xvii}	60.48 (2)	Ti2^{xxi}—Bi2—Bi3^{xxv}	105.657 (5)
Bi2^{xii}—Ti2—Ti1^{xvii}	56.631 (18)	Ti2^{xxii}—Bi2—Bi3^{xxv}	105.657 (5)
Bi2^{xiii}—Ti2—Ti1^{xvii}	123.369 (18)	Ti4—Bi2—Bi3^{xxv}	105.07 (4)
Bi2^{xiv}—Ti2—Ti1^{xvii}	117.005 (19)	Ti1^{xxiii}—Bi2—Bi3^{xxv}	52.029 (19)
Bi2^{xv}—Ti2—Ti1^{xvii}	62.995 (19)	Ti1^{xxiv}—Bi2—Bi3^{xxv}	52.029 (19)
Ti1^{xvi}—Ti2—Ti1^{xvii}	117.99 (4)	Ti3^{xxii}—Bi2—Bi3^{xxv}	179.25 (4)
Ti1^{v}—Ti2—Ti1^{xvii}	62.01 (4)	Bi2^{xviii}—Bi2—Bi3^{xxv}	122.853 (2)
Bi1—Ti2—Ti1^{xviii}	60.48 (2)	Bi2^{iv}—Bi2—Bi3^{xxv}	122.853 (2)
Bi1^{xi}—Ti2—Ti1^{xviii}	119.52 (2)	Ti1^{iv}—Bi3—Ti1^{iii}	137.96 (3)
Bi2^{xii}—Ti2—Ti1^{xviii}	123.369 (18)	Ti1^{iv}—Bi3—Ti1^{xxvi}	137.96 (3)
Bi2^{xiii}—Ti2—Ti1^{xviii}	56.631 (18)	Ti1^{iii}—Bi3—Ti1^{xxvi}	60.96 (4)
Bi2^{xiv}—Ti2—Ti1^{xviii}	62.995 (19)	Ti1^{iv}—Bi3—Ti1^{xxvii}	60.96 (4)
Bi2^{xv}—Ti2—Ti1^{xviii}	117.005 (19)	Ti1^{iii}—Bi3—Ti1^{xxvii}	137.96 (3)
Ti1^{xvi}—Ti2—Ti1^{xviii}	62.01 (4)	Ti1^{xxvi}—Bi3—Ti1^{xxvii}	137.96 (3)
Ti1^{v}—Ti2—Ti1^{xviii}	117.99 (4)	Ti1^{iv}—Bi3—Bi2^{xxviii}	160.38 (2)
Ti1^{xvii}—Ti2—Ti1^{xviii}	180.00 (4)	Ti1^{iii}—Bi3—Bi2^{xxviii}	56.443 (9)
Bi1^{v}—Ti3—Bi1^{iv}	66.09 (4)	Ti1^{xxvi}—Bi3—Bi2^{xxviii}	56.443 (9)
Bi1^{v}—Ti3—Bi1^{xviii}	66.09 (4)	Ti1^{xxvii}—Bi3—Bi2^{xxviii}	99.42 (2)
Bi1^{iv}—Ti3—Bi1^{xviii}	100.91 (7)	Ti1^{iv}—Bi3—Bi2^{xxv}	56.443 (9)
Bi1^{v}—Ti3—Bi1	100.91 (7)	Ti1^{iii}—Bi3—Bi2^{xxv}	160.38 (2)
Bi1^{iv}—Ti3—Bi1	66.09 (4)	Ti1^{xxvi}—Bi3—Bi2^{xxv}	99.42 (2)
Bi1^{xviii}—Ti3—Bi1	66.09 (4)	Ti1^{xxvii}—Bi3—Bi2^{xxv}	56.443 (9)
Bi1^{v}—Ti3—Bi2^{xiii}	145.571 (2)	Bi2^{xxviii}—Bi3—Bi2^{xxv}	114.292 (4)
Bi1^{iv}—Ti3—Bi2^{xiii}	88.805 (5)	Ti1^{iv}—Bi3—Bi2^{xxix}	56.443 (9)
Bi1^{xviii}—Ti3—Bi2^{xiii}	145.571 (2)	Ti1^{iii}—Bi3—Bi2^{xxix}	99.42 (2)
Bi1—Ti3—Bi2^{xiii}	88.805 (5)	Ti1^{xxvi}—Bi3—Bi2^{xxix}	160.38 (2)
Bi1^{v}—Ti3—Bi2^{xv}	145.571 (2)	Ti1^{xxvii}—Bi3—Bi2^{xxix}	56.443 (9)
Bi1^{iv}—Ti3—Bi2^{xv}	145.571 (2)	Bi2^{xxviii}—Bi3—Bi2^{xxix}	114.292 (4)
Bi1^{xviii}—Ti3—Bi2^{xv}	88.805 (5)	Bi2^{xxv}—Bi3—Bi2^{xxix}	100.208 (7)
Bi1—Ti3—Bi2^{xv}	88.805 (5)	Ti1^{iv}—Bi3—Bi2^{xviii}	99.42 (2)
Bi2^{xiii}—Ti3—Bi2^{xv}	66.51 (4)	Ti1^{iii}—Bi3—Bi2^{xviii}	56.443 (9)
Bi1^{v}—Ti3—Bi2^{ii}	88.805 (5)	Ti1^{xxvi}—Bi3—Bi2^{xviii}	56.443 (9)
Bi1^{iv}—Ti3—Bi2^{ii}	88.805 (5)	Ti1^{xxvii}—Bi3—Bi2^{xviii}	160.38 (2)

Bi1^{xviii}—Ti3—Bi2^{ii}	145.571 (2)	Bi2^{xxviii}—Bi3—Bi2^{xviii}	100.208 (7)
Bi1—Ti3—Bi2^{ii}	145.571 (2)	Bi2^{xxv}—Bi3—Bi2^{xviii}	114.292 (4)
Bi2^{xiii}—Ti3—Bi2^{ii}	66.51 (4)	Bi2^{xxix}—Bi3—Bi2^{xviii}	114.292 (4)
Bi2^{xv}—Ti3—Bi2^{ii}	101.70 (7)	Ti1^{xxvii}—O1—Ti1^{xxx}	111.62 (3)
Bi1^{v}—Ti3—Bi2^{xix}	88.805 (5)	Ti1^{xxvii}—O1—Ti1^{iv}	105.25 (7)
Bi1^{iv}—Ti3—Bi2^{xix}	145.571 (2)	Ti1^{xxx}—O1—Ti1^{iv}	111.62 (3)
Bi1^{xviii}—Ti3—Bi2^{xix}	88.805 (5)	Ti1^{xxvii}—O1—Ti1^{i}	111.62 (3)
Bi1—Ti3—Bi2^{xix}	145.571 (2)	Ti1^{xxx}—O1—Ti1^{i}	105.25 (7)
Bi2^{xiii}—Ti3—Bi2^{xix}	101.70 (7)	Ti1^{iv}—O1—Ti1^{i}	111.62 (3)

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*; (ii) −*x*+1/2, −*y*+1/2, *z*−1; (iii) −*x*+1, −*y*+1, −*z*+1; (iv) *y*, −*x*+1/2, *z*; (v) −*x*+1/2, −*y*+1/2, *z*; (vi) −*x*+1/2, −*y*+3/2, *z*; (vii) *y*−1/2, −*x*+1, −*z*; (viii) −*y*+1, *x*+1/2, −*z*; (ix) *y*+1/2, −*x*+1, −*z*+1; (x) −*y*, *x*+1/2, −*z*+1; (xi) −*x*, −*y*, −*z*; (xii) −*y*, *x*−1/2, −*z*+1; (xiii) *y*, −*x*+1/2, *z*−1; (xiv) −*x*, −*y*, −*z*+1; (xv) *x*, *y*, *z*−1; (xvi) *x*−1/2, *y*−1/2, −*z*; (xvii) *y*−1/2, −*x*, −*z*; (xviii) −*y*+1/2, *x*, *z*; (xix) −*y*+1/2, *x*, *z*−1; (xx) −*x*+1/2, −*y*+1/2, *z*+1; (xxi) −*y*+1/2, *x*, *z*+1; (xxii) *x*, *y*, *z*+1; (xxiii) *y*−1/2, −*x*, −*z*+1; (xxiv) −*y*+1, *x*−1/2, −*z*+1; (xxv) −*x*+1, −*y*, −*z*+1; (xxvi) *x*+1/2, *y*−1/2, −*z*+1; (xxvii) −*y*+3/2, *x*, *z*; (xxviii) *y*+1, −*x*+1/2, *z*; (xxix) *x*+1/2, *y*+1/2, −*z*+1; (xxx) *x*+1/2, *y*−1/2, −*z*.