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# Ge<sub>0.57</sub>Ti<sub>0.43</sub>O<sub>2</sub>: a new high-pressure material with rutile-type crystal structure

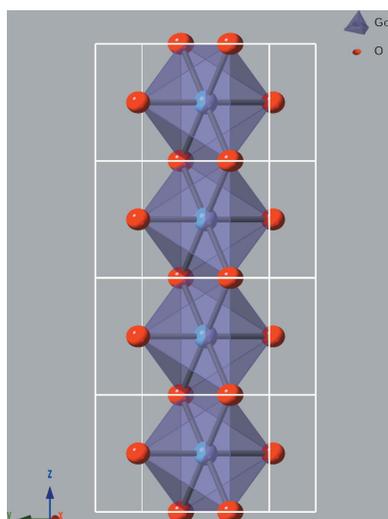
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Single crystals of a GeO<sub>2</sub>–TiO<sub>2</sub> solid solution with the corresponding composition Ge<sub>0.57</sub>Ti<sub>0.43</sub>O<sub>2</sub> (germanium titanium tetraoxide) were obtained by devitrification of germania-titania glass at high pressure and temperature. The new compound crystallizes in the rutile structure type (space group *P4<sub>2</sub>mm*), where Ge and Ti share the same position *M* (site symmetry *m.mm*), with occupancy values of 0.57 (3) and 0.43 (3), respectively, and one O-atom position (*m.2m*). The *M* site is in a sixfold O-atom coordination and, as in the original TiO<sub>2</sub> rutile structure, an elongation of the O–M–O bonds along the *c*-axis direction of the coordination polyhedron and deviation of the angles from 90° lead to a decrease in the coordination symmetry from octahedral to tetragonal. The Ge and Ti atoms are fully disordered in the structure, which indicates that the rutile structure is surprisingly pliant given the differing sizes of the two cations.

## 1. Chemical context

At ambient pressure, the GeO<sub>2</sub>–TiO<sub>2</sub> phase diagram shows the formation of three phases: rutile-type GeO<sub>2</sub>, stable up to 1323 K, β-quartz-type GeO<sub>2</sub>, stable above 1323 K and TiO<sub>2</sub> in the form of rutile. A metastable α-quartz-type structured GeO<sub>2</sub> has also been reported as the result of the cooling of the β-quartz-type structure (Sarver, 1961). Additionally, at ambient pressure GeO<sub>2</sub> and TiO<sub>2</sub> exhibit only limited mutual solubility. The GeO<sub>2</sub>–TiO<sub>2</sub> phase diagram at elevated pressures and temperatures has not been studied in great detail and the mutual solubility of Ge and Ti in the phases stable at these conditions is still largely unknown. GeO<sub>2</sub> is dimorphous at ambient atmospheric conditions, represented by both rutile-type and α-quartz-structured phases depending on the temperature, but with increasing pressure the GeO<sub>2</sub> rutile becomes more stable, and is the primary phase above two GPa (Micoulaut *et al.*, 2006). At pressures above 25 GPa, the tetragonal rutile-type phase transforms into an orthorhombic CaCl<sub>2</sub>-type phase (Haines *et al.*, 2000). TiO<sub>2</sub> rutile undergoes two phase transitions under high pressure of up to 12 GPa: rutile-to-α-PbO<sub>2</sub>-type at around 7 GPa and α-PbO<sub>2</sub>-to-baddeleyite at 12 GPa (Gerward & Staun Olsen, 1997). We synthesized the title compound while investigating the GeO<sub>2</sub>–TiO<sub>2</sub> phase diagram at a pressure of 8 GPa at 2028 K by means of the multi-anvil high-pressure technique. Instead of forming Ge-bearing TiO<sub>2</sub> and Ti-bearing GeO<sub>2</sub>, we discovered that the high pressure and temperature conditions led to the formation of a crystalline, single solid-solution material. At temperatures above 1873 K, crystal growth was significant and high-quality



**Table 1**

Selected geometric parameters (Å, °).

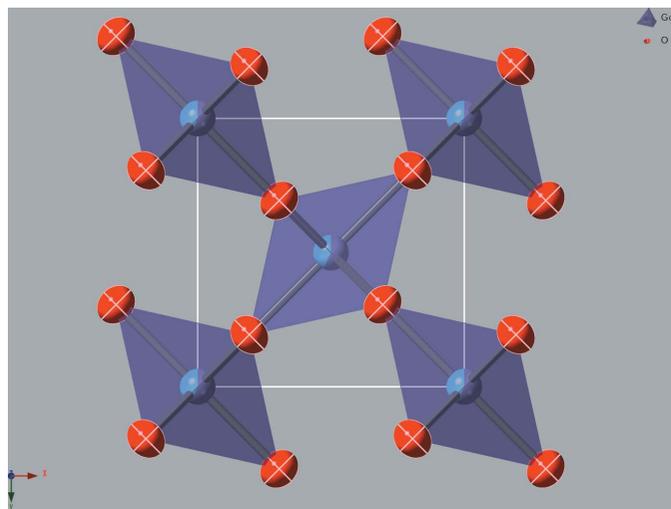
Ge1–O1 <sup>i</sup>	1.9080 (12)	Ge1–Ti1 <sup>ii</sup>	2.9121 (13)
Ge1–O1	1.9441 (19)		
O1 <sup>i</sup> –Ge1–O1 <sup>iii</sup>	99.48 (8)	Ti1 <sup>ii</sup> –Ge1–Ti1 <sup>vi</sup>	180
O1 <sup>i</sup> –Ge1–O1 <sup>iv</sup>	80.52 (8)	Ti1 <sup>vii</sup> –O1–Ti1 <sup>viii</sup>	99.48 (8)
O1 <sup>v</sup> –Ge1–O1	180	Ge1 <sup>vii</sup> –O1–Ge1	130.26 (4)

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

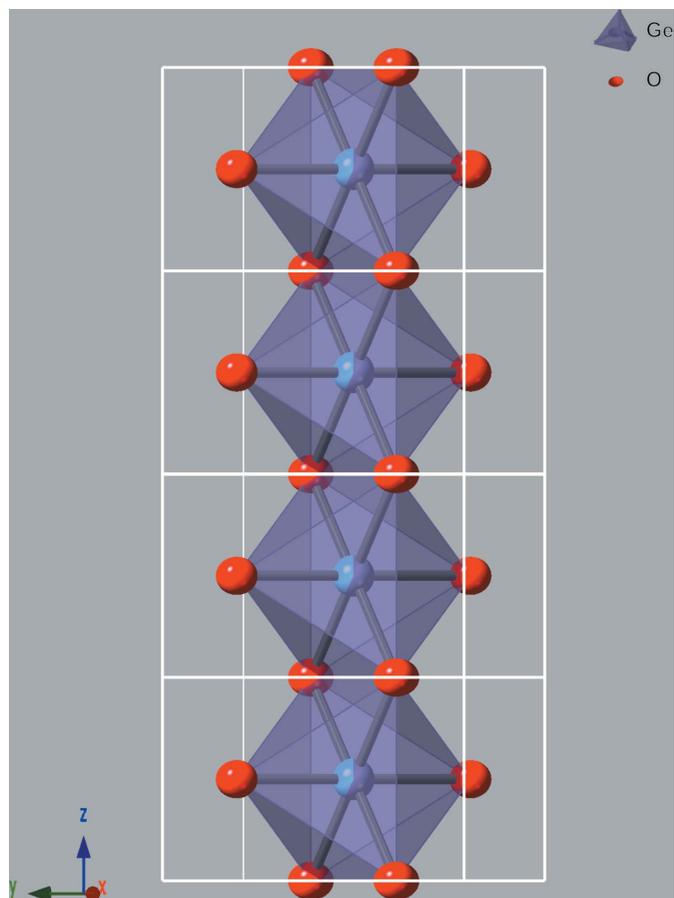
single crystals of the solid solution with a composition near TiGeO<sub>4</sub> could be obtained.

## 2. Structural commentary

The crystal structure of Ge<sub>0.57</sub>Ti<sub>0.43</sub>O<sub>2</sub> corresponds to the TiO<sub>2</sub> rutile type (space group  $P4_2/mnm$ ). The shared metal site *M* is in Wyckoff position *2a* and is surrounded by six O atoms, thus forming a sixfold coordination polyhedron. 57% of the *2a* positions are occupied by Ge and the remaining 43% are occupied by Ti. Each oxygen atom occupies a *4f* position and is surrounded by three *M* sites, forming triangular *MO*<sub>3</sub> groups in the (110) lattice plane (Fig. 1). The structure is represented by chains of edge-sharing *MO*<sub>6</sub> octahedra running parallel to the *c*-axis direction (Fig. 2) and connected to each other by shared corners. Relevant bond lengths and angles are presented in Table 1. In the *MO*<sub>6</sub> coordination polyhedra, the *M*–O distances in the *xy* plane are 1.9080 (12) Å, while the *M*–O distances along the *z* axis increase to 1.9441 (19) Å. The *M*···*M* distances are equal to 2.9121 (13) Å. The elongation of O–*M*–O bonds along the *z* direction of the *MO*<sub>6</sub> coordina-


**Figure 1**

View of the structure of Ge<sub>0.57</sub>Ti<sub>0.43</sub>O<sub>2</sub> looking down the *c* axis. The unit cell is outlined in white. The red ellipsoids represent the oxygen atoms and show the orientation of the displacement ellipsoids for 99% probability. The Ti atom is represented by light blue and the Ge atom by purple, with the percentage occupancy of the *M* site represented as a pie chart on the atom. *MO*<sub>6</sub> octahedra are represented as transparent polyhedra.


**Figure 2**

View of the edge-sharing chain of *MO*<sub>6</sub> octahedra in Ge<sub>0.57</sub>Ti<sub>0.43</sub>O<sub>2</sub>. The symbols are the same as in Fig. 1.

tion polyhedron and the deviation of the angles from 90° lead to a decrease in point group symmetry from octahedral *O<sub>h</sub>* to tetragonal *D<sub>4h</sub>*. The unit-cell volume of Ge<sub>0.57</sub>Ti<sub>0.43</sub>O<sub>2</sub> [58.79 (6) Å<sup>3</sup>] falls in between the rutile-type GeO<sub>2</sub> [55.3424 (17) Å<sup>3</sup>] (Gullikson *et al.*, 2015) and TiO<sub>2</sub> rutile [62.435 Å<sup>3</sup>] (Howard *et al.*, 1991) and indicates a linear relationship between the unit-cell volume and molar fraction of GeO<sub>2</sub>, adhering to Vegard's Law.

The somewhat large difference in the ionic radii of the sixfold coordinated Ge<sup>4+</sup> and Ti<sup>4+</sup> (0.53 and 0.605 Å, respectively; Shannon, 1976) may be the reason for the limited mutual solubility of Ge and Ti in the rutile structured oxides at ambient pressure. This might explain why the single solid-solution phase is absent in the GeO<sub>2</sub>–TiO<sub>2</sub> system, and why the synthesis of a material with composition near TiGeO<sub>4</sub> requires high-pressure and high-temperature conditions. Disorder at high temperatures (significantly above the ambient-pressure melting point) could assist in the stability of the solid solution even with the two different sized cations.

## 3. Synthesis and crystallization

The title compound was synthesized by using an industrial multi-anvil high-pressure apparatus. The starting material was

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	Ge <sub>1.14</sub> Ti <sub>0.86</sub> O <sub>4</sub>
$M_r$	187.88
Crystal system, space group	Tetragonal, $P4_2/mnm$
Temperature (K)	298
$a, c$ (Å)	4.493 (2), 2.9121 (13)
$V$ (Å <sup>3</sup> )	58.79 (6)
$Z$	1
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	17.23
Crystal size (mm)	0.08 × 0.08 × 0.07
Data collection	
Diffractometer	Bruker SMART APEX
Absorption correction	Multi-scan ( <i>SADABS</i> ; Bruker, 2014)
$T_{\min}, T_{\max}$	0.31, 0.40
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	722, 77, 76
$R_{\text{int}}$	0.022
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.772
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.018, 0.050, 1.20
No. of reflections	77
No. of parameters	10
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.60, -0.93

Computer programs: *APEX2* and *SAINT* (Bruker, 2014), *SHELXT* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b), *CrystalMaker* (Palmer, 2015) and *pubCIF* (Westrip, 2010).

a GeO<sub>2</sub>-TiO<sub>2</sub> glass produced from the corresponding oxide powders with a molar ratio of 60:40 (Sem-Com Company, Toledo, OH). A Pt foil capsule was loaded with the powdered glass and was subjected to high-pressure/high-temperature (HPHT) conditions of 8 GPa and 2028 K for 30 minutes, followed by cooling for 15 minutes to room temperature and releasing pressure non-isobarically to atmospheric pressure to recover the sample. The temperature was monitored with a W3%Re-W26%Re (C-type) thermocouple. The pressure was estimated by recovering and analyzing SiO<sub>2</sub>-GeO<sub>2</sub> glass that was loaded in the Pt foil capsule and pressed in the same high-pressure cell. Thus, the pressure standard and the GeO<sub>2</sub>-TiO<sub>2</sub> glass were treated at the same conditions. The details on the pressure calibration technique can be found elsewhere (Gullikson *et al.*, 2015; Leinenweber *et al.*, 2015). The applied temperature was sufficient to produce high-quality single crystals with uniform extinction in the optical microscope. A

clear colourless tabular-like crystal from the recovered GeO<sub>2</sub>-TiO<sub>2</sub> sample was used for the X-ray crystallographic analysis.

#### 4. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Structure data were standardized according to the *STRUCTURE-TIDY* program (Gelato & Parthé, 1987).

#### Acknowledgements

We acknowledge the use of facilities within the Eyring Materials Center at Arizona State University. The GeO<sub>2</sub>-TiO<sub>2</sub> crystals were grown in-house at Sandvik Hyperion.

#### Funding information

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## supporting information

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## Ge<sub>0.57</sub>Ti<sub>0.43</sub>O<sub>2</sub>: a new high-pressure material with rutile-type crystal structure

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### Computing details

Data collection: *APEX2* (Bruker, 2014); cell refinement: *SAINTE* (Bruker, 2014); data reduction: *SAINTE* (Bruker, 2014); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *CrystalMaker* (Palmer, 2015); software used to prepare material for publication: *publCIF* (Westrip, 2010).

### Germanium titanium tetraoxide

#### Crystal data

Ge<sub>1.14</sub>Ti<sub>0.86</sub>O<sub>4</sub>

$M_r = 187.88$

Tetragonal,  $P4_2/mnm$

$a = 4.493$  (2) Å

$c = 2.9121$  (13) Å

$V = 58.79$  (6) Å<sup>3</sup>

$Z = 1$

$F(000) = 87$

$D_x = 5.307$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 538 reflections

$\theta = 4.5$ – $33.3^\circ$

$\mu = 17.23$  mm<sup>-1</sup>

$T = 298$  K

Tabular, clear colourless

$0.08 \times 0.08 \times 0.07$  mm

#### Data collection

Bruker SMART APEX

diffractometer

Radiation source: fine-focus sealed tube, sealed tube

Graphite monochromator

Detector resolution: 8.3330 pixels mm<sup>-1</sup>

$\omega$  and  $\varphi$  scans

Absorption correction: multi-scan  
(*SADABS*; Bruker, 2014)

$T_{\min} = 0.31$ ,  $T_{\max} = 0.40$

722 measured reflections

77 independent reflections

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

$R_{\text{int}} = 0.022$

$\theta_{\max} = 33.3^\circ$ ,  $\theta_{\min} = 6.4^\circ$

$h = -6 \rightarrow 6$

$k = -6 \rightarrow 6$

$l = -4 \rightarrow 4$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.018$

$wR(F^2) = 0.050$

$S = 1.20$

77 reflections

10 parameters

0 restraints

Primary atom site location: iterative

Secondary atom site location: notdet

$w = 1/[\sigma^2(F_o^2) + (0.0347P)^2 + 0.0217P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.60$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.93$  e Å<sup>-3</sup>

Extinction correction: *SHELXL2014*  
(Sheldrick, 2015b)

Extinction coefficient: 0.58 (7)

*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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Ge1	0	0	0	0.0049 (3)	0.57 (3)
Ti1	0	0	0	0.0049 (3)	0.43 (3)
O1	0.3059 (3)	0.3059 (3)	0	0.0077 (6)	

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Ge1	0.0059 (4)	0.0059 (4)	0.0029 (4)	-0.00019 (9)	0	0
Ti1	0.0059 (4)	0.0059 (4)	0.0029 (4)	-0.00019 (9)	0	0
O1	0.0084 (7)	0.0084 (7)	0.0065 (8)	-0.0014 (5)	0	0

*Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )*

Ge1—O1 <sup>i</sup>	1.9080 (12)	Ge1—Ti1 <sup>vii</sup>	2.9121 (13)
Ge1—O1 <sup>ii</sup>	1.9080 (12)	Ge1—Ge1 <sup>vi</sup>	2.9121 (13)
Ge1—O1 <sup>iii</sup>	1.9080 (12)	Ge1—Ge1 <sup>vii</sup>	2.9121 (13)
Ge1—O1 <sup>iv</sup>	1.9080 (12)	O1—Ti1 <sup>viii</sup>	1.9080 (12)
Ge1—O1 <sup>v</sup>	1.9440 (19)	O1—Ge1 <sup>viii</sup>	1.9080 (12)
Ge1—O1	1.9441 (19)	O1—Ti1 <sup>ix</sup>	1.9080 (12)
Ge1—Ti1 <sup>vi</sup>	2.9121 (13)	O1—Ge1 <sup>ix</sup>	1.9080 (12)
O1 <sup>i</sup> —Ge1—O1 <sup>ii</sup>	99.48 (8)	O1 <sup>i</sup> —Ge1—Ge1 <sup>vi</sup>	40.26 (4)
O1 <sup>i</sup> —Ge1—O1 <sup>iii</sup>	80.52 (8)	O1 <sup>ii</sup> —Ge1—Ge1 <sup>vi</sup>	139.74 (4)
O1 <sup>ii</sup> —Ge1—O1 <sup>iii</sup>	180.0	O1 <sup>iii</sup> —Ge1—Ge1 <sup>vi</sup>	40.26 (4)
O1 <sup>i</sup> —Ge1—O1 <sup>iv</sup>	180.0	O1 <sup>iv</sup> —Ge1—Ge1 <sup>vi</sup>	139.74 (4)
O1 <sup>ii</sup> —Ge1—O1 <sup>iv</sup>	80.52 (8)	O1 <sup>v</sup> —Ge1—Ge1 <sup>vi</sup>	90.0
O1 <sup>iii</sup> —Ge1—O1 <sup>iv</sup>	99.48 (8)	O1—Ge1—Ge1 <sup>vi</sup>	90.0
O1 <sup>i</sup> —Ge1—O1 <sup>v</sup>	90.0	Ti1 <sup>vi</sup> —Ge1—Ge1 <sup>vi</sup>	0
O1 <sup>ii</sup> —Ge1—O1 <sup>v</sup>	90.0	Ti1 <sup>vii</sup> —Ge1—Ge1 <sup>vi</sup>	180.0
O1 <sup>iii</sup> —Ge1—O1 <sup>v</sup>	90.0	O1 <sup>i</sup> —Ge1—Ge1 <sup>vii</sup>	139.74 (4)
O1 <sup>iv</sup> —Ge1—O1 <sup>v</sup>	90.0	O1 <sup>ii</sup> —Ge1—Ge1 <sup>vii</sup>	40.26 (4)
O1 <sup>i</sup> —Ge1—O1	90.0	O1 <sup>iii</sup> —Ge1—Ge1 <sup>vii</sup>	139.74 (4)
O1 <sup>ii</sup> —Ge1—O1	90.0	O1 <sup>iv</sup> —Ge1—Ge1 <sup>vii</sup>	40.26 (4)
O1 <sup>iii</sup> —Ge1—O1	90.0	O1 <sup>v</sup> —Ge1—Ge1 <sup>vii</sup>	90.0
O1 <sup>iv</sup> —Ge1—O1	90.0	O1—Ge1—Ge1 <sup>vii</sup>	90.0
O1 <sup>v</sup> —Ge1—O1	180.0	Ti1 <sup>vi</sup> —Ge1—Ge1 <sup>vii</sup>	180.0
O1 <sup>i</sup> —Ge1—Ti1 <sup>vi</sup>	40.26 (4)	Ti1 <sup>vii</sup> —Ge1—Ge1 <sup>vii</sup>	0
O1 <sup>ii</sup> —Ge1—Ti1 <sup>vi</sup>	139.74 (4)	Ge1 <sup>vi</sup> —Ge1—Ge1 <sup>vii</sup>	180.0
O1 <sup>iii</sup> —Ge1—Ti1 <sup>vi</sup>	40.26 (4)	Ti1 <sup>viii</sup> —O1—Ge1 <sup>viii</sup>	0

O1 <sup>iv</sup> —Ge1—Ti1 <sup>vi</sup>	139.74 (4)	Ti1 <sup>viii</sup> —O1—Ti1 <sup>ix</sup>	99.48 (8)
O1 <sup>v</sup> —Ge1—Ti1 <sup>vi</sup>	90.0	Ge1 <sup>viii</sup> —O1—Ti1 <sup>ix</sup>	99.48 (8)
O1—Ge1—Ti1 <sup>vi</sup>	90.0	Ti1 <sup>viii</sup> —O1—Ge1 <sup>ix</sup>	99.5
O1 <sup>i</sup> —Ge1—Ti1 <sup>vii</sup>	139.74 (4)	Ge1 <sup>viii</sup> —O1—Ge1 <sup>ix</sup>	99.48 (8)
O1 <sup>ii</sup> —Ge1—Ti1 <sup>vii</sup>	40.26 (4)	Ti1 <sup>ix</sup> —O1—Ge1 <sup>ix</sup>	0
O1 <sup>iii</sup> —Ge1—Ti1 <sup>vii</sup>	139.74 (4)	Ti1 <sup>viii</sup> —O1—Ge1	130.3
O1 <sup>iv</sup> —Ge1—Ti1 <sup>vii</sup>	40.26 (4)	Ge1 <sup>viii</sup> —O1—Ge1	130.26 (4)
O1 <sup>v</sup> —Ge1—Ti1 <sup>vii</sup>	90.0	Ti1 <sup>ix</sup> —O1—Ge1	130.3
O1—Ge1—Ti1 <sup>vii</sup>	90.0	Ge1 <sup>ix</sup> —O1—Ge1	130.26 (4)
Ti1 <sup>vi</sup> —Ge1—Ti1 <sup>vii</sup>	180.0		

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

Atomic coordinates and equivalent isotropic atomic displacement parameters ( $\text{\AA}^2$ ) for  $\text{TiGeO}_4$ .  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	$x/a$	$y/b$	$z/c$	$U(\text{eq})$
Ge(1)	0.0	0.0	0.0	0.0049 (3)
Ti(1)	0.0	0.0	0.0	0.0049 (3)
O(1)	0.3059 (3)	0.3059 (3)	0.0	0.0077 (6)

Anisotropic atomic displacement parameters ( $\text{\AA}^2$ ) for  $\text{TiGeO}_4$ .

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Ge(1)	0.0059 (4)	0.0059 (4)	0.0029 (4)	0	0	-0.00019 (9)
Ti(1)	0.0059 (4)	0.0059 (4)	0.0029 (4)	0	0	-0.00019 (9)
O(1)	0.0084 (7)	0.0084 (7)	0.0065 (8)	0	0	-0.0014 (5)

Selected interatomic distances ( $\text{\AA}$ ) and angles for  $\text{TiGeO}_4$ .

Ge(1)—O(1)	1.9080 (12)	Ge(1)—O(1)	1.9441 (19)
Ge1—Ti1	2.9121 (13)	O1—Ti1	1.9080 (12)
O1—Ge1	1.9080 (12)		
O(1)—Ge(1)—O(1)	99.48 (8)	O(1)—Ge(1)—O(1)	80.52 (8)
O(1)—Ge(1)—O(1)	180.0	O(1)—Ge(1)—O(1)	90.0
O(1)—Ge(1)—Ti(1)	139.74 (4)	O(1)—Ge(1)—Ti(1)	40.26 (4)
O(1)—Ge(1)—Ti(1)	90.0	Ti(1)—Ge(1)—Ti(1)	180.0
Ge1—O1—Ti1	99.48 (8)	Ti1—O1—Ge1	130.26 (4)