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Redetermination of the γ-form of tellurium dioxide

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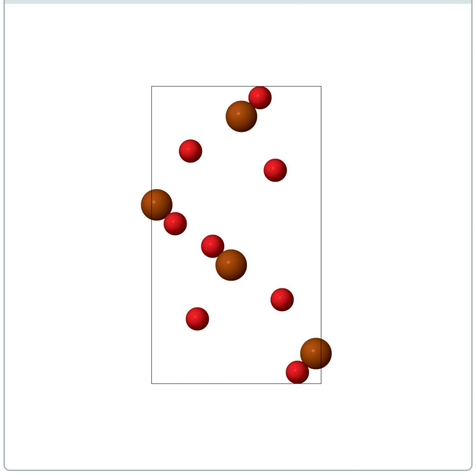
The crystal structure of γ-TeO_2 was redetermined on the basis of single-crystal X-ray diffraction data. The previous structure determination of this modification was based on laboratory powder X-ray diffraction data [Champarnaud-Mesjard *et al.* (2000). *J. Phys. Chem. Solids*, **61**, 1499–1507]. The current redetermination revealed all atoms with anisotropic displacement parameters, accompanied with a much higher accuracy and precision in terms of bond lengths and angles, and the determination of the absolute structure. The crystal structure consists of TeO_4 bisphenoids that combine through corner-sharing of all their oxygen atoms into a three-dimensional framework.

3D view



Structure description

In a continuation of hydrothermal phase formation studies to incorporate tetrahedral XO_4 groups (X = S, Se) into framework structures of divalent metal oxotellurates(IV) (metal = Ca, Cd, Hg, Mg, Pb, Sr, Zn; Weil & Shirkhanlou, 2015, 2017*a*,*b*,*c*), the system Mn/Se/Te/O was investigated. In one of these experiments, single crystals of γ-TeO_2 were obtained serendipitously as a minor by-product.

Tellurium dioxide is polymorphic, with three reported crystalline forms at ambient pressure: the α-form (Lindqvist, 1968), the β-form (Beyer, 1967) and the γ-form (Champarnaud-Mesjard *et al.*, 2000). Whereas the α- and β-forms can be found in nature as the rare minerals paratellurite and tellurite, respectively, the γ-form is synthetic and can usually be obtained as a polycrystalline material by recrystallizing TeO_2 glasses at low temperatures. This was also the procedure to prepare material for the previous structure determination of γ-TeO_2 that was based on laboratory X-ray diffraction data and refined using the Rietveld method (Champarnaud-Mesjard *et al.*, 2000). The results of the current rerefinement using modern CCD data are reported here. The previous structure model is confirmed, however, with higher accuracy and precision, as exemplified by a comparison

Table 1
Comparison of bond lengths (Å) and angles (°) in the current and the previous refinement of γ-TeO_2.

	Current refinement	Previous refinement ^{a}
Te1—O1	1.839 (3)	1.86 (2)
Te1—O2^{i}	1.906 (3)	1.94 (2)
Te1—O2^{ii}	2.048 (3)	2.02 (2)
Te1—O1^{iii}	2.241 (4)	2.20 (2)
O1—Te1—O2^{i}	100.36 (17)	99.2 (4)
O1—Te1—O2^{ii}	93.14 (17)	91.8 (5)
O1—Te1—O1^{iii}	91.69 (9)	91.9 (5)
O2^{i}—Te1—O2^{ii}	78.68 (9)	77.6 (5)
O2^{i}—Te1—O1^{iii}	75.60 (14)	76.1 (4)
O2^{ii}—Te1—O1^{iii}	154.28 (13)	153.6 (5)
Te1—O1—Te1^{iv}	131.6 (2)	133.1 (5)
Te1^{v}—O2—Te1^{vi}	125.18 (18)	125.1 (5)

Symmetry codes: (i) $x, y, z - 1$; (ii) $-x + \frac{3}{2}, -y, z - \frac{1}{2}$; (iii) $x + \frac{1}{2}, -y + \frac{1}{2}, -z$; (iv) $x - \frac{1}{2}, -y + \frac{1}{2}, -z$; (v) $x, y, z + 1$; (vi) $-x + \frac{3}{2}, -y, z + \frac{1}{2}$. Notes: (*a*) Champarnaud-Mesjard *et al.* (2000); lattice parameters a = 4.898 (3), b = 8.576 (4), c = 4.351 (2) Å at room temperature.

of the bond lengths and angles (Table 1). Moreover, the absolute structure of γ-TeO_2 was determined (Table 2).

In the crystal structure, the tellurium atom is surrounded by four oxygen atoms in the shape of a bisphenoid, with a Te—O bond lengths range of 1.839 (3) – 2.241 (4) Å. Each TeO_4 polyhedron is linked to four symmetry-related TeO_4 polyhedra by sharing corners, which leads to the formation of a three-dimensional framework structure. Characteristic for the crystal chemistry of tellurium(IV) oxides or oxotellurates(IV) (Christy *et al.*, 2016), the $5s^2$ electron lone pair situated at the Te^{IV} atom is stereochemically active and points towards the open space of this arrangement (Fig. 1).

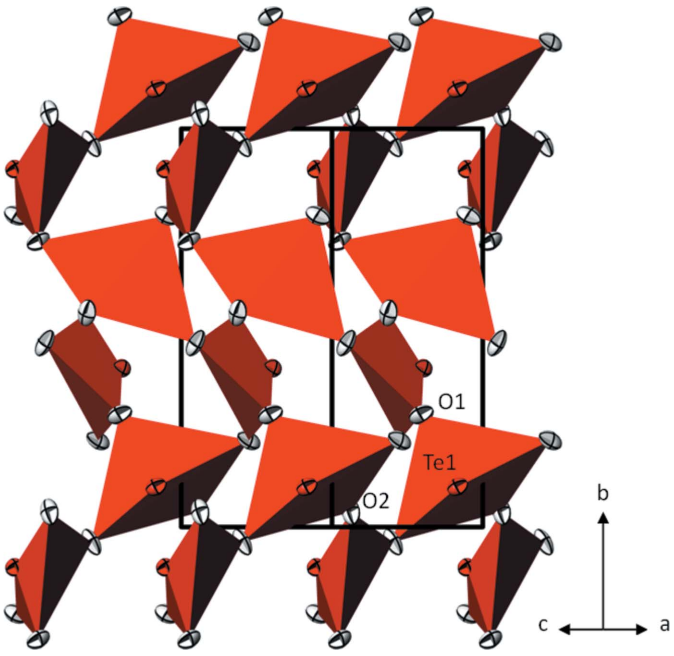


Figure 1
Projection of the crystal structure of γ-TeO_2 along [101]. TeO_4 groups are given as polyhedra (Te atoms red, O atoms colourless) with anisotropic displacement ellipsoids drawn at the 74% probability level.

Table 2
Experimental details.

Crystal data	
Chemical formula	TeO_2
M_r	159.60
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	296
a, b, c (Å)	4.8809 (2), 8.5668 (4), 4.3433 (2)
V (Å^3)	181.61 (1)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	15.91
Crystal size (mm)	0.18 × 0.01 × 0.01
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2015)
T_{min}, T_{max}	0.552, 0.747
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7370, 893, 816
R_{int}	0.056
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.844
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.025, 0.037, 1.02
No. of reflections	893
No. of parameters	28
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.81, −1.28
Absolute structure	Flack x determined using 296 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter	−0.03 (4)

Coordinates were taken from a previous refinement. Computer programs: *APEX2* and *SAINT* (Bruker, 2015), *SHELXL2014/7* (Sheldrick, 2015), *ATOMS* (Dowty, 2006) and *publCIF* (Westrip, 2010).

Synthesis and crystallization

100 mg TeO_2, 350 mg $MnSeO_4 \cdot H_2O$ and 70 mg KOH were mixed and placed in a 5 ml capacity Teflon container that was subsequently filled with 2 ml water. The container was closed with a Teflon lid and placed in a steel autoclave for ten days at 483 K under autogenous pressure. After cooling down to room temperature, the solid reaction product was filtered off and washed with water and ethanol. The obtained material consisted of a dark-brown to black powder as the main product besides few light-brown plate-like crystals and very few colourless needles. Powder X-ray diffraction of the dark-brown material revealed Mn_2TeO_6 (Hund, 1971), and single-crystal X-ray diffraction showed the plate-like crystals to be spiroffite-type $Mn_2Te_3O_8$ (Cooper & Hawthorne, 1996); the colourless needles correspond to the title compound.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Coordinates and atom labels were taken from the previous refinement (Champarnaud-Mesjard *et al.*, 2000). The maximum and minimum electron density peaks are located 0.68 and 0.73 Å, respectively, from atom Te1.

Acknowledgements

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full crystallographic data

IUCrData (2017). **2**, x171757 [https://doi.org/10.1107/S2414314617017576]

Redetermination of the γ-form of tellurium dioxide

Matthias Weil

(I)

Crystal data

O_2Te
$M_r = 159.60$
Orthorhombic, $P2_12_12_1$
$a = 4.8809\ (2)$ Å
$b = 8.5668\ (4)$ Å
$c = 4.3433\ (2)$ Å
$V = 181.61\ (1)$ Å^3
$Z = 4$
$F(000) = 272$
$D_x = 5.837$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2511 reflections
$\theta = 4.8–32.2°$
$\mu = 15.91$ mm^{-1}
$T = 296$ K
Needle, colourless
0.18 × 0.01 × 0.01 mm

Data collection

Bruker APEXII CCD diffractometer
ω–scans′
Absorption correction: multi-scan (SADABS; Bruker, 2015)
$T_{\min} = 0.552$, $T_{\max} = 0.747$
7370 measured reflections
893 independent reflections
816 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.056$
$\theta_{\max} = 36.9°$, $\theta_{\min} = 4.8°$
$h = -8 \rightarrow 8$
$k = -14 \rightarrow 14$
$l = -7 \rightarrow 7$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.037$
$S = 1.02$
893 reflections
28 parameters
0 restraints
Primary atom site location: isomorphous structure methods
$w = 1/[\sigma^2(F_o^2) + (0.014P)^2 + 0.0171P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.81$ e Å^{-3}
$\Delta\rho_{\min} = -1.28$ e Å^{-3}
Absolute structure: Flack x determined using 296 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: −0.03 (4)

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Te1	0.96976 (6)	0.10122 (4)	0.13698 (7)	0.01056 (7)
O1	0.7704 (7)	0.2822 (4)	0.1778 (9)	0.0147 (8)
O2	0.8602 (7)	0.0379 (4)	0.7347 (8)	0.0140 (7)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Te1	0.01128 (12)	0.00983 (11)	0.01058 (11)	0.00182 (11)	−0.00163 (11)	−0.00096 (13)
O1	0.0143 (16)	0.0114 (17)	0.018 (2)	0.0056 (12)	−0.0012 (14)	0.0006 (15)
O2	0.0144 (18)	0.0200 (19)	0.0075 (15)	−0.0067 (14)	0.0006 (13)	−0.0036 (14)

Geometric parameters (Å, º)

Te1—O1	1.839 (3)	O1—Te1$^{\mathrm{iv}}$	2.241 (3)
Te1—O2$^{\mathrm{i}}$	1.906 (3)	O2—Te1$^{\mathrm{v}}$	1.906 (3)
Te1—O2$^{\mathrm{ii}}$	2.048 (3)	O2—Te1$^{\mathrm{vi}}$	2.048 (3)
Te1—O1$^{\mathrm{iii}}$	2.241 (4)		
O1—Te1—O2$^{\mathrm{i}}$	100.36 (17)	O2$^{\mathrm{i}}$—Te1—O1$^{\mathrm{iii}}$	75.60 (14)
O1—Te1—O2$^{\mathrm{ii}}$	93.14 (17)	O2$^{\mathrm{ii}}$—Te1—O1$^{\mathrm{iii}}$	154.28 (13)
O2$^{\mathrm{i}}$—Te1—O2$^{\mathrm{ii}}$	78.68 (9)	Te1—O1—Te1$^{\mathrm{iv}}$	131.6 (2)
O1—Te1—O1$^{\mathrm{iii}}$	91.69 (9)	Te1$^{\mathrm{v}}$—O2—Te1$^{\mathrm{vi}}$	125.18 (18)

Symmetry codes: (i) *x*, *y*, *z*−1; (ii) −*x*+3/2, −*y*, *z*−1/2; (iii) *x*+1/2, −*y*+1/2, −*z*; (iv) *x*−1/2, −*y*+1/2, −*z*; (v) *x*, *y*, *z*+1; (vi) −*x*+3/2, −*y*, *z*+1/2.