

GeTe₂O₆, a germanium tellurate(IV) with an open framework

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The structure of an already evidenced but still uncharacterized GeTe₂O₆ phase consists of isolated GeO₆ octahedra connected *via* isolated TeO₃ units. The germanium cations occupy a site with $\bar{1}$ symmetry. The Te and O atoms are in general positions of the $P2_1/n$ space group. This structure corresponds to a new type of tetravalent tellurate and is different from other AB₂X₆ structures in which the B cation presents a stereochemically active electronic lone pair. It derives from the pseudo-hexagonal MI₂O₆ ($M = \text{Mg, Mn, Co and Fe}$) type by a strong monoclinic distortion caused by the much smaller size of Ge⁴⁺ compared with the divalent M cations.

Comment

Germanium oxide has been used as a building element to form a number of open frameworks with novel topologies. The structure of the germanate framework can be formed by GeO₄ (tetrahedra), GeO₆ (octahedra) and sometimes GeO₅ (square pyramid or trigonal bipyramid) polyhedra (Liu *et al.*, 2008). Meanwhile, our laboratory has systematically developed the investigation of tellurium(IV) compounds for their potential nonlinear optical properties (Laval *et al.*, 2008). We have attempted to combine the building capability of Ge^{IV} oxide with Te^{IV} oxide in an effort to obtain novel germanium oxyfluorotellurates. In this paper, we report the structure of the oxide GeTe₂O₆, which was inadvertently obtained in one of our reactions. The powder X-ray diffraction pattern has been reported (PDF No. 00-051-0288; Gospodinov, 1999); however, the pattern calculated from the present crystal structure differs from the reference pattern, suggesting that the PDF file does not correspond to a pure phase or to the same polymorph. Bond valence calculations (Brown, 1981) confirm that the studied crystal corresponds to an oxide and not to an oxyfluoride as expected (Table 2).

In this structure, the Ge atom is sixfold coordinated, occupying the center of an almost regular octahedron (Fig. 1). The Ge—O distances are essentially the same within experimental

uncertainty (Table 1) and are typical for germanates (Monge *et al.*, 2000; Cascales *et al.*, 1998; Xu *et al.*, 2004).

The configuration of the Te atom is the same as that in MTeO₃F ($M = \text{Fe, Ga and Cr}$; Laval *et al.*, 2008), *i.e.* strongly bonded to three O atoms (O1, O2 and O3; Table 1) at the center of a tetrahedron whose fourth corner corresponds to the direction of the stereochemically active lone pair E (Fig. 2). Three additional weak Te—O bonds can be added to the coordination environment of the Te atom. In that case, the corresponding polyhedron can be roughly described as a distorted octahedron. The lone pair E points towards the face formed by atoms O1ⁱ, O1ⁱⁱ and O3ⁱⁱⁱ [symmetry codes: (i) $-x + 1, -y, -z + 1$; (ii) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (iii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$].

The GeTe₂O₆ structure is based on the association, by corner-sharing, of GeO₆ octahedra and TeO₃ trigonal pyramids. Each Te atom is bonded to three different Ge atoms *via* oxygen vertices, and conversely each GeO₆ octahedron is linked *via* six TeO₃ bridges to ten other GeO₆ octahedra. Projections on to the three main planes of the almost orthorhombic structure (Fig. 3) show that the GeO₆ octahedra are tilted along the [010] direction and form layers perpendicular to [001], each one alternating with a wavy layer of tellurium. The three-dimensional framework of Te and Ge cations derives from a hexagonal packing, but with great distortion [$a/b = 0.749$ for the monoclinic, near-orthorhombic ($\beta = 91.66^\circ$), unit cell, instead of $a/b = 3/2^{1/2}$ for the orthorhombic supercell derived from a hexagonal unit cell].

If the weak Te—O bonds are considered, Te₄O₂₀ units are formed. These units are connected *via* O1 vertices to form

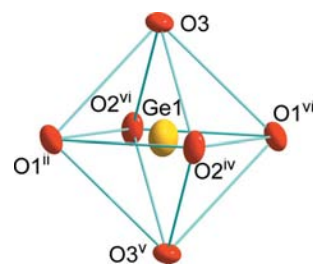


Figure 1

The coordination polyhedron of Ge1 in the GeTe₂O₆ structure. [Symmetry codes: (ii) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (iv) $x - \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (v) $-x + 1, -y + 1, -z + 2$; (vi) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (vii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$].

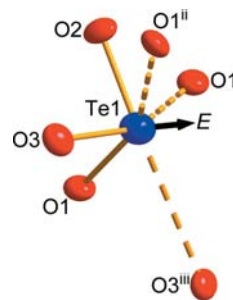


Figure 2

The anionic polyhedron around the Te⁴⁺ cation in the GeTe₂O₆ structure. The arrow indicates the direction in which the lone pair E points. Broken lines represent weak Te—O bonds. [Symmetry codes: (i) $-x + 1, -y, -z + 1$; (ii) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (iii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$].

infinite rows along [010] with cavities of irregular cross section (Fig. 4a). The GeO_6 octahedra ensure the connection of these rows (Fig. 4b).

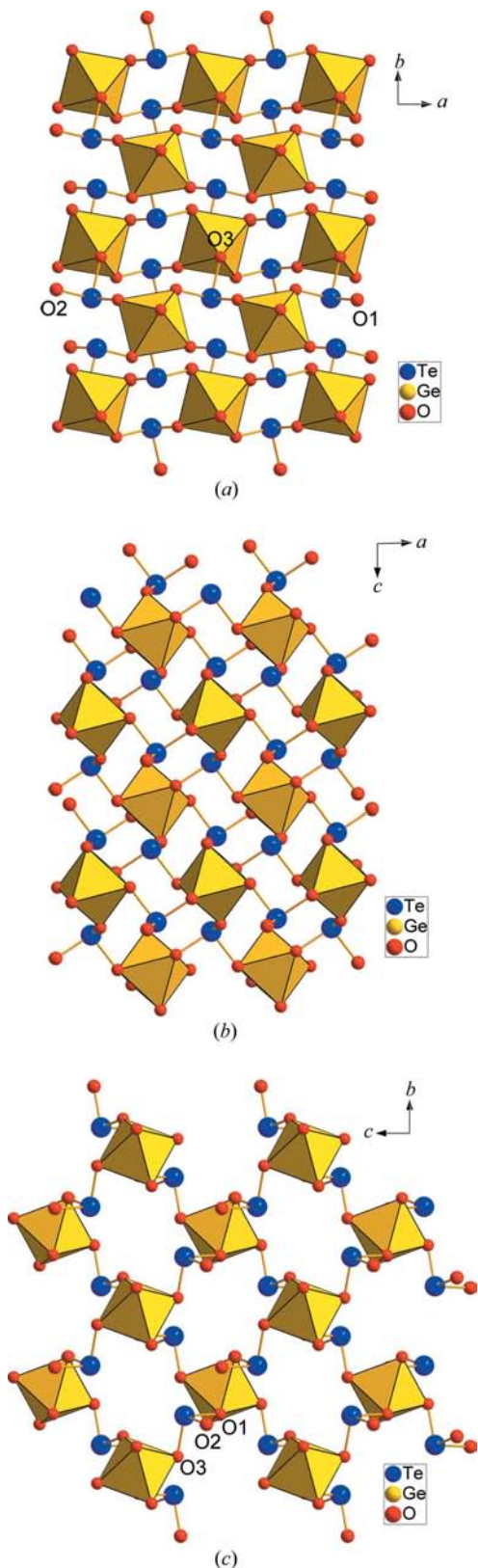


Figure 3
Projections on to (a) the xy , (b) the xz and (c) the yz planes, showing the GeO_6 octahedra and their connection via TeO_3 polyhedra.

The $M_x\text{Te}_y\text{O}_z$ tellurates(IV) present many M/Te compositions, from 5/1 ($\text{Mo}_5\text{TeO}_{16}$) to 1/6 ($\text{ZnTe}_6\text{O}_{13}$). However, the main M/Te ratios for di-, tri-, tetra-, penta- or hexavalent metal oxides are 1/1 [e.g. CoTeO_3 , VTeO_4 , $\text{Ta}_2(\text{V}_2)\text{Te}_2\text{O}_9$], 3/2 [e.g. $\text{Ni}_2\text{Te}_3\text{O}_8$, $\text{Fe}_2(\text{or In}_2)\text{Te}_3\text{O}_9$, $\text{Nb}_2\text{Te}_3\text{O}_{11}$], 1/2 [e.g. MgTe_2O_5 , $\text{Cr}_2(\text{or Ln}_2)\text{Te}_4\text{O}_{11}$, $\text{Th}(\text{or Ce or Pu})\text{Te}_2\text{O}_6$, $\text{Nb}_2\text{Te}_4\text{O}_{13}$, MoTe_2O_7], 5/2 [e.g. $\text{Sc}_2(\text{or Lu}_2)\text{Te}_5\text{O}_{13}$], 1/3 [e.g. $\text{Zr}(\text{or Sn or Hf})\text{Te}_3\text{O}_8$], 1/5 (e.g. $\text{PbTe}_5\text{O}_{11}$) and 1/6 (e.g. $\text{ZnTe}_6\text{O}_{13}$) (FIZ/NIST, 2008).

These phases present a very rich crystallochemistry, with structures generally consisting of more or less complex associations (groups, chains or layers) of MO_6 octahedra and of TeO_3 or TeO_4 polyhedra. GeTe_2O_6 is a new structure type for tetravalent tellurates and is simpler than most of the phases noted above. In fact, few tellurates(IV) contain isolated MO_6

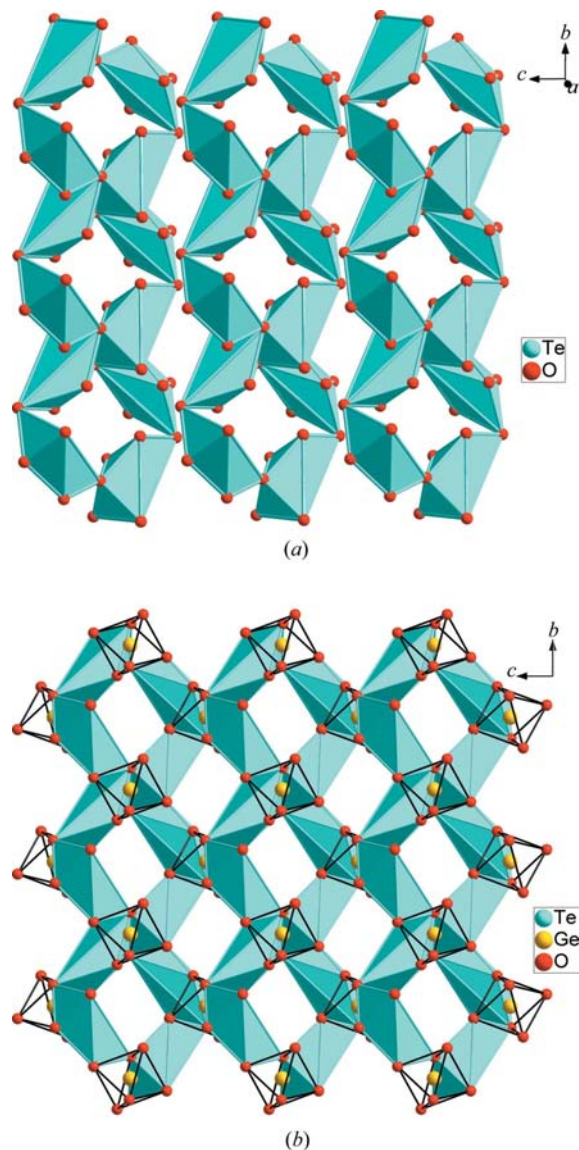


Figure 4
(a) A perspective view showing the double chains of TeO_6 distorted octahedra. (b) A projection on to yz showing the global structure of GeTe_2O_6 with the six-membered-ring channels.

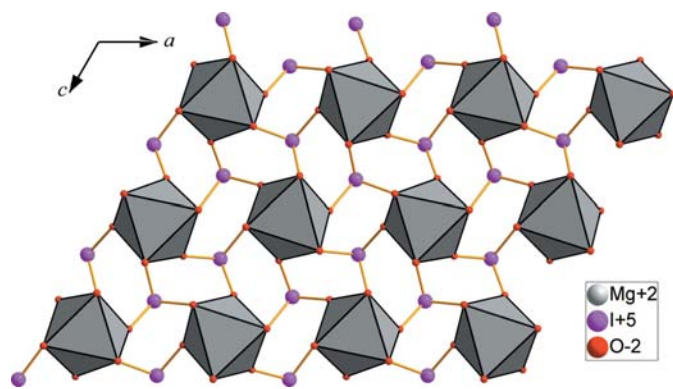


Figure 5
A projection on to the xz plane of the MgI_2O_6 structure for comparison with $GeTe_2O_6$ (Fig. 3a).

octahedra, except $ZnTe_6O_{13}$. The other MTe_2O_6 tellurates adopt a structure type deriving from fluorite, suitable for tetravalent cations of greater size, such as Ce, Pu and Th (Lopez *et al.*, 1991; Krishnan *et al.*, 2000).

The new $GeTe_2O_6$ type is structurally closer to the MI_2O_6 series of iodates(V) with divalent cations Mg, Mn, Co, Ni and Zn (Phanon *et al.*, 2006). These MI_2O_6 compounds are isostructural and crystallize in the monoclinic system (space group $P2_1$), but are very close to hexagonal symmetry ($\beta \simeq 120^\circ$). The general organization of the structures is similar, but $GeTe_2O_6$ is much more distant from ideal hexagonal symmetry than the MI_2O_6 series, as discussed above and as is easily observed by comparing Figs. 3(a) and 5. This higher distortion likely results from the smaller size of the Ge^{4+} cation ($R = 0.53 \text{ \AA}$) compared with the size of the M cations of the MI_2O_6 series (about $0.65\text{--}0.75 \text{ \AA}$). This prevents the TeO_3 polyhedra from adopting a nearly regular hexagonal framework and causes a tilting of the GeO_6 octahedra.

Experimental

Small single crystals of $GeTe_2O_6$ were obtained accidentally in experiments initially intended to synthesize new oxyfluorotellurates(IV). TeO_2 was prepared in the laboratory by decomposition at 823 K under flowing oxygen of commercial H_6TeO_6 (Aldrich, 99.9%) and GeO_2 was a commercial product (Aldrich, 99.9%). An equimolar mixture of GeO_2 and TeO_2 was dissolved in hydrofluoric acid (40%) in a Teflon beaker and heated at 453 K. Then, after slow evaporation, the product was crushed and heated at 673 K in a platinum crimped tube for 48 h. Small colorless tablets of $GeTe_2O_6$, air stable and suitable for structural study, were obtained instead of the expected germanium oxyfluorotellurate(IV).

Crystal data

$GeTe_2O_6$	$V = 266.52 (8) \text{ \AA}^3$
$M_r = 423.79$	$Z = 2$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 5.2201 (8) \text{ \AA}$	$\mu = 16.43 \text{ mm}^{-1}$
$b = 6.9730 (13) \text{ \AA}$	$T = 293 \text{ K}$
$c = 7.3252 (15) \text{ \AA}$	$0.02 \times 0.01 \times 0.003 \text{ mm}$
$\beta = 91.66 (2)^\circ$	

Table 1
Selected bond lengths (\AA).

Te1—O3	1.873 (5)	Te1—O3 ⁱⁱⁱ	2.968 (5)
Te1—O2	1.874 (5)	Ge1—O3	1.870 (5)
Te1—O1	1.903 (5)	Ge1—O1 ⁱⁱ	1.877 (4)
Te1—O1 ⁱ	2.852 (5)	Ge1—O2 ^{iv}	1.878 (5)
Te1—O1 ⁱⁱ	2.877 (5)		

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

Table 2
Bond valences (ν_{ij}) for $GeTe_2O_6$.

Atoms	Te1	Ge1	ν_{ij}
O1	1.223/0.094/0.088	2×0.704	2.11
O2	1.321	2×0.704	2.03
O3	1.326/0.069	2×0.719	2.11
V_{ij}	4.12	4.25	

Data collection

Nonius KappaCCD diffractometer	5004 measured reflections
Absorption correction: multi-scan (SADABS; Bruker 2001)	771 independent reflections
$T_{\min} = 0.735, T_{\max} = 0.952$	551 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.105$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$	44 parameters
$wR(F^2) = 0.055$	$\Delta\rho_{\max} = 2.24 \text{ e \AA}^{-3}$
$S = 1.05$	$\Delta\rho_{\min} = -1.72 \text{ e \AA}^{-3}$
771 reflections	

Data collection: *KappaCCD Server Software* (Nonius, 1998); cell refinement: *DIRAX/LSQ* (Duisenberg, 1992); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3186). Services for accessing these data are described at the back of the journal.

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