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Stoichiometric $ZrGeTe_4$

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Key indicators: single-crystal X-ray study; T = 150 K; mean σ(Zr–Ge) = 0.002 Å; R factor = 0.036; wR factor = 0.080; data-to-parameter ratio = 23.8.

Zirconium germanium tetratelluride, $ZrGeTe_4$, is isostructural with $Hf_{0.85}GeTe_4$ [Mar & Ibers (1993). *J. Am Chem. Soc.* **115**, 3227–3238], but the Zr site in $ZrGeTe_4$ is fully occupied and the compound is stoichiometric. $ZrGeTe_4$ adopts a layered structural type. Each layer is composed of two unique one-dimensional chains of face-sharing Zr-centered bicapped trigonal prisms and corner-sharing Ge-centered tetrahedra.

Related literature

The synthesis and characterization of $Hf_{0.85}GeTe_4$ have been published (Mar & Ibers, 1993). The Zr analogue of this phase has also been found but detailed structural studies on $ZrGeTe_4$ have not been reported yet. The title compound, $ZrGeTe_4$, is isostructural with $Hf_{0.85}GeTe_4$. However, the Zr site in $ZrGeTe_4$ is fully occupied.

For related literature, see: Furuseth *et al.* (1973).

Experimental

Crystal data

$ZrGeTe_4$	V = 697.02 (7) $Å^3$
M_r = 674.24	Z = 4
Orthorhombic, $Cmc2_1$	Mo $K\alpha$ radiation
a = 3.9794 (2) Å	μ = 22.09 mm^{-1}
b = 15.9296 (10) Å	T = 150 (1) K
c = 10.9957 (6) Å	0.50 × 0.03 × 0.02 mm

Data collection

Rigaku R-AXIS RAPID diffractometer	3351 measured reflections
Absorption correction: numerical (*NUMABS*; Higashi, 2000)	904 independent reflections
T_{min} = 0.482, T_{max} = 0.625	899 reflections with $I > 2\sigma(I)$
	R_{int} = 0.081

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036	$\Delta\rho_{max}$ = 1.40 e $Å^{-3}$
$wR(F^2)$ = 0.080	$\Delta\rho_{min}$ = −2.31 e $Å^{-3}$
S = 1.07	Absolute structure: Flack (1983), 420 Friedel pairs
904 reflections	Flack parameter: −0.01 (3)
38 parameters	
1 restraint	

Table 1
Selected geometric parameters (Å, °).

Zr—Ge	2.8413 (17)	Zr—Te2^{i}	2.9806 (11)
Zr—Te1	2.9612 (11)	Zr—Te4	3.0507 (15)
Zr—Te1^{i}	2.9612 (11)	Ge—Te4^{ii}	2.6716 (10)
Zr—Te3^{i}	2.9637 (11)	Ge—Te4^{iii}	2.6716 (10)
Zr—Te3	2.9637 (11)	Ge—Te3^{iii}	2.6903 (16)
Zr—Te2	2.9806 (11)	Te1—Te2	2.7361 (12)
Te4^{ii}—Ge—Te4^{iii}	96.28 (5)	Te4^{iii}—Ge—Zr	123.34 (4)
Te4^{iii}—Ge—Te3^{iii}	93.17 (5)	Te3^{iii}—Ge—Zr	119.81 (6)

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

Data collection: *RAPID-AUTO* (Rigaku, 2006); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: locally modified version of *ORTEP* (Johnson, 1965); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FI2044).

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supplementary materials

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Stoichiometric $ZrGeTe_4$

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Comment

The title compound is isostructural with $Hf_{0.85}GeTe_4$ (Mar & Ibers, 1993). A view of the structure down the *a* axis in Fig. 1 shows the layered nature of the compound. Fig 2. shows that an individual layer is composed of two unique one-dimensional chains of face-sharing Zr-centered bicapped trigonal prisms and corner-sharing Ge-centered tetrahedra.

The Zr atom is surrounded by six Te atoms in a trigonal prismatic manner, the vertices of two base sides of the prism are composed of six Te atoms. Atoms Te1, Te2, and Te3 form a triangle that is isosceles, the Te1—Te2 distance (2.736 (1) Å) being much shorter than the other two (> 3.0 Å). This short Te1—Te2 separation is typical of $(Te—Te)^{2-}$ pair (Furuseth *et al.*, 1973). Te4 and Ge cap two of the rectangular faces of the trigonal prism to complete the Zr-centered bicapped trigonal prismatic coordination. These trigonal prisms share their triangular faces to form an infinite chain, $_\infty{}^1[ZrGeTe_4]$ along the direction of the *a* axis.

The Ge atom is surrounded by three Te and one Zr atoms in a distorted tetrahedral fashion. These tetrahedra share their corners through the Te4 atom to form an infinite chain. The bicapped trigonal prismatic and the tetrahedral chains are fused through Zr—Ge bonds to form a double chain and finally these chains are connected along the *c* axis to complete the two-dimensional layer. These layers then stack on top of each other to form the three-dimensional structure with an undulating van der Waals gap shown in Fig. 1.

We have checked many crystals from different reactions with various starting Zr/Te and Hf/Te ratios. We were not able to find nonstoichiometric $M_{0.85}GeTe_4$ (M=Zr, Hf) phases and we believe that the nature of the nonstoichiometry varies depending on the synthetic method.

Experimental

$ZrGeTe_4$ was obtained from a reaction of Zr(CERAC, 99.7%), Ge(CERAC, 99.999%) and Te(CERAC, 99.95%) in an elemental ratio of 1:1:4 in the presence of KCl as flux. The mass ratio of reactants and flux was 1:2. The starting materials were placed in a fused-silica tube. The tube was evacuated to 10^{-3} torr, sealed, and heated to 973 K at a rate of 15 K/hr, where it was kept for 72 hrs. The tube was cooled at a rate of 8 K/hr to 373 K and the furnace was shut off. Air- and water-stable metallic shiny needle-shaped crystals were isolated after the flux was removed with water. Qualitative analysis of the crystals with a WDX-equipped scanning electron microscope indicated the presence of Zr, Ge, and Te. No other element was detected.

Refinement

Although the anisotropic displacement parameters (ADPs) of the Zr atom were comparable to those of the other atoms, the nonstoichiometry of Zr in $ZrGeTe_4$ was checked by refining the occupancy and ADPs of Zr while those of the other atoms were fixed. With the nonstoichiometric model, both parameter were not changed significantly and the residuals (wR2, R1 indices) were remained the same. The highest peak/deepest hole in the Fourier map are found 1.74Å from Te2 and 0.73Å from Te3.

Figures

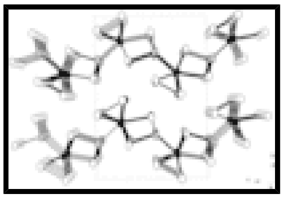

Fig. 1. View of $ZrGeTe_4$ down the *a* axis, showing the layered nature of the compound. Filled, grey, and open circles represent Zr, Ge, and Te atoms, respectively. Displacement ellipsoids are drawn at the 90% probability level.

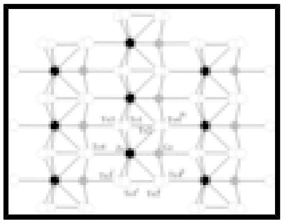

Fig. 2. View of $ZrGeTe_4$ down the *b* axis, showing a two-dimensional layer. Atoms are as marked in Fig. 1. [Symmetry code: (i) $-1 + x, y, z$; (ii) $-1/2 - x, 1/2 - y, 1/2 + z$; (iii) $1/2 - x, 1/2 - y, 1/2 + z$.]

Zirconium germanium tetratelluride

Crystal data

$Zr_1Ge_1Te_4$

$M_r = 674.24$

Orthorhombic, *Cmc*2$_1$

Hall symbol: C 2c -2

$a = 3.9794$ (2) Å

$b = 15.9296$ (10) Å

$c = 10.9957$ (6) Å

$V = 697.02$ (7) Å^3

$Z = 4$

$F_{000} = 1120$

$D_x = 6.425$ Mg m^{-3}

Mo *K*α radiation
λ = 0.71073 Å

Cell parameters from 3442 reflections

θ = 3.2–27.5°

$\mu = 22.09$ mm^{-1}

$T = 150$ (1) K

Needle, metallic silver

0.50 × 0.03 × 0.02 mm

Data collection

Rigaku R-AXIS RAPID diffractometer

$T = 150(1)$ K

ω scans

Absorption correction: numerical (NUMABS; Higashi, 2000)

$T_{min} = 0.482$, $T_{max} = 0.625$

3351 measured reflections

904 independent reflections

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

$R_{int} = 0.081$

$\theta_{max} = 27.5°$

$\theta_{min} = 3.2°$

$h = -5 \rightarrow 4$

$k = -20 \rightarrow 20$

$l = -13 \rightarrow 14$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0268P)^2 + 0.122P]$ where $P = (F_o^2 + 2F_c^2)/3$
Least-squares matrix: full	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.036$	$\Delta\rho_{max} = 1.40$ e Å^{-3}
$wR(F^2) = 0.080$	$\Delta\rho_{min} = -2.31$ e Å^{-3}
$S = 1.07$	Extinction correction: SHELXL97 (Sheldrick, 1997), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
904 reflections	Extinction coefficient: 0.0134 (6)
38 parameters	Absolute structure: Flack (1983), 420 Friedel pairs
1 restraint	Flack parameter: −0.01 (3)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Zr	0.0000	0.34835 (8)	0.77333 (11)	0.0065 (3)
Ge	0.0000	0.22779 (8)	0.96377 (13)	0.0077 (3)
Te1	0.5000	0.48455 (5)	0.74420 (8)	0.0083 (2)
Te2	0.5000	0.39999 (5)	0.96079 (7)	0.0084 (2)
Te3	0.5000	0.22096 (6)	0.69689 (7)	0.0070 (2)
Te4	0.0000	0.38129 (5)	0.50002 (7)	0.0073 (2)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zr	0.0068 (5)	0.0086 (6)	0.0042 (5)	0.000	0.000	0.0001 (5)
Ge	0.0079 (5)	0.0108 (7)	0.0044 (5)	0.000	0.000	0.0008 (5)
Te1	0.0089 (3)	0.0097 (5)	0.0065 (4)	0.000	0.000	0.0001 (3)
Te2	0.0087 (3)	0.0117 (5)	0.0048 (4)	0.000	0.000	−0.0012 (3)
Te3	0.0082 (3)	0.0087 (4)	0.0042 (4)	0.000	0.000	−0.0010 (3)
Te4	0.0071 (3)	0.0094 (4)	0.0053 (4)	0.000	0.000	0.0006 (3)

Geometric parameters (Å, °)

Zr—Ge	2.8413 (17)	Ge—Te4^{iii}	2.6716 (10)
Zr—Te1	2.9612 (11)	Ge—Te3^{iii}	2.6903 (16)
Zr—Te1^{i}	2.9612 (11)	Te1—Te2	2.7361 (12)
Zr—Te3^{i}	2.9637 (11)	Te1—Zr^{iv}	2.9612 (11)
Zr—Te3	2.9637 (11)	Te2—Zr^{iv}	2.9806 (11)
Zr—Te2	2.9806 (11)	Te3—Ge^{v}	2.6903 (16)
Zr—Te2^{i}	2.9806 (11)	Te3—Zr^{iv}	2.9637 (11)
Zr—Te4	3.0507 (15)	Te4—Ge^{vi}	2.6716 (10)
Ge—Te4^{ii}	2.6716 (10)	Te4—Ge^{v}	2.6716 (10)
Ge—Zr—Te1	125.10 (4)	Te1^{i}—Zr—Te4	76.55 (4)

Ge—Zr—Te1^{i}	125.10 (4)	Te3^{i}—Zr—Te4	80.70 (3)
Te1—Zr—Te1^{i}	84.43 (4)	Te3—Zr—Te4	80.70 (3)
Ge—Zr—Te3^{i}	75.30 (4)	Te2—Zr—Te4	129.33 (3)
Te1—Zr—Te3^{i}	157.24 (5)	Te2^{i}—Zr—Te4	129.33 (3)
Te1^{i}—Zr—Te3^{i}	91.14 (2)	Te4^{ii}—Ge—Te4^{iii}	96.28 (5)
Ge—Zr—Te3	75.30 (4)	Te4^{ii}—Ge—Te3^{iii}	93.17 (5)
Te1—Zr—Te3	91.14 (2)	Te4^{iii}—Ge—Te3^{iii}	93.17 (5)
Te1^{i}—Zr—Te3	157.24 (5)	Te4^{ii}—Ge—Zr	123.34 (4)
Te3^{i}—Zr—Te3	84.34 (4)	Te4^{iii}—Ge—Zr	123.34 (4)
Ge—Zr—Te2	71.15 (3)	Te3^{iii}—Ge—Zr	119.81 (6)
Te1—Zr—Te2	54.84 (3)	Te2—Te1—Zr	62.94 (3)
Te1^{i}—Zr—Te2	108.73 (5)	Te2—Te1—Zr^{iv}	62.94 (3)
Te3^{i}—Zr—Te2	146.43 (5)	Zr—Te1—Zr^{iv}	84.43 (4)
Te3—Zr—Te2	86.38 (2)	Te1—Te2—Zr	62.22 (3)
Ge—Zr—Te2^{i}	71.15 (3)	Te1—Te2—Zr^{iv}	62.22 (3)
Te1—Zr—Te2^{i}	108.73 (5)	Zr—Te2—Zr^{iv}	83.76 (4)
Te1^{i}—Zr—Te2^{i}	54.84 (3)	Ge^{v}—Te3—Zr^{iv}	93.58 (4)
Te3^{i}—Zr—Te2^{i}	86.38 (2)	Ge^{v}—Te3—Zr	93.58 (4)
Te3—Zr—Te2^{i}	146.43 (5)	Zr^{iv}—Te3—Zr	84.34 (4)
Te2—Zr—Te2^{i}	83.76 (4)	Ge^{vi}—Te4—Ge^{v}	96.28 (5)
Ge—Zr—Te4	147.38 (6)	Ge^{vi}—Te4—Zr	92.01 (4)
Te1—Zr—Te4	76.55 (4)	Ge^{v}—Te4—Zr	92.01 (4)

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

Fig. 1

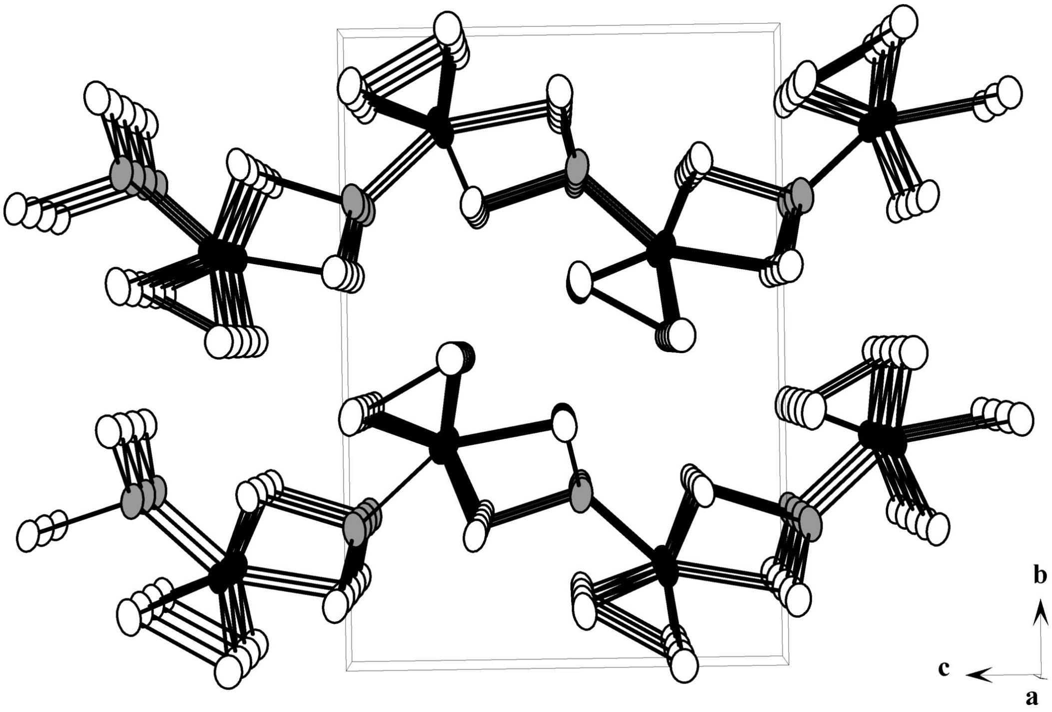

Fig. 2