inorganic compounds

Titanium germanium antimonide, TiGeSb

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TiGeSb adopts the PbFCl- or ZrSiS-type structure, with Ti atoms ($4mm$ symmetry) centred within monocapped square antiprisms generated by the stacking of denser square nets of Ge atoms ($\overline{4}m2$ symmetry) alternating with less dense square nets of Sb atoms ($4mm$ symmetry).

Related literature

For PbFCl- or ZrSiS-type structures, see: Tremel & Hoffmann (1987). For a previous report on TiGeSb, see: Dashjav & Kleinke (2002). The Ti—Ge—Sb phase diagram at 670 K was reported by Kozlov & Pavlyuk (2004). For the related ZrGeSb, see: Lam & Mar (1997). For background to solid solutions in this class of compounds, see: Soheilnia *et al.* (2003); Kozlov & Pavlyuk (2004). Metallic radii were taken from Pauling (1960).

Experimental

Crystal data

TiGeSb	$Z = 2$
$M_r = 242.24$	Mo $K\alpha$ radiation
Tetragonal, $P4/nmm$	$\mu = 28.18$ mm^{-1}
$a = 3.7022$ (5) Å	$T = 295$ K
$c = 8.2137$ (12) Å	$0.12 \times 0.11 \times 0.01$ mm
$V = 112.58$ (3) Å^3	

Data collection

Enraf–Nonius CAD-4 diffractometer	181 independent reflections
Absorption correction: numerical (*SHELXTL*; Sheldrick, 2008)	178 reflections with $I > 2\sigma(I)$
$T_{min} = 0.117$, $T_{max} = 0.718$	$R_{int} = 0.125$
1906 measured reflections	3 standard reflections frequency: 120 min intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$	10 parameters
$wR(F^2) = 0.081$	$\Delta\rho_{max} = 1.95$ e Å^{-3}
$S = 1.17$	$\Delta\rho_{min} = -2.53$ e Å^{-3}
181 reflections	

Table 1
Selected bond lengths (Å).

Ti—Ge	2.7570 (10)	Ti—Sb	3.0129 (14)
Ti—Sb^i	2.8452 (7)	Ge—Ge^{ii}	2.6179 (4)

Symmetry codes: (i) $-x, -y, -z+1$; (ii) $-x+1, -y, -z$.

Data collection: *CAD-4-PC* (Enraf–Nonius, 1993); cell refinement: *CAD-4-PC*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *ATOMS* (Dowty, 1999); software used to prepare material for publication: *SHELXTL*.

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supporting information

Titanium germanium antimonide, TiGeSb

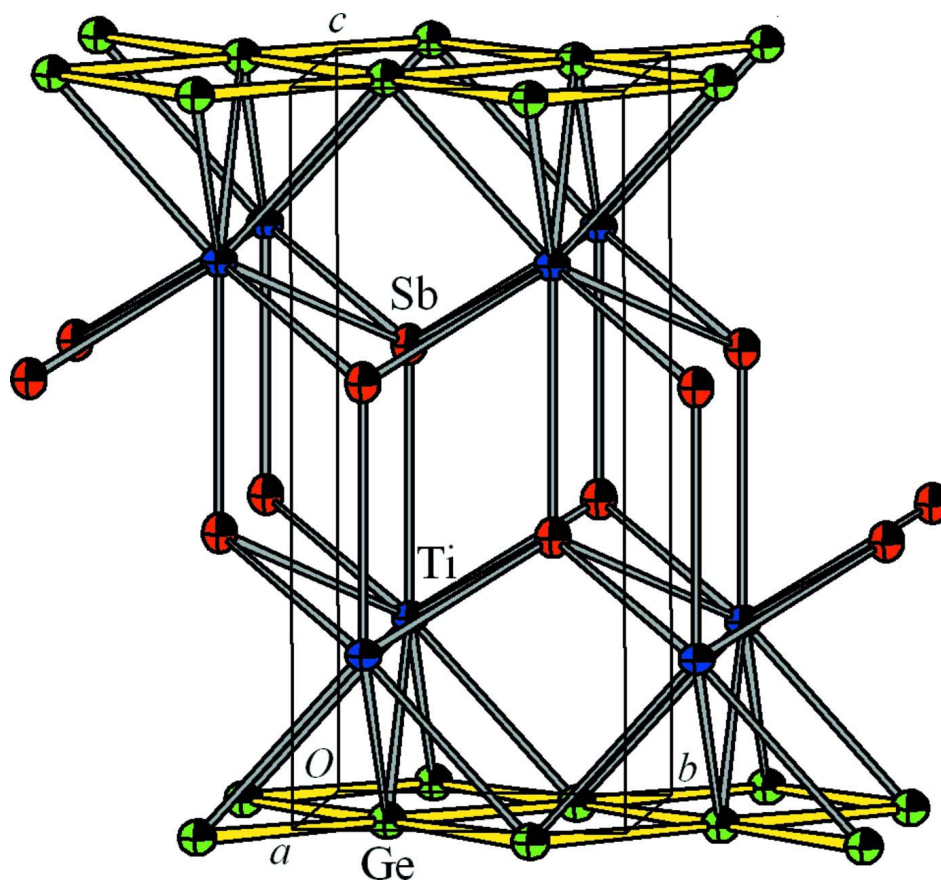**Robert Lam and Arthur Mar**

S1. Comment

After a report of the ternary antimonide ZrGeSb (Lam & Mar, 1997), the corresponding Ti and Hf analogues were later described in a conference proceeding, but full crystallographic details have not been forthcoming (Dashjav & Kleinke, 2002). The complete structure of TiGeSb, which is absent in the Ti—Ge—Sb phase diagram at 670 K (Kozlov & Pavlyuk, 2004) but was prepared here at 1273 K, is presented. Common to many equiatomic compounds of the formulation *MAB* (*M* = large transition-metal atom; *A*, *B* = main group atoms), TiGeSb adopts the PbFCl- or ZrSiS-type structure, among other names (Tremel & Hoffmann, 1987). Square nets of each type of atom, with the Ge net being twice as dense as the other two, are stacked along the *c* axis (Fig. 1). The Zr atoms are nine-coordinate, centred within monocapped square antiprisms. The Ge–Ge distances are 0.13 Å longer than the sum of the Pauling metallic radii (2.48 Å; Pauling, 1960), indicative of weak polyanionic bonding. The solid solutions $ZrGe_xSb_{1-x}$ and $HfGe_xSb_{1-x}$ (up to $x = 0.2$) form related orthorhombic $PbCl_2$-type structures (Soheilnia *et al.*, 2003), whereas $TiGe_xSb_{1-x}$ adopts a NiAs-type structure (Kozlov & Pavlyuk, 2004).

S2. Experimental

A 0.25 g mixture of Ti (99.98%, Cerac), Ge (99.999%, Cerac), and Sb (99.995%, Aldrich) powders in a 1:1:3 molar ratio was placed in an evacuated fused-silica tube. The tube was heated at 873 K for 2 d and 1273 K for 2 d. Silver plate-shaped crystals were obtained, which were found by semiquantitative energy-dispersive X-ray (EDX) analysis to have a composition (at%) of 32 (2)% Ti, 35 (2)% Ge, and 33 (2)% Sb, in good agreement with the formula TiGeSb.

S3. Refinement

Analysis of Weissenberg photographs on a plate-shaped crystal, subsequently transferred to the four-circle diffractometer, established Laue symmetry 4/*mmm* and provided approximate cell parameters of $a = 3.71$ Å and $c = 8.22$ Å. In the final Fourier map based on origin choice 2 of space group *P*4/*nmm* the maximum peak and deepest hole are located 0.67 Å and 0.02 Å, respectively, from the Sb atom.

Figure 1

Projection of the TiGeSb structure approximately along the *a* axis. Displacement ellipsoids are drawn at the 90% probability level.

titanium germanium antimonide

Crystal data

TiGeSb	$D_x = 7.146$ Mg m^{-3}
$M_r = 242.24$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Tetragonal, $P4/nmm$	Cell parameters from 24 reflections
Hall symbol: -P 4a 2a	$\theta = 11.0$–$23.3°$
$a = 3.7022$ (5) Å	$\mu = 28.18$ mm^{-1}
$c = 8.2137$ (12) Å	$T = 295$ K
$V = 112.58$ (3) Å^3	Plate, silver
$Z = 2$	$0.12 \times 0.11 \times 0.01$ mm
$F(000) = 210$	

Data collection

Enraf–Nonius CAD-4 diffractometer	$T_{min} = 0.117$, $T_{max} = 0.718$
Radiation source: fine-focus sealed tube	1906 measured reflections
Graphite monochromator	181 independent reflections
$\theta/2\theta$ scans	178 reflections with $I > 2\sigma(I)$
Absorption correction: numerical (*SHELXTL*; Sheldrick, 2008)	$R_{int} = 0.125$
	$\theta_{max} = 34.8°$, $\theta_{min} = 2.5°$
	$h = -5 \rightarrow 5$

$k = -5 \rightarrow 5$

$l = -13 \rightarrow 13$

3 standard reflections every 120 min

intensity decay: none

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.032$	$w = 1/[\sigma^2(F_o^2) + (0.044P)^2 + 0.3679P]$
$wR(F^2) = 0.081$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.17$	$(\Delta/\sigma)_{max} < 0.001$
181 reflections	$\Delta\rho_{max} = 1.95$ e Å^{-3}
10 parameters	$\Delta\rho_{min} = -2.53$ e Å^{-3}
0 restraints	Extinction correction: *SHELXTL* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.038 (9)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

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

	x	y	z	$U_{iso}*/U_{eq}$
Ti	0.2500	0.2500	0.24875 (16)	0.0054 (3)
Ge	0.7500	0.2500	0.0000	0.0063 (3)
Sb	0.2500	0.2500	0.61556 (6)	0.0063 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ti	0.0060 (4)	0.0060 (4)	0.0043 (6)	0.000	0.000	0.000
Ge	0.0065 (4)	0.0065 (4)	0.0059 (4)	0.000	0.000	0.000
Sb	0.0056 (3)	0.0056 (3)	0.0076 (4)	0.000	0.000	0.000

Geometric parameters (Å, º)

Ti—Ge[i]	2.7570 (10)	Ge—Ge[ix]	2.6179 (3)
Ti—Ge[ii]	2.7570 (10)	Ge—Ti[i]	2.7570 (10)
Ti—Ge[iii]	2.7570 (10)	Ge—Ti[x]	2.7570 (10)
Ti—Ge	2.7570 (10)	Ge—Ti[iii]	2.7570 (10)
Ti—Sb[iv]	2.8452 (7)	Sb—Ti[iv]	2.8452 (7)
Ti—Sb[v]	2.8452 (7)	Sb—Ti[v]	2.8452 (7)
Ti—Sb[vi]	2.8452 (7)	Sb—Ti[vi]	2.8452 (7)
Ti—Sb[vii]	2.8452 (7)	Sb—Ti[vii]	2.8452 (7)
Ti—Sb	3.0129 (14)	Sb—Sb[v]	3.2337 (7)
Ge—Ge[viii]	2.6179 (4)	Sb—Sb[iv]	3.2337 (7)

Ge—Geⁱ	2.6179 (4)	Sb—Sb^{vii}	3.2337 (7)
Ge—Geⁱⁱⁱ	2.6179 (4)	Sb—Sb^{vi}	3.2337 (7)
Geⁱ—Ti—Geⁱⁱ	56.69 (2)	Tiⁱ—Ge—Ti^x	123.31 (2)
Geⁱ—Ti—Geⁱⁱⁱ	84.35 (4)	Ge^{viii}—Ge—Ti	118.344 (11)
Geⁱⁱ—Ti—Geⁱⁱⁱ	56.69 (2)	Geⁱ—Ge—Ti	61.656 (11)
Geⁱ—Ti—Ge	56.69 (2)	Geⁱⁱⁱ—Ge—Ti	61.656 (11)
Geⁱⁱ—Ti—Ge	84.35 (4)	Ge^{ix}—Ge—Ti	118.344 (11)
Geⁱⁱⁱ—Ti—Ge	56.69 (2)	Tiⁱ—Ge—Ti	123.31 (2)
Geⁱ—Ti—Sb^{iv}	136.65 (2)	Ti^x—Ge—Ti	84.35 (4)
Geⁱⁱ—Ti—Sb^{iv}	136.65 (2)	Ge^{viii}—Ge—Tiⁱⁱⁱ	61.656 (11)
Geⁱⁱⁱ—Ti—Sb^{iv}	81.574 (14)	Geⁱ—Ge—Tiⁱⁱⁱ	118.344 (11)
Ge—Ti—Sb^{iv}	81.574 (14)	Geⁱⁱⁱ—Ge—Tiⁱⁱⁱ	61.656 (11)
Geⁱ—Ti—Sb^v	81.574 (14)	Ge^{ix}—Ge—Tiⁱⁱⁱ	118.344 (11)
Geⁱⁱ—Ti—Sb^v	81.574 (14)	Tiⁱ—Ge—Tiⁱⁱⁱ	84.35 (4)
Geⁱⁱⁱ—Ti—Sb^v	136.65 (2)	Ti^x—Ge—Tiⁱⁱⁱ	123.31 (2)
Ge—Ti—Sb^v	136.65 (2)	Ti—Ge—Tiⁱⁱⁱ	123.31 (2)
Sb^{iv}—Ti—Sb^v	133.88 (5)	Ti^{iv}—Sb—Ti^v	133.88 (5)
Geⁱ—Ti—Sb^{vi}	136.65 (2)	Ti^{iv}—Sb—Ti^{vi}	81.17 (2)
Geⁱⁱ—Ti—Sb^{vi}	81.574 (14)	Ti^v—Sb—Ti^{vi}	81.17 (2)
Geⁱⁱⁱ—Ti—Sb^{vi}	81.574 (14)	Ti^{iv}—Sb—Ti^{vii}	81.17 (2)
Ge—Ti—Sb^{vi}	136.65 (2)	Ti^v—Sb—Ti^{vii}	81.17 (2)
Sb^{iv}—Ti—Sb^{vi}	81.17 (2)	Ti^{vi}—Sb—Ti^{vii}	133.88 (5)
Sb^v—Ti—Sb^{vi}	81.17 (2)	Ti^{iv}—Sb—Ti	113.06 (3)
Geⁱ—Ti—Sb^{vii}	81.574 (14)	Ti^v—Sb—Ti	113.06 (3)
Geⁱⁱ—Ti—Sb^{vii}	136.65 (2)	Ti^{vi}—Sb—Ti	113.06 (3)
Geⁱⁱⁱ—Ti—Sb^{vii}	136.65 (2)	Ti^{vii}—Sb—Ti	113.06 (3)
Ge—Ti—Sb^{vii}	81.574 (14)	Ti^{iv}—Sb—Sb^v	167.11 (4)
Sb^{iv}—Ti—Sb^{vii}	81.17 (2)	Ti^v—Sb—Sb^v	59.01 (3)
Sb^v—Ti—Sb^{vii}	81.17 (2)	Ti^{vi}—Sb—Sb^v	103.295 (14)
Sb^{vi}—Ti—Sb^{vii}	133.88 (5)	Ti^{vii}—Sb—Sb^v	103.295 (14)
Geⁱ—Ti—Sb	137.823 (19)	Ti—Sb—Sb^v	54.051 (16)
Geⁱⁱ—Ti—Sb	137.823 (19)	Ti^{iv}—Sb—Sb^{iv}	59.01 (3)
Geⁱⁱⁱ—Ti—Sb	137.823 (19)	Ti^v—Sb—Sb^{iv}	167.11 (4)
Ge—Ti—Sb	137.823 (19)	Ti^{vi}—Sb—Sb^{iv}	103.295 (14)
Sb^{iv}—Ti—Sb	66.94 (3)	Ti^{vii}—Sb—Sb^{iv}	103.295 (14)
Sb^v—Ti—Sb	66.94 (3)	Ti—Sb—Sb^{iv}	54.051 (16)
Sb^{vi}—Ti—Sb	66.94 (3)	Sb^v—Sb—Sb^{iv}	108.10 (3)
Sb^{vii}—Ti—Sb	66.94 (3)	Ti^{iv}—Sb—Sb^{vii}	103.295 (14)
Ge^{viii}—Ge—Geⁱ	180.0	Ti^v—Sb—Sb^{vii}	103.295 (14)
Ge^{viii}—Ge—Geⁱⁱⁱ	90.0	Ti^{vi}—Sb—Sb^{vii}	167.11 (4)
Geⁱ—Ge—Geⁱⁱⁱ	90.0	Ti^{vii}—Sb—Sb^{vii}	59.01 (3)
Ge^{viii}—Ge—Ge^{ix}	90.0	Ti—Sb—Sb^{vii}	54.051 (16)
Geⁱ—Ge—Ge^{ix}	90.0	Sb^v—Sb—Sb^{vii}	69.840 (16)
Geⁱⁱⁱ—Ge—Ge^{ix}	180.0	Sb^{iv}—Sb—Sb^{vii}	69.840 (16)
Ge^{viii}—Ge—Tiⁱ	118.344 (11)	Ti^{iv}—Sb—Sb^{vi}	103.295 (14)
Geⁱ—Ge—Tiⁱ	61.656 (11)	Ti^v—Sb—Sb^{vi}	103.295 (14)
Geⁱⁱⁱ—Ge—Tiⁱ	118.344 (11)	Ti^{vi}—Sb—Sb^{vi}	59.01 (3)

Ge^{ix}—Ge—Ti^{i}	61.656 (11)	Ti^{vii}—Sb—Sb^{vi}	167.11 (4)
Ge^{viii}—Ge—Ti^{x}	61.656 (11)	Ti—Sb—Sb^{vi}	54.051 (16)
Ge^{i}—Ge—Ti^{x}	118.344 (11)	Sb^{v}—Sb—Sb^{vi}	69.840 (16)
Ge^{iii}—Ge—Ti^{x}	118.344 (11)	Sb^{iv}—Sb—Sb^{vi}	69.840 (16)
Ge^{ix}—Ge—Ti^{x}	61.656 (11)	Sb^{vii}—Sb—Sb^{vi}	108.10 (3)

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