

TiGeS₃

Pilsoo Kim and Hoseop Yun*

Division of Energy Systems Research and Department of Chemistry, Ajou University, Suwon 443-749, Republic of Korea

Correspondence e-mail: hsyun@ajou.ac.kr

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Key indicators: single-crystal X-ray study; $T = 290$ K; mean $\sigma(\text{Ti}-\text{S}) = 0.001$ Å; R factor = 0.032; wR factor = 0.076; data-to-parameter ratio = 17.2.

The new ternary titanium(II) thio germanate(IV), TiGeS₃, was synthesized using the reactive halide flux method. The title compound shows features of a ribbon-type structure formed from double chains composed of edge-sharing octahedral TiS₆ and pyramidal GeS₃ units, with all atoms in the asymmetric unit positioned on mirror planes. While the TiS₆ octahedron is regular, the coordination around the Ge atom is rather irregular, which can be described as [3 + 3]. Three S atoms build up a triangle that is bound to the Ge atom, the coordination of which is augmented by three additional S atoms at considerably longer distances. The charge balance can formally be described as [Ti⁴⁺][Ge²⁺][S²⁻]₃.

Related literature

For related structures, see: Brasseur & Pauling (1938) for NH₄CdCl₃; Kniep *et al.* (1982) for Sn^{II}Sn^{IV}S₃. For isostructural compounds, see: Lelieveld & Ijdo (1978) for PbZrS₃; Gressier *et al.* (1987) for Sn_{1.2}Ti_{0.8}S₃. For usual bond lengths and angles for the TiS₆ octahedron, see: Jandali *et al.* (1980) for TiP₂S₆. A similar coordination of Ge to that observed in the title compound can be found in divalent germanium sulfide, GeS, see: Bissert & Hesse (1978).

Experimental

Crystal data

TiGeS ₃	$V = 410.39$ (7) Å ³
$M_r = 216.68$	$Z = 4$
Orthorhombic, <i>Pnma</i>	Mo $K\alpha$ radiation
$a = 8.9263$ (8) Å	$\mu = 10.56$ mm ⁻¹
$b = 3.4673$ (3) Å	$T = 290$ K
$c = 13.2596$ (15) Å	$0.60 \times 0.08 \times 0.06$ mm

Data collection

Rigaku R-Axis RAPID diffractometer	3802 measured reflections
Absorption correction: multi-scan (<i>ABSCOR</i> ; Higashi, 1995)	550 independent reflections
$T_{\min} = 0.674$, $T_{\max} = 1.000$	525 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.031$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$	32 parameters
$wR(F^2) = 0.076$	$\Delta\rho_{\text{max}} = 1.69$ e Å ⁻³
$S = 1.16$	$\Delta\rho_{\text{min}} = -1.44$ e Å ⁻³
550 reflections	

Table 1

Selected bond lengths (Å).

Ti—S1 ⁱ	2.4238 (12)	Ge—S2 ⁱⁱⁱ	2.3970 (8)
Ti—S2	2.4246 (12)	Ge—S2	2.3970 (8)
Ti—S3 ⁱⁱ	2.4286 (8)	Ge—S3	2.4754 (11)
Ti—S3	2.4286 (8)	Ge—S1 ^{iv}	3.0558 (11)
Ti—S1	2.4469 (8)	Ge—S3 ^v	3.4360 (10)
Ti—S1 ⁱⁱ	2.4469 (8)	Ge—S3 ^{vi}	3.4360 (10)

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

Data collection: *RAPID-AUTO* (Rigaku, 2006); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; 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: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RU2041).

References

- Bissert, G. & Hesse, K.-F. (1978). *Acta Cryst.* **B34**, 1322–1323.
 Brandenburg, K. (1999). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
 Brasseur, H. & Pauling, L. (1938). *J. Am. Chem. Soc.* **60**, 2886–2890.
 Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
 Gressier, P., Meerschaut, A. & Rouxel, J. (1987). *Mater. Res. Bull.* **22**, 1573–1580.
 Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
 Jandali, M. Z., Eulenberg, G. & Hahn, H. (1980). *Z. Anorg. Allg. Chem.* **470**, 39–44.
 Kniep, R., Mootz, D., Severin, U. & Wunderlich, H. (1982). *Acta Cryst.* **B38**, 2022–2023.
 Lelieveld, R. & Ijdo, D. J. W. (1978). *Acta Cryst.* **B34**, 3348–3349.
 Rigaku (2006). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

supporting information

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TiGeS₃**Pilsoo Kim and Hoseop Yun****S1. Comment**

During an effort to find a new phase in the A—Ti—Ge—S system (A=alkali metals), a new compound was isolated. Here we report the synthesis and structure of the new ternary thiogermanate, TiGeS₃.

The title compound shows the features of the ribbon-type structure (Fig. 1). Its structure is closely related to that of NH₄CdCl₃ (Brasseur & Pauling, 1938) and it is isostructural with the previously reported SnⁿSn^{IV}S₃ (Kniep *et al.*, 1982), PbZrS₃ (Lelieveld & Ijdo, 1978), and Sn_{1.2}Ti_{0.8}S₃ (Gressier *et al.*, 1987). The Ti atom is coordinated by six sulfur atoms in an octahedral arrangement (Fig. 2). The TiS₆ octahedra share an edge to form the one-dimensional chains along the *b* axis. These chains are fused together sharing two S atoms to form the double chain. These double octahedral chains are capped by the Ge atom to complete the one-dimensional chain.

While the TiS₆ octahedra are regular and the Ti—S distances are in good agreement with those found in other titanium sulfides (Jandali *et al.*, 1980), the coordination around the Ge atom is rather irregular. It can be described as [3 + 3]. Three S atoms built up a triangle that is bound to the Ge atom (Ge—S, 2.397 (1)–2.475 (1) Å; S—Ge—S, 91.13 (3)–92.65 (4) °), the coordination of which is augmented by three additional S atoms at considerably longer distances of 3.056 (1)–3.436 (1) Å. The similar Ge coordination observed in the title compound can be found in divalent germanium sulfide, GeS (Bissert & Hesse, 1978) and the charge balance can be described by [Ti⁴⁺][Ge²⁺][S²⁻]₃.

S2. Experimental

The title compound, TiGeS₃ was prepared by the reaction of elements with the use of the reactive halide-flux technique. A combination of the pure elements, Ti powder (Aldrich 99.7%), Ge powder (CERAC 99.9%) and S powder (Aldrich 99.999%) were mixed in a fused silica tube in molar ratio of Ti:Ge:S=4:2:7 and then KCl (CERAC 99.9%) was added. The mass ratio of the reactants and the halide was 1:2. The tube was evacuated to 0.133 Pa, sealed, and heated gradually (20 K/h) to 923 K, where it was kept for 72 h. The tube was cooled to room temperature at the rate 3 K/h. The excess halide was removed with distilled water and black needle-shaped crystals were obtained. The crystals are stable in air and water. A qualitative X-ray fluorescence analysis of the needles indicated the presence of Ti, Ge, and S. The composition of the compound was determined by single-crystal X-ray diffraction.

S3. Refinement

The Ti site in Sn_{1.2}Ti_{0.8}S₃ has been reported to be occupied by disordered Ti⁴⁺ and Sn⁴⁺ ions (Gressier *et al.*, 1987) and the nonstoichiometry of the Ti site in the title compound was checked by refining the occupancy and anisotropic displacement parameters while those of the other atoms were fixed. With the nonstoichiometric model, both parameters were not changed significantly and the residuals (wR2, R1 indices) remained the same. The highest peak (1.69 e/Å⁻³) and the deepest hole (-1.44 e/Å⁻³) are 0.77 Å and 0.86 Å from the atom Ge, respectively.

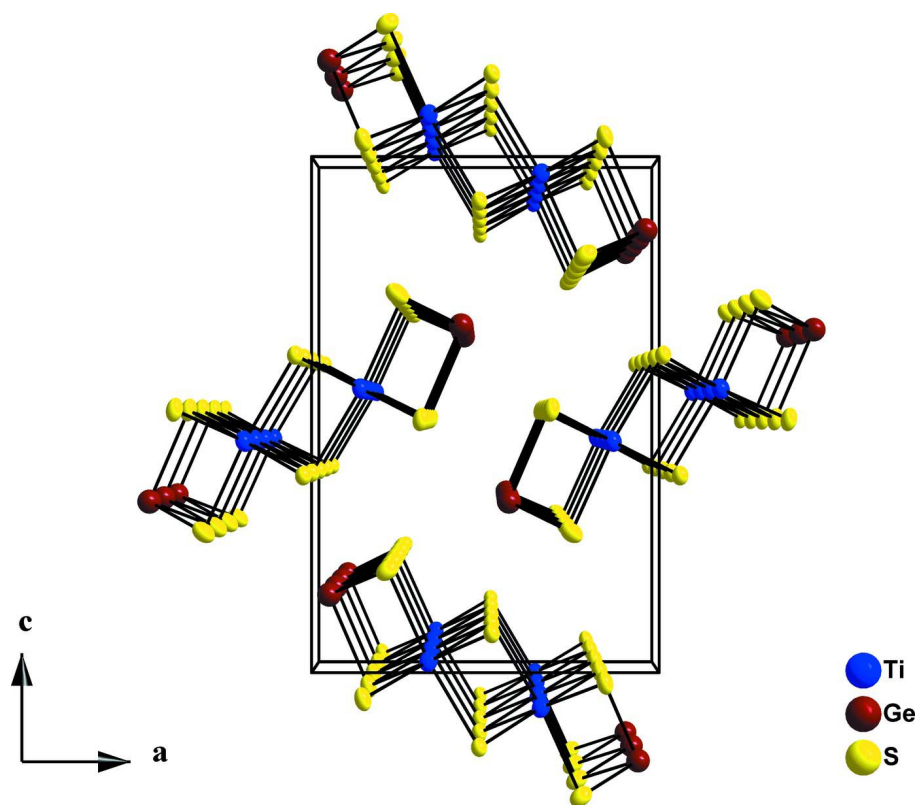


Figure 1

A perspective view of TiGeS₃ down the *b* axis showing the ribbon-type structure of the chain.

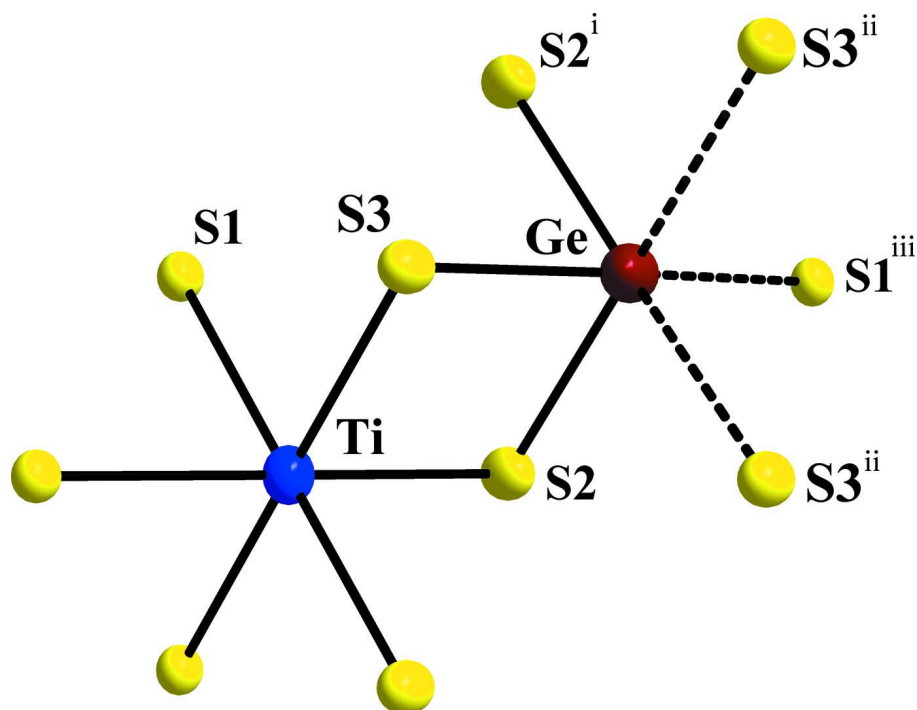


Figure 2

A view showing the local coordination environments of Ti and Ge atoms with the atom labelling scheme. Displacement ellipsoids are drawn at the 80% probability level. [Symmetry codes: (i) $x, 1+y, z$; (ii) $-x, 1/2+y, -z$; (iii) $-1/2+x, 1/2-y, 1/2-z$.]

Titanium(II) thiogermanate(IV)

Crystal data

TiGeS₃

$M_r = 216.68$

Orthorhombic, *Pnma*

Hall symbol: $-P\ 2ac\ 2n$

$a = 8.9263\ (8)\ \text{\AA}$

$b = 3.4673\ (3)\ \text{\AA}$

$c = 13.2596\ (15)\ \text{\AA}$

$V = 410.39\ (7)\ \text{\AA}^3$

$Z = 4$

$F(000) = 408$

$D_x = 3.507\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 3487 reflections

$\theta = 3.1\text{--}27.4^\circ$

$\mu = 10.56\ \text{mm}^{-1}$

$T = 290\ \text{K}$

Needle, black

$0.60 \times 0.08 \times 0.06\ \text{mm}$

Data collection

Rigaku R-AXIS RAPID
diffractometer

Graphite monochromator

ω scans

Absorption correction: multi-scan
(*ABSCOR*; Higashi, 1995)

$T_{\min} = 0.674, T_{\max} = 1.000$

3802 measured reflections

550 independent reflections

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

$R_{\text{int}} = 0.031$

$\theta_{\max} = 27.4^\circ, \theta_{\min} = 3.1^\circ$

$h = -11 \rightarrow 11$

$k = -4 \rightarrow 4$

$l = -17 \rightarrow 17$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0422P)^2 + 0.885P]$
$R[F^2 > 2\sigma(F^2)] = 0.032$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.076$	$(\Delta/\sigma)_{\max} < 0.001$
$S = 1.16$	$\Delta\rho_{\max} = 1.69 \text{ e } \text{\AA}^{-3}$
550 reflections	$\Delta\rho_{\min} = -1.44 \text{ e } \text{\AA}^{-3}$
32 parameters	Extinction correction: <i>SHELXL97</i> (Sheldrick, 2008)
0 restraints	Extinction coefficient: 0.049 (3)
Primary atom site location: structure-invariant direct methods	

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Ti	0.34548 (8)	-0.25	0.04861 (5)	0.0133 (3)
Ge	0.06572 (5)	0.25	0.16292 (4)	0.0227 (2)
S1	0.51690 (10)	0.25	0.10897 (7)	0.0102 (3)
S2	0.23401 (12)	-0.25	0.21536 (7)	0.0146 (3)
S3	0.17500 (11)	0.25	-0.00866 (8)	0.0125 (3)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ti	0.0111 (4)	0.0142 (4)	0.0145 (4)	0	0.0012 (3)	0
Ge	0.0145 (3)	0.0144 (3)	0.0393 (4)	0	0.00642 (19)	0
S1	0.0083 (5)	0.0108 (5)	0.0116 (5)	0	-0.0002 (3)	0
S2	0.0167 (5)	0.0124 (5)	0.0148 (5)	0	0.0045 (4)	0
S3	0.0089 (5)	0.0111 (5)	0.0174 (5)	0	-0.0021 (3)	0

Geometric parameters (\AA , $^\circ$)

Ti—S1 ⁱ	2.4238 (12)	Ge—S3	2.4754 (11)
Ti—S2	2.4246 (12)	Ge—S1 ^{iv}	3.0558 (11)
Ti—S3 ⁱⁱ	2.4286 (8)	Ge—S3 ^v	3.4360 (10)
Ti—S3	2.4286 (8)	Ge—S3 ^{vi}	3.4360 (10)
Ti—S1	2.4469 (8)	S1—Ti ⁱ	2.4238 (12)
Ti—S1 ⁱⁱ	2.4469 (8)	S1—Ti ⁱⁱⁱ	2.4469 (8)
Ge—S2 ⁱⁱⁱ	2.3970 (8)	S2—Ge ⁱⁱ	2.3970 (8)
Ge—S2	2.3970 (8)	S3—Ti ⁱⁱⁱ	2.4286 (8)

S1 ⁱ —Ti—S2	173.78 (5)	S1—Ti—S1 ⁱⁱ	90.22 (4)
S1 ⁱ —Ti—S3 ⁱⁱ	92.75 (4)	S2 ⁱⁱⁱ —Ge—S2	92.65 (4)
S2—Ti—S3 ⁱⁱ	91.60 (4)	S2 ⁱⁱⁱ —Ge—S3	91.13 (3)
S1 ⁱ —Ti—S3	92.75 (4)	S2—Ge—S3	91.13 (3)
S2—Ti—S3	91.60 (4)	Ti ⁱ —S1—Ti	92.00 (3)
S3 ⁱⁱ —Ti—S3	91.10 (4)	Ti ⁱ —S1—Ti ⁱⁱⁱ	92.00 (3)
S1 ⁱ —Ti—S1	88.00 (3)	Ti—S1—Ti ⁱⁱⁱ	90.22 (4)
S2—Ti—S1	87.61 (3)	Ge ⁱⁱ —S2—Ge	92.65 (4)
S3 ⁱⁱ —Ti—S1	179.11 (4)	Ge ⁱⁱ —S2—Ti	89.58 (3)
S3—Ti—S1	89.33 (2)	Ge—S2—Ti	89.58 (3)
S1 ⁱ —Ti—S1 ⁱⁱ	88.00 (3)	Ti ⁱⁱⁱ —S3—Ti	91.10 (4)
S2—Ti—S1 ⁱⁱ	87.61 (3)	Ti ⁱⁱⁱ —S3—Ge	87.68 (3)
S3 ⁱⁱ —Ti—S1 ⁱⁱ	89.33 (2)	Ti—S3—Ge	87.68 (3)
S3—Ti—S1 ⁱⁱ	179.11 (4)		

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