Reinvestigation of Ge$_4$Se$_9$ based on single-crystal data

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Tetragermanium nonaselenide, Ge$_4$Se$_9$, adopts a two-dimensional layered structure. The layer is made up of infinite chains of corner-sharing GeSe$_4$ tetrahedra and the chains are connected *via* the Ge$_2$Se$_7$ unit to form the two-dimensional layer. These layers are stacked to form the three-dimensional structure with a van der Waals gap. A previous structure report on Ge$_4$Se$_9$ based on powder diffraction data [Fjellvåg, Kongshaug & Stølen (2001). *J. Chem. Soc. Dalton Trans.* pp. 1043–1045] is comparable with our results except for the absolute structure determination.

Comment

The synthesis of polycrystalline Ge$_4$Se$_9$ has been reported and its structure was previously determined *ab initio* from X-ray powder diffraction data (Fjellvåg *et al.*, 2001). Single crystals of reasonable quality and size suitable for a single-crystal X-ray diffraction study were not obtained using traditional solid-state synthetic techniques. We have used alkali metal halides as fluxes to prepare single crystals of metal chalcogenides, and this synthetic technique appears to be of general utility in preparing crystalline chalcogenides (Do & Yun, 1996; Kim *et al.*, 1997). We describe here the synthesis and structural characterization of Ge$_4$Se$_9$ single crystals.
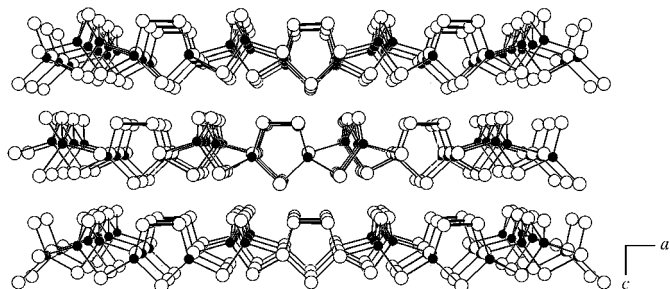

Figure 1
Ge$_4$Se$_9$, viewed down the *b* axis, showing the stacking of the layers. Filled circles are Ge atoms and open circles are Se atoms.
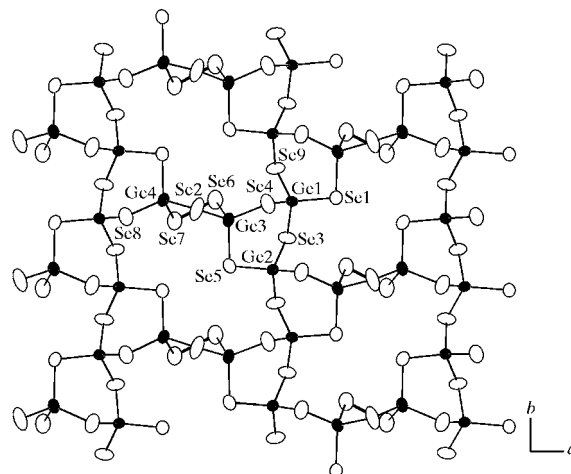

Figure 2
A view of Ge$_4$Se$_9$ down the *c* axis, showing an individual layer and the coordination around the Ge atoms. Atoms are labelled as in Fig. 1. The short Se—Se distances are denoted by thick lines for clarity.

The general features of the structure of Ge$_4$Se$_9$ are the same as previously reported (Fjellvåg *et al.*, 2001). A view down the *b* axis clearly shows the layered nature of the structure (Fig. 1). Fig. 2 shows that an individual layer is composed of infinite chains of corner-sharing Ge tetrahedra. The chains are connected *via* Ge$_2$Se$_7$ units parallel to the *a* axis to form a two-dimensional layer, and these layers are stacked to complete the three-dimensional structure with a van der Waals gap, as shown in Fig. 1. There is no bonding interaction, only van der Waals forces, between the layers.

The structure of Ge$_4$Se$_9$ is closely related to that of monoclinic α-GeSe$_2$ (Dittmar & Schäfer, 1976). One-dimensional chains composed of corner-sharing tetrahedral GeSe$_4$ units are found in both structures. While the edge-sharing Ge$_2$Se$_6$ unit (Fig. 3a) bridges the chains in GeSe$_2$, the corner-sharing Ge$_2$Se$_7$ link (Fig. 3b) connects the chains in Ge$_4$Se$_9$.

The Ge—Se distances [2.331 (2)–2.370 (2) Å] are in good agreement with those calculated from the covalent radii of Ge and Se (1.22 and 1.16 Å, respectively; Webelements, 2005) and are comparable with those of other selenogermanates, such as SrCu$_2$GeSe$_4$ [2.345 (5)–2.370 (4) Å; Tampier & Johrendt, 2001]. As would be expected, the Ge—Se distances found here from single-crystal diffraction data are more regular than those reported previously with powder diffraction data [2.287 (8)–2.405 (6) Å]. The bond angles found in the GeSe$_4$ tetrahedra do not deviate significantly from the ideal tetrahedral value, except for the Se3—Ge2—Se9^{ii} angle [93.49 (6)°; symmetry code: (ii) *x*, *y* − 1, *z*].

The short Se6—Se7 separation [2.3638 (14) Å] found in the Ge$_2$Se$_7$ unit is consistent with a typical (Se—Se)$^{2-}$ pair (Sunshine & Ibers, 1987). The electrostatic bond valence sums calculated for the present structure (Adams, 2001) are 4.1008–4.1748 for the Ge atoms, 1.1761 and 1.1651 for atoms Se6 and Se7, respectively, and 2.0281–2.1271 for the other Se atoms, which are in good agreement with the estimated oxidation states from classical charge balance, [Ge^{4+}]$_4$[Se^{2-}]$_7$[Se$_2^{2-}$]. The global instability index, GII = 0.1108 v.u., is a value typical for an unstrained structure (Adams, 2001).
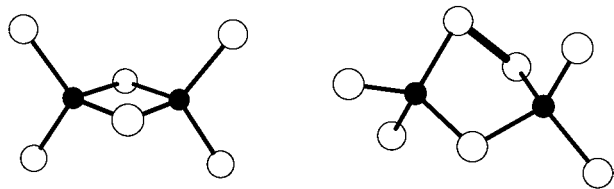
Figure 3
A sketch of the bridging units in GeSe$_2$ (left) and Ge$_4$Se$_9$ (right). Filled circles are Ge atoms and open circles are Se atoms.

Experimental

Ge$_4$Se$_9$ was prepared by the reaction of elemental Ta, Ge and Se by use of the flux technique. A combination of the pure elements, *viz*. Ta powder (CERAC, 99.999%), Ge powder (CERAC, 99.5%) and Se powder (CERAC, 99.95%), were mixed in silica tubes in an atomic ratio of Ta:Ge:Se = 1:2:10, and then RbCl was added in a weight ratio of TaGe$_2$Se$_{10}$:RbCl = 1:2. The tubes were evacuated to 10^{-2} Torr (1 Torr = 133.322 Pa), sealed, and heated gradually (50 K h^{-1}) to 1073 K in a box furnace, where they were kept for 96 h. The tubes were cooled slowly to 473 K at a rate of 4 K h^{-1} and quenched. The excess halide was removed with distilled water. Orange block-shaped crystals of up to 0.3 mm in length were obtained. The crystals are stable in air and water.

Crystal data

Ge$_4$Se$_9$
$M_r = 1001.08$
Orthorhombic, $Pca2_1$
$a = 17.805$ (6) Å
$b = 7.002$ (2) Å
$c = 12.071$ (6) Å
$V = 1504.8$ (10) Å^3
$Z = 4$
$D_x = 4.419$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 11241 reflections
$\theta = 3.1–27.5°$
$\mu = 29.64$ mm^{-1}
$T = 291$ (2) K
Block, orange
$0.30 \times 0.10 \times 0.05$ mm

Data collection

Rigaku R-AXIS RAPID-S diffractometer
ω scans
Absorption correction: numerical (*NUMABS*; Higashi, 2000)
$T_{min} = 0.042$, $T_{max} = 0.220$
13705 measured reflections

3410 independent reflections
2837 reflections with $I > 2\sigma(I)$
$R_{int} = 0.060$
$\theta_{max} = 27.5°$
$h = -21 \rightarrow 23$
$k = -9 \rightarrow 8$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.074$
$S = 1.06$
3410 reflections
118 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0242P)^2 + 4.9288P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.32$ e Å^{-3}
$\Delta\rho_{min} = -0.93$ e Å^{-3}
Absolute structure: Flack (1983), with 1615 Friedel pairs
Flack parameter: 0.11 (6)

Systematic absences are consistent with the orthorhombic space groups *Pbcm* and *Pca2$_1$*. The initial positions for all atoms were determined by direct methods with the program *SHELXS97* (Sheldrick, 1997). A solution with a low figure of merit could only be found in the non-centrosymmetric space group *Pca2$_1$*. No additional symmetry, as tested by *PLATON* (Spek, 2003), was detected in this structure. The absolute structure cannot be determined from powder data because Friedel pairs are overlapped. Refinement with the positional parameters from the previous report based on the powder study (Fjellvåg *et al.*, 2001) gave a value of 0.86 (6) for the Flack

Table 1
Selected geometric parameters (Å, °).

Ge1—Se4	2.3307 (18)	Ge3—Se2	2.3587 (17)
Ge1—Se1	2.3427 (14)	Ge3—Se6	2.3630 (18)
Ge1—Se3	2.3523 (15)	Ge3—Se5	2.3689 (14)
Ge1—Se9	2.3550 (15)	Ge4—Se2	2.3553 (16)
Ge2—Se5	2.3431 (14)	Ge4—Se8	2.3600 (15)
Ge2—Se8^{i}	2.3450 (17)	Ge4—Se1^{iii}	2.3652 (14)
Ge2—Se9^{ii}	2.3580 (15)	Ge4—Se7	2.3699 (18)
Ge2—Se3	2.3628 (15)	Se6—Se7	2.3638 (14)
Ge3—Se4	2.3528 (15)		
Se4—Ge1—Se1	107.79 (7)	Se4—Ge3—Se2	102.44 (7)
Se4—Ge1—Se3	112.73 (5)	Se4—Ge3—Se6	115.74 (6)
Se1—Ge1—Se3	108.08 (5)	Se2—Ge3—Se6	107.54 (6)
Se4—Ge1—Se9	110.11 (5)	Se4—Ge3—Se5	110.86 (5)
Se1—Ge1—Se9	115.98 (5)	Se2—Ge3—Se5	106.98 (6)
Se3—Ge1—Se9	102.19 (6)	Se6—Ge3—Se5	112.37 (6)
Se5—Ge2—Se8^{i}	111.17 (7)	Se2—Ge4—Se8	100.67 (6)
Se5—Ge2—Se9^{ii}	108.85 (5)	Se2—Ge4—Se1^{iii}	106.78 (5)
Se8^{i}—Ge2—Se9^{ii}	116.55 (5)	Se8—Ge4—Se1^{iii}	113.00 (5)
Se5—Ge2—Se3	115.71 (5)	Se2—Ge4—Se7	107.77 (6)
Se8^{i}—Ge2—Se3	110.19 (5)	Se8—Ge4—Se7	115.65 (5)
Se9^{ii}—Ge2—Se3	93.49 (6)	Se1^{iii}—Ge4—Se7	111.84 (6)

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

parameter (Flack, 1983) ($wR_2 = 0.0804$). Refinement of the inverse structure, which is the setting reported in this work, leads to a Flack parameter of 0.11 (6) and an improved reliability factor ($wR_2 = 0.074$). The highest residual electron density is 1.13 Å from the Ge1 site and the deepest hole is 1.65 Å from the Se5 site. The anisotropic displacement parameters of atoms Se1, Se2 and Se5 are larger than those of the other Se atoms and this is probably due to the ample free space around those atoms.

Data collection: *RAPID-AUTO* (Rigaku, 2005); 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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