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Crystal structure of Ge_4Se_9: a new germanium selenide with Se_2 pairs breaking the edge-sharing $GeSe_4$ tetrahedra in $GeSe_2$

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Received 4th December 2000, Accepted 7th February 2001
First published as an Advance Article on the web 8th March 2001

The crystal structure of the new germanium selenide Ge_4Se_9 has been determined by powder X-ray diffraction. It shows a new feature for this class of compounds; corner sharing of tetrahedra *via* Se_2 dimers with short Se–Se bonds. Structurally, Ge_4Se_9 is related to $GeSe_2$ in that the edge-sharing tetrahedra in ambient pressure $GeSe_2$ are split by the introduction of Se_2 pairs.

Introduction

GeSe and $GeSe_2$ have long been considered to be the only binary compounds in the Ge–Se system.[1] An apparently metastable germanium selenide has, however, been reported to form on thermal evolution of glasses with composition in the range 68 to 85 at.% Se. The phase appeared to be slightly Se-rich compared to $GeSe_2$ and electron probe microanalysis indicated a composition near Ge_3Se_7.[2] It has recently been shown to be stable and to decompose peritectically to $GeSe_2$ and a liquid with $x_{Se} = 0.85 \pm 2$ at 658 ± 5 K. Electron probe microanalysis suggests the phase to contain 69.2 ± 0.6 at.% Se and the experimental density of the phase is 4.37 g cm^{-3}. It can be indexed using an orthorhombic unit cell with $a = 7.003$, $b = 17.820$ and $c = 12.082$ Å.[3] The crystal structure of this new germanium selenide, Ge_4Se_9, is presently described and the structural relationship with $GeSe_2$ discussed.

$GeSe_2$ takes a structure with $GeSe_4$ tetrahedra as the main structural entity. The connectivity between the tetrahedra is unique, with 50% edge-sharing and 50% corner-sharing tetrahedra.[4] The edge-sharing entities reduce the connectivity of the structure and $GeSe_2$ therefore has a two-dimensional structure. They and the layer like structure have also been reported for Ge–Se glasses, based on spectroscopy and diffraction measurements.[5,6] A three-dimensional $GeSe_2$ modification with just corner sharing of tetrahedra is stable for pressures above ≈1 GPa.[7–9]

Experimental

High-purity Se (99.999%) and Ge (99.999%) from Goodfellow Inc. UK were used as starting materials for the synthesis. The sample was prepared in evacuated and sealed vitreous silica ampoules. Stoichiometric amounts were annealed at 623 K for 240 h. Further details on synthesis and characterization have been published elsewhere.[3]

Powder X-ray diffraction data were collected in transmission geometry with a Siemens D5000 diffractometer using monochromatic Cu-Kα_1 radiation (germanium monochromator) and a Braun position sensitive detector (PSD). The sample was put on a Scotch magic tape using a flat transmission sample holder, for which the zero point position was adjusted manually by means of earlier measurements on silicon powder. 5129 Data points were collected between $2\theta = 10$ and 89.75°. Experiments were also conducted in Bragg–Brentano geometry. Comparison of the data showed that preferred orientation affects the measured intensities to a significant extent. This was taken as an indication of a chain or layered nature of the crystal structure.

Crystal structure analysis

The diffraction pattern was completely indexed using the program TREOR 90,[10] suggesting a unit cell with dimensions $a = 7.003$, $b = 17.820$ and $c = 12.085$ Å, $M(20) = 59$. On the basis of the measured density, $\rho_{exp} = 4.37$ g cm^{-3}, the unit cell was considered to contain four formula units of Ge_4Se_9 (calculated density 4.42 g cm^{-3}). The related hexagonal solution $a_h = 2a$, $b_h = c\sqrt{3}$ and $c_h = b$ did not give a satisfactory Le Bail fit of the observed pattern, in particular at higher angles. Careful search for systematic extinctions indicated $0kl$ to be absent for $k = 2n + 1$ and $h0l$ absent for $h + l = 2n + 1$, consistent with the space groups $Pbn2_1$ (33) or $Pbnm$ (62). Integrated intensities were extracted with EXTRA.[11] Structure solution was possible, although difficult, by direct methods (EXPO,[12] SIRPOW[13]) and subsequent cycles of refinements and Fourier difference calculations. However, the Rietveld type refinements gave large displacement parameters for some of the atoms and the fit was not satisfactory. For that reason other space groups were considered. The correct solution was obtained for space group $Pca2_1$ (note; interchange of a and b axes, $0kl$ absent for $l = 2n + 1$ and $h0l$ for $h = 2n + 1$). The direct methods approach immediately gave all the four non-equivalent Ge and nine non-equivalent Se atoms of the unit cell. This solution deviated only in certain details from the $Pbn2_1$ model.

Rietveld type refinements were performed with the GSAS program package.[14] No distance restraints were introduced (however, such are absolutely required in $Pbn2_1$). The background was modelled using a 24-term cosine Fourier series polynomial and the peak shape was described by profile function #3 in GSAS, which allows asymmetry correction in the pseudo Voigt profile function. Details on the refinements are given in Table 1. Corrections were made for preferred orientation of the crystallites using the March–Dollase model implemented in the GSAS program. Atomic coordinates are listed in Table 2, selected interatomic distances and bond angles in Table 3. The fit between observed and calculated intensities is displayed in Fig. 1.

DOI: 10.1039/b009794m

Table 1 Experimental conditions and relevant parameters for Rietveld refinement of Ge_4Se_9

Pattern range 2θ/°	10–89.75
Step size $\Delta 2\theta$/°	0.015552[a]
λ/Å	1.540598
Space group	$Pca2_1$
a/Å	17.8204(1)
b/Å	7.0029(1)
c/Å	12.0854(1)
Z	4
V/Å^3	1508.2(2)
No. observations	5129
No. reflections	675
No. refined parameters	75
R_{wp}	0.039
$R_F{}^2$	0.047

[a] As defined by the PSD setting.

Table 2 Refined atomic coordinates and displacements factors for Ge_4Se_9. Calculated standard deviations are given in parentheses. U_{iso} are 0.022 Å^2 for Ge and 0.032 Å^2 for Se. z(Se7) is fixed to zero

Atom	x	y	z
Ge1	0.2738(3)	0.8147(7)	0.1976(5)
Ge2	0.3303(2)	0.3135(7)	0.2059(5)
Ge3	0.4598(2)	0.6772(7)	0.1302(4)
Ge4	0.1477(3)	0.1798(7)	0.1444(4)
Se1	0.2550(3)	0.2989(6)	0.0529(5)
Se2	0.2865(2)	0.5612(4)	0.3333(5)
Se3	0.9927(2)	0.1710(6)	0.2985(5)
Se4	0.3203(2)	0.0415(5)	0.3278(5)
Se5	0.1476(2)	0.8402(6)	0.1505(5)
Se6	0.3507(3)	0.7984(7)	0.0400(4)
Se7	0.0533(3)	0.2587(7)	0.0000
Se8	0.4551(2)	0.3354(6)	0.1582(5)
Se9	0.1093(2)	0.3249(6)	0.2993(5)

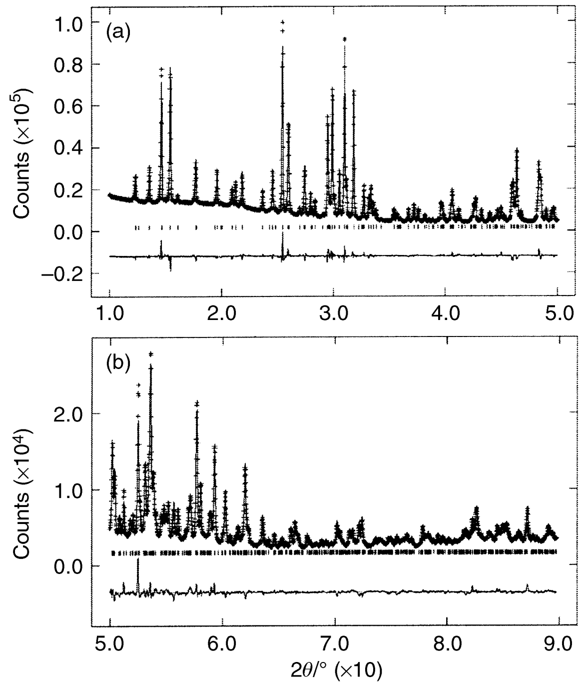

Fig. 1 Observed, calculated and difference intensity profiles for refinements of powder X-ray diffraction data of Ge_4Se_9 at 298 K (λ = 1.540598 Å).

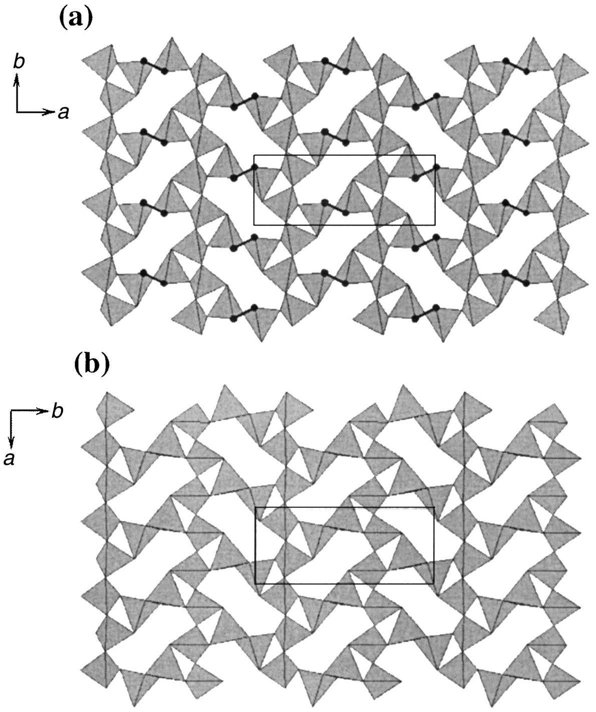

Fig. 2 Two-dimensional layers in (a) Ge_4Se_9 and (b) monoclinic $GeSe_2$. $Se_2{}^{2-}$ anion pairs are marked in black (a).

Discussion

The crystal structure of Ge_4Se_9 contains two-dimensional layers that are bonded by weak van der Waals interactions along [001]. This layered nature explains the strong tendency towards preferred orientation. The unit cell of Ge_4Se_9 has clear similarities with that of monoclinic $GeSe_2$[4] ($P2_1/c$ with a = 7.016, b = 16.796 and c = 11.831 Å, b = 90.65°). The 2D-layers of these structures are compared in Fig. 2.

The crystal structure of Ge_4Se_9 is based on tetrahedral $GeSe_4$ units that basically share corners. In one case the connection is made *via* a Se_2 pair. In monoclinic $GeSe_2$ basically the same layers and pattern of connected polyhedra exists. However, half of the tetrahedra form dimers by edge sharing. As can be seen from Fig. 3, the additional selenium in Ge_4Se_9 is introduced *via* Se_2 pairs that open up the edge-shared tetrahedra in $GeSe_2$.

The chemical formula Ge_4Se_9 can now be understood in view of the additional Se–Se pairs that connect neighbouring $GeSe_4$ tetrahedra. This structural feature is also known in the ternary germanium selenide based compounds K_2GeSe_4 and Rb_2GeSe_4[15] and $Cs_4Ge_2Se_8$.[16] K_2GeSe_4 and Rb_2GeSe_4 contain infinite chains in which $GeSe_4$ tetrahedra are linked *via* Se–Se bonds, while $Cs_4Ge_2Se_8$ contains a dinuclear anion composed of two $GeSe_4$ tetrahedra linked *via* two Se–Se bonds.

Ge_4Se_9 can be described as a valence compound $(Ge^{4+})_4(Se^{2-})_7(Se_2{}^{2-})$ with tetravalent germanium and divalent selenium as confirmed by bond valence calculations[17] (Table 4). The material is expected to remain semiconducting like $GeSe_2$. The Se–Se distance is 2.340(4) Å. This concurs well with findings in the mentioned ternary germanium selenides,[15,16] as well with pyrite- and marcasite-type selenides with separations in the range 2.33 ($CuSe_2$[18]) to 2.54 Å ($FeSe_2$[18]).

Edge-sharing tetrahedra and a layer like structure have been proposed for Ge–Se glasses based on spectroscopy and diffraction measurements.[5,6] Ge–Se liquids with composition near $GeSe_2$ are strong glass formers and the main structural entities in the corresponding crystals are expected to be retained in the liquid. However, since Ge_4Se_9 decomposes peritectically to $GeSe_2$ and a selenium rich melt at 658 K, the new findings do not exclude edge-sharing tetrahedra in the melt. Temperature induced changes in the structure of the undercooled melt and corresponding differences between the structure of melts and

Table 3 Selected interatomic distances (Å) and bond angles (°) for Ge_4Se_9. Calculated standard deviations in parentheses

Ge1–Se2	2.347(6)	Se2–Ge1–Se4	94.5(3)
Ge1–Se4	2.306(7)	Se2–Ge1–Se5	108.0(2)
Ge1–Se5	2.327(6)	Se2–Ge1–Se6	115.6(3)
Ge1–Se6	2.349(7)	Se4–Ge1–Se5	116.6(3)
		Se4–Ge1–Se6	109.6(3)
		Se5–Ge1–Se6	111.7(3)
Ge2–Se1	2.287(8)	Se1–Ge2–Se2	108.8(3)
Ge2–Se2	2.372(7)	Se1–Ge2–Se4	112.7(3)
Ge2–Se4	2.343(6)	Se1–Ge2–Se8	108.7(3)
Ge2–Se8	2.336(5)	Se2–Ge2–Se4	103.0(3)
		Se2–Ge2–Se8	116.4(3)
		Se4–Ge2–Se8	107.4(2)
Ge3–Se3	2.369(7)	Se3–Ge3–Se6	115.7(2)
Ge3–Se6	2.385(7)	Se3–Ge3–Se7	108.4(3)
Ge3–Se7	2.335(6)	Se3–Ge3–Se8	112.2(3)
Ge3–Se8	2.405(6)	Se6–Ge3–Se7	101.8(3)
		Se6–Ge3–Se8	111.5(3)
		Se7–Ge3–Se8	106.1(3)
Ge4–Se1	2.306(8)	Se1–Ge4–Se5	113.3(3)
Ge4–Se5	2.387(6)	Se1–Ge4–Se7	102.1(3)
Ge4–Se7	2.404(7)	Se1–Ge4–Se9	116.7(3)
Ge4–Se9	2.339(7)	Se5–Ge4–Se7	106.5(2)
		Se5–Ge4–Se9	111.3(3)
		Se7–Ge4–Se9	105.7(2)
Se1–Ge2	2.287(8)		
Se1–Ge4	2.306(8)	Ge2–Se1–Ge4	99.1(3)
Se2–Ge1	2.347(6)		
Se2–Ge2	2.372(7)	Ge1–Se2–Ge2	101.4(3)
Se3–Ge3	2.369(7)		
Se3–Se9	2.340(4)	Ge3–Se3–Se9	90.9(3)
Se4–Ge1	2.306(7)		
Se4–Ge2	2.343(6)	Ge1–Se4–Ge2	102.9(3)
Se5–Ge1	2.327(6)		
Se5–Ge4	2.387(6)	Ge1–Se5–Ge4	95.5(2)
Se6–Ge1	2.349(7)		
Se6–Ge3	2.385(7)	Ge1–Se6–Ge3	97.0(3)
Se7–Ge3	2.335(6)		
Se7–Ge4	2.404(7)	Ge3–Se7–Ge4	95.1(2)
Se8–Ge2	2.336(5)		
Se8–Ge3	2.405(6)	Ge2–Se8–Ge3	97.2(3)
Se9–Ge4	2.339(7)		
Se9–Se3	2.340(4)	Ge4–Se9–Se3	93.3(3)

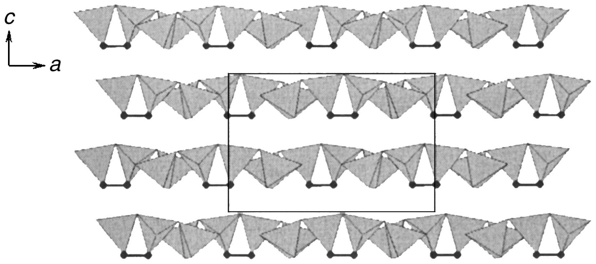

Fig. 3 Packing of 2-D layers and position of Se_2^{2-} anion pairs connecting $GeSe_4$ tetrahedra in Ge_4Se_9. Projection of the structure along [010].

Table 4 Calculated bond valences for Ge_4Se_9

	Ge1	Ge2	Ge3	Ge4	Se3	Se9	Σ
Se1		1.19		1.13			2.32
Se2	1.01	0.94					1.95
Se3			0.95			1.06	2.01
Se4	1.13	1.02					2.15
Se5	1.06			0.90			1.96
Se6	1.00		0.91				1.91
Se7			1.04	0.86			1.90
Se8		1.04	0.98				2.02
Se9				1.03	1.06		2.09
Σ	4.20	4.19	3.88	3.92			

glasses should, however, be considered. Large temperature induced changes in the intermediate-range order in liquid $GeSe_2$ have recently been suggested based on neutron diffraction[19] and first-principles molecular dynamics.[20]

The volume of Ge_4Se_9 is about 0.3% larger than that of a corresponding two-phase mixture of $GeSe_2$ and Se. Ge_4Se_9 is accordingly (assuming the bulk modulus to be equal for Ge_4Se_9 and a corresponding mixture of $GeSe_2$ and Se) destabilized by pressure.

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