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$Pr_4Ge_3S_{12}$: structure determination from high-resolution powder diffraction data

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Key indicators

Powder synchrotron study
T = 293 K
Mean σ(Ge–S) = 0.009 Å
R factor = 0.084
wR factor = 0.108
Data-to-parameter ratio = 16

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The structure of praseodymium germanium sulfide, $Pr_4Ge_3S_{12}$, has been determined in the course of the determination of the amount of contamination of the title compound by the starting products. Its structure was assumed to be isostructural with the structure of $La_4Ge_3S_{12}$. One Pr atom lies on a threefold axis.

Comment

The title compound belongs to a class of materials that are of great interest for optical telecommunication systems because of their qualities as amplifiers (Simons, 1995). The Ge atom is tetrahedrally surrounded by S atoms, while both Pr atoms are surrounded by a trigonal prism of six S atoms, with the 'square' faces capped by three further S atoms at larger distances. These surroundings are displayed in Figs. 1, 2 and 3, respectively. Checking the bond valences (Brown, 2000) of the compound results in a Global Instability Index (GII; the r.m.s. deviation between the bond valence sums and the formal ionic charge) of 0.26. This deviation is mainly caused by atom S2, which has a bond valence of 2.50, and indicates that the S2 bonds are too short. However, performing the same calculations for the isostructural compound $La_4Ge_3S_{12}$, which has been refined from single-crystal data (Mazurier & Etienne, 1974), gives a deviation of the same order of magnitude for the GII (0.21) and the bond valence of atom S2 (2.40), indicating that this deviation is inherent in the structure.

Experimental

$Pr_4Ge_3S_{12}$ was prepared by melting the starting materials GeS_2 and Pr_2S_3 in a sealed silica ampoule in a vacuum of 10^{-1}–10^{-2} kPa. The ampoule was rotated (horizontally) at the glass melting temperature of 1273 K for at least 8 h in order to mix the constituents thoroughly; the contents were allowed to crystallize and then remelted over a

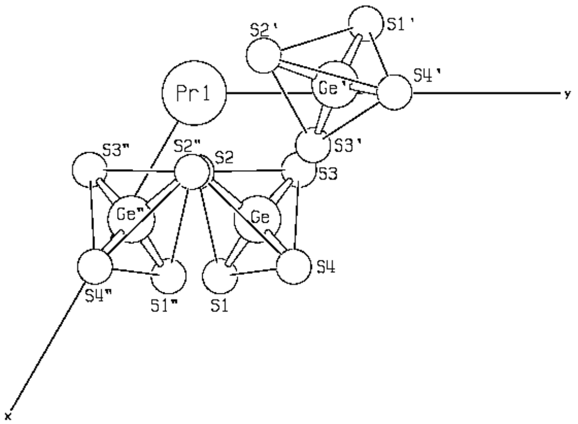

Figure 1
The tetrahedral surrounding of Ge by S atoms.

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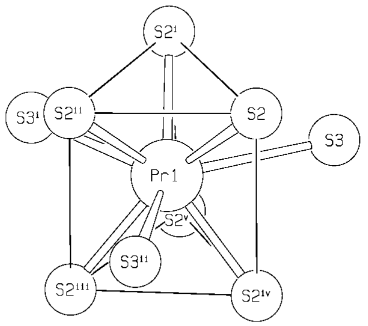

Figure 2
The prismatic surrounding of Pr1 by S atoms and the three extra S3 atoms (S′) at a longer distance capping the 'square' faces.

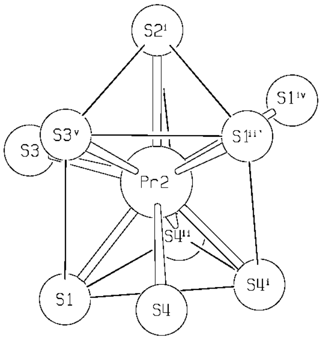

Figure 3
The same as Fig. 2 for the prismatic surrounding of Pr2; $S1_{iv}$, S3 and S4 are the three extra capping S atoms at longer distances.

period of about 4 h. Several Guinier–Johannson photographs were taken using Cu $K\alpha_1$ radiation ($\lambda = 1.54056$ Å) at different exposure times to collect very weak and very strong reflections. Using a Johannson LS18 microdensitometer, the Guinier films were digitized in steps of 0.01° 2θ. From these data, the following cell parameters have been obtained using the program *LSPAID* (Visser, 1986): $a = b = 19.29$ (1) Å and $c = 7.983$ (5) Å. From the extinctions, the rhombohedral space group $R3c$ was obtained. The XRPD pattern of the compound has been recorded at the high-resolution X-ray powder diffraction station at beamline BM16 (ESRF, Grenoble, France; Fitch, 1996) with a fixed wavelength of $\lambda = 0.65296$ Å. A 0.5 mm capillary filled with powder was rotated during exposure. Continuous scans were made from 0.5 to 47.98° 2θ, with a rate of 0.5° 2θ min^{-1} and a sampling time of 50 ms, and were binned at 0.002° 2θ.

Crystal data

$Pr_4Ge_3S_{12}$
$M_r = 1166.18$
Trigonal, $R3c$
$a = 19.2856$ (1) Å
$c = 7.98049$ (3) Å
$V = 2570.55$ (2) Å^3
$Z = 6$
$D_x = 4.52$ Mg m^{-3}
Synchrotron radiation
Wavelength of incident radiation: 0.65296 Å
Cell parameters from 38 reflections
$\theta = 9$–49°
$\mu = 12.86$ mm^{-1}
$T = 293$ (1) K
Cylinder, green
Specimen prepared at 0.05 (5) kPa, 1273 K

Data collection

ESRF BM16 diffractometer
ESRF Grenoble
Specimen mounting: glass capillary
Specimen mounted in transmission mode
Absorption correction: cylindrical (*ABSCYL*; Lelieveld, R. & Helmholdt, R. B., unpublished)
$T_{\min} = 0.012$, $T_{\max} = 0.023$
349 measured reflections
$2\theta_{\min} = 3.0$, $2\theta_{\max} = 40.0°$
Increment in $2\theta = 0.002°$

Refinement

$R_p = 0.084$
$R_{wp} = 0.108$
$R_{exp} = 0.031$
$S = 3.5$
The following 12 excluded regions were introduced because some contamination is present: 8.532–8.768, 9.682–9.750, 10.856–10.990, 11.198–11.268, 11.992–12.216, 13.134–13.196, 14.256–14.372, 14.952–15.094, 15.768–15.910, 17.294–17.440, 20.016–20.154, 21.064–21.952
Profile function: pseudo-Voigt
63 parameters

Table 1
Selected interatomic distances (Å).

Pr1^{i}—S2^{ii}	2.836 (7)	Pr2^{i}—S3^{iii}	2.995 (8)
Pr1^{i}—S2^{iii}	2.889 (7)	Pr2^{i}—S3^{vii}	3.028 (8)
Pr1^{i}—S3^{iv}	3.409 (7)	Pr2^{i}—S1^{viii}	3.546 (8)
Pr2^{i}—S4^{ii}	2.830 (7)	Pr2^{i}—S4^{ix}	3.702 (8)
Pr2^{i}—S1^{i}	2.884 (7)	Ge^{ii}—S2^{ii}	2.178 (9)
Pr2^{i}—S2^{ii}	2.932 (7)	Ge^{ii}—S3^{iv}	2.186 (8)
Pr2^{i}—S4^{v}	2.933 (8)	Ge^{ii}—S1^{viii}	2.196 (8)
Pr2^{i}—S1^{vi}	2.976 (8)	Ge^{ii}—S4^{x}	2.203 (8)

Symmetry codes: (i) $\frac{2}{3}+x, \frac{1}{3}+y, \frac{1}{3}+z$; (ii) $\frac{2}{3}-y, \frac{1}{3}+x-y, \frac{1}{3}+z$; (iii) $\frac{2}{3}-x+y, \frac{1}{3}+y, z-\frac{1}{6}$; (iv) $\frac{2}{3}-y, \frac{1}{3}+x-y, z-\frac{2}{3}$; (v) $1-x+y, 1-x, z$; (vi) $\frac{1}{3}-x+y, \frac{2}{3}-x, \frac{2}{3}+z$; (vii) $\frac{2}{3}+x, \frac{1}{3}+y, z-\frac{2}{3}$; (viii) $\frac{1}{3}+x, \frac{2}{3}+x-y, \frac{1}{6}+z$; (ix) $\frac{1}{3}+x, \frac{2}{3}+y, \frac{2}{3}+z$; (x) $x, x-y, \frac{1}{2}+z$.

Table 2
Full pattern decomposition results for different models.

	A	*B*	*C*	*D*
R	0.094	0.073	0.075	0.097
R_{wp}	0.149	0.094	0.100	0.157
GOF	5.5	3.5	3.9	6.1

2θ range 3–23°; *A*: only one phase ($Pr_4Ge_3S_{12}$); *B*: one phase ($Pr_4Ge_3S_{12}$ + 12 excluded regions); *C*: two phases [$Pr_4Ge_3S_{12}$ + GeS_2(HT)]; *D*: two phases ($Pr_4Ge_3S_{12}$ + Pr_2S_3).

Table 3
Rietveld refinement results for different models.

	A	*B*	*C*	*D*
R	0.099	0.084	0.099	0.100
R_{wp}	0.148	0.108	0.147	0.148
GOF	4.8	3.5	4.8	4.8
$Pr_4Ge_3S_{12}$ (%)	100.0	100.0	97.9	98.6
GeS_2/Pr_2S_3 (%)	–	–	0.8	0.0

2θ range 3–40°; *A*: only one phase ($Pr_4Ge_3S_{12}$); *B*: one phase ($Pr_4Ge_3S_{12}$ + 12 excluded regions); *C*: two phases [$Pr_4Ge_3S_{12}$ + GeS_2(HT)]; D: two phases ($Pr_4Ge_3S_{12}$ + Pr_2S_3)

$Pr_4Ge_3S_{12}$ belongs to a class of rare earth compounds with general formula $M_4Ge_3S_{12}$, of which the structure of $La_4Ge_3S_{12}$ has been determined by Mazurier & Etienne (1974). The atomic coordinates of that structure have been taken as starting coordinates for solving the structure of $Pr_4Ge_3S_{12}$. The intensities have been corrected for absorption ($\mu = 128.58$ cm^{-1}), assuming an apparent density of 50%. The full pattern decomposition (FPD) procedure in MRIA suggests that the extra peaks in the diffractogram may be assigned to a second phase, *e.g.* one of the starting materials (GeS_2, high-temperature modification; Dittmar and Schäfer, 1975). Similar R_p and S values are obtained for the FPD procedure with 12 excluded regions as for the FPD procedure with two phases (*e.g.* $Pr_4Ge_3S_{12}$ and GeS_2; columns *B* and *C* of Table 1). The Rietveld refinement procedure was applied to the 2θ range 3–40°, resulting in R_p, R_{wp} and goodness of fit (GOF)

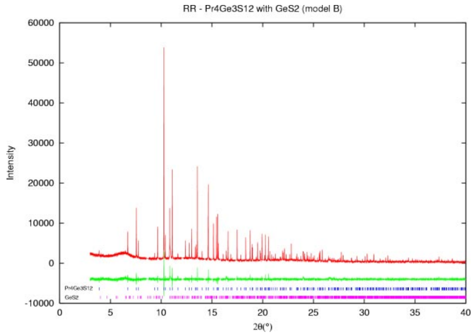

Figure 4
Synchrotron powder diffraction pattern of $Pr_4Ge_3S_{12}$. The upper pattern is the observed pattern and the lower pattern is the difference between the observed and calculated patterns. The reflection positions are indicated for $Pr_4Ge_3S_{12}$ and GeS_2, respectively.

values of, respectively, 0.084, 0.108 and 3.5. To obtain these results, 12 regions in the diffractogram have to be excluded because they contain peaks that could not be accounted for by the space group *R*3*c*. Although nine of these peaks are very close to the peak positions of the high-temperature phase of GeS_2, a multiphase refinement did not result in a better fit. This multiphase refinement shows that about 1% of the powder consists of GeS_2, while the height of the extra diffraction peaks is not explained by this contamination (see Table 2 and Fig. 4). The full pattern decomposition, on the other hand, strongly benefits from this second phase (Table 1). The interatomic distances are given in Table 3.

Cell refinement: *LSPAID* (Visser, 1986); data reduction: *MRIA* (Zlokazov & Chernysev, 1992); program(s) used to refine structure: *GSAS* (Larson & Von Dreele, 1985–2000); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *VaList* (Wills & Brown, 1999) and *Xtal* (Hall *et al.*, 1995).

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