Crystal structure of tetracesium decasulfidotetragermanate, $Cs_4Ge_4S_{10}$

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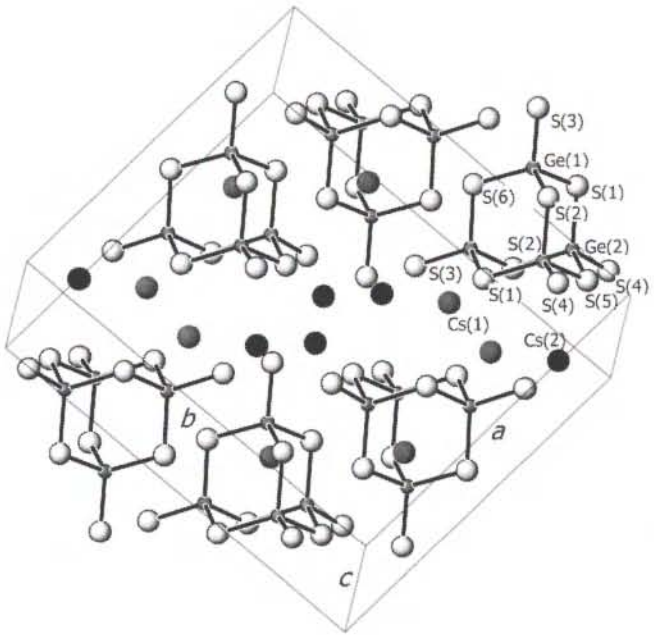

Abstract

$Cs_4Ge_4S_{10}$, monoclinic, $C12/c1$ (No. 15), a = 15.714(3) Å, b = 15.858(2) Å, c = 9.491(2) Å, β = 106.74(2)°, V = 2264.9 Å^3, Z = 4, $R_{gt}(F)$ = 0.027, $wR(F)$ = 0.025, T = 294 K.

Source of material

The title compound was prepared by reacting Cs_2S (627 mg = 2.104 mmol), obtained from high purity elements in liquid ammonia with GeS_2 (573 mg = 4.19 mmol) at 1123 K in an evacuated silica ampoule, allowing the melt to attain ambient temperature at a controlled rate of 2 K min^{-1}. The reaction product was of homogeneous appearance and consisted of polyhedral crystals of globular shape.

Discussion

The crystal structure of $Cs_4Ge_4S_{10}$ is characterized by the formation of discrete adamantane like complex anions $[Ge_4S_{10}]^{4-}$ built up by four corner sharing GeS_4 tetrahedra. Bonds to bridging sulfur atoms lie within a narrow range (d(Ge—S)$_b$ from 2.223(2) Å to 2.245(2) Å). Bond lengths for the terminal sulfur atoms are 2.113 Å and 2.119 Å, respectively. The mean Ge—S bond length in the anion is 2.208 Å, somewhat shorter than the sum of the crystal radii for tetracoordinate Ge and S (2.230 Å) [1]. The atomic arrangement of $Cs_4Ge_4S_{10}$ corresponds to $Ba_4Ga_4S_{10}$ [2] with which it is isoelectronic. The crystal structure determination of $Cs_4Ge_4S_{10}$ completes the series of chalcogenogermanates, $A_4Ge_4Q_{10}$, (A = Na-Cs, Q = S, Se) all of which were found to contain adamantane type anions. Depending on the radius ratio $r(A^+)/r(Q^{2-})$ three different structure types are adopted. Both sodium compounds, $Na_4Ge_4S_{10}$ [3] and $Na_4Ge_4Se_{10}$ [4], are isostructural with $Na_4Si_4S_{10}$ [3] while $K_4Ge_4Se_{10}$ crystallizes with an idiosyncratic structure [5]. $K_4Ge_4S_{10}$, $Rb_4Ge_4S_{10}$, $Rb_4Ge_4Se_{10}$ as well as $Cs_4Ge_4Se_{10}$ are isostructural and crystallize with the $Ba_4Ga_4S_{10}$ type [6]. $Cs_4Ge_4S_{10}$ characterized by the highest $r(A^+)/r(Q^{2-})$ value still follows this trend. On the other hand the compound with the lowest radius ratio, $Na_4Ge_4Se_{10}$, is actually dimorphic. Its second modification is characterized by infinite anionic layers formed by corner sharing $GeSe_4$ tetrahedra [7].

Table 1. Data collection and handling.

Crystal:	colourless, polyhedral, size 0.05 × 0.05 × 0.05 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	123.58 cm^{-1}
Diffractometer, scan mode:	Enraf-Nonius CAD4, θ/2θ
$2\theta_{max}$:	53.94°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2648, 2462
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 3\ \sigma(I_{obs})$, 1956
$N(param)_{refined}$:	84
Programs:	MolEN [8], ATOMS [9]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cs(1)	8*f*	0.15335(3)	0.36379(3)	0.87171(5)	0.0380(2)	0.0346(2)	0.0305(2)	–0.0083(2)	0.0083(2)	0.0004(2)
Cs(2)	8*f*	0.13530(3)	0.07036(3)	0.64501(5)	0.0374(2)	0.0373(2)	0.0328(2)	–0.0006(2)	0.0151(1)	–0.0082(2)
Ge(1)	8*f*	0.10476(4)	0.36854(4)	0.39799(7)	0.0232(3)	0.0208(3)	0.0244(3)	–0.0037(3)	0.0089(2)	–0.0019(3)
Ge(2)	8*f*	0.43581(4)	0.29524(4)	0.87865(7)	0.0243(3)	0.0204(3)	0.0210(3)	0.0025(3)	0.0119(2)	0.0003(3)
S(1)	8*f*	0.1694(1)	0.2855(1)	0.2654(2)	0.0239(7)	0.0302(9)	0.0326(8)	–0.0013(7)	0.0119(6)	–0.0054(7)
S(2)	8*f*	0.4580(1)	0.2169(1)	0.4718(2)	0.0329(8)	0.0285(8)	0.0227(7)	–0.0089(7)	0.0117(6)	–0.0035(7)

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Table 2. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(3)	8*f*	0.2030(1)	0.4424(1)	0.5452(2)	0.0302(8)	0.0304(9)	0.0289(8)	–0.0100(7)	0.0077(6)	–0.0041(7)
S(4)	8*f*	0.1157(1)	0.1304(1)	0.9794(2)	0.0376(8)	0.0327(9)	0.0274(7)	0.0074(7)	0.0183(6)	–0.0047(7)
S(5)	4*e*	0	0.1197(1)	1/4	0.035(1)	0.019(1)	0.029(1)	0	0.0182(8)	0
S(6)	4*e*	0	0.4495(2)	1/4	0.033(1)	0.022(1)	0.044(1)	0	0.003(1)	0

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