Crystal structure of tetrarubidium hexathiodigermananate(IV), $\text{Rb}_4\text{Ge}_2\text{S}_6$

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Abstract

$\text{Ge}_2\text{Rb}_4\text{S}_6$, monoclinic, $C12/m1$ (No. 12), $a = 13.43(5)$ Å, $b = 6.898(3)$ Å, $c = 11.15(3)$ Å, $\beta = 135.06(9)^\circ$, $V = 729.7$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.043$, $wR_{\text{ref}}(F) = 0.052$, $T = 296$ K.

Source of material

Colourless single crystals of $\text{Rb}_4\text{Ge}_2\text{S}_6$ were obtained by reacting an intimate mixture of 875.8 mg Rb_2S (prepared from the elements in liquid ammonia), 209.5 mg 99.999 % Ge and 139 mg 99.99 % S (approximate molar ratio 3:2:3) in a sealed and evacuated silica tube. The sample was gradually heated to 1073 K, held at this temperature for 12 h and allowed to cool to ambient temperature at a controlled rate of 4 K/h.

Discussion

The crystal structure of $\text{Rb}_4\text{Ge}_2\text{S}_6$ is characterized by binuclear complex anions built up by two edge sharing GeS_4 tetrahedra (shortest interanionic contact $d(\text{S1}—\text{S1}) = 3.550(4)$ Å). The bond lengths of the two independent terminal $\text{Ge}—\text{S}$ bonds ($d(\text{Ge}—\text{S2}) = 2.150(2)$ Å, $d(\text{Ge}—\text{S3}) = 2.153(2)$ Å) are significantly shorter than the bridging $\text{Ge}—\text{S}$ bonds ($d(\text{Ge1}—\text{S1}) = 2.289(2)$ Å). In accord with this findings the bond angle involving the terminal

chalcogen ligands deviates considerably from the ideal tetrahedral value ($\angle \text{S2}—\text{Ge}—\text{S3} = 118.22(8)^\circ$) as does that involving the bridging atoms ($\angle \text{S1}—\text{Ge}—\text{S1} = 93.68(8)^\circ$). The symmetry of the anion is close to D_{2h} . The coordinations of the two alkali cations differ appreciably. Rb(1) is in a distorted square pyramidal chalcogen coordination ($d(\text{Rb1}—\text{S}) = 3.357(2)$ Å to $3.485(1)$ Å). Two S atoms cap the basal plane at a considerably larger distance ($d(\text{Rb}—\text{S1}) = 3.870(1)$ Å) while Rb(2) is in a true seven-fold coordination with bond distances ranging from $3.274(2)$ Å to $3.488(1)$ Å. The crystal structure of $\text{Rb}_4\text{Ge}_2\text{S}_6$ may be rationally described as a stacking of virtually planar mixed atom layers which run parallel to $(10\bar{2})$ and are formed by the alkali and chalcogen atoms occupying the nodes of a complex square-triangle net. Tetrahedral interstices between these layers host the Ge atoms.

The crystal structure of $\text{Rb}_4\text{Ge}_2\text{S}_6$ is isotypic with that of $\text{Cs}_4\text{Sn}_2\text{Se}_6$ [1] and $\text{Rb}_4\text{Ge}_2\text{Se}_6$ [2]. A less symmetric variant of this atomic arrangement is realized with the $\text{Ti}_4\text{Ge}_2\text{S}_6$ structure type (space group $P\bar{1}$, $Z = 1$) [3] which is also adopted by $\text{Ti}_4\text{Ge}_2\text{Se}_6$ [4], $\text{K}_4\text{Ge}_2\text{Se}_6$ [5], $\text{K}_4\text{Sn}_2\text{Se}_6$ [6] and $\text{Rb}_4\text{Sn}_2\text{Se}_6$ [7].

Table 1. Data collection and handling.

Crystal:	colourless, irregular fragment, size $0.15 \times 0.18 \times 0.20$ mm
Wavelength:	Mo $K\alpha$ radiation (0.7107 Å)
μ :	181.71 cm^{-1}
Diffractometer, scan mode:	Enraf Nonius CAD4, $\omega/2\theta$
$2\theta_{\text{max}}$:	53.9°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	902, 864
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 775
$N(\text{param})_{\text{refined}}$:	36
Programs:	SIR92 [8], Crystal Structure [9], DIFABS [10], ATOMS [11]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rb(1)	4i	$-0.1223(1)$	0	$0.1861(1)$	$0.0310(5)$	$0.0418(5)$	$0.0206(4)$	0	$0.0156(4)$	0
Rb(2)	4i	$0.28174(9)$	0	$0.3629(1)$	$0.0274(4)$	$0.0361(5)$	$0.0144(4)$	0	$0.0141(3)$	0
Ge(1)	4i	$0.43522(8)$	0	$0.81595(9)$	$0.0170(4)$	$0.0237(4)$	$0.0071(4)$	0	$0.0071(3)$	0
S(1)	4g	$1/2$	$0.2426(3)$	0	$0.037(1)$	$0.0213(8)$	$0.0116(8)$	0	$0.0131(8)$	0
S(2)	4i	$0.5697(2)$	0	$0.7754(3)$	$0.022(1)$	$0.048(1)$	$0.019(1)$	0	$0.0144(9)$	0
S(3)	4i	$0.2107(2)$	0	$0.5969(2)$	$0.0165(9)$	$0.038(1)$	$0.0114(9)$	0	$0.0066(8)$	0

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