Crystal structure of tetrarubidium tetrathioostannate(IV), Rb_4SnS_4

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Abstract

Rb_4SnS_4 , cubic, $P\bar{4}3n$ (No. 218), $a = 13.4524(7)$ Å, $V = 2434.4$ Å³, $Z = 8$, $R_{\text{gt}}(F) = 0.036$, $wR_{\text{obs}}(F) = 0.028$, $T = 294$ K.

Source of material

Colourless single crystals of Rb_4SnS_4 were obtained by prolonged annealing of an intimate mixture of Rb_2S , Sn and S (molar ratio 2:1:2) in a sealed silica ampoule at 673 K, followed by controlled cooling to ambient temperature at a constant cooling rate of $3 \text{ K} \cdot \text{h}^{-1}$.

Discussion

The crystal structure of Rb_4SnS_4 is characterized by the formation of discrete tetrahedral complex anions, $[\text{SnS}_4]^{4-}$. The atomic arrangement (see upper figure) is isostructural with Ba_4SiAs_4 [1]. The Sn—S bond lengths in the two crystallographically independent anions are identical within experimental error: ($d(\text{Sn1—S1}) = 2.378(2)$ Å, $d(\text{Sn2—S2}) = 2.378(3)$ Å). The Rb^+ cations are coordinated to 6 S in distorted octahedral configurations. They cap the triangular faces of the tetrahedra, forming stellae quadrangulae (see lower figure) which are connected with each other via the remaining three Rb—S bonds ($d(\text{Rb1—S2}) = 3.383(4)$ Å (3×); $d(\text{Rb2—S1}) = 3.298(4)$ Å, $3.333(2)$ Å and $3.389(4)$ Å). Rb_4SnS_4 is the only chalcogenostannate so far which crystallizes with the Ba_4SiAs_4 structure. As a contrast the chalcogenogermanates A_4GeQ_4 ($\text{A} = \text{K}, \text{Rb}, \text{Cs}$; $\text{Q} = \text{S}, \text{Se}$) [2] uniformly adopt this structure type which has also been reported for the chalcogenosilicates Cs_4SiSe_4 [3] and Cs_4SiTe_4 [4]. Samples of Rb_4SnS_4 when prepared from the melt, however, yield a hexagonal phase with $a = 20.53(2)$ Å, $c = 10.773(8)$ Å, probable space group $P6_322$. Similar cell metrics have been reported in 1978 for K_4TiS_4 [5] (structure unknown). If the structure determination corroborates the anticipated formula type, Rb_4SnS_4 would be the first among the complex ionic $\text{A}_4[\text{MX}_4]$ compounds to exhibit dimorphism.

Table 1. Data collection and handling.

Crystal:	colourless prismatic fragment, size $0.05 \times 0.08 \times 0.08$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	181.77 cm^{-1}
Diffractionmeter, scan mode:	Enraf-Nonius CAD4, $\theta/2\theta$
$2\theta_{\text{max}}$:	53.92°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	2648, 969
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 3 \sigma(I_{\text{obs}})$, 522
$N(\text{param})_{\text{refined}}$:	29
Programs:	MolEN [6], ATOMS [7]

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}
Sn(1)	2a	0	0	0	0.0155(6)	U_{11}	U_{11}	0	0	0
Sn(2)	6d	$1/4$	0	$1/2$	0.0165(7)	0.0141(4)	U_{22}	0	0	0
Rb(1)	8e	0.65438(9)	x	x	0.0297(5)	U_{11}	U_{11}	$-0.0028(6)$	U_{12}	U_{12}
Rb(2)	24i	0.41629(8)	0.1534(1)	0.36292(8)	0.0263(6)	0.0303(6)	0.0282(6)	$-0.0021(6)$	0.0010(6)	0.0030(5)
S(1)	8e	0.3980(2)	x	x	0.028(1)	U_{11}	U_{11}	$-0.008(1)$	U_{12}	U_{12}
S(2)	24i	0.1537(2)	0.1114(2)	0.4022(2)	0.025(2)	0.024(1)	0.029(2)	0.006(2)	$-0.006(1)$	0.005(1)

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