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Rubidium thiogallate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(Ga–S) = 0.006 Å
R factor = 0.053
wR factor = 0.186
Data-to-parameter ratio = 19.7

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

$RbGaS_2$, for which only cell parameters were previously known, consists of GaS_2 layers interleaved with Rb atoms.

Comment

There are eight AGaS$_2$ (A = alkali metal, Tl, Cu and Ag) compounds known. They contain gallium in tetrahedral coordination and have four types of diverse structures, ranging from one-dimensional to three-dimensional. For $RbGaS_2$ and $TlGaS_2$, only unit-cell parameters are available, whereas for the five AGaS$_2$ (A = Li, K, Cs, Ag Cu) compounds, structures have been determined by single-crystal X-ray diffraction. $LiGaS_2$ is derived from zincite, wherein Li and Ga atoms occupy the tetrahedral sites in an hcp array of S atoms in an ordered fashion (Leal-Gonzalez *et al.*, 1990). The structure of $KGaS_2$ was solved in the non-centrosymmetric space group *Aa* (Lemoine *et al.*, 1984) but is actually the same as that of layered $TlGaSe_2$, with the centrosymmetric space group *C*2/*c* (Müller & Hahn, 1978; Henkel *et al.*, 1982). $NaGaS_2$, $RbGaS_2$ and $TlGaS_2$ are believed to have the same $TlGaSe_2$ structure

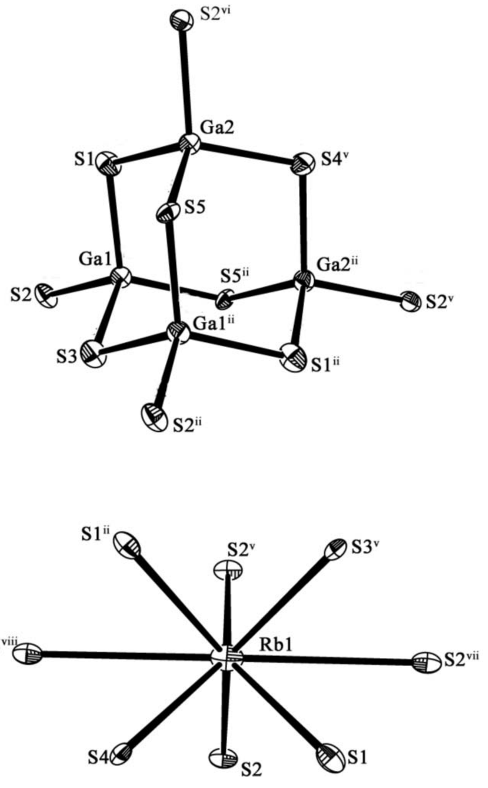

Figure 1
ORTEP-3 (Farrugia, 1997) diagrams of the tetrahedral Ga_4S_{10} unit (top) and bicapped trigonal prism of $Rb1S_8$ (bottom). Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes as in Table 1.]

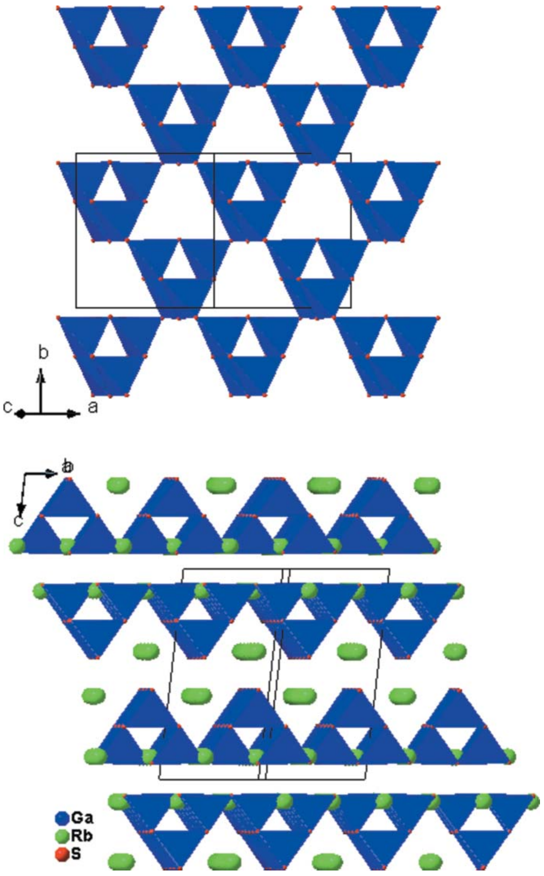

Figure 2
Polyhedral representation of the GaS_2 layer viewed along [101] (top), and the unit cell contents of $RbGaS_2$ viewed along the *a* axis (bottom).

(Hoppe, 1965; Schubert & Hoppe, 1970; Klepp, 1992; Müller *et al.*, 1974). $CsGaS_2$ is a one-dimensional compound, in which a GaS_4 tetrahedron shares edges with two other tetrahedra to form GaS_2 chains that are separated by Cs atoms (Schmitz & Bronger, 1975). $CuGaS_2$ and $AgGaS_2$ compounds are of chalcopyrite type (Abrahams & Bernstein, 1973*a*,*b*). We report here the single-crystal X-ray structure of $RbGaS_2$, confirming that it is isotypic with $TlGaSe_2$. It is noteworthy that the crystal structure elucidation of $RbGaS_2$ has so far remained elusive, because of twinning and stacking faults that are common for crystals of such layered compounds (Kienle *et al.*, 2004). $KInS_2$ (Lowe-Ma *et al.*, 1991; Eisenmann & Hofmann, 1991*a*), $KInSe_2$ (Krebs, 1983), $RbInS_2$ (Müller & Hahn, 1978), $CsInS_2$, $KTlS_2$, $RbTlS_2$, $CsTlS_2$ (Schubert & Hoppe, 1970), $TlAlSe_2$, $TlAlS_2$, $TlInS_2$ (Müller *et al.*, 1974) and $NaAlSe_2$ (Eisenmann & Hofmann, 1991*b*) are the other known compounds with the $TlGaSe_2$ structure.

In $RbGaS_2$, four GaS_4 tetrahedra form adamantane-like Ga_4S_{10} units (Fig. 1). These units are connected by corners to one another to give rise to GaS_2 layers, which are stacked along the *c* axis and interleaved with Rb atoms (Fig. 2). The Rb atoms have bicapped trigonal prismatic coordination, as shown for Rb1 in Fig. 1. Bond lengths and angles compare well with those reported in the literature (Devi & Vidyasagar, 2002; Schmitz & Bronger, 1975; Lemoine *et al.*, 1984; Yao & Ibers, 2004).

Experimental

The chemicals used for synthesis were of greater than 99% purity and were purchased from CERAC Inc. and Alfa Aesar. A mixture of Rb_2CO_3 (0.2 g, 0.086 mmol), Ga_2S_3 (0.0139 g, 0.059 mmol) and S (0.1388 g, 4.32 mmol) was sealed in an evacuated fused-silica tube of 13 cm length and 1.3 cm diameter, heated in a furnace at 1023 K for 4 d and then cooled to room temperature over a period of 4 d. The product was washed with water to dissolve away the rubidium polysulfide flux, enabling the isolation of single-phase $RbGaS_2$ in the form of plate-like red–brown crystals (0.0608 g, 75% based on Ga_2S_3). The powder X-ray diffraction pattern of the sample compares well with that simulated using the program *LAZY PULVERIX* (Yvon *et al.*, 1977) on the basis of the single-crystal X-ray structure.

Crystal data

$RbGaS_2$
$M_r = 219.31$
Monoclinic, $C2/c$
$a = 10.484\ (15)$ Å
$b = 10.468\ (15)$ Å
$c = 15.390\ (16)$ Å
$\beta = 99.69\ (10)^\circ$
$V = 1665\ (4)$ Å^3
$Z = 16$

$D_x = 3.499$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10$–15°
$\mu = 18.99$ mm^{-1}
$T = 293\ (2)$ K
Block, brown
$0.2 \times 0.1 \times 0.1$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.076$, $T_{max} = 0.150$
3083 measured reflections
1476 independent reflections
895 reflections with $I > 2\sigma(I)$

$R_{int} = 0.077$
$\theta_{max} = 25.0^\circ$
$h = -12 \rightarrow 8$
$k = -12 \rightarrow 8$
$l = -18 \rightarrow 18$
2 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.186$
$S = 1.19$
1476 reflections
75 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0817P)^2 + 20.9393P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.32$ e Å^{-3}
$\Delta\rho_{min} = -1.35$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.00029 (8)

Table 1
Selected interatomic distances (Å).

Ga1—S1	2.263 (5)	Rb1—S2^{vi}	3.380 (6)
Ga1—S3^{i}	2.268 (6)	Rb1—S1^{vii}	3.384 (6)
Ga1—S5^{i}	2.294 (5)	Rb1—S2	3.717 (7)
Ga1—S2	2.300 (5)	Rb1—S2^{v}	3.734 (7)
Ga2—S1	2.263 (5)	Rb2—S5^{viii}	3.318 (6)
Ga2—S4^{ii}	2.271 (6)	Rb2—S2^{ix}	3.350 (6)
Ga2—S5	2.288 (5)	Rb2—S1^{x}	3.419 (6)
Ga2—S2^{iii}	2.296 (5)	Rb2—S1	3.424 (6)
Rb1—S5^{iv}	3.330 (6)	Rb2—S3^{i}	3.425 (5)
Rb1—S3^{v}	3.365 (7)	Rb2—S4	3.425 (4)
Rb1—S4	3.366 (7)	Rb2—S5^{xi}	3.728 (7)
Rb1—S1	3.370 (5)	Rb2—S5	3.731 (7)

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

The highest peak and the deepest hole in the final Fourier map are located 0.85 Å from Ga2 and 1.18 Å from Ga1, respectively.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* in *WinGX* (Farrugia, 1999); program(s) used to solve structure: *SHELXL86* (Sheldrick, 1986); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999) and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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