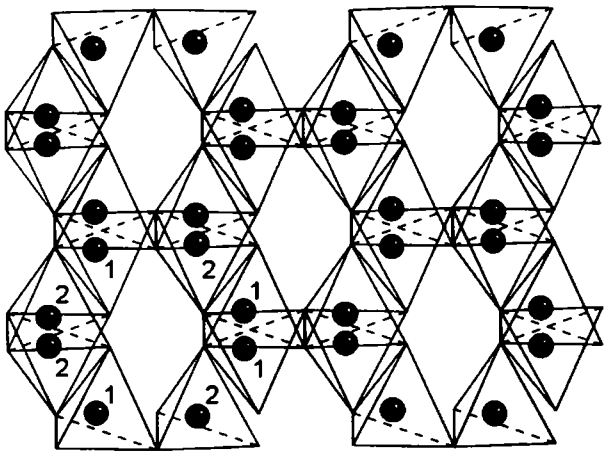
Refinement of the crystal structure of digallium trisulfide, Ga_2S_3

C. Y. Jones*[I], J. C. Bryan[II], K. Kirschbaum[III] and J. G. Edwards[III]

[I] Oak Ridge National Laboratory, Metals and Ceramics Division, Oak Ridge, TN 37831, USA
[II] Oak Ridge National Laboratory, Chemical and Analytical Sciences Division, Oak Ridge, TN 37831, USA
[III] University of Toledo, Department of Chemistry, Toledo, OH 43606, USA

Received February 21, 2001, CSD-No. 409550



● Ga

Abstract

Ga_2S_3, monoclinic, $Clc1$ (No. 9), $a = 11.107(2)$ Å, $b = 6.395(1)$ Å, $c = 7.021(1)$ Å, $\beta = 121.17(3)°$, $V = 426.7$ Å^3, $Z = 4$, $R_{gt}(F) = 0.035$, $wR_{ref}(F^2) = 0.084$, $T = 294$ K.

Source of material

A pale, yellow crystal of Ga_2S_3 was selected from crystals grown by vapor deposition from Ga_2S_3 powder in an effusion cell [1]. The selected crystal had smooth, uniformly-reflecting facet surfaces.

Experimental details

The unit cell parameters and atomic coordinates from this determination agree with the previously published structure [2], but are systematically smaller, possibly because of a difference in the temperature. An extinction coefficient, 0.142, is reported here for the first time.

Discussion

Gallium sulfide, Ga_2S_3, is a III-VI semiconductor whose monoclinic phase possesses at room-temperature a blue-green luminescence [3-5]. Often referred to as α-Ga_2S_3, the monoclinic Ga_2S_3 crystallizes in space group Cc and contains ordered vacancies [2]. In addition to its luminescence properties, Ga_2S_3 also exhibits partial vapor pressures of $Ga_2S(g)$ that increase with decreasing temperature and decrease with increasing temperature in the range 1230 K < T < 1260 K, where a phase transformation was postulated [6]. Its anomalous vapor-pressure behavior has made Ga_2S_3 a model system for the study of a class of high-temperature condensed-phase transformations in it and other sulfides and chalcogenides exhibiting anomalous temperature dependence of vapor pressure. Recent data, from the first time-of-flight neutron powder diffraction experiments performed on samples undergoing effusion [1], revealed a disordering, monoclinic-to-hexagonal phase transformation in the same temperature range as the anomalous vapor pressure, 1240 K – 1260 K [7]. For the monoclinic phase of Ga_2S_3, four single-crystal structures have been published [2,8,9,10]. Work on the high-temperature structures of Ga_2S_3 determined by neutron scattering has made it desirable to reanalyze its single-crystal structure at a specified temperature. The figure shows the corner-sharing GaS_4 tetrahedra of the structure as viewed along the [001] direction and the channels created by the ordered vacancies.

Table 1. Data collection and handling.

Crystal:	yellow, irregular, size 0.30 × 0.30 × 0.40 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	13.87 cm^{-1}
Diffractometer, scan mode:	Enraf-Nonius CAD4, $\omega/2\theta$
$2\theta_{max}$:	52°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	436, 436
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 432
$N(param)_{refined}$:	47
Programs:	SHEXTL [11], SHELXL-97 [12], PLATON [13]

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}
Ga(1)	4a	0.04213(8)	0.4023(2)	0.1251(1)	0.0068(7)	0.0130(6)	0.0096(7)	0.0007(4)	0.0042(5)	0.0005(4)
Ga(2)	4a	0.20026(9)	0.9321(2)	0.1156(1)	0.0065(7)	0.0133(6)	0.0102(7)	–0.0003(4)	0.0045(5)	–0.0012(4)
S(1)	4a	–0.0050(3)	1.0861(4)	–0.0162(6)	0.007(1)	0.016(1)	0.018(1)	–0.0001(8)	0.004(1)	–0.0048(9)
S(2)	4a	0.3378(3)	0.9075(3)	0.4999(4)	0.004(1)	0.015(1)	0.010(2)	–0.0009(8)	0.004(1)	–0.0019(8)
S(3)	4a	0.1741(3)	0.5840(3)	0.0084(4)	0.008(1)	0.012(1)	0.010(1)	–0.0017(8)	0.006(1)	–0.0010(8)

* Correspondence author (e-mail: jonescy@ornl.gov)

Acknowledgment. We thank the College of Arts and Sciences of the University of Toledo for use of the X-ray diffractometer and computer facilities in the Arts and Sciences Instrumentation Center.

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