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Crystal structure of thallium arsenic diselenide, $TlAsSe_2$

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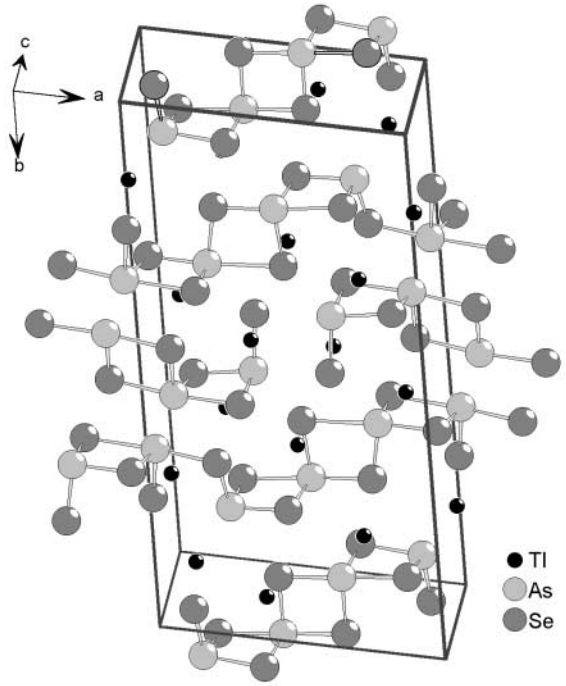

Abstract

$AsSe_2Tl$, monoclinic, $P12_1/n1$ (No. 14), a = 12.141(3) Å, b = 23.633(6) Å, c = 6.243(1) Å, β = 102.85(4)°, V = 1746.4 Å^3, Z = 16, $R_{gt}(F)$ = 0.059, $wR_{gt}(F)$ = 0.064, T = 293 K.

Source of material

$TlAsSe_2$ was prepared from a stoichiometric reaction of the high-purity elements in an evacuated and sealed silica-glass ampoule. The probe was heated from room temperature to 773 K with a rate of 100 K/h, and held at this temperature for one week.

Experimental details

Due to the irregular form and low quality of the crystal under study, it was not possible to apply a reasonable absorption correction. The R_{gt} value for a refinement with anisotropic displacement parameters did not improved significantly (R_{gt} = 0.058 for 145 parameters) and the standard deviations for the parameters became much larger. From this point of view, we renounced to a refinement with anisotropic displacement parameters.

Discussion

Lattice parameters calculated from single crystal data for $TlAsSe_2$ were first given by Majid and Prager [1]. Comparing unit cell parameters with those of the mineral lorandite ($TlAsS_2$) [2] they concluded an analogy between the two crystal structures. Indexed powder pattern of this compound are different from unindexed one published by Dembowskii et al. [3] and those calculated by the authors, with parameters given in Table 2. From the point of view of powder pattern, we ascertain real structural differences for the three phases with identical chemical composition.

Arrangement of structural (As_2Se_5) units in the a,c-plane at $y \approx 0$ and $y \approx 1/4$ implies a tabular grown crystal species. Within these units, one of the As atoms is 3-fold (trigonal Se based with As at the apical pyramid position) and the second one is 4-fold (3 basal and 1 apical positions of a Se octahedron) coordinated. The closest As—Se distances range from 2.366 Å to 2.514 Å correspond to the sum of atomic (ionic As^{+3} and Se^{-2}) radii. For the fourth bond a As—Se distance of 2.731 Å for As(2) and 2.914 Å for As(3) was calculated. The next closest As—Se distances follow outside the limit 3.191 Å.

Table 1. Data collection and handling.

Crystal:	metallic grey thin fragment, size 0.06 × 0.15 × 0.25 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	628.2 cm^{-1}
Diffractometer, scan mode:	Philips PW1100, $2\theta/\omega$
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6514, 2988
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 3\ \sigma(I_{obs})$, 2721
$N(param)_{refined}$:	64
Programs:	CRYMIS [4], DIAMOND [5]

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

Atom	Site	x	y	z	B_{iso}
Tl(1)	4*e*	0.2779(1)	0.1782(1)	0.7281(2)	2.32(3)
Tl(2)	4*e*	–0.0049(1)	0.1716(1)	0.1585(2)	3.11(3)
Tl(3)	4*e*	0.8962(1)	0.0642(1)	0.5414(2)	2.60(3)
Tl(4)	4*e*	0.6166(1)	0.0743(1)	0.9646(2)	2.45(3)
As(1)	4*e*	0.1402(4)	0.0540(2)	0.0503(7)	3.70(8)
As(2)	4*e*	0.3914(3)	0.0562(2)	0.4712(7)	3.75(8)
As(3)	4*e*	0.4949(3)	0.2027(2)	0.2101(6)	3.47(8)
As(4)	4*e*	0.2526(3)	0.3106(1)	0.1291(5)	1.95(6)
Se(1)	4*e*	0.1639(2)	0.0650(1)	0.4383(5)	1.82(6)
Se(2)	4*e*	0.3521(2)	0.0674(1)	0.0813(5)	1.68(6)
Se(3)	4*e*	0.8714(2)	0.0442(1)	0.0316(4)	1.48(5)
Se(4)	4*e*	0.6150(2)	0.0416(1)	0.4600(5)	1.86(6)
Se(5)	4*e*	0.0188(2)	0.1957(1)	0.6661(5)	1.63(5)
Se(6)	4*e*	0.5487(2)	0.1938(1)	0.6123(4)	1.41(5)
Se(7)	4*e*	0.2804(2)	0.2148(1)	0.2236(4)	1.30(5)
Se(8)	4*e*	0.2373(2)	0.3097(1)	0.7478(4)	1.38(5)

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