JOURNAL OF SOLID STATE CHEMISTRY **124,** 305–308 (1996)
ARTICLE NO. 0241

Redetermination of the Crystal Structure of γ-In_2Se_3 by Twin Crystal X-Ray Method

A. Pfitzner and H. D. Lutz

Anorganische Chemie I, Universität Siegen, D-57068 Siegen, Germany

Received April 4, 1996; accepted April 10, 1996

DEDICATED TO PROFESSOR ROGER BLACHNIK ON THE OCCASION OF HIS 60TH BIRTHDAY

The crystal structure of γ-In_2Se_3 ($P6_1$ or $P6_5$, $Z = 6$, $a = 712.86(5)$, $c = 1938.1(2)$ pm) was redetermined by X-ray structure determination methods confirming the results of Likforman *et al.* reported in 1978 (8). The crystals (hexagonal pyramids and bipyramids, and small plates) obtained by chemical transport with iodine as transporting agent were multiple twins. The collected data of two twinned crystal specimens were refined (final $R1 = 0.0315$ and 0.0559 for 1553 and 1602 independent reflections with $I > 2\sigma_I$, respectively). The structure is built up by In(1)Se_5 trigonal bipyramids and distorted In(2)Se_4 tetrahedra resulting in a distorted wurtzite-type-like arrangement. γ-In_2Se_3 is the room-temperature polymorph of indium(III) selenide contrary to some other reports in the literature, e.g., Julien *et al.* (1985) (3).

INTRODUCTION

The crystal structures of the various In_2Se_3 polymorphs (1–6) have been not reported so far with the exception of two older papers on α-, β-, and γ-In_2Se_3 (7, 8). After Osamura *et al.* (7), α- and β-In_2Se_3 crystallize in layer structures with indium in tetrahedral and octahedral holes formed by selenium, respectively. Likforman *et al.* (8) determined the structure of γ-In_2Se_3 revealing two different indium sites, viz. tetrahedrally coordinated In^{3+} ions and those in a trigonal bipyramidal coordination. These results, however, were only qualitatively considered to be confirmed (9). Thus, it was concluded from the densities of the polymorphs under discussion that the coordination of the In^{3+} ions is equal for α- and β-In_2Se_3 but larger than in the case of the γ modification (5). Additional X-ray structure studies promised at that time (5) failed because of multiple twinning of the crystals obtained. Furthermore, the phase relationships of the In_2Se_3 polymorphs are not fully established. In the older literature as well as that by Likforman *et al.* (2) (in contrast to Likforman *et al.* (8)) and by Julien *et al.* (3), γ-In_2Se_3 was claimed to be a high-temperature modification. In 1988, we argued for γ-In_2Se_3 as the room-temperature polymorph (5). Full confirmation of this reverse order, however, is lacking until now. In some recent papers (6, 10) this problem was negated.

The structure data reported by Likforman *et al.* (8) give no hints on the normally observed twinning of this compounds although the reliability factor of the refinement ($R = 0.066$ for $I > 2\sigma_I$) reveals some problems with the crystal studied. We therefore redetermined the crystal structure of γ-In_2Se_3.

γ-In_2Se_3 crystallizes in the enantiomorphous space groups $P6_1$ or $P6_5$ with 6 formula units in the unit cell. The specimen studied by Likforman *et al.* (8) belonged to space group $P6_1$. We obtained twins showing Laue symmetry $6/mmm$ (possible space groups $P6_122$ or $P6_522$ with respect to the reflection condition $00l$ with $l = 6n$) as well as crystals showing small deviations from Laue symmetry $6/mmm$ resulting in $6/m$ (possible space groups $P6_1$ or $P6_5$).

EXPERIMENTAL

Crystals of γ-In_2Se_3 were grown by chemical vapor transport in closed silica tubes using iodine as the transporting agent (11–13). The transport occurs from the cold to the hot zone, i.e., from 700 to 800 K (13). The transporting rate depends strongly on the I_2 concentration in the tube. Using 5 mg/cm^3, crystals as large as 2 mm in diameter were obtained within 2 days. The typical habit of the black (dark red in transmission) crystals were hexagonal pyramids, hexagonal bipyramids, and some amounts of small plates. The composition of one of the crystals has been determined by a microprobe (Cam Scan 44 with EDAX detector) to be 60.7 mol% Se (calc. 60 mol%) and 39.3 mol% In (40 mol%).

Various small plates were transferred to an Enraf–Nonius CAD 4 diffractometer. Graphite-monochromatized Mo$K\alpha$ radiation was used. The intensity data were corrected for Lorentz and polarization effects with NRCVAX (14). Empirical absorption corrections were performed by ψ scans. The variations in intensity throughout the data collection were less than 1%. The structure

0022-4596/96 $18.00

was refined by full-matrix least-squares refinement of positional and anisotropic thermal parameters, extinction coefficient, and scale factor using scattering factors for neutral atoms (15) using the program SHELXL-93 (16). In the last stage, racemic twinning has been taken into consideration. Additional twinning by a mirror plane, e.g. parallel to (010), or by the equivalent twofold rotation axis, e.g. parallel to [100], was refined.

RESULTS AND DISCUSSION

The refinements converged to a final $R1$ of 5.64% for 1602 unique reflections ($I > 2\sigma_I$) of the nearly monocrystal specimen 2, data set 2, regarded as a monocrystal, and to 5.59% for its refinement as a rotation twin (relative volume 98.4 and 1.6(2)%), and to 3.15% for 1553 reflections for specimen 1, refined as racemic and rotation twin, data set 1. The crystallographic data and the data of structure refinement of specimen 1 are given in Table 1. A final decision on the real twinning symmetry element of the obtained crystals is not possible.

The structure data obtained for the various refinements only differ within the range of experimental errors. The final results for specimens 1 and 2 are listed in Table 2 together with those reported by Likforman *et al.* (8) for comparison; the anisotropic displacement parameters are given in Table 3 and selected bond lengths and angles are given in Table 4.[1] The two $InSe_n$ polyhedra are shown in Fig. 1 and the arrangement of the polyhedra in the structure are shown in Fig. 2. Three isostructural sulfides, viz. Al_2S_3 (tbp), $AlInS_3$, and $GaInS_3$, and isostructural $GaInSe_3$ have been reported recently (18–21).

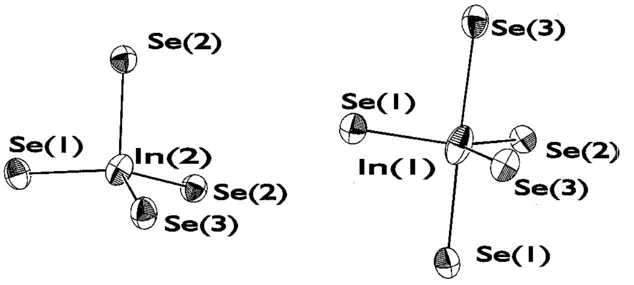

FIG. 1. Coordination polyhedra of the In atoms in γ-In_2Se_3. (90% probability).

TABLE 1
Crystallographic Data and Data of Structure Refinement of γ-In_2Se_3 (Data Set No. 1)

	Crystal data		
Formula weight	466.52	Density	5.449 Mg m^{-3}
Space group	$P6_1$	$a =$	712.86(5) pm
Z	6	$c =$	1938.1(2) pm
Cell volume	852.9(1) × 10^6 pm^3		
	Data collection		
Temperature	293(2) K	Range of hkl	$-10 < h < 8$
Wavelength	71.073 pm		$0 < k < 10$
Theta range	1.05°–30.04°		$-27 < l < 27$
Parameters	49		
	Data of structure refinement		
Crystal size (mm^3)			0.13 × 0.15 × 0.15
Absorption coefficient μ (mm^{-1})			27.146
Reflections collected			3673
Independent reflections, R_{int}			1648, 0.050
Reflections with $I > 2\sigma_I$			1553
F (000)			1200
Goodness-of-fit on F^2			1.073
$R1$ ($I > 2\sigma_I$), $R1$ (all data)			0.0315, 0.0350
$wR2^a$ ($I > 2\sigma_I$), $wR2^a$ (all data)			0.0693, 0.0702
Extinction coefficient			0.00083(8)
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (10^{-6} e pm^{-3})			−1.39, 2.61
Relative volumina of the twins (%)			65 : 5 : 27 : 3

[a] $w = 1/[\sigma^2(F_0^2) + (a * P)^2 + b * P]$ with $a = 0.0301$, $b = 1.7027$, and $P = [\max(F_0^2, 0) + 2 * F_c^2]/3$.

As already described in (8), the structure of γ-In_2Se_3 is built up by distorted In(1)Se_5 trigonal bipyramids and In(2)Se_4 tetrahedra. These polyhedra are connected by common corners and edges resulting in a distorted wurtzite-type-like arrangement (18). In the crystal structure of γ-In_2Se_3 two different screws are built up by the 6_1 axis. One is formed by corner sharing In(2)Se_4 tetrahedra, and the other by In(1)Se_5 trigonal bipyramids sharing common edges. The screws of one type are interlinked only by those of the other type and vice versa.

The In–Se equatorial distances vary from 257.7 to 262.2 pm, and the axial distances from 287.4 and 297.4 pm (trigonal bipyramid) and 255.2–263.4 pm (tetrahedron), with Se–In–Se angles ranging from 94.55° to 118.88° (tetrahedron). Those of the $InSe_5$ polyhedron do not largely deviate from 90°, 120°, and 180°, respectively (see Table 4).

The structure proposed for γ-In_2Se_3 by Likforman *et al.* (8) and, hence, the coordination numbers of the two kinds of In^{3+} ions, viz. 4 and 5, are confirmed (see Table 4). This means that because of the higher densities the coordination numbers of both the α- and β-polymorphs must be greater, i.e., probably 6, than those of the γ modification. These conclusions are in agreement with the results of infrared and Raman spectroscopic measurements, which reveal

---

[1] Additional material to this paper can be ordered by referring to CSD 380097, the names of the authors, and citations of the paper at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany. The list of the F_o/F_c data is available from the author up to one year after the publication has appeared.

TABLE 2
Atomic Coordinates and Isotropic Displacement Parameters U_{eq} (10^6 pm^2)[a]

	x	y	z	U_{eq} [B_{iso}]
In(1)	0.0117(1)	0.3137(1)	0	2.29(2)
	0.0118(2)	0.3137(2)	0	2.13(3)
	[0.0111(6)	0.3142(7)	0	1.76(2)]
In(2)	0.3417(1)	0.0152(1)	0.30489(5)	1.88(2)
	0.3411(1)	0.0149(2)	0.30476(5)	1.64(3)
	[0.3416(6)	0.0156(7)	0.3055(3)	1.56(2)]
Se(1)	0.0742(2)	0.3470(2)	0.14696(6)	1.78(2)
	0.0739(2)	0.3467(2)	0.14707(7)	1.71(3)
	[0.0728(8)	0.3470(9)	0.1469(4)	1.33(2)]
Se(2)	0.3473(1)	0.0436(1)	0.1693(1)	1.60(2)
	0.3472(2)	0.0438(2)	0.16950(6)	1.37(3)
	[0.3463(9)	0.0437(8)	0.1703(4)	1.30(2)]
Se(3)	0.3662(2)	0.0250(1)	0.51459(6)	1.93(2)
	0.3656(2)	0.0249(2)	0.51472(8)	1.54(3)
	[0.3646(9)	0.0250(9)	0.5150(3)	1.46(2)]

Note. First line, data set No. 1; second line, data set No. 2; data according to Likforman *et al.* (8) in square brackets.

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

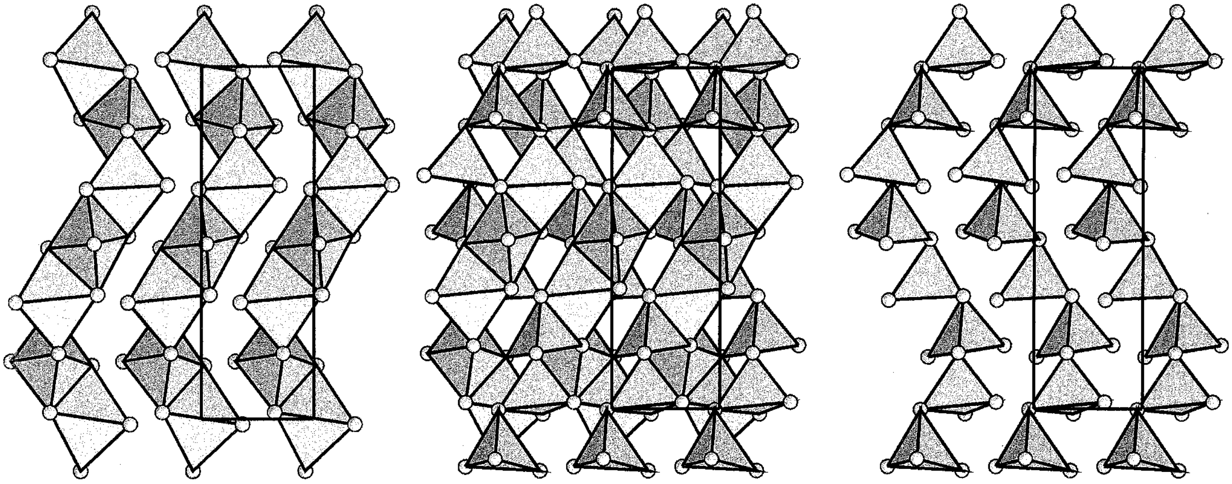

FIG. 2. Arrangement of the $InSe_n$ polyhedra in the crystal structure of γ-In_2Se_3 (projected along the b-axis); screws of the In(2)Se_4 tetrahedra (right) and In(1)Se_5 trigonal bipyramids (left) build up the three-dimensional structure.

TABLE 3
Anisotropic Displacement Parameters U_{ij} (100 pm^2)[a] of γ-In_2Se_3 (Data Set No. 1)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
In(1)	1.78(3)	1.51(3)	3.52(4)	0.77(3)	0.72(3)	−0.09(3)
In(2)	1.62(3)	1.75(3)	2.19(3)	0.80(2)	0.33(2)	−0.11(2)
Se(1)	1.57(4)	1.67(4)	2.17(4)	0.88(3)	0.00(3)	0.16(3)
Se(2)	1.57(4)	1.61(4)	1.69(4)	0.84(3)	−0.08(3)	−0.14(3)
Se(3)	1.68(4)	1.59(4)	2.36(4)	0.70(3)	−0.20(4)	0.17(3)

[a] The anisotropic displacement factor exponent takes the form $-2\pi^2 \Sigma_i \Sigma_j U_{ij} h_i h_j a_i^* a_j^*$.

TABLE 4
Selected Bond Lengths (pm) and Angles (°) of γ-In_2Se_3 (Data Set No. 1)

In(1)^{i}–Se(1)^{i}	287.4(1)	Se(1)^{i}–In(1)^{i}–Se(1)^{ii}	92.42(3)
In(1)^{i}–Se(1)^{ii}	257.7(1)	Se(1)^{i}–In(1)^{i}–Se(2)^{iv}	88.00(4)
In(1)^{i}–Se(2)^{iv}	262.2(1)	Se(1)^{ii}–In(1)^{i}–Se(2)^{iv}	121.17(4)
In(1)^{i}–Se(3)^{iii}	258.1(1)	Se(1)^{i}–In(1)^{i}–Se(3)^{iii}	90.86(4)
In(1)^{i}–Se(3)^{v}	297.4(1)	Se(1)^{i}–In(1)^{i}–Se(3)^{v}	172.60(4)
		Se(1)^{ii}–In(1)^{i}–Se(3)^{iii}	120.26(4)
		Se(1)^{ii}–In(1)^{i}–Se(3)^{v}	88.73(3)
		Se(2)^{iv}–In(1)^{i}–Se(3)^{iii}	118.56(4)
		Se(2)^{iv}–In(1)^{i}–Se(3)^{v}	85.16(4)
		Se(3)^{iii}–In(1)^{i}–Se(3)^{v}	94.88(4)
In(2)^{i}–Se(1)^{vi}	256.9(1)	Se(1)^{vi}–In(2)^{i}–Se(2)^{i}	94.55(4)
In(2)^{i}–Se(2)^{i}	263.4(1)	Se(1)^{vi}–In(2)^{i}–Se(2)^{vii}	115.34(4)
In(2)^{i}–Se(2)^{vii}	258.6(1)	Se(1)^{vi}–In(2)^{i}–Se(3)^{ii}	118.88(4)
In(2)^{i}–Se(3)^{ii}	255.2(1)	Se(2)^{i}–In(2)^{i}–Se(2)^{vii}	99.59(3)
		Se(2)^{i}–In(2)^{i}–Se(3)^{ii}	111.99(3)
		Se(2)^{vii}–In(2)^{i}–Se(3)^{ii}	112.95(4)

Symmetry transformations used to generate equivalent atoms: (i) x, y, z; (ii) $y, -x + y, z - 1/6$; (iii) $-x, -y, z - 1/2$; (iv) $y, -x + y + 1, z - 1/6$; (v) $-y, x - y, z - 2/3$; (vi) $x - y + 1, x, z + 1/6$; (vii) $x - y, x, z + 1/6$.

higher frequency lattice modes and, hence, lower coordination numbers of the In^{3+} ions in γ-In_2Se_3 compared to those of the α, α', β, and β' polymorphs (5, 17). The results of Osmura *et al.* (7), namely that the indium ions of α-In_2Se_3 are located in tetrahedral sites, therefore must be doubted.

REFERENCES

1. S. Popovic, A. Tonejc, B. Grzeta-Plenkovic, B. Celustka, and R. Troiko, *J. Appl. Crystallogr.* **12,** 416 (1979).
2. A. Likforman, P. H. Fourcroy, M. Guittard, J. Flahaut, R. Poirier, and N. Szydlo, *J. Solid State Chem.* **33,** 91 (1980).
3. C. Julien, M. Eddrief, M. Balkanski, E. Hatzkraniotis, and K. Kambas, *Phys. Status Solidi A* **88,** 687 (1985).
4. C. Manolikas, *J. Solid State Chem.* **74,** 319 (1985).
5. H. D. Lutz, M. Fischer, H.-B. Baldus, and R. Blachnik, *J. Less-Common Met.* **143,** 83 (1988).
6. B. Grzeta and S. Popovic, *J. Appl. Crystallogr.* **23,** 340 (1990).
7. K. Osamura, Y. Murakami, and Y. Tomiie, *J. Phys. Soc. Jpn.* **21,** 1848 (1966).
8. A. Likforman, D. Carré, and R. Hillel, *Acta Crystallogr. Sect. B* **34,** 1 (1978).
9. K. Krusch and J. A. Gardner, *Phys. Rev. B* **24,** 4587 (1981).
10. C. Julien and M. Eddrief, *Mater. Sci. Eng. Sect. B* **13,** 247 (1992).
11. Z. S. Medvedeva and T. N. Guliev, *Izv. Akad. Nauk SSSR, Neorg. Mater.* **1,** 848 (1965); *Inorg. Mater.* **1,** 779 (1965).
12. Ja.Kh. Grinberg, V. A. Boriakova, V. F. Chevel'kov, R. Hillel, and J. Bouix, *J. Inorg. Nucl. Chem.* **38,** 383 (1976).
13. M. Fischer, Ph.D. thesis, University of Siegen, Germany (1988).
14. E. J. Gabe, Y. LePage, J.-P. Charland, F. L. Lee, and P. S. White, *J. Appl. Crystallogr.* **22,** 384 (1989).
15. "International Tables for Crystallography," Vol. C. Kluwer Academic, Dordrecht, 1992.
16. G. M. Sheldrick, "SHELXL-93, Program for Crystal Structure Refinement." University of Göttingen, 1993.
17. K. Kambas, C. Julien, M. Jouanne, A. Likforman, and M. Guittard, *Phys. Status Solidi B* **124,** K105 (1984).
18. B. Krebs, A. Schiemann, and M. Läge, *Z. Anorg. Allg. Chem.* **619,** 983 (1993).
19. M. Schulte-Kellinghaus and V. Krämer, *Acta Crystallogr. Sect. B* **35,** 3016 (1979).
20. P. Dubcek and B. Etlinger, *Phys. Status Solidi B* **185,** 123 (1994).
21. G. G. Guseinov, I. R. Amiraslanov, A. S. Kuliev, and K. S. Mamedov, *Izv. Akad. Nauk SSSR, Neorg. Mater.* **23,** 854 (1987).