X-ray Diffraction Study of the Crystal Structure of the Tl Ternary Chalcogenides $Tl_{2x}In_{2(1-x)}Se_2$, $x = 0.2, 0.3,...0.9$

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Abstract

A series of thallium ternary chalcogenides with the composition $Tl_{2x}In_{2(1-x)}Se_2$, $x = 0.2, 0.3,...0.9$, have been studied by X-ray powder and, for some of them, single-crystal diffraction. They are tetragonal, space group $I4/mcm$, $Z = 4$, and isostructural with the binary semiconductor TlSe. Their crystal structures have been solved by direct methods and refined by the Rietveld method to a precision which is satisfactorily comparable to single-crystal results. As x is changed from $x = 0.2$ to $x = 0.9$ the unit-cell parameters and volume decrease or increase following Kurnakov's law, which is valid for solid solutions. Refined positional parameters of Se, In—Se and Tl—Se bond lengths vary with x also according to the same law. The distribution of In and Tl cations in $4(a)$ and $4(b)$ sites depends on the stoichiometry x and the crystals are composed of $[In^{3+}Se_2]^-_\infty$ chains along the c axis in which $InSe_4$ tetrahedra share edges; the chains are interconnected with $Tl^+(In^+)$ ions.

1. Introduction

$TlInSe_2$ has attracted interest and is still being studied because it is a p-type semiconductor exhibiting switching and memory capability and nonlinear electrical behavior described by S-type (I-U) characteristics with voltage oscillations in the negative differential resistance (NDR) region, *i.e.* physical properties pointing to possible technological applications such as switching and memory devices, oscillators, thermistors *etc.* (Abdullaev & Aliev, 1980; Hanias *et al.*, 1986).

Recently, we have reported in detail the crystal growth of the nonstoichiometric compounds $Tl_{2x}In_{2(1-x)}Se_2$ for $x = 0.2,...0.9$ and their energy-gap variation as a function of the stoichiometry x (Hatzisymeon *et al.*, 1996). Since only the crystal structure of the stoichiometric $TlInSe_2$ has been studied so far it was deemed worthwhile to carry out an X-ray crystal structure analysis for the whole family of the above nonstoichiometric thallium chalcogenides and to find out the way in which their structural parameters vary when the stoichiometry x is altered.

2. Experimental

Crystals of the $Tl_{2x}In_{2(1-x)}Se_2$ family were grown by the total synthesis and/or the Bridgmann–Stockbarger methods from appropriate amounts of high-purity elements (99.999%) of Tl, In and Se. Details of the growth procedure are given in our report mentioned above. The crystals grown by both techniques were bundles of black thin parallel fibers. They were very easily cleaved along two mutually perpendicular planes, parallel to the (110) planes of their tetragonal unit cells (Guseinov *et al.*, 1978), giving birth to long rectangular needles. Owing to this easy and continuous cleavage, separating many small fragments, it was difficult to isolate single crystals suitable for data collection on a four-circle diffractometer. This was achieved only for $Tl_{0.6}In_{1.4}Se_2$, $Tl_{0.8}In_{1.2}Se_2$ and $Tl_{1.2}In_{0.8}Se_2$. It was, therefore, necessary to use powder diffraction methods, but for these three compounds single-crystal structure analyses were also carried out for comparison purposes. The stoichiometry of the crystals grown was checked using a microanalysis unit (AN 1000 LINK) adapted to a Scanning Electron Microscope (SEM), type JSM-804A by Jeol Co. Experimental values of x agreed with the corresponding nominal ones to within 5%.

2.1. *Single-crystal data collection and structure determination*

Details of the single-crystal data, data collection and structure refinement results are given in Table 1. Fractional atomic coordinates and selected geometric data are given in Tables 2 and 3, respectively.†

2.2. *Powder data collection, structure solution and refinement*

All samples were ground in a conventional hand mortar and periodically sieved during grinding through a 400 mesh (38 μm) sonic shifter sieve, which was the finest available, in order to minimize the influence of

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† A list of structure factors and the numbered intensity of each measured point on the profile have been deposited with the IUCr (Reference: HA0154). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Experimental details*

	(1)	(2)	(3)
Crystal data			
Chemical formula	$Tl_{0.6}In_{1.4}Se_2$	$Tl_{0.8}In_{1.2}Se_2$	$Tl_{1.2}In_{0.8}Se_2$
Chemical formula weight	441.296	459.208	495.536
Cell setting	Tetragonal	Tetragonal	Tetragonal
Space group	*I4/mcm*	*I4/mcm*	*I4/mcm*
a (Å)	8.054 (1)	8.056 (1)	8.057 (1)
b (Å)	8.054 (1)	8.056 (1)	8.057 (1)
c (Å)	6.805 (3)	6.826 (2)	6.830 (1)
V (Å^3)	441.4 (2)	443.00 (15)	443.37 (15)
Z	4	4	4
D_x (Mg m^{-3})	6.627	6.895	7.410
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.7107	0.7107	0.7107
No. of reflections for cell parameters	25	25	25
θ range (°)	10.19–28.15	10.19–28.15	10.19–28.15
μ (mm^{-1})	45.455	51.518	63.914
Temperature (K)	293 (2)	293 (2)	293 (2)
Crystal form	Parallelepiped	Parallelepiped	Parallelepiped
Crystal size (mm)	$0.37 \times 0.15 \times 0.13$	$0.5 \times 0.28 \times 0.12$	$0.55 \times 0.17 \times 0.10$
Crystal color	Metallic black	Metallic black	Metallic black
Data collection			
Diffractometer	Philips PW1100 (upgraded by Stoe GmbH)	Philips PW1100 (upgraded by Stoe GmbH)	Philips PW1100 (upgraded by Stoe GmbH)
Data collection method	θ–2θ scans	θ–2θ scans	θ–2θ scans
Absorption correction	Empirical *via* ψ scans (*EMPIR*; Stoe, 1990*b*)	Empirical *via* ψ scans (*EMPIR*; Stoe, 1990*b*)	Empirical *via* ψ scans (*EMPIR*; Stoe, 1990*b*)
T_{min}	0.107	0.158	0.192
T_{max}	0.572	0.631	0.661
No. of measured reflections	1240	1240	1244
No. of independent reflections	283	283	284
No. of observed reflections	211	251	238
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.0684	0.0618	0.1215
θ_{max} (°)	34.93	34.9	34.99
Range of h, k, l	$-12 \rightarrow h \rightarrow 12$	$-12 \rightarrow h \rightarrow 12$	$-12 \rightarrow h \rightarrow 12$
	$-9 \rightarrow k \rightarrow 9$	$-9 \rightarrow k \rightarrow 9$	$-9 \rightarrow k \rightarrow 9$
	$0 \rightarrow l \rightarrow 10$	$0 \rightarrow l \rightarrow 10$	$0 \rightarrow l \rightarrow 10$
No. of standard reflections	3	3	3
Frequency of standard reflections (min)	120	120	120
Refinement			
Refinement on	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$	0.0619	0.0426	0.0870
$wR(F^2)$	0.1298	0.0969	0.2332
S	1.221	1.172	1.105
No. of reflections used in refinement	283	283	284
No. of parameters used	10	10	10
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0341P)^2 + 22.4966P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0485P)^2 + 2.7550P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1125P)^2 + 107.0340P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.004	0.007	0.005
$\Delta\rho_{max}$ (e Å^{-3})	3.25	2.89	3.26
$\Delta\rho_{min}$ (e Å^{-3})	-5.19	-4.88	-1.37
Extinction method	*SHELXL*97 (Sheldrick, 1997)	*SHELXL*97 (Sheldrick, 1997)	*SHELXL*97 (Sheldrick, 1997)
Extinction coefficient	0.0040 (7)	0.0033 (6)	0.0013 (8)
Source of atomic scattering factors	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Computer programs			
Data collection	*DIF*4–*COSY* (Stoe, 1990*a*)	*DIF*4–*COSY* (Stoe, 1990*a*)	*DIF*4–*COSY* (Stoe, 1990*a*)
Cell refinement	*DIF*4 (Stoe, 1990*a*)	*DIF*4 (Stoe, 1990*a*)	*DIF*4 (Stoe, 1990*a*)
Data reduction	*DIF*4–*REDU*4 (Stoe, 1990*a*)	*DIF*4–*REDU*4 (Stoe, 1990*a*)	*DIF*4–*REDU*4 (Stoe, 1990*a*)
Structure solution	*SHELXS* (Sheldrick, 1990)	*SHELXS* (Sheldrick, 1990)	*SHELXS* (Sheldrick, 1990)
Structure refinement	*SHELXL*97 (Sheldrick, 1997)	*SHELXL*97 (Sheldrick, 1997)	*SHELXL*97 (Sheldrick, 1997)

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($\mathring{A}^2$)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$

	Wyckoff position	x	y	z	U_{eq}	Site composition
(1) $Tl_{0.6}In_{1.4}Se_2$, $x = 0.3$						
Tl	4(a)	0.0	0.0	1/4	0.0390 (6)	0.6
In1	4(a)	0.0	0.0	1/4	0.0390 (6)	0.4
In	4(b)	0.0	1/2	1/4	0.0152 (5)	
Se	8(h)	0.1718 (1)	0.6718 (1)	0.0000	0.0145 (5)	
(2) $Tl_{0.8}In_{1.2}Se_2$, $x = 0.4$						
Tl	4(a)	0.0	0.0	1/4	0.0323 (3)	0.8
In1	4(a)	0.0	0.0	1/4	0.0323 (3)	0.2
In	4(b)	0.0	1/2	1/4	0.0155 (3)	
Se	8(h)	0.1731 (1)	0.6731 (1)	0.0000	0.0146 (3)	
(3) $Tl_{1.2}In_{0.8}Se_2$, $x = 0.6$						
Tl	4(a)	0.0	0.0	1/4	0.0351 (8)	0.8
Tl1	4(b)	0.0	1/2	1/4	0.0216 (7)	0.2
In	4(b)	0.0	1/2	1/4	0.0216 (7)	
Se	8(h)	0.1759 (1)	0.6759 (1)	0.0000	0.0149 (7)	

Table 3. *Selected bond lengths ($\mathring{A}$) and angles (°)*

	Tetrahedra		Square antiprism		
Compound	In—Se	Se—In—Se^i	Tl—Se	Se—Tl—Se^{ii}	Se—Tl—Se^{iii}
$Tl_{0.6}In_{1.4}Se_2$	2.593 (1)	115.50 (1)	3.435 (1)	75.80 (1)	67.99 (2)
$Tl_{0.8}In_{1.2}Se_2$	2.608 (1)	115.35 (1)	3.434 (1)	75.70 (1)	67.92 (1)
$Tl_{1.2}In_{0.8}Se_2$	2.633 (1)	114.87 (1)	3.427 (1)	75.62 (1)	67.54 (1)

Symmetry codes: (i) $x, \frac{1}{2} - x, \frac{1}{2}$; (ii) $\frac{1}{2} + x, 1 - x, 0$; (iii) $\frac{1}{2} - x, 1 - x, \frac{1}{2}$.

factors encountered with coarse grain size (extinction, microabsorption and particle statistics) and thus improve the accuracy of X-ray diffraction intensities and peak positions. Despite grinding and sieving, the compounds exhibit an intense preferred orientation, when packed into a sample holder, owing to their easy cleavage. This undesirable effect was drastically reduced, but not eliminated completely, by mixing a quantity of each compound with ~50% silica gel. A mixture of the sample powder with an amorphous material surrounds the particles of interest in a homogeneous nonorienting medium, reducing the preferred orientation to a satisfactory degree (Bish & Reynolds, 1989).

Diffraction data were collected on a Phillips PW 1710 diffractometer with Cu $K\alpha$ radiation over the angular range $2\theta = 15$–80° in steps of 0.02° (2θ) and counting time 10 s per step.†

The recorded X-ray powder diffraction patterns are similar to the corresponding ones of TlSe, calculated from published data (Wyckoff, 1965), and $TlInSe_2$ (Banys *et al.*, 1990), indicating that all the nonstoichiometric compounds discussed here have the tetragonal TlSe-type structure with space group $I4/mcm$ and $Z = 4$.

Although the known structure of stoichiometric $TlInSe_2$ could be used as a starting model, *ab initio* solution by direct methods using the programs *EXTRA* (Altomare *et al.*, 1995) and *SIRPOW* (Altomare *et al.*,

1994) was attempted; it was successful, despite the problems arising from peak overlap and preferred orientation.

2.3. *Rietveld structure refinement*

Least-squares refinement by the Rietveld method was carried out with the program *RIETHAR* (Hewat, 1973; Ahtee *et al.*, 1989; Järvinen, 1993). The advantage of this program is that the effects of preferred orientation are included in the refinement by expanding the pole-density orientation distribution in a sum of spherical harmonic terms, the number of which depends on the degree of preferred orientation. This method is considered as a variant of the experimental determination of pole-density distributions by a multiaxis diffractometer (Dollase, 1986). The Voigt function was used to represent individual reflection profiles, the background was estimated from the minima between the reflection peaks and 21 parameters were involved in the refinement, *i.e.* four structural and isotropic temperature parameters, one scale factor, one asymmetry and two unit-cell parameters along with five halfwidth, two zero-point shift parameters and five coefficients for the preferred orientation definition.

The refinement was carried out by assuming thallium and indium cation distribution in 4(a) and 4(b) sites, in accordance with the value of stoichiometry x. Thus, for the stoichiometric $TlInSe_2$ ($x = 0.5$) it was considered that Tl^+ cations fill up the octahedral sites in 4(a) and

† See deposition footnote on p. 358.

Table 4. *Final reliability indices and refined unit-cell parameters from powder data*

R factors are as defined by Hewat (1973).

Compound	R (%)	R_{exp} (%)	a axis (Å)	c axis (Å)	V (Å^3)
$Tl_{0.4}In_{1.6}Se_2$	10.60	9.43	8.0475 (13)	6.7901 (14)	439.7 (1)
$Tl_{0.6}In_{1.4}Se_2$	5.60	8.73	8.0520 (9)	6.8062 (9)	441.3 (1)
$Tl_{0.8}In_{1.2}Se_2$	5.34	7.48	8.0558 (10)	6.8206 (10)	442.6 (1)
$TlInSe_2$	7.67	7.89	8.0591 (6)	6.8300 (5)	443.6 (1)
$Tl_{1.2}In_{0.8}Se_2$	7.13	7.24	8.0550 (14)	6.8426 (14)	444.0 (1)
$Tl_{1.4}In_{0.6}Se_2$	8.26	7.10	8.0478 (3)	6.8725 (3)	445.1 (1)
$Tl_{1.6}In_{0.4}Se_2$	9.43	6.70	8.0370 (6)	6.9233 (1)	447.2 (1)
$Tl_{1.8}In_{0.2}Se_2$	4.33	6.83	8.0149 (2)	6.9497 (1)	446.4 (1)

In^{3+} ions the tetrahedral ones in 4(b), rather than being distributed among these two equivalent positions. This ordering arrangement was suggested by Guseinov *et al.* (1978) after considering the electron configuration of Tl and In and their consequent tendency to appear in monovalent and trivalent states, respectively. Following the same reasoning in the case of nonstoichiometric compounds it was plausible to assume that for $0.5 < x < 1.0$, when thallium is in excess with respect to In, Tl$^+$ occupies all eight-coordinate 4(a) positions, while both Tl^{3+} and In^{3+} are statistically distributed in the tetrahedral 4(b) sites. For $0 < x < 0.5$, when indium is in excess

with respect to thallium, all 4(b) positions are occupied by In^{3+} ions, while both Tl$^+$ and In$^+$ fill the 4(a) positions. Cations on the same site were given the same atomic displacement parameters. Occupancy numbers, calculated on the basis of the known stoichiometry, were kept fixed. The refinement proceeded well and converged to R values less than 10% (except for $Tl_{0.4}In_{1.6}Se_2$). The preferred orientation weights ranged from 0.4542 to 1.3079.

In order to further check the validity of the above cation distributions a test was made for $Tl_{1.2}In_{0.8}Se_2$ and $Tl_{0.6}In_{1.4}Se_2$, *i.e.* one compound with stoichiometry in the range $0.5 < x < 1.0$ and another in the range $0 < x < 0.5$. In this case it was assumed that for $0.5 < x < 1.0$ In cations occupy not only 4(b) sites as above, but are statistically distributed in both 4(a) and 4(b) sites. Similarly, for $0 < x < 0.5$ it was assumed that Tl cations occupy not only 4(a) sites as above, but are also found in both 4(a) and 4(b) positions. The refinement was repeated for various combinations of the relevant occupancy factors, which were kept fixed and under the constrains

$$n_{Tl4(a)} + n_{In4(a)} = n_{Tl4(b)} + n_{In4(b)} = 1 \text{ and}$$
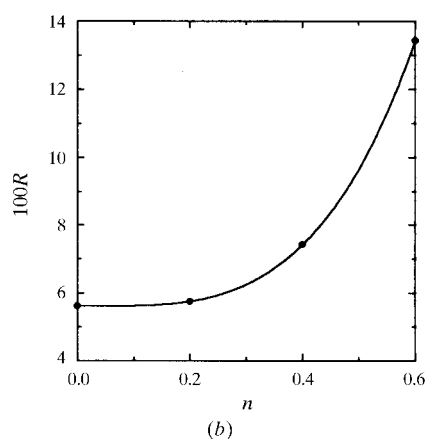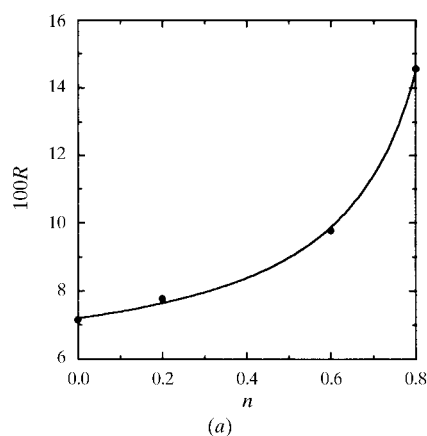$$n_{Tl4(a)} + n_{Tl4(b)} = 2x.$$

Fig. 1. Variation of R index as a function of the occupancy factor (a) $n = n_{In4(a)}$ for $Tl_{1.2}In_{0.8}Se_2$ and (b) $n = n_{Tl4(b)}$ for $Tl_{0.6}In_{1.4}Se_2$.
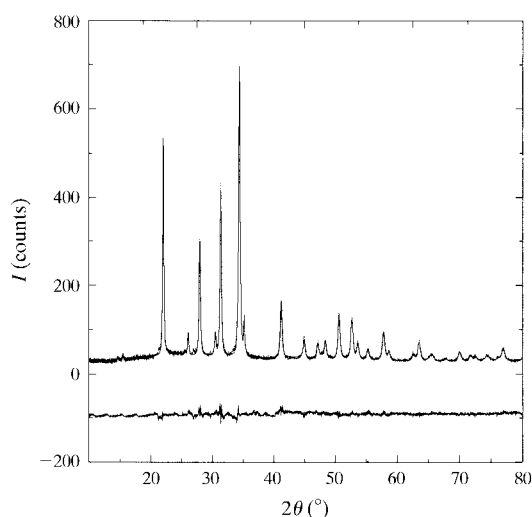

Fig. 2. The observed and calculated powder patterns of $Tl_{0.8}In_{1.2}Se_2$.

Table 5. *Refined atomic and isotropic displacement parameters B_{iso} ($\AA^2$) from powder data ($B = 8\pi U$)*

Compound	x_{Se}	B(Tl)	B(In)	B(Se)
$Tl_{0.4}In_{1.6}Se_2$	0.1705 (5)	8.834 (8)	4.030 (4)	4.112 (2)
$Tl_{0.6}In_{1.4}Se_2$	0.1713 (6)	4.403 (1)	1.300 (1)	1.567 (1)
$Tl_{0.8}In_{1.2}Se_2$	0.1735 (6)	3.425 (1)	0.741 (1)	1.264 (2)
$TlInSe_2$	0.1745 (6)	2.992 (1)	0.837 (1)	1.494 (2)
$Tl_{1.2}In_{0.8}Se_2$	0.1768 (9)	2.547 (1)	2.008 (1)	1.367 (3)
$Tl_{1.4}In_{0.6}Se_2$	0.1780 (6)	1.661 (1)	1.932 (2)	1.288 (2)
$Tl_{1.6}In_{0.4}Se_2$	0.1798 (8)	2.707 (1)	1.549 (3)	0.858 (2)
$Tl_{1.8}In_{0.2}Se_2$	0.1804 (3)	3.044 (2)	1.944 (3)	2.284 (1)

Table 6. *Bond lengths ($\AA$) and angles ($°$)*

| | Tetrahedra | | Square antiprism | | |
Compound	In—Se	Se—Tl—Se	Tl—Se	Se—Tl—Se	Se—Tl—Se
$Tl_{0.4}In_{1.6}Se_2$	2.578 (3)	115.6 (2)	3.435 (4)	75.9 (2)	68.1 (1)
$Tl_{0.6}In_{1.4}Se_2$	2.589 (4)	115.6 (1)	3.436 (4)	75.8 (1)	68.1 (1)
$Tl_{0.8}In_{1.2}Se_2$	2.611 (4)	115.3 (1)	3.432 (4)	75.7 (1)	67.8 (1)
$TlInSe_2$	2.621 (4)	115.1 (1)	3.431 (4)	75.7 (1)	67.7 (1)
$Tl_{1.2}In_{0.8}Se_2$	2.642 (4)	114.8 (2)	3.425 (6)	75.6 (1)	67.5 (1)
$Tl_{1.4}In_{0.6}Se_2$	2.656 (4)	114.7 (1)	3.423 (4)	75.4 (1)	67.6 (1)
$Tl_{1.6}In_{0.4}Se_2$	2.678 (5)	114.7 (2)	3.422 (6)	75.2 (1)	67.7 (1)
$Tl_{1.8}In_{0.2}Se_2$	2.683 (2)	114.8 (1)	3.416 (2)	75.0 (1)	67.9 (1)

The values of the R factors for the cation distribution models assumed are shown in Figs. 1(a) and 1(b). The smallest values of R obtained indicate that the cation distributions originally considered in 4(a) and 4(b) positions are correct.

The observed and calculated powder patterns of $Tl_{0.8}In_{1.2}Se_2$ are presented in Fig. 2 as an example of the results of the Rietveld refinement for the studied compounds. Final structure and isotropic temperature parameters are given in Tables 4, 5 and 6. In the case of $Tl_{0.6}In_{1.4}Se_2$, $Tl_{0.8}In_{1.2}Se_2$ and $Tl_{1.2}In_{0.8}Se_2$ the values of the unit-cell parameters and the refined x coordinate of the Se atom are in good agreement with those from single-crystal data refinement, indicating that the results of our powder diffraction study are reasonably accurate. In the case of x_{Se}, particularly, a previous observation, according to which positional parameters from powder and single-crystal diffraction results differ by less than 1–2 e.s.d.'s, while e.s.d.'s themselves differ by an order of magnitude (Bénard *et al.*, 1991; Young, 1995), seems to hold once more. Table 6 lists interatomic distances and angles derived from the final atomic parameters.

3. Crystal structure

The nonstoichiometric $Tl_{2x}In_{2(1-x)}Se_2$ compounds, for all stoichiometries considered ($x = 0.2,...0.9$), share the tetragonal crystal structure of the stoichiometric $TlInSe_2$. The latter, resembling the structure of the binary semiconductor TlSe, was described as being composed of two types of structural unit, tetrahedra and eight-coordinate groups (Guseinov *et al.*, 1978). Indeed, each In^{3+} cation in 4(b) is covalently bonded to four Se atoms in a slightly distorted tetrahedral coordination (Table 6). The $In^{3+}Se_4$ tetrahedra, connected to each other through a common Se–Se edge, form columns

along the c axis. These $[In^{3+}Se_2]_\infty^-$ chains, furthermore, are interconnected through the Tl^+ cations in 4(a), each one of which is surrounded by eight Se atoms at a Tl—Se distance corresponding to the sum of the ionic radii (Fig. 3), forming a square antiprism.

According to the proposed cation distribution when stoichiometry increases from $x = 0.5$ (stoichiometric compound $TlInSe_2$) to $x = 0.9$, towards the composition TlSe, trivalent In^{3+} ions in the tetrahedra are replaced randomly by trivalent Tl^{3+} [while all eight-coordinate 4(a) sites are occupied by Tl^+]. On the other hand, when x decreases from $x = 0.5$ to $x = 0.2$, towards the composition InSe, monovalent Tl^+ ions in the eight-coordinate sites are replaced by monovalent In^+ [while all tetrahedral 4(b) sites are occupied by In^{3+}]. As a result, the family $Tl_{2x}In_{2(1-x)}Se_2$, $x = 0.2–0.9$, may be considered as consisting of a series of random substitutional solid solutions.

The changes in the structure above, through stoichiometry modification, affect, as expected, the unit cell and other structural parameters. In Figs. 4(a) and 4(b) the variation of the lattice constants a and c is shown as full circles, while the square indicates the TlSe values from Wyckoff (1965). The solid lines represent the best fits obtained using the equation

$$y = Ax + B(1 - x) + C(1 - x)x$$

of the well known Kurnakov's law (Kurnakov, 1965), generally valid for solid solutions with the following parameter values

for the a axis: $A = 8.012$, $B = 8.029$, $C = 0.141$

c axis: $A = 6.999$, $B = 6.803$, $C = -0.289$.

The unit-cell volume V varies according to the same law, from 439.7 (1) to 446.4 (1) $\AA^3$. The tetrahedral In—Se

bond lengths increase from 2.578 (3) to 2.683 (2) Å, while, at the same time, the square antiprism Tl—Se bond lengths decrease slightly from 3.435 (4) to
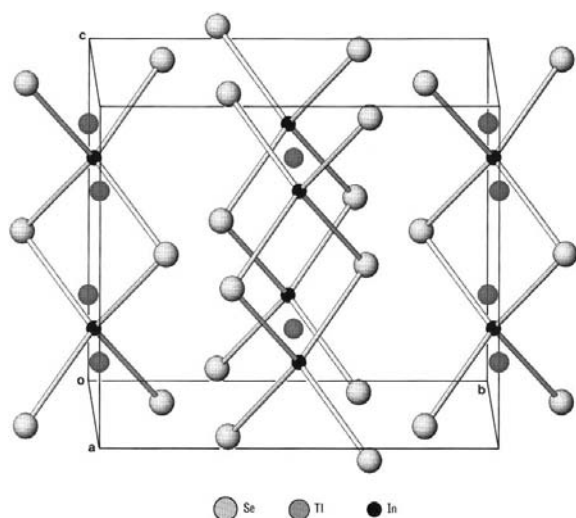

Fig. 3. Perspective view of the unit-cell contents for TlInSe$_2$ showing the [In^{3+}Se$_2$]$_\infty^-$ chains. Tl—Se ionic bonds are not drawn for clarity.

3.416 (2) Å, preserving their covalent and ionic character, respectively. These changes are accompanied by a change in the interatomic Se—Se distances. The variation of x_{Se}, the bond lengths and the Se—Se distances also appears to follow Kurnakov's law, since their fitting by this equation gave goodness-of-fit values better than those by linear fit (Figs. 5a and 5b). The parameters for fitting these variations are

$$\text{for Tl—Se:} \ A = 3.417, B = 3.443, C = -0.006$$
$$\text{In—Se:} \ A = 2.687, B = 2.528, C = 0.079.$$

Further, the energy gap, the conductivity, the band discontinuity and the microhardness of the Tl$_{2x}$In$_{2(1-x)}$Se$_2$ compounds studied were found to vary with the stoichiometry x according to Kurnakov's law also (Yanchev *et al.*, 1995; Hatzisymeon *et al.*, 1996).

4. Concluding remarks

The crystal structures of Tl$_{2x}$In$_{2(1-x)}$Se$_2$ for $x = 0.2$, 0.3,...0.9 were successfully solved and refined from
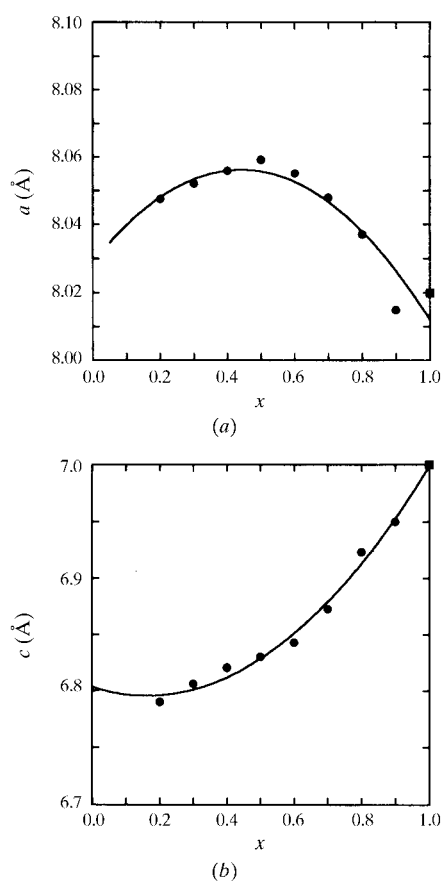

Fig. 4. Variation of lattice constants a and c as a function of stoichiometry.
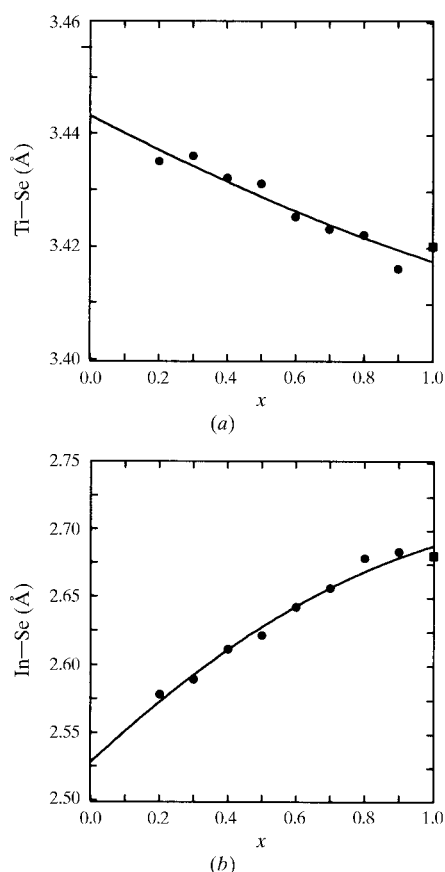

Fig. 5. Variation of bond lengths Tl—Se and In—Se as a function of stoichiometry.

powder data; for three members of the series single-crystal structure solution and refinement were carried out and the results agree.

Peak overlapping and preferred orientation, reduced by careful sample preparation, were easily overcome using *EXTRA* (Altomare *et al.*, 1995) and *SIRPOW* (Altomare *et al.*, 1994), the software packages used for the structure solution, in this case where the structures are relatively simple.

The variation of stoichiometry x from 0.2 to 0.9 alters the distribution of Tl and In cations in $4(a)$ and $4(b)$ sites and results in changes of unit cell and other structural parameters. The functional form of these changes was found to be that of Kurnakov's law and certain physical properties of the crystals vary in this way also.

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