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The Crystal Structure of Tetraindium Tritelluride

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The crystal structure of tetraindium tritelluride (In_4Te_3) has been determined from X-ray photographic data taken with Mo $K\alpha$ radiation and refined to a residual of 0·08. The phase, which is shown to be isomorphous with In_4Se_3, is orthorhombic, space group *Pnnm*, with $a=15{\cdot}630$, $b=12{\cdot}756$, $c=4{\cdot}441$ Å, $Z=4$. The material is composed of two centrosymmetrically related interlocking continuous sheets of atoms running perpendicular to **a**. These are constructed of interlinked five-membered indium–tellurium rings forming chains parallel to **c**, the chains being cross-linked by strongly bound In–In–In units forming, in ionic terms, the homonuclear triatomic cation $(In_3)^{5+}$.

Introduction

In their review of the phase diagram of the binary system In–Te Grochowski, Mason, Schmitt & Smith (1964) found no evidence for the existence of the phase In_2Te reported by Klemm & von Vogel (1934). Instead they proposed the existence of In_9Te_7. In a recent investigation of the In–Se system (Hogg, Sutherland & Williams, 1971), the phase reported by Man & Semilitov (1965) as In_2Se was shown as a result of structural analysis to be In_4Se_3, a finding confirmed by Likforman & Etienne (1972). This phase has unit-cell parameters almost identical with those quoted by Man & Semilitov for In_2Se and very similar to those for In_2Te given by Schubert, Dörre & Günzel (1954). In view of this a full structural investigation was undertaken by the authors which showed the existence of a phase In_4Te_3, isomorphous with In_4Se_3, whose parameters match those given for In_2Te. Further, the formula In_4Te_3 more closely agrees with the composition of 43% Te reported for the phase by Grochowski *et al.* (1964) than the formula In_9Te_7 which they proposed. It is concluded that the correct formula for In_2Te and In_9Te_7 is In_4Te_3.

Preparation of the phase

Mixtures of indium and tellurium in the correct stoichiometric proportions to produce In_2Te and In_9Te_7 were placed in sealed evacuated tubes and heated to 600 °C. This temperature was maintained for 24 hr whilst the tubes were shaken to ensure mixing; subsequently the samples were subjected to directional freezing over a period of 3 days to a temperature of 400 °C at which they were held for two days before cooling. The resultant boules were, in both cases, inhomogeneous but both contained black shiny needle crystals very similar in appearance to crystals of In_4Se_3. Several crystals were extracted and subsequent structural investigation proved them to be In_4Te_3.

Unit cell and space group

Unit-cell parameters were obtained by the method of Farquhar & Lipson (1946) with Cu $K\alpha$ radiation, wavelengths $K\alpha_1=1{\cdot}54051$ and $K\alpha_2=1{\cdot}54433$ Å. The cell is orthorhombic with $a=15{\cdot}630$ (3), $b=12{\cdot}756$ (3) and $c=4{\cdot}441$ (2) Å. These compare with the parameters given by Schubert, Dörre & Günzel (1954) for In_2Te $a=15{\cdot}35$, $b=12{\cdot}62$, $c=4{\cdot}46$ Å.

The space group indicated by systematic absences is either *Pnnm* or *Pnn*2. As a result of refinement the correct space group emerged as *Pnnm* (No. 58). There are four formula units per unit cell giving a calculated density of 6·32, a figure which proved impossible to check experimentally due to the exceedingly small amount of the pure material which could be isolated.

Structure determination

1754 reflexions, of which 687 were recorded as zero, were collected from Weissenberg photographs taken about **c** with multiple-film packs and Mo $K\alpha$ radiation. Reflexion intensities were measured with a Joyce–Loebl flying-spot integrating densitometer. Very weak reflexions were measured visually, and the two sets of data placed on the same scale by measuring with the densitometer the more intense reflexions of the calibrated scale used for visual estimation. Data were corrected for Lorentz and polarization factors and, in the case of visual data, for spot elongation on upper layers. No absorption correction was made since the dimensions of the crystal, which was a needle of approximately circular cross-section, gave a μR value of only 0·4. Approximate values of absolute scale and temperature factors were determined by Wilson's (1942) method. Interlayer scaling was achieved through common reflexions on precession photographs and final scaling was carried out during the least-squares refinement.

The overall intensity data bore a remarkable similarity to those of In_4Se_3 as did the Patterson projection down **c**. The similarity in unit-cell parameters has already been remarked upon. In view of this the obvious starting point for refinement was with the atomic coordinates taken from In_4Se_3. During the refinement it became clear that because of the proximity of indium and tellurium in the periodic table it would not prove possible to identify atom types from the X-ray data. At this stage it was assumed that the telluride and sele-

nide were isomorphous and on this basis refinement of positional coordinates and anisotropic thermal parameters by block-diagonal least squares with the 1067 observed reflexions proceeded very rapidly. Refinement ceased at $R=0{\cdot}08$, at which point parameter shifts were negligible. Packing and bonding considerations confirmed the choice of atom types. The weighting scheme employed was

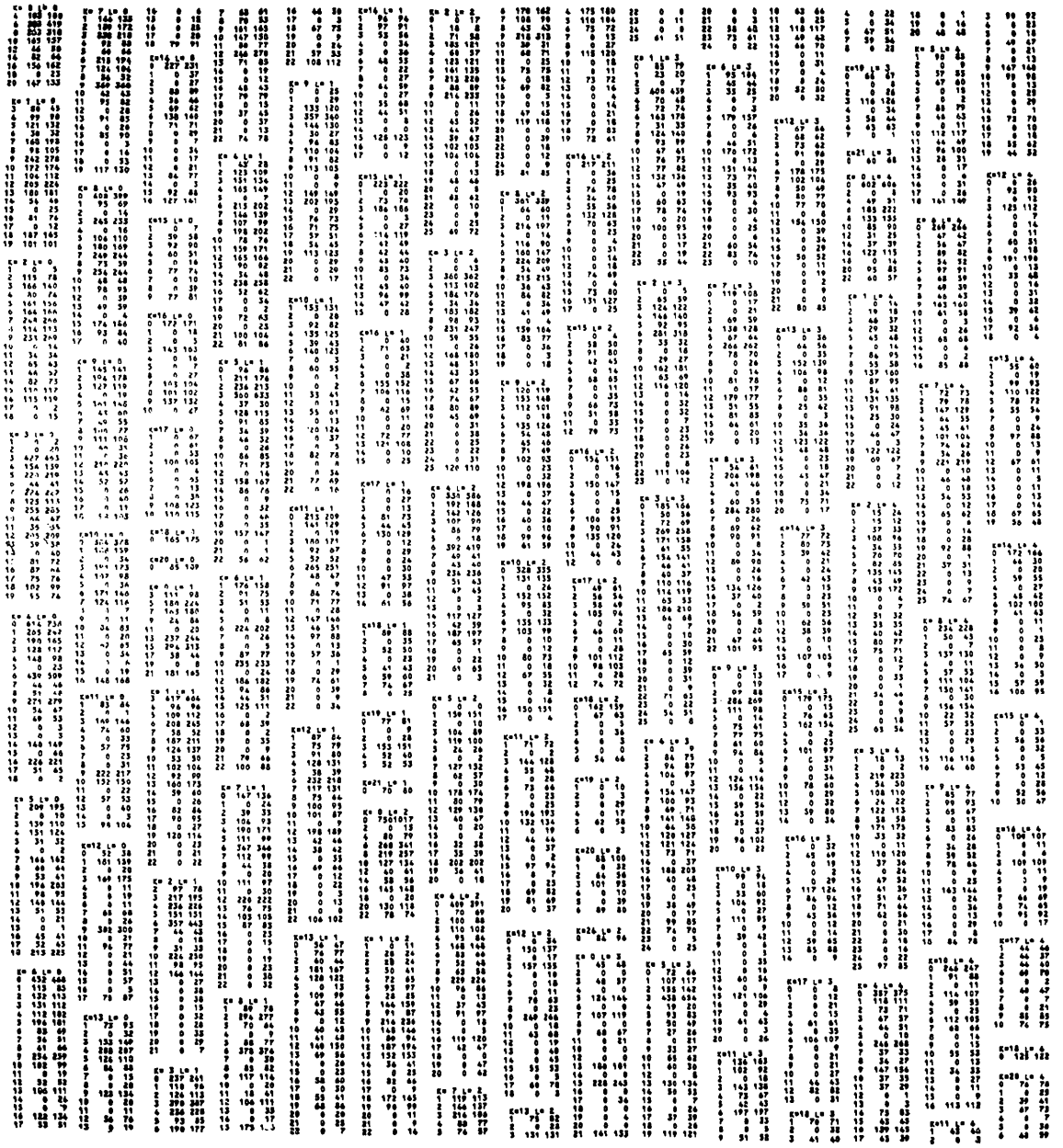
$$w=1\Big/\left[2|F_{\min}|+|F_o|+\frac{2|F_o|^2}{|F_{\max}|}+\frac{5|F_o|^3}{|F_{\max}|^2}\right].$$

Ten reflexions were omitted from the refinement due to suspected extinction but were included in the final R. The refinement, which was carried out with scattering factors for indium and tellurium taken from *International Tables for X-ray Crystallography* (1962), took place in space group *Pnnm*. Subsequent refinement in *Pnn*2 also ceased at $R=0{\cdot}08$ at which stage the z parameters did not differ significantly from 0 and $\frac{1}{2}$. It was therefore concluded that the space group was *Pnnm* with all the atoms lying on the mirror planes.

Observed and calculated structure factors are given

Table 1. *Observed and calculated structure factors*

Data in each block are arranged in columns of h, F_o and F_c.



in Table 1; atomic coordinates and anisotropic thermal parameters with their standard deviations are quoted in Table 2. A projection of the structure viewed down **c** is shown in Fig. 1.

Table 2. *Fractional coordinates* ($\times 10^4$) *and anisotropic thermal parameters* ($\times 10^4$, Å^2) *with e.s.d.'s in parentheses*

Thermal parameters are defined as
$\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{23}klb^*c^*+2U_{31}lhc^*a^*+2U_{12}hka^*b^*)]$.

	x	y	z
In(1)	7154 (2)	3449 (2)	0
In(2)	8169 (2)	5248 (2)	0
In(3)	9640 (2)	6459 (2)	0
In(4)	4276 (2)	3981 (3)	0
Te(1)	9035 (1)	8605 (2)	0
Te(2)	7739 (1)	1374 (2)	0
Te(3)	4223 (1)	1481 (2)	0

	U_{11}	U_{22}	U_{33}	$2U_{12}$
In(1)	225 (10)	130 (9)	162 (11)	55 (19)
In(2)	242 (11)	179 (10)	253 (12)	124 (21)
In(3)	195 (10)	139 (8)	140 (10)	34 (18)
In(4)	307 (13)	244 (12)	293 (15)	7 (24)
Te(1)	182 (8)	112 (7)	124 (9)	0 (16)
Te(2)	172 (9)	132 (8)	124 (10)	−1 (16)
Te(3)	169 (8)	122 (8)	106 (9)	−41 (15)

Description of the structure

The structure, which is essentially isomorphous with that of In_4Se_3, is planar with all the atoms lying in sheets on $z=0,\frac{1}{2}$. An analysis of interatomic distances indicates that the material is composed of endless chains of atoms running parallel to **c** based on a five-membered In–Te ring system [In(1), Te(2), In(2_1), In(3_1), Te(1_1)] the chains being cross-linked by strong In–In–In bonds [In(1), In(2), In(3)] to form a continuous sheet of atoms perpendicular to **a**. The structure contains two such centrosymmetrically related sheets (one of which is shown in Fig. 2) which interlock in the manner shown in Fig. 1. Bond lengths and angles within the sheets of atoms are given in Table 3. Other relevant interatomic distances including those between the centrosymmetrically related sheets are given in Table 4.

The strongly bound In–In–In group has almost exactly the same spatial configuration in both In_4Te_3 and In_4Se_3 (Hogg, Sutherland & Williams, 1973) with average bond lengths in the two materials of 2·78 and 2·77 Å and bond angles about the central atom of 158·6 and 157·8° respectively. In ionic terms, this grouping could be regarded as a triatomic cation $(In_3)^{5+}$ (Hogg, Sutherland & Williams, 1971) leading to the formula $In^+(In_3)^{5+}3Te^{2-}$. The structure, however, cannot be regarded as purely ionic, if only because of the low coordination number of all the atoms except In(4). This suggests a high degree of covalency within the $(In_3Te_3)^-$ group. Each tellurium atom is surrounded by three indium atoms in an approximately tetrahedral configuration (Fig. 2) indicating that they exist in a state of sp^3 hybridization, each forming two ordinary covalent bonds and one donor bond with the three indium atoms and each carrying one lone pair. The end members of the In–In–In group [In(1), In(3)] are also situated in roughly tetrahedral cnordination with three tellurium atoms, again indicating sp^3 hybridization.

Table 3. *Bond lengths* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

Atomic positions are as shown in Figs. 1 and 2. Subscripts 1 and 2 indicate atoms with $z=+\frac{1}{2}$ and $-\frac{1}{2}$ respectively

Te(1)—In(3)	2·896 (4)
In(3)—In(2)	2·770 (4)
In(2)—In(1)	2·790 (4)
In(2)—Te($3_1''$)	3·537 (3)
In(1)—Te(2)	2·800 (4)
Te(2)—In(2_1)	3·001 (2)
Te(1_1)—In(1)	2·902 (2)
In(3_1)—Te(3)	2·844 (2)
Te(3)—In(4)	3·190 (5)

In(3)—In(2)—In(1)	158·6 (1)
Te(2_1)—In(2)—Te(2_2)	95·4 (1)
Te(2_1)—In(2)—In(3)	97·2 (1)
Te(2_1)—In(2)—In(1)	97·2 (1)
Te($3_1''$)—In(2)—Te($3_2''$)	77·8 (1)
Te($3_1''$)—In(2)—In(3)	87·8 (1)
Te($3_1''$)—In(2)—In(1)	75·6 (1)
In(2)—In(1)—Te(2)	126·3 (1)
Te(1_1)—In(1)—Te(1_2)	99·8 (1)
Te(1_1)—In(1)—In(2)	107·9 (1)
Te(1_1)—In(1)—Te(2)	105·9 (1)
In(1)—Te(1_1)-In(3_1)	98·3 (1)
Te(1_1)—In(3_1)–In(2_1)	104·8 (1)
Te(1_1)—In(3_1)–Te(3)	101·2 (1)
In(2_1)—In(3_1)–Te(3)	121·6 (1)
In(3_1)—Te(3)–In(3_2)	102·7 (1)
In(3_1)—Te(3)–In(4)	89·6 (1)
In(2_1)—Te(2)–In(1)	107·3 (1)

Table 4. *Relevant interatomic distances* (Å) *with e.s.d.'s in parentheses*

In–Te and In–In distances < 4 Å and Te–Te distances < 4·8 Å are given.

In(4)—In(4′)	3·447 (5)
In(4)—Te(1′)	3·815 (4)
In(4)—Te(1_1)	3·483 (3)
In(4)—Te(2′)	3·303 (3)
Te(3)—In(1′)	3·924 (3)
Te(3)—In(2′)	3·537 (3)
In(3_1)—In(3′)	3·889 (4)
In(2)—In(4′)	3·946 (4)
Te(1_1)—Te(2_1)	4·072 (3)
Te(1_1)—Te(1′)	4·665 (3)
Te(1_1)—Te(3)	4·437 (3)
Te(1_1)—Te(2)	4·552 (3)
Te(3)—Te(2′)	4·219 (3)
Te(3)—Te(3′)	4·492 (3)
Te(2)—Te(3′)	4·761 (3)

The coordination around the central indium atom in this group [In(2)] does not, however, correspond to any simple hybridization. If In(2) is regarded as *sp* hybridized the group would be linear but the In(1)–In(2)–In(3) bond angle of 158·6° is somewhat less than 180°. Conversely, if In(2) is sp^3 hybridized the angle would be 109·5°. Under d^2sp^3 hybridization the angle would again be 180° with an octahedral arrangement of atoms around In(2), but whilst In(2) does indeed have six neighbours in a roughly octahedral array [In(1), In(3), $Te(2_1)$, $Te(2_2)$, $Te(3_1'')$, $Te(3_2'')$] there are considerable variations in bond distances within this grouping. In particular the bonds to atoms $Te(3_1'')$ and $Te(3_2'')$, which lie in the neighbouring sheet of atoms (Fig. 1), are some 0·5 Å longer than those to $Te(2_1)$ and $Te(2_2)$, a point noted by Likforman & Etienne (1972) in their discussion of the structure of In_4Se_3. On a covalent model this implies hybridization of In(2) some-

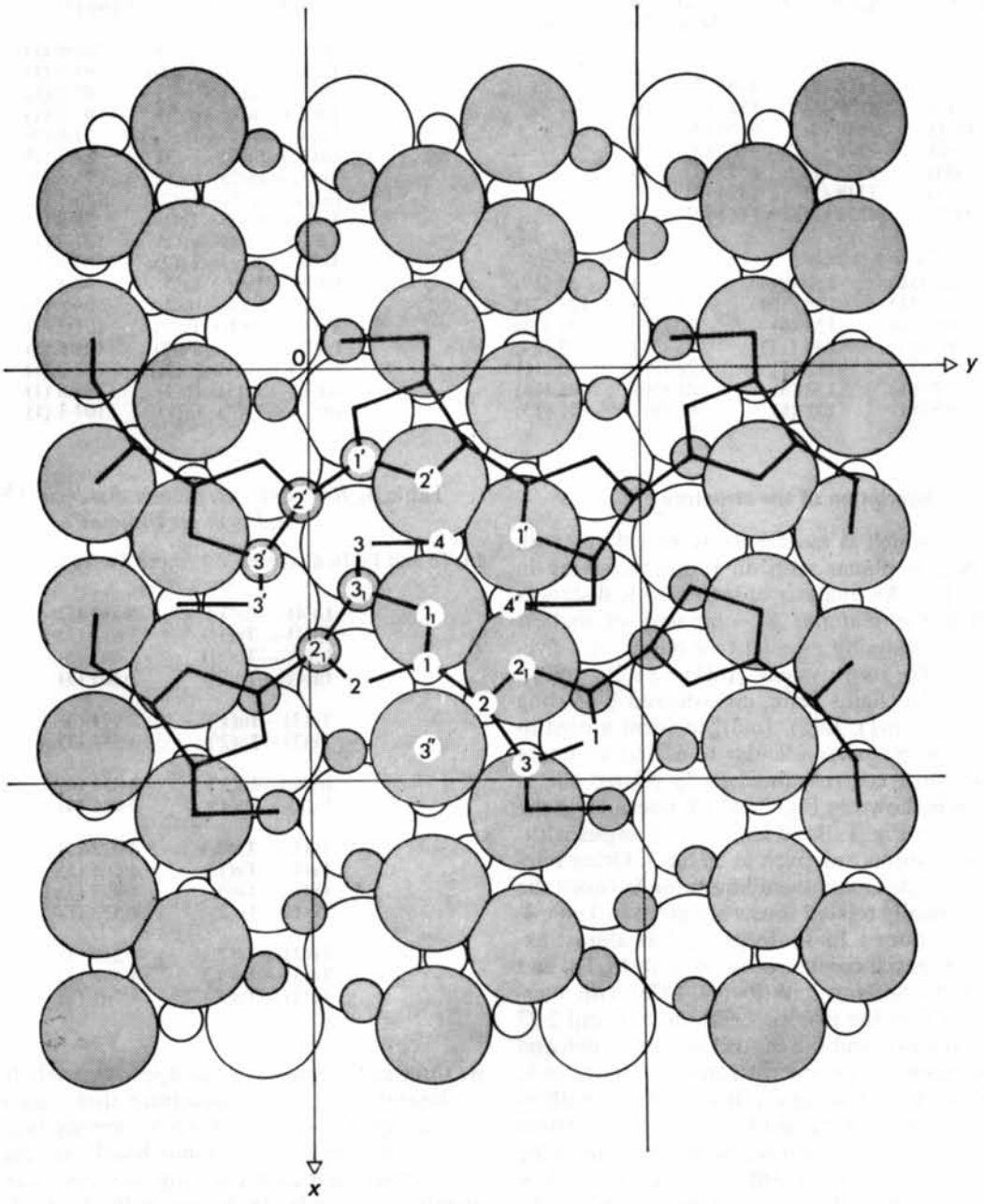


Fig. 1. In_4Te_3. A projection of the structure down **c** showing the method of bonding. The atoms are scaled to the respective ionic radii of In^{3+}(0·81 Å) and Te^{2-} (2·22 Å). Shaded and non-shaded atoms lie on $z=\frac{1}{2}$ and 0 respectively. Atom numbers refer to Tables 2, 3 and 4.

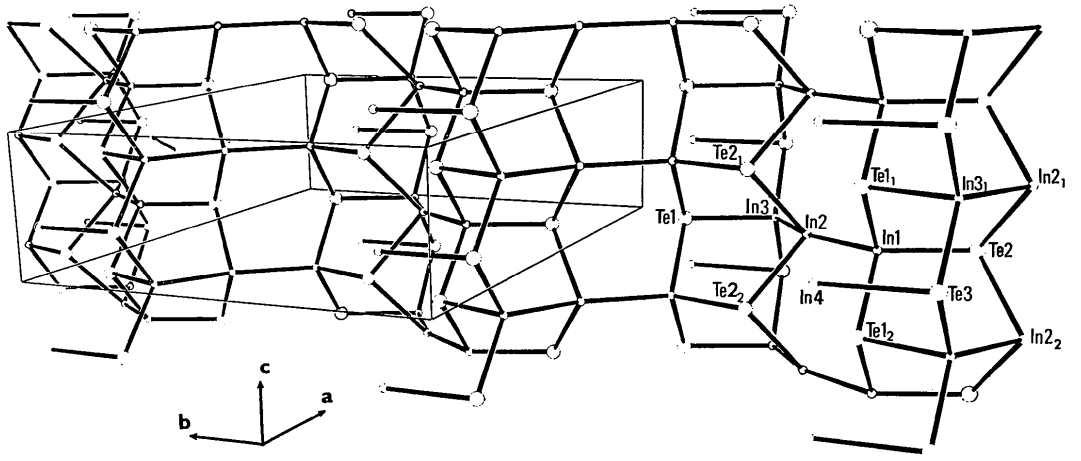


Fig. 2. One of the centrosymmetrically related continuous sheets of atoms in the structure of In_4Te_3 (drawn by *ORTEP*, Johnson, 1965). Small circles are In atoms, large circles are Te atoms. The part of the structure shown covers 3 cell translations in **b** and 2·5 in **c**. Atom designations refer to Tables 2, 3 and 4.

where between these three extremes. It needs to be remembered, however, that the material is black and lustrous, which could imply a degree of metallic bonding as well.

The remaining indium atom, In(4), is surrounded by seven tellurium atoms at distances of 3·2 to 3·8 Å plus In(4′) at 3·4 Å. This environment is consistent with the extreme ionic formulation In^+ for this indium atom.

A comparison of cell dimensions of In_4Te_3 and In_4Se_3 reveals that the *c* parameter in both cases is determined by the diameter of the appropriate anion Te^{2-}, Se^{2-}. However, neither the *a* nor *b* cell parameters of the two materials differ in proportion to the size of the anion, there being only a slight increase in these parameters from selenide to telluride. This small increase is adequately accounted for by the spatial rigidity of the $(In_3)^{5+}$ cation, which has the same configuration in both materials, plus the stabilizing influence of the tightly bound five membered In–Te/Se ring systems coupled with the changes in the (001) projected bond lengths.

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