JOURNAL OF SOLID STATE CHEMISTRY 117, 351–355 (1995)

The Crystal Structure of Tl_2GeTe_3: A Tellurogermanate(IV) with Bitetrahedral Anions

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Received September 3, 1992; in revised form April 27, 1993; accepted May 4, 1993

Black lustrous single crystals of Tl_2GeTe_3 were prepared from the melt. Tl_2GeTe_3 is orthorhombic, *oP*48, s.g. *Pnma* with a = 8.303(4) Å, b = 21.514(9) Å, c = 8.453(6) Å, Z = 8. The crystal structure was refined to a conventional R of 0.047 (R_w = 0.043, 1151 F_0's, 58 variables). The crystal structure is characterized by discrete bitetrahedral $[Ge_2Te_6]^{4-}$ groups aligned parallel to [010], which are separated by Tl^+-cations. The atomic arrangement is isostructural with Tl_2SnSe_3. © 1995 Academic Press, Inc.

INTRODUCTION

The binary systems of Si, Ge, and Sn with tellurium differ from those with the lighter chalcogens by the apparent absence of intermediate compounds in which the IVB elements attain their maximum group oxidation number (1). However, this oxidation state may easily be stabilized in ternary tellurides with electropositive metals where the group IV element and Te take part in the formation of complex anions. Thus Na_4SnTe_4 (2), Tl_2SnTe_3 (3), and the polytellurides K_2SnTe_5 (4), K_2GeTe_4 (5), Tl_2SnTe_5 (6), and Tl_2GeTe_5 (7, 8), with tetrahedrally coordinated IVB, atoms have been prepared recently.

With the exception of K_2GeTe_4 and Tl_2GeTe_5 the tellurogermanates known so far contain Ge in a formal oxidation state of +III which is obtained through the formation of complex anions containing Ge–Ge pairs. Discrete anions, $[Te_3Ge\text{–}GeTe_3]^{6-}$, have been reported for $K_6Ge_2Te_6$ (9), $Na_6Ge_2Te_6$ (10), and $Tl_6Ge_2Te_6$ (11). Condensation of such units via common tellurium atoms leads to the cyclic anions of the dimorphic $Na_8Ge_4Te_{10}$ (12, 13) or to the infinite chains of $LiGeTe_2$ (14).

While no phase analytical data have been reported for the ternary systems A–Ge–Te containing alkali–metals, a detailed thermoanalytical study of the system Tl–Ge–Te has been published recently (15), where among others the existence of Tl_2GeTe_3 has been claimed.

These findings could now be corroborated in the course of a roentgenographic investigation of this system (16). Based on single crystal data, the crystal structure of this new tellurogermanate(IV) could be determined.

EXPERIMENTAL

Synthesis of Tl_2GeTe_3. High purity elements in compact form (thallium ingots, 4*N*8; germanium lumps, 5*N*8, and tellurium pieces 5*N*8) were used as starting materials. For the synthesis of Tl_2GeTe_3 the congruently melting compound Tl_5Te_3 was prepared by reacting thallium metal (purified by melting under hydrogen and filtered under vacuum) with tellurium in a sealed Duran ampoule at 500°C, followed by slow cooling. Two grams of a stoichiometric mixture of powdered Tl_5Te_3, Ge, and Te was then sealed into an evacuated silica ampoule (inner diameter: 6 mm) and allowed to react at 750°C for 3 days. The thermal treatment was finished by a controlled cooling (2.5 deg hr^{-1}) to ambient temperature.

The crushed ingot was of uniform and homogeneous appearance under the microscope. Its fragments were black and lustrous and did not show metallic conductivity. The compound is stable in air. Single crystal specimen did not show characteristic crystal habits.

The comparison of the Guinier powder pattern with a theoretical powder diagram obtained by FINAX (17) based on the structural parameters obtained by the single crystal investigation confirmed that the sample was essentially single phase Tl_2GeTe_3, though the compound according to Abba-Touré *et al.* (15) is formed by a peritectic reaction at 378°C. This may be taken as an indication that the cooling rate was sufficiently low to attain phase equilibrium. The crystal data reported for Tl_2GeTe_3 by these authors (s.g. *Immm*, $I2_12_12_1$ or *I*222, a = 4.13 Å, b = 12.02 Å, c = 8.48 Å) could, however, not be confirmed in the present study. Since neither explicit experimental information on how these data were obtained nor an empirical powder diagram have been given, a sound discussion of this discrepancy is not possible. No phase transformation has been reported for Tl_2GeTe_3 (15) nor do our

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0022-4596/95 $12.00

TABLE 1
Crystallographic Data and Structure Refinement of Tl_2GeTe_3

Pearson symbol	*oP*48
Lattice dimensions	
a	8.303(4) Å
b	21.514(9) Å
c	8.453(6) Å
Space group	*Pnma* (No. 62)
Z	8
V	1509.5 Å^3
d_{calc}	7.61 g cm^{-3}
M_r	864.1
$\mu_{MoK\alpha}$	583 cm^{-1}
Unique reflections	1687
$F_0^2 > 3\sigma(F_0^2)$	1151
Refined variables	58
$R = \sum \|\|F_0\| - \|F_c\|\| / \sum \|F_0\|$	0.047
$R_w = [\sum w(\|F_0\| - \|F_c\|)^2 / \sum w\|F_0\|^2]^{1/2}$	0.043
$w = [\sigma(F_0^2)^2 + (0.002 \times F_0^2)^2]^{-1/2}$	
Largest diff. peak	2.8 *e* Å^{-3}

investigations give any indications for a potential dimorphism of this compound.

Structure determination. Preliminary investigations by single crystal film methods revealed orthorhombic symmetry. The systematic extinctions ($0kl$: $k + l \neq 2n$ and $hk0$: $h \neq 2n$) led to *Pnma* and $Pn2_1a$ as possible space groups. For the data collection a prismatic single crystal was cut to the approximate dimensions 0.1 × 0.1 × 0.06 mm, mounted on a glass fiber and transferred to a four circle diffractometer (ENRAF NONIUS CAD4) operated with graphite monochromated Mo$K\alpha$-radiation (λ = 0.71069 Å). The unit cell dimensions were refined using 25 independent reflections in the 2θ-range 25–35° centered at four different settings. They are listed in Table 1 together with other crystallographically relevant data. The intensity data were collected over one octant of the reflection sphere up to 2θ = 54° (ω–2θ-scans, scan-width 1° + 0.35° tan θ, maximum scan time 140 sec). Evaluation of the periodically determined control reflections showed only statistical fluctuations.

The crystal structure was solved by direct methods [MULTAN 82] (18) in the centrosymmetric space group *Pnma*, yielding the complete structure. Full matrix least squares refinements (*F*-refinement) rapidly converged to a conventional *R* of 0.047. The final shift over error ratio was less than 0.005. A difference Fourier map calculated at this stage of refinement revealed no physically significant peaks.

All calculations were performed on a DEC Microvax-3520 computer using programs of the MOLEN crystallographic software package (19). Atomic scattering factors for the neutral atoms and coefficients for anomalous dispersion effects were taken from the International Tables (20). Absorption effects were approximately accounted for by a spherical correction (μR = 1.8). The final positional parameters are listed in Table 2. Structure factor tables and a list of anisotropic thermal parameters have been deposited under the deposition number C.S.D. 56186 with the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information m.b.H., D-76344 Eggenstein Leopoldshafen 2, Germany.

TABLE 2
Positional Parameters and Equivalent Isotropic Temperature Factors for Tl_2GeTe_3[a]

Atom	*x*	*y*	*z*	B_{eq} (Å^2)
Tl(1)	0.1793(1)	0.16876(6)	0.5181(1)	1.76(2)
Tl(2)	0.2194(2)	0.00756(6)	0.4508(2)	2.62(2)
Ge(1)	0.1762(3)	0.1675(1)	0.0094(3)	0.78(4)
Te(1)	0.0065(3)	0.250	0.1705(3)	0.88(4)
Te(2)	0.3369(3)	0.250	0.8402(3)	0.86(4)
Te(3)	0.5136(2)	0.09135(8)	0.6678(2)	1.19(3)
Te(4)	0.3752(2)	0.10792(8)	0.1883(2)	0.88(3)

[a] $B_{eq} = \frac{1}{3}(B_{11} + B_{22} + B_{33})$

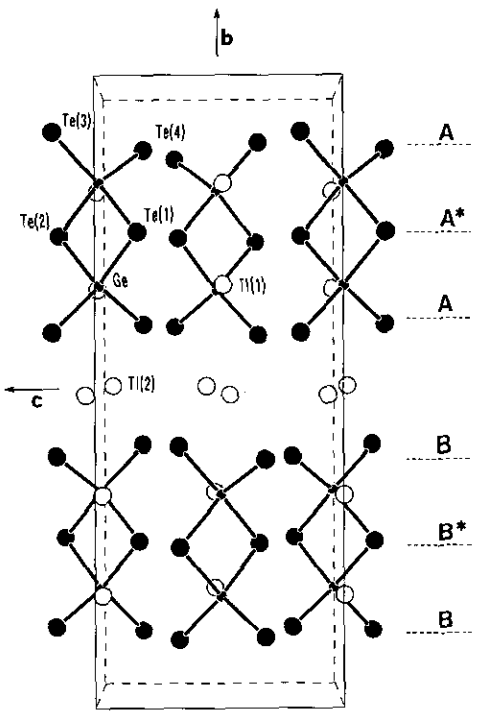

FIG. 1. Perspective view of the structure of Tl_2GeTe_3 along [100]. The capital letters to the right indicate the different stacking positions of the 3^2434-layers of tellurium atoms (see text).

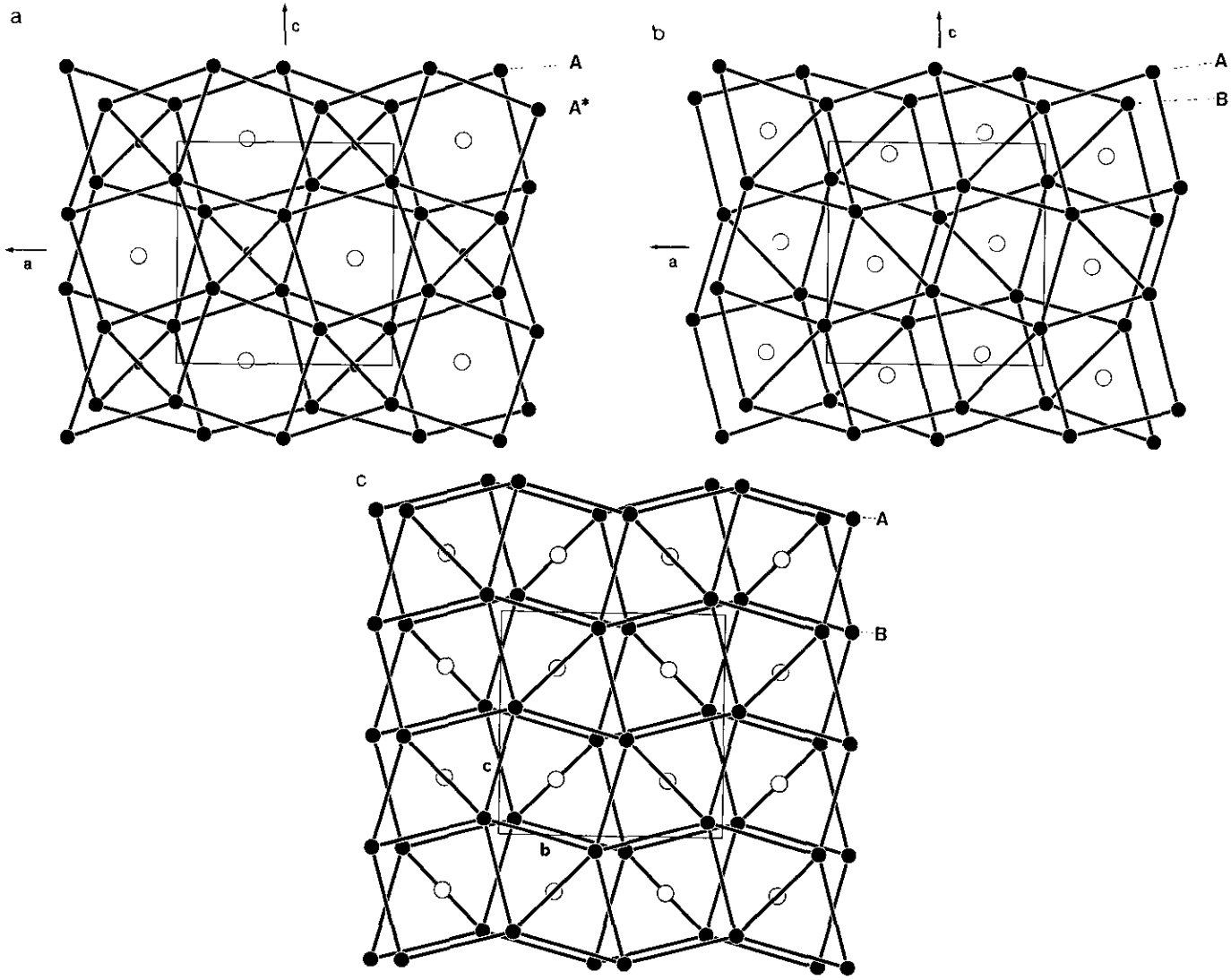

FIG. 2. (a) The antisymmetric stacking (AA^* or BB^*) of two square triangle 3^2434-layers of tellurium atoms (full circles) in the structure of Tl_2GeTe_3. The distorted square antiprismatic sites are occupied by Tl(1) (open circles), tetrahedral sites by Ge. (b) The AB stacking of square triangle 3^2434-layers of tellurium atoms in the structure of Tl_2GeTe_3. The asymmetric interstitial sites formed by this stacking are occupied by Tl(2) (open circles). (c) The AB stacking of square triangle 3^2434-layers of selenium atoms (full circles) in $K_4Sn_3Se_8$. Interstitial sites occupied be K-ions (open circles).

RESULTS AND DISCUSSION

In contrast to the homologous chalcogenides Tl_2GeS_3 (21) and Tl_2GeSe_3 (22) ($aP12$), the atomic arrangement of Tl_2GeTe_3 is isostructural with that of Tl_2SnSe_3 (23). The only other compound so far know to adopt this orthorhombic structure type is Tl_2SnTe_3 (3). All the compounds mentioned above are, in a partial ionic description, characterized by discrete anionic moieties $[M_2^{IV}Q_6]^{4-}$ which are built up by two distorted MQ_4-tetrahedra sharing one common edge.

Figure 1 shows a projection of the crystal structure of Tl_2GeTe_3 along [001] and indicates the atom labeling adopted for its description. Interatomic distances and bond angles are listed in Table 3. The bitetrahedral anionic groups are oriented along [010]. They are arranged in slabs parallel to (010) which are separated from each other by the Tl(2)-cations, whereas the Tl(1)-ions separate the groups within the slabs.

The symmetry of the groups is C_S, the common edge of the $GeTe_4$-tetrahedra lying in the mirror plane. As may be expected Ge–Te-bond distances to the terminal Te-atoms are shorter ($\overline{d}_{(Ge-Te)t}$ = 2.589 Å) than those to the bridging tellurium atoms ($\overline{d}_{(Ge-Te)b}$ = 2.642 Å). Compared to the values found in K_2GeTe_4 ($\overline{d}_{(Ge-Te)t}$ = 2.526 Å, $\overline{d}_{(Ge-Te)b}$ = 2.635 Å) (5) the difference is however rather small. A better agreement is found with the corresponding distances in the redetermined structure of Tl_2GeTe_5 (16):

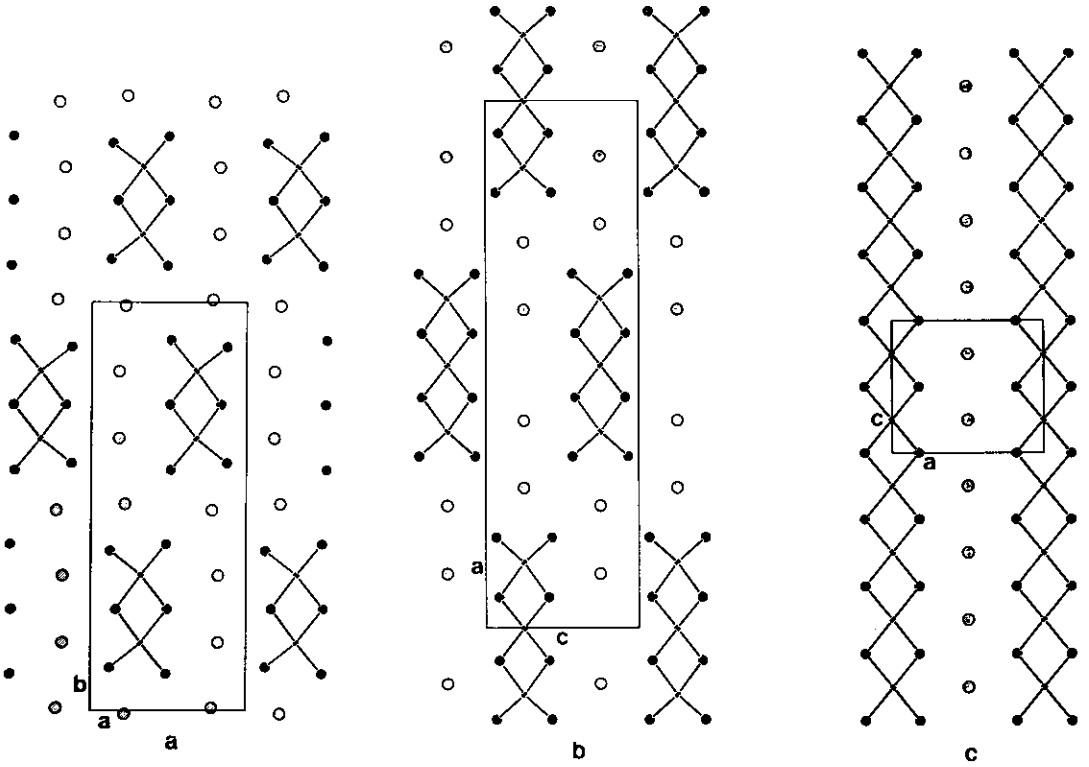

FIG. 3. The crystal structures of Tl_2GeTe_3 (a), $K_4Sn_3Se_8$ (b), and TlSe (c) in comparative representation. For the sake of clarity only one half of the translation period is shown along the projection axis.

$d_{(Ge-Te)t}$ = 2.601(4) Å, $d_{(Ge-Te)b}$ = 2.644(5) Å. The apparently larger $d_{Ge-Te)t}$ values in the thallium compounds may possibly be due to covalent contributions in the Tl–Te-bonding. As with many bitetrahedral groups the largest deviation of the bond angles from the regular tetrahedral value are found between the bridging atoms (∠Te(1)–Ge–Te(2) = 95.5(1)°).

TABLE 3
Interatomic Distances (up to 4 Å) and Bond Angles for Tl_2GeTe_3

Tl(1)–Te(4)	3.334(2)		Tl(2)–Te(3)	3.231(2)
Tl(1)–Te(3)	3.422(2)		Tl(2)–Te(4)	3.289(2)
Tl(1)–Te(3)	3.473(2)		Tl(2)–Te(4)	3.355(2)
Tl(1)–Te(4)	3.481(2)		Tl(2)–Te(3)	3.545(2)
Tl(1)–Te(2)	3.489(3)		Tl(2)–Te(3)	3.740(2)
Tl(1)–Te(2)	3.544(2)		Tl(2)–Te(4)	3.768(2)
Tl(1)–Te(1)	3.600(3)		Tl(2)–Tl(2)	3.748(3)
Tl(1)–Te(1)	3.706(3)		Tl(2)–Ge	3.897(3)
Tl(1)–Tl(1)	3.496(3)			
Tl(1)–Tl(2)	3.531(2)			
Ge–Te(4)	2.580(3)		Te(1)–Ge–Te(2)	95.5(1)°
Ge–Te(3)	2.598(3)		Te(2)–Ge–Te(4)	109.2(1)°
Ge–Te(2)	2.640(3)		Te(3)–Ge–Te(4)	110.9(1)°
Ge–Te(1)	2.643(3)		Te(1)–Ge–Te(4)	111.9(1)°
Ge–Ge	3.550(5)		Te(2)–Ge–Te(3)	112.0(1)°
Ge–Te(4)	3.795(3)		Te(1)–Ge–Te(3)	116.4(1)°
Te(1)–Te(4)	3.458(2)	2×	Ge–Te(1)–Ge	84.4(1)°
Te(1)–Te(2)	3.911(3)			
Te(2)–Te(3)	3.991(2)	2×	Ge–Te(2)–Ge	84.5(1)°

The two crystallographically independent thallium atoms have very different chalcogen coordinations. Tl(1) is surrounded by eight Te-atoms in a distorted square antiprismatic configuration ($d_{Tl(1)-Te}$ = 3.334–3.706 Å). The coordination around Tl(2) is even less regular: Six Te-atoms coordinate in a rather polar configuration ($d_{Tl(2)-Te}$ = 3.231–3.768 Å) which may indicate an, in comparison with Tl(1), more pronounced stereochemical activity of the s^2 pair on Tl(2).

An apparent metrical peculiarity of the structure of Tl_2GeTe_3 is its pseudotetragonal axial ratio a/c = 0.982. In fact its atomic arrangement can be conceived as to contain fragment blocks, $Tl(1)_2Ge_2Te_6$, of the tetragonal ($tI16$) TlSe ($Tl^{I}Tl^{III}Se_2$) structure type (24) which are separated from each other by the Tl(2)-layers. A common geometrical feature of both structures is the layered arrangement of the chalcogen atoms which occupy the nodes of square triangle 3^2434 nets. In TlSe neighboring layers overlie antrisymmetrically along [001] (they are mutually shifted by $\frac{1}{2}$ of the a-translation periods). This stacking, which may be denoted as $\ldots AA^*\ldots$ stacking, leads to tetrahedral sites occupied by Tl^{III} forming $^1_\infty$-$[TlSe]^{2-}$-chains of edge sharing tetrahedra while the monovalent cations occupy distorted square antiprismatic

interstices. In Tl_2GeTe_3 corresponding, though distorted chalcogen layers can be made out perpendicular to [010]. A slightly corrugated 3^2434 layer (denoted as *A* and *B* in Figs. 1 and 2a) is formed by Te(3) and Te(4) whereas by Te(1) and Te(2) build up a planar layer (denoted as *A** and *B**) passing through the mirror plane. The stacking sequence *AA*A* yielding the sites occupied by Tl(1) and Ge is repeated by the symmetrically related sequence *BB*B*. *A*- and *B*-type layers have essentially the same orientation, but are shifted against each other by a pseudo-glide (predominantly effective) along [100] ($|\Delta x| \approx 0.4$) (Fig. 2b). This stacking creates very asmmetric interstices (formed by overlying squares and triangles) well suited to host the stereochemically active Tl(2)-ions.

A similarly close relationship to the TlSe-structure type can be found in the atomic arrangement of $K_4Sn_3Se_8$ (25), which like Tl_2GeTe_3 is also characterized by finite anionic chains of edge sharing tetrahedra. In this metrically pseudotetragonal structure (*oC*60, s.g. *Ccca*, $a = 27.766$ Å $b = 8.191$ Å, $c = 8.187$ Å, $Z = 4$), the square triangle layers of the chalcogen atoms are stacked along [100]; the stacking sequence is $\cdots AA^*AA^*B^*BB^*B\cdots$, yielding discrete triple chains $[Sn_3Se_8]^{4-}$. One half of the K^+-ions (K(1)) occupies the distorted square antiprismatic sites of this packing, while the other (K(2)) occupies sites created through the $AB(A^*B^*)$ stacking step (Fig. 2c). In contrast to Tl_2GeTe_3 the neighboring *A*- and *B*-type layers are now related by a true crystallographic glide operation (the *c*-glide normal to [100]) yielding sites which allow a fairly regular sixfold coordination of the alkali cations ($d_{K(2)-Se} = 3.363$–3.438 Å). A comparative representation of the related crystal structures of Tl_2GeTe_3, $K_4Sn_3Se_8$ and TlSe is given in Fig. 3.

ACKNOWLEDGMENT

Support through the Austrian Federal Ministry of Science and Research and through the Linzer Hochschulfonds is gratefully acknowledged.

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