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Thallium Silver Chalcogenides of the Ordered *anti*-$PbCl_2$-Structure Type

Short Communication

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TlAgS, TlAgSe and TlAgTe crystallize with the ordered *anti*-$PbCl_2$-structure type, space group Pnma, $Z = 4$. The lattice constants are: TlAgS: $a = 722.8(3)$, $b = 446.6(1)$, $c = 833.1(2)$ pm. TlAgSe: $a = 747.56(3)$, $b = 463.75(2)$, $c = 869.0(1)$ pm. TlAgTe: $a = 775.9(1)$, $b = 486.8(1)$, $c = 877.3(2)$ pm. The crystal structure of TlAgSe was refined from single crystal diffractometer data to a conventional R-factor of 0.045. The relationship with the $BaCu_2S_2$-structure type is discussed.

(Keywords: Chalcogenides; Crystal structure; Thallium silver chalcogenides; Thallium silver selenide)

Thallium-Silber-Chalkogenide vom anti-$PbCl_2$*-Strukturtyp*
(Kurze Mitteilung)

TlAgS, TlAgSe und TlAgTe kristallisieren im geordneten *anti*-$PbCl_2$-Strukturtyp, Raumgruppe Pnma, $Z = 4$. Die Gitterkonstanten betragen: TlAgS: $a = 722{,}8(3)$, $b = 446{,}6(1)$, $c = 833{,}1(2)$ pm. TlAgSe: $a = 747{,}56(3)$, $b = 463{,}75(2)$, $c = 869{,}0(1)$ pm. TlAgTe: $a = 775{,}9(1)$, $b = 486{,}8(1)$, $c = 877{,}3(2)$ pm. Die Kristallstruktur von TlAgSe wurde aus Einkristalldiffraktometerdaten zu einem konventionellen R-Wert von 0,045 verfeinert. Die Verwandtschaft zum $BaCu_2S_2$-Strukturtyp wird diskutiert.

The compounds TlAgS, TlAgSe and TlAgTe were prepared by annealing stoichiometric mixtures of thallium chalcogenide, silver and the corresponding chalcogen at 570 K in sealed and evacuated silica tubes. The sintered reaction products showed bright metallic lustre. *Guinier* photographs (CuKα-radiation) were taken. The similarity of the diffraction diagrams indicated that the three compounds were isotypic. Preliminary crystallographic investigations (*Weissenberg*- and rotating crystal photographs) showed orthorhombic symmetry with systematic extinctions for $hk0$: $h = 2n + 1$ and $0kl$: $k + l = 2n + 1$, indicating Pnma and $Pna2_1$ as possible groups.

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Intensity data were collected for a single crystal of TlAgSe on an automatic four circle diffractometer (Philips PW 1100) using graphite monochromated MoKα-radiation (θ-2θ-scans, $6° < 2\theta < 54°$, $196\,I_0$). Atomic scattering factors were taken from *Cromer* and *Mann*[1], a spherical absorption correction and corrections for anomalous dispersion[2] were applied. Composition, symmetry and cell dimensions suggested isotypy with NaCdSb, which crystallizes with the *anti*-$PbCl_2$-structure type[3]. Its positional parameters were taken as starting values in a full matrix least squares refinement (XRAY 76[4]) which after several cycles converged to an R-value of 0.045 [$R_w = 0.053$, $w = 1/\sigma^2(F)$]. The final atomic parameters are listed in Table 1. On the basis of these parameters powder diagrams were calculated for TlAgS and TlAgTe (LAZY PULVERIX[5]). They showed satisfactory agreement with the observed powder diagrams.

Table 1. *Atomic coordinates and averaged isotropic temperature factors for* TlAgSe *with anti*-$PbCl_2$-*structure type, space group Pnma. All atoms are on equipoint 4 (c). The temperature factor is expressed as* $T = \exp(-2\pi^2 U s^2)$, *where* $s = 1/d_{hkl}$. *E.s.d.'s are given in parentheses*

Atom	x	y	z	U (pm^2)
Tl	0.5005(3)	1/4	0.6772(2)	257(5)
Ag	0.6706(6)	1/4	0.0822(5)	310(10)
Se	0.3179(6)	1/4	0.1048(5)	170(10)

The interatomic distances are listed in Table 2, a projection of the crystal structure is shown in Fig. 1. Ag is coordinated to four Se, which form a stretched tetrahedron. The Ag-atom is very close to one of the tetrahedral faces, a feature also observed in the thioargentates $K_2Ag_4S_3$[6] and $CsAg_3S_2$[7]. The average Ag—Se distance, $\bar{d}_{\mathrm{Ag—Se}} = 272\,\mathrm{pm}$, indicates an important covalent contribution to the Ag—Se bonding ($r_{\mathrm{Ag}}^{\mathrm{cov}} + r_{\mathrm{Se}}^{\mathrm{cov}} = 144 + 116 = 260\,\mathrm{pm}$; $r_{\mathrm{Ag^+}} + r_{\mathrm{Se^{2-}}} = 126 + 198 = 324\,\mathrm{pm}$). The $AgSe_4$-tetrahedra share two skew edges thus forming infinite chains. These chains are in turn linked by corner sharing of tetrahedra, which results in the formation of an $\overset{3}{\infty}$-dimensional network with large channels parallel to [010]. The Tl-atoms, located in these channels, are coordinated to six Se in an irregular octahedral configuration. The average Tl—Se-distance, $\bar{d}_{\mathrm{Tl—Se}} = 335\,\mathrm{pm}$, indicates predominantly ionic bonding ($r_{\mathrm{Tl^+}} + r_{\mathrm{Se^{2-}}} = 140 + 198 = 338\,\mathrm{pm}$). The coordination of Tl is completed by six Ag in the range between 324 and 363 pm, which also form a distorted octahedron.

Some of these Tl—Ag distances are remarkably shorter than corresponding distances in the thio- and selenoargentates of K^+ and Rb^+[6–8], whose ionic radii are close to that of Tl^+. The shortest K—Ag distance in $K_2Ag_4S_3$[6] for instance amounts to 353 pm, the shortest

Table 2. *Interatomic distances (pm) for* TlAgSe *up to 400 pm (standard deviations are given in parentheses)*

Tl —	2 Se	315.9(4)	Ag —	Se	264.5(6)	Se —	Ag	264.5(6)
—	2 Se	328.5(4)	—	2 Se	269.4(4)	—	2 Ag	269.4(4)
—	Se	335.2(5)	—	Se	284.7(6)	—	Ag	284.7(6)
—	Se	384.3(5)						
			—	2 Tl	324.0(4)	—	2 Tl	315.9(4)
—	2 Ag	324.0(4)	—	Tl	328.8(5)	—	2 Tl	328.5(4)
—	Ag	328.8(5)	—	2 Tl	339.0(4)	—	Tl	335.2(5)
—	2 Ag	339.0(4)	—	Tl	362.6(5)	—	Tl	384.3(5)
—	Ag	362.6(5)						
			—	2 Ag	362.6(5)	—	2 Se	391.9(5)
—	2 Tl	369.1(3)						
—	2 Tl	393.3(3)						

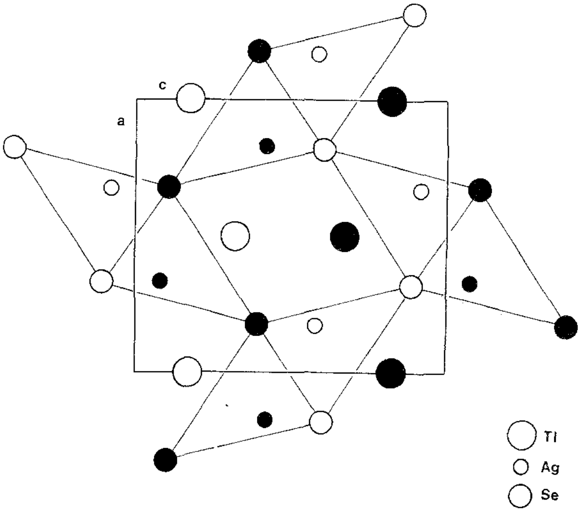

Fig. 1. Projection of the crystal structure of TlAgSe along [010]. Atoms at $y = 1/4$ are represented by full circles, atoms at $y = 3/4$ by open circles

Rb—Ag distance in $RbAg_3Se_2$[8] to 384 pm. Short Tl—Ag distances are on the other hand also observed in other chalcogenides (in which, on the basis of the Tl-chalcogen distances thallium appears to be present as Tl^+) such as $TlAgSe_2$[9] ($d_{Tl—Se}$: 311-384 pm, $d_{Tl—Ag}$: 315 and 339 pm) or $TlAg_{5.4}S_{3.4}$[10] ($d_{Tl—S}$: 332 pm, $d_{Tl—Ag}$: 341 pm). In view of the scarcity of structural data and the lack of physical measurements it is at present not possible to deduce particular Tl—Ag interactions in these compounds.

Neglecting the difficulty in the interpretation of the Tl—Ag distances, TlAgSe may be represented by an ionic formula. Since the channels formed by the AgSe-network take up two Tl^+-cations per translation period an adequate formulation is given by $(Tl^+)_2[Ag_2Se_2]^{2-}$, which sheds light upon the relationship with the isoelectronic $[Cu_2S_2]^{2-}$-anion found in $BaCu_2S_2$[11]. The anionic network of the latter is also built up by tetrahedral chains linked by corner sharing. Its structure is however more complex, since two different types of tetrahedra take part in the formation of the chains. The resulting channels are more narrow thans those in the $[Ag_2Se_2]^{2-}$-network and hence contain only one Ba^{++}-cation per translation period, thus leading to a different stoichiometry.

The title compounds are the first chalcogenides found to crystallize with the *anti*-$PbCl_2$-structure type. Their existence is a further indication for the high ability of this structure type to accomodate the coordination requirements of its constituent atoms by relatively small changes of axial ratios and atomic parameters. A classification of this structure type on the basis of axial ratios has recently been given by *Flahaut* and *Thévet*[12], according to which the present compounds belong to the Co_2P-branch[13] of this structure type.

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