

The Crystal Structure of AgTlX Phases ($X = S, Se, Te$)

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The isomorphism of ternary compounds AgTlX ($X = S, Se, Te$) is pointed out. The compounds have an orthorhombic unit cell with four formulas and the space group is *Pnam*. The crystal structure of AgTlTe has been solved with a final *R* value of 0.098. Silver and tellurium atoms are covalently bonded in chains of AgTe₄ tetrahedra delimiting channels where thallium atoms are located.

1. Introduction

In the last few years interesting investigations into the physical properties of ternary compounds AgTlX ($X = S, Se, Te$) have been carried out. They have shown that AgTlS has a high thermoelectric power (2500 $\mu V/^{\circ}C$, 4.5 $\mu W/cm^{\circ}C$) (1). However, no overall work has ever really studied the structural aspect of these compounds. The first work in the field is that of Kamsu Kom (2). He prepared the two phases AgTlS and AgTlSe and proposed a cubic unit cell for them. In 1971 Soulard and Tournoux investigated the ternary system AgTlS (3). The phases AgTlS, Ag₃TlS₂, and AgTlS₂ were confirmed in particular by their crystallographic data. In 1970 and 1975 Kovaleva *et al.* (4, 5) studied the ternary system Ag-Tl-Te in quasi-binary sections Ag₂Te-Tl₂Te and Ag₂Te-Tl₂Te₃ and showed the formation of AgTlTe and AgTlTe₂ (6). We have undertaken the crystallographic investigation of AgTlSe and AgTlTe hoping to establish some correlation between struc-

ture and electrical properties. The present paper concerns the structural study of these phases.

2. Experimental Procedures

A. Preparation of Specimens

The specimens of the three phases (AgTlS, AgTlSe, AgTlTe) were synthesized by melting stoichiometric quantities of the elements in quartz tubes sealed under vacuum (10^{-3} Torr). The samples were heated up to 800°C, cooled slowly, and

TABLE I
LATTICE PARAMETERS FOR AgTlX COMPOUNDS

	AgTlS (3)	AgTlSe	AgTlTe
<i>a</i> (Å)	8.323(5)	8.386(3)	8.775(2)
<i>b</i> (Å)	7.238(5)	7.470(3)	7.763(2)
<i>c</i> (Å)	4.464(5)	4.633(2)	4.867(1)
<i>V</i> (Å ³)	269(1)	290.2(8)	331.5(5)
<i>dx</i> (g/cm ³)	8.51	8.93	8.80
<i>Z</i>	4	4	4

annealed for 3 days at 300°C. The crystal used to determine the structure of AgTlTe was obtained by crystal growth following Bridgman's method. The products were maintained in the liquid state for at least 1 day before the beginning of the run. The ampoule travel rate was 0.5 mm/hr. The temperature near the

TABLE II
OBSERVED AND CALCULATED
INTERRETICULAR SPACINGS OF THE X-RAY
POWDER DIFFRACTION PATTERN FOR AgTlSe

<i>h k l</i>	D_{calc}	D_{obs}	I/I_0
2 0 0	4.193	4.183	10
0 1 1	3.937	3.927	15
0 2 0	3.735	3.723	<5
1 1 1	3.564	3.556	<5
2 0 1	3.109	3.101	<5
2 1 1	2.870	2.864	85
2 2 0	2.789	2.784	25
1 2 1	2.747	2.743	100
3 1 0	2.618	2.614	30
1 3 0	2.387	2.383	30
0 0 2	2.316	2.314	45
0 2 1	2.193	2.190	40
1 1 2	2.139	2.138	<5
1 3 1	2.122	2.119	<5
4 0 0	2.096	2.094	10
2 0 2	2.028	2.026	<5
0 2 2	1.9686	1.9662	<5
2 5 1	1.9435	1.9433	<5
0 4 0	1.8675	1.8659	10
3 3 0	1.8593	1.8581	10
4 1 1	1.8505	1.8489	25
4 2 0	1.8282	1.8273	<5
2 2 2	1.7820	1.7806	15
3 1 2	1.7348	1.7335	25
0 3 2	1.6960	1.6931	10
1 3 2	1.6624	1.6608	15
4 0 2	1.5544	1.5532	<5
0 1 3	1.5123	1.5122	<5
1 3 0	1.4708	1.4708	20
5 2 1	1.4528	1.4519	15
2 0 3	1.4491	1.4486	10
4 2 2	1.4351	1.4343	<5
2 1 3	1.4226	1.4219	20
2 5 0	1.4073	1.4066	15
6 0 0	1.3977	1.3973	<5
5 3 0	1.3911	1.3904	<5

TABLE III
OBSERVED AND CALCULATED
INTERRETICULAR SPACINGS OF THE X-RAY
POWDER DIFFRACTION PATTERN FOR AgTlTe

<i>h k l</i>	D_{calc}	D_{obs}	I/I_0
2 0 0	4.387	4.384	15
0 1 1	4.124	4.126	10
2 1 1	3.005	3.003	100
2 2 0	2.907	2.904	30
1 2 1	2.868	2.867	95
3 1 0	2.737	2.736	55
1 3 0	2.482	2.481	30
0 0 2	2.434	2.434	70
3 1 1	2.386	2.384	5
0 3 1	2.285	2.284	40
4 0 0	2.194	2.195	10
3 2 1	2.106	2.107	10
2 3 1	2.026	2.026	10
4 1 1	1.9368	1.9363	5
2 2 2	1.8660	1.8667	20
3 1 2	1.8187	1.8184	25
1 3 2	1.7376	1.7372	15
3 4 1	1.5347	1.5349	35
0 4 2	1.5173	1.5176	20
3 3 2	1.5160	1.5149	45
2 1 3	1.4932	1.4929	15
1 2 3	1.4755	1.4758	20
6 0 0	1.4625	1.4625	25

solidification point was stabilized with an accuracy of 0.5°C.

B. Data Determination

For unit-cell determination suitable AgTlSe and AgTlTe crystals were chosen. X-Ray crystal analysis using the Weissenberg method shows that these compounds crystallize in the orthorhombic system. The systematic extinctions observed were consistent with the $Pna2_1$ and $Pnam$ space groups. The centrosymmetric group was chosen later, during the structural determination. The density measurement indicates four molecules per unit cell. The AgTlSe powder pattern is very similar to that of Soulard and Tournoux. It can be indexed on the basis of the same orthorhombic cell with lattice parameters close to those

TABLE IV
FINAL ATOMIC PARAMETERS FOR AgTlTe^a

	<i>X/a</i>	<i>Y/b</i>	<i>Z/c</i>	<i>B</i> (Å ²)		
Tl	0.5106(4)	0.6742(4)	$\frac{1}{4}$	1.08(8)		
Te	0.1867(5)	0.3925(6)	$\frac{1}{4}$	0.35(9)		
Ag	0.8389(9)	0.4236(8)	$\frac{1}{4}$	1.10(10)		
	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Tl	0.0077(9)	0.012(1)	0.004(1)	0.001(1)	0	0
Te	0.0020(2)	0.0017(2)	0.014(1)	0.005(2)	0	0
Ag	0.038(4)	0.013(4)	0.008(2)	-0.016(3)	0	0

^a $\exp[-2\pi^2 (h^2 a^{*2} U_{11} + k^2 b^{*2} U_{22} + l^2 c^{*2} U_{33} + hka^* b^* U_{12} + hla^* c^* U_{13} + klb^* c^* U_{23})]$. Standard deviations of the least significant figure are given in parentheses.

of AgTlSe and AgTlTe. This evidence suggests that the three compounds are isomorphous. Table I presents lattice parameters for the three compounds. Tables II and III show the diffraction planes, interreticular spacings, and relative intensities for AgTlSe and AgTlTe.

3. Structure Analysis

The crystal used in the structural deter-

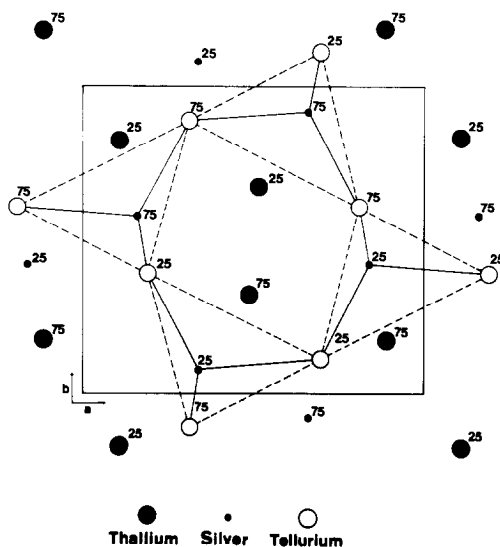


FIG. 1. Projection of AgTlTe structure along *c* axis.

mination was elongated along the *c* axis. The dimensions of this crystal were $0.113 \times 0.138 \times 0.0078 \times 0.02$ mm for the trapezoidal base and 0.2 mm for the height. Scattering intensities were collected with an Enraf-Nonius CAD 4 diffractometer using the $K\alpha$ molybdenum radiation. Using ω - 2θ scanning 634 independent reflections with $\sigma(I)/I \leq 0.3$ were selected for the determination and refinement of the structure. All the intensities were collected for Lorentz and polarization effects. The structure was solved in the centrosymmetric space group *Pnam* by interpreting Patterson's three-dimensional maps.

Initially, thallium atoms were located in the $4c (x, y, \frac{1}{4})$ position. The first refinement, followed by a Fourier difference summation using the thallium contribution, allows the localization of silver and tellurium atoms also in $x, y, \frac{1}{4}$ positions.

All reflections were corrected for absorption effects, after which three refinement cycles using anisotropic temperature factors reduced *R* to the final value of 0.098.

The final atomic parameters are listed in Table IV as well as isotropic and anisotropic atomic temperature factors obtained during the subsequent least-squares refinement. Scattering factors given by

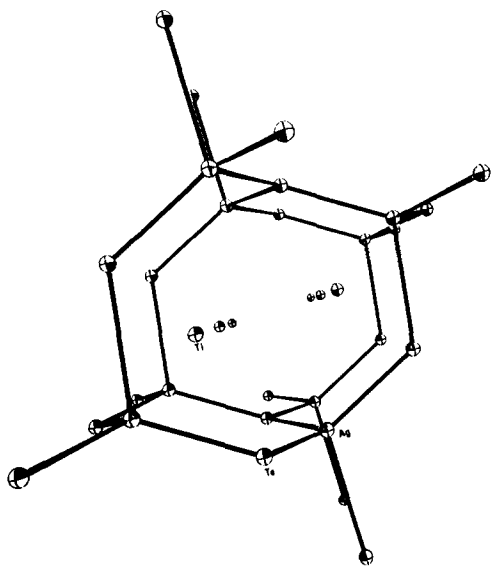


FIG. 2. Stereoscopic view of the structure along c axis for two networks showing the channeling structure.

Doyle and Turner (7) were used for silver and thallium and those given by Cromer and Waber for tellurium (8).

4. Discussion

The AgTlTe structure is given in Fig. 1 using an x y projection. The crystal structure is built up from an AgTe_4 tetrahedra arrangement. Each tetrahedron shares two corners with two other tetrahedra forming chains along the c axis. Four neighboring chains are connected by tellurium atoms delimiting a channel. Thallium atoms are located in this channel bonding to the tellurium atoms (Fig. 1). This channeling structure can be seen more easily in the stereographic projection (Fig. 2). The basic AgTe_4 pattern is shown in Fig. 3. Tetrahedra are distorted. The deviation from the tetrahedral symmetry is essentially due to the opening of angles Te-Ag-Te (up to 117.89°). Interactions between the thallium Tl^+ ions present in the channels and the

tellurium atoms may explain this fact. With regard to angle values and bond distances several other comments can be made. Silver-tellurium distances varying from 2.782 to 3.051 Å are observed (see Table V), equivalent to covalent bonds in comparison to the ionic radii sum (3.21 according to Shannon (9)) and to the covalent radii sum (2.81 according to Van Vechten and Philips (10)). In fact these distances are entirely comparable to those determined in Ag_2Te (2.87 and 2.91 Å; 2.99 and 3.04 Å (11)) and in the petzite Ag_3AuTe_2 (2.90 and 2.95 Å (12)) for silver atoms in tetrahedral coordination.

The tellurium atom's nearest neighbors are four silver atoms in a deformed tetrahedral coordination. This distortion is induced by thallium-tellurium interactions; the Tl-Te distances are about 3.640 Å.

Thallium atoms have a specific position (Fig. 2). Located in the channels, they are held by Tl-Te bonds and also by Tl-Tl interactions: thus distances between neighboring thallium atoms are 3.642 Å. This effect may be described as a metal-metal interaction through the thallium(I) $6s^2$ lone pair.

5. Conclusion

In a series of isomorphous compounds

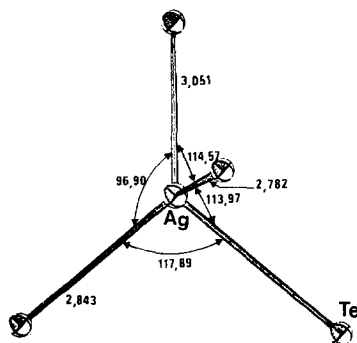


FIG. 3. The AgTe_4 tetrahedron in AgTlTe .

TABLE V
ANGLE AND BOND DISTANCES IN (AgTe₄)_n CHAINS

Distances Ag-Te (Å)	Distances Te-Te (Å)
Te-Ag = 3.051(9)	Te-Te ⁱ = 4.413(7)
Te ⁱ -Ag = 2.843(4)	Te-Te ⁱⁱ = 4.909(4)
Te ⁱ -Ag = 2.843(4)	Te ⁱ Te ⁱ = 4.871(1)
Te ⁱⁱ -Ag = 2.782(8)	Te ⁱ -Te ⁱⁱ = 4.717(2)
Angles Te-Ag-Te (°)	Angles Ag-Te-Ag (°)
Te-Ag-Te 96.90(20)	Ag-Te-Ag ⁱ 83.10(20)
Te-Ag-Te ⁱⁱ 114.57(24)	Ag-Te-Ag ⁱⁱ 123.21(23)
Te ⁱ -Ag-Te ⁱ 117.89(27)	Ag ⁱ -Te-Ag ⁱ 117.89(27)
Te ⁱ -Ag-Te ⁱⁱ 113.97(17)	Ag ⁱ -Te-Ag ⁱⁱ 119.05(13)

AgTlX (with X = S, Se, Te) the structure of AgTlTe has been solved with a final *R* value of 0.098. This structure is quite different from those of equivalent compounds. The silver and tellurium atoms are covalently bonded in chains of AgTe₄ tetrahedra delimiting channels where thallium atoms are located. The details of the structure will be of interest in explaining the physical

properties, the study of which is presently in progress.

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