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A new phase in the Tl–Ag–Te system: crystal structure of $Tl_2Ag_{16}Te_{11}$

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Abstract

A new phase in the ternary Tl–Ag–Te system has been identified. X-ray diffraction examination of single crystals was used to establish the crystal structure of $Tl_2Ag_{16}Te_{11}$. The hexagonal space group is $R\bar{3}c$ and the lattice parameters are $a = 1.1442(3)$ nm, $c = 4.1971(5)$ nm and $Z = 6$.

The structure is described as a three-dimensional array of large hexagonal channels of silver and tellurium atoms hosting linear chains of atoms. These channels are parallel to the crystallographic c axis. Each channel is built up with hexagonal prisms centred by thallium atoms and with tellurium-centred silver octahedra. The refinement indicates partial occupation of all silver positions.

1. Introduction

Brun *et al.* [1] have surveyed studies of the Tl–Ag–Te system. Recently Moreau *et al.* [2] determined the exact composition and the crystal structure of a new compound $Tl_4Ag_{18}Te_{11}$, which is related to $Tl_2Ag_8Te_5$ [1].

In this paper, we report the structure and lattice parameters of another new compound $Tl_2Ag_{16}Te_{11}$.

2. Experimental details

Small crystals suitable for X-ray analysis were obtained from the annealed samples, with the stoichiometric formula $TlAg_9Te_5$, by mechanical means. The crystal intensities were measured using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,69$ Å) on a CAD-4 Enraf–Nonius diffractometer in the θ–2θ scan mode.

The accurate cell dimensions determined by the least-squares analysis of 25 θ values were $a = b = 1.1442(3)$ nm and $c = 4.1971(5)$ nm. Three

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standard reflections were monitored at intervals of 3600 s. The intensity variation during the data collection was about 7%. The intensities of 1777 independent reflections up to the limit of $\theta = 30°$ were measured and corrected for background, Lorentz and polarization factors with the program *START* Examination of systematic extinctions led to the space groups $R3c$ or $R\bar{3}c$. The structure was solved by direct methods using the *MULTAN* program. Least-squares refinements of positional and thermal parameters of eight atoms (fully occupied sites) converged but the R factor (given by $\Sigma|\Delta F|/\Sigma|F|$) using 480 reflections with $I > 3\sigma(I)$ was not less than 0.16. Fourier maps revealed the presence of atoms at (0.55, 0.49, 0.25). This site could be only half occupied because of too short distances (1.3 Å) in the centrosymmetric space group $R\bar{3}c$. Finally the best R factor, with the correct thermal parameters, was obtained with all silver atom sites partially occupied. The least-squares refinement of 56 positional and anisotropic parameters converged, using F values of 480 reflections with $I > 3\sigma(I)$. The final R was 0.089. All calculations were performed on a PDP 11/23 computer using the SDP program system [3]. The atomic position parameters and temperature factors are listed in Table 1. The final composition was $Tl_{12}Ag_{96.5}Te_{66}$ or $Tl_2Ag_{16}Te_{11}$ with 174 atoms per unit cell.

3. Discussion

The structure of $Tl_2Ag_{16}Te_{11}$ with centrosymmetric rhombohedral symmetry can be described in a cell with height $c/6$ (Fig. 1). The projection of one sixth of the unit cell along the c axis (Fig. 2) shows that the atoms are situated in equidistant plans where they occupy the vertices of triangles (silver atoms) or hexagons (alternatively silver or tellurium atoms) or are located on the threefold axis in intermediate planes. So, around each threefold axis are formed three different hexagonal blocks with height $c/6$, denoted

TABLE 1

Positional parameters and their estimated standard deviations for $Tl_2Ag_{16}Te_{11}$ (space group, $R\bar{3}c$)

Atom	Site	x	y	z	Occupation factor	B (Å^2)
Tl	12c	0.000	0.000	0.1959(2)	1	3.18(7)
Ag(1)	12c	0.000	0.000	0.1137(4)	0.84	4.2(2)
Ag(2)	18e	0.732(1)	0.000	0.250	0.81	3.8(3)
Ag(3)	36f	0.4011(7)	0.0962(8)	0.1934(2)	0.88	4.3(2)
Ag(4)	36f	0.1958(9)	0.3935(9)	0.1935(3)	0.65	4.3(2)
Ag(5)	36f	0.560(1)	0.495(1)	0.2554(3)	0.46	4.0(4)
Te(1)	12c	0.000	0.000	0.0477(2)	1	3.7(2)
Te(2)	18e	0.2275(6)	0.000	0.25	1	2.4(1)
Te(3)	36f	0.4392(4)	0.3632(4)	0.1939(1)	1	2.24(9)

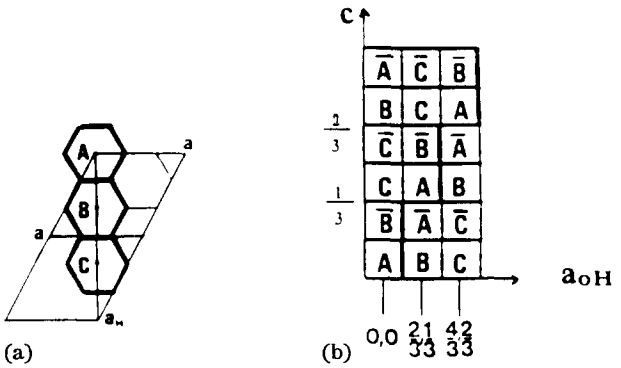

Fig. 1. The hexagonal cell can be described by (a) the blocks A, B and C, along the a_{0H} axis of the orthohexagonal cell and (b) the stacking of blocks, along the c axis, with rhombohedral (translation ($\frac{2}{3}$, $\frac{1}{3}$, $\frac{1}{3}$)) and central symmetry ($\bar{1}$). The blocks denoted $\bar{A}$, $\bar{B}$ and $\bar{C}$ are obtained by a central symmetry from the blocks A, B and C on the (0, 0) axis.

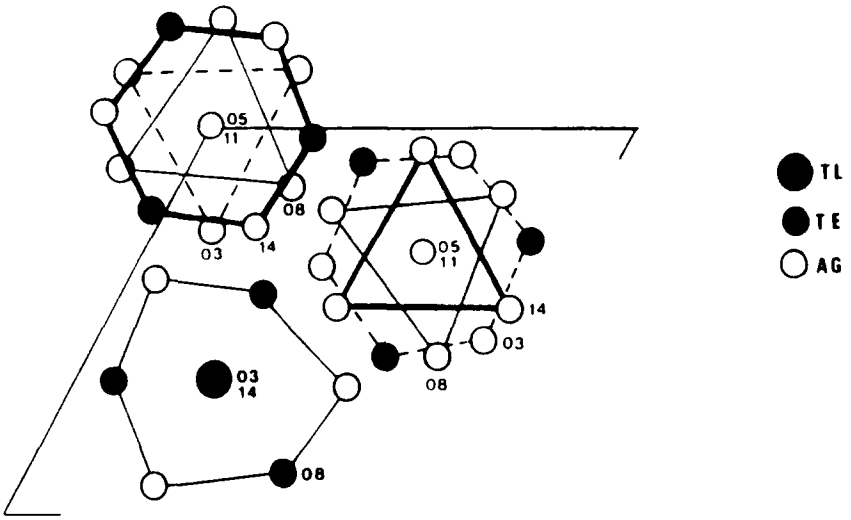

Fig. 2. Projection along the c axis of the $Tl_2Ag_{16}Te_{11}$ crystal structure, situated between the planes $z=0$ and $z=\frac{1}{6}$. The numbers indicate the positional z parameters multiplied by 100.

A, B and C (Fig. 3). The blocks A and C are derived from one another by a rotation of 180° around the a_{0H} axis. Each contains a tellurium-centred octahedron of silver atoms facing upwards in block A and downwards in block C, a silver atom on the threefold axis and then a hexagon of silver and tellurium atoms. The description of the complete structure, as explained in Fig. 1, is needed to describe the blocks $\bar{A}$, $\bar{B}$ and $\bar{C}$, obtained by central symmetry ($\bar{1}$) from blocks A, B and C; block $\bar{A}$ is identical with block C, and block $\bar{B}$ is identical with block B, but in each case with an interchange of the silver and tellurium atoms in the hexagons. The stacking of blocks along the (0, 0) axis as indicated in Fig. 1 leads to the formation (Fig. 4) of two base-supported hexagonal prisms, slightly distorted with lines nearly

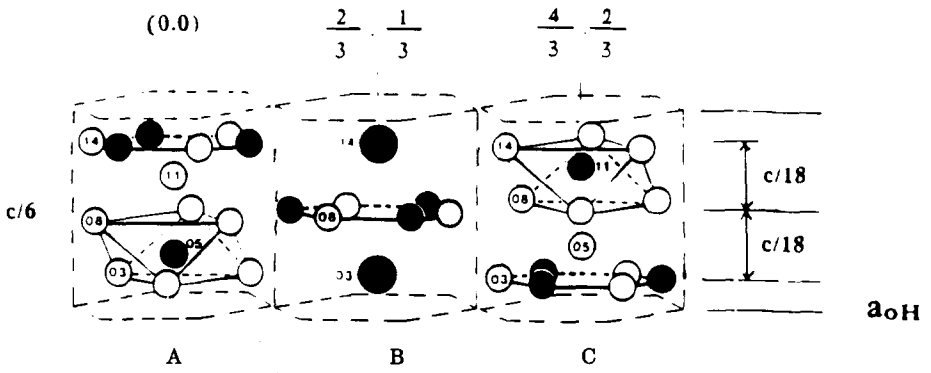

Fig. 3. The three structure blocks A, B and C along the a_{OH} axis form the building elements of the $Tl_2Ag_{16}Te_{11}$ structure; all atoms are in equidistant layers. The most compact layers are separated by $c/18$.

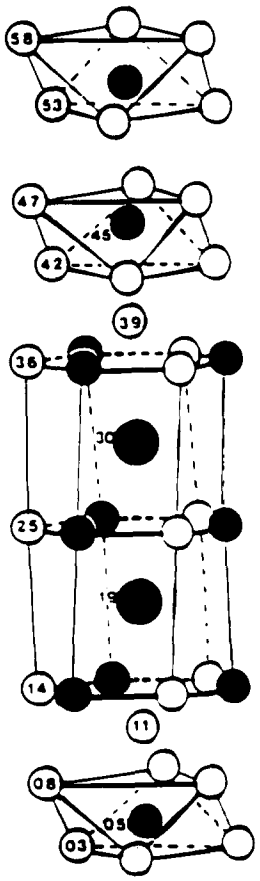

Fig. 4. Tellurium-centred octahedra of silver atoms and thallium-centred hexagonal polyhedra of silver and tellurium atoms, along the (0, 0) axis (in the centrosymmetric group $R\bar{3}c$). The numbers indicate the positional z parameter multiplied by 100.

TABLE 2

Interatomic distances in $Tl_2Ag_{16}Te_{11}$ (space group $R\bar{3}c$) up to 4

	Distance (Å)			Distance (Å)	
Tl–1Ag(1)	3.45		Ag(1)–1Te(1)	2.77	Tetrahedron
–3Te(2)	3.45	Hexagonal prism	–3Te(3)	2.99	
–3Te(3)	3.66		–3Ag(5)	3.07	
–3Ag(3)	3.72		–3Ag(3)	3.09	
–3Ag(2)	3.81		–1Tl	3.45	
–3Ag(4)	3.90				
Te(1)–1Ag(1)	2.77		Ag(2)–2Te(2)	2.87	Tetrahedron
–3Ag(4)	2.84	Octahedron	–2Te(3)	2.90	
–3Ag(5)	2.96		–2Ag(5)	3.04	
			–2Ag(4)	3.09	
			–2Tl	3.82	
Te(2)–3Ag(2)	2.87		–2Ag(3)	3.85	
–2Ag(5)	2.89				
–2Ag(3)	2.94		Ag(3)–1Te(3)	2.82	Tetrahedron
–2Ag(4)	3.16		–1Te(3)	2.86	
			–1Te(3)	2.88	
Te(3)–1Ag(3)	2.82		–1Te(2)	2.93	
–1Ag(3)	2.86		–1Ag(5)	2.96	
–1Ag(4)	2.87		–1Ag(4)	2.97	
–1Ag(3)	2.87		–1Ag(5)	3.00	
–1Ag(5)	2.93		–1Ag(1)	3.09	
–1Ag(5)	2.96		–1Ag(4)	3.21	
–1Ag(4)	2.97		–1Ag(3)	3.54	
–1Ag(1)	2.99		–1Tl	3.72	
			–1Ag(2)	3.85	
Ag(5)–1Te(2)	2.88	Tetrahedron	Ag(4)–1Te(1)	2.84	Tetrahedron
–1Te(3)	2.93		–1Te(3)	2.87	
–1Te(3)	2.96		–1Te(3)	2.97	
–1Te(1)	2.96		–1Ag(3)	2.97	
–1Ag(3)	2.96		–1Ag(2)	3.09	
–1Ag(3)	3.00		–1Te(2)	3.16	
–1Ag(2)	3.04		–1Ag(3)	3.21	
–1Ag(1)	3.07		–1Ag(5)	3.22	
–1Ag(4)	3.22		–2Ag(4)	3.52	
–1Ag(5)	3.66		–1Ag(5)	3.66	
			–1Tl	3.90	

parallel to the *c* axis and alternatively occupied by silver or tellurium atoms, each with a thallium atom at the centre. These two prisms are followed by two tellurium-centred octahedra of silver atoms; the group of two hexagonal prisms is separated from the group of two octahedra by a silver atom situated on the *c* axis. These chains of polyhedra along each threefold axis are shifted from one axis to the other so that three faces of each hexagonal prism of one chain are capped by silver atoms forming part of the octahedra of the

neighbouring chain. All thallium and tellurium atom sites are fully occupied whereas the silver atom sites of the hexagonal prisms or those on the threefold axis are only 85% occupied and the silver atom sites in the octahedra are about half occupied, which is partially explained by the short Ag(5)–Ag(5) distance (1.3 Å).

Examination of the interatomic distances, reported in Table 2, leads to similar conclusions as for most structures of the Ag–Tl–Te system.

(1) The thallium atoms are located inside large hexagonal prisms with a radius about 2.6 Å and are hence larger than the radius of a thallium atom.

(2) All Tl–Te distances are larger than 3.3 Å, indicating an ionic bonding as found by Ayral-Marin *et al.* [4] for AgTlTe. The Ag–Te interatomic distances vary from 2.77 to 3.16 Å; it is difficult to say whether the bonds are covalent or ionic.

(3) Finally, this structure can be described by large channels of silver and tellurium atoms, parallel to the crystallographic c axis; these channels host a column of atoms.

The $Tl_2Ag_{16}Te_{11}$ (space group $R\bar{3}c$) and $Tl_4Ag_{24-x}Te_{15-y}$ (space group $P\bar{6}$) [5] crystal structures are related by similar elements. The cell parameters a are equal and the c value of the first is $\frac{9}{2}c$ of the second; both structures contain hexagonal prisms of silver and tellurium atoms, hosting a thallium atom, with height 4.7 Å, and identical tellurium-centred octahedra of silver atoms; each cell contains as many hexagonal prisms as octahedra but the occupation factors of the atom sites are different.

The first structure is characterized by identical channels parallel to the c axis, shifted by $c/3$, and built up by the stacking of two types of polyhedron (hexagonal prisms and octahedra). The second structure is characterized by two types of channel parallel to the c axis: one channel of octahedra and two channels of hexagonal prisms.

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