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A new phase in the Tl–Ag–Te system: crystal structure of $Tl_4Ag_{24-x}Te_{15-y}$

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Abstract

A new stable phase $Tl_4Ag_{24-x}Te_{15-y}$ in the ternary Tl–Ag–Te system has been identified by X-ray diffraction on single crystals. The space group is $P\bar{6}$ and the lattice parameters are $a = 1.1418(4)$ nm and $c = 0.9220(1)$ nm with one formula per unit cell ($Z = 1$). The structure is described as an arrangement of two types of channels parallel to the [001] direction. Two-thirds of these channels are hexagonal and built up with silver and tellurium atoms, hosting thallium atoms. One-third are octahedral chains of silver atoms with centres statistically occupied by tellurium atoms. In addition, the refinement indicates partial occupation of some silver positions.

1. Introduction

According to previous investigations on the phase equilibria and structural chemistry in the Tl–Ag–Te system, a new ternary phase has been reported with $TlAg_5Te_3$ composition and hexagonal cell [1]. Also reported in the literature were the structural analyses of ternary compounds: TlAgTe [2], $TlAgSe_2$ [3], $TlAgTe_2$ [4], $TlAg_3Te_2$ [5] and $Tl_4Ag_{18}Te_{11}$ [6].

Furthermore, a preliminary study of $TlAg_{5.4}S_{3.5}$ has been reported [7] with a half-size hexagonal cell ($a = 1.0614$ nm; $c = 0.4246$ nm) and the space group $P6_3/m$.

2. Experimental details and structure refinement

Small crystals of size about 60 μm, suitable for X-ray analysis, were obtained from the annealed samples by mechanical means. The crystal

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intensities were measured in the θ–2θ scan mode with Mo Kα radiation ($\lambda = 0.071\,069$ nm) on a CAD-4 Enraf-Nonius diffractometer equipped with a graphite single-crystal monochromator. Accurate cell dimensions, determined by a least-squares analysis of 25 θ values, were $a = 1.1418(4)$ and $c = 0.9220(1)$ nm.

Three standard reflections were monitored at intervals of 3600 s with an intensity variation during the data collection of 2%. The intensities of 3520 reflections up to a limit of $\theta = 30°$ were measured and corrected for background, Lorentz and polarization factors with the program START. Because of the small size and the good symmetry of the crystal, no absorption correction has been applied. No systematic extinctions have been observed and an examination of the intensities with $I(hkl) \neq I(khl)$ led to space group $P6$, $P\bar{6}$ or $P6/m$.

The intensities of the hkl reflections with $l \neq 2n$ were weak, owing to the existence of a pseudocell with $c' = c/2$. Partial results of the direct method using the MULTAN [8] program indicated layers of atoms at positions $z = 0$, 1/4, 1/2, 3/4. A least-squares refinement on the $hk0$ reflections gave the projection of the atomic structure on the x–y plane. The observation of the Fourier maps with all the hkl reflections gave the atomic positions of tellurium atoms located at (2/3, 1/3, z), but the too-small interatomic distances required a partial occupation of these sites. Then, after averaging equivalent reflections with the program PAINT, a least-squares refinement of the atomic positions and anisotropic thermal parameters converged using F values of 915 independent reflections with $I > 3\sigma(I)$. The final R factor (given by $\Sigma|\Delta F|/\Sigma|F|$) was 0.10 for the results given in Table 1. Calculations were performed on a PDP 11/23 computer using the SDP program [9]. The final composition is $Tl_4Ag_{24-x}Te_{15-y}$ with $x = 2$ and $y = 0.1$. A single crystal with a volume of a few cubic millimetres has been grown with the Bridgman technique, and a composition analysis with a Castaing microprobe gave the same formula.

3. Discussion

The crystal structure can be described as a stacking of two types of polyhedra (Fig. 1).

On the one hand, hexagonal Ag_6Te_6 prisms with thallium atoms at the centre form a column parallel to the [001] direction, at position (0, 0, z) and (1/3, 2/3, z). The Ag(3) site of these prisms is partially occupied (0.67), and three faces are capped by silver atoms.

On the other hand, octahedra formed with silver atoms only are stacked along the [001] direction as well. The tellurium atoms located inside exhibit a very high anisotropic temperature factor along the c axis, revealing a high mobility along this direction.

TABLE 1

Positional parameters and their estimated standard deviations for $Tl_4Ag_{24-x}Te_{15-y}$ (space group $P\bar{6}$)

Atom	Site	Occupation factor	x	y	z	B (Å^2)
Tl(1)	1a	1.0	0.0	0.0	0.0	2.7(1)
Tl(2)	1b	1.0	0.0	0.0	0.5	2.5(1)
Tl(3)	2h	1.0	1/3	2/3	0.244(2)	2.8(1)
Ag(1)	6l	1.0	0.0192(6)	0.2633(6)	0.2290(9)	3.4(2)
Ag(2)	3j	1.0	0.0872(9)	0.685(1)	0.0	2.0(2)
Ag(3)	3k	0.667	0.058(1)	0.665(1)	0.5	2.3(3)
Ag(4)	3j	1.0	0.381(1)	0.176(1)	0.0	2.5(2)
Ag(5)	3k	0.667	0.381(1)	0.189(1)	0.5	2.8(3)
Ag(6)	6l	1.0	0.5411(7)	0.0584(7)	0.2259(9)	3.8(2)
Te(1)	6l	1.0	0.2472(4)	0.2276(4)	0.2621(8)	1.8(1)
Te(2)	3j	1.0	0.3455(7)	0.9082(7)	0.5	1.4(1)
Te(3)	3k	1.0	0.3575(7)	0.9113(7)	0.5	1.5(1)
Te(4)	1e	0.62	2/3	1/3	0.0	2.6(5)
Te(5)	2i	0.38	2/3	1/3	0.147(3)	1.4(3)
Te(6)	2i	0.5	2/3	1/3	0.305(3)	1.3(2)
Te(7)	1f	0.5	2/3	1/3	0.5	1.5(3)

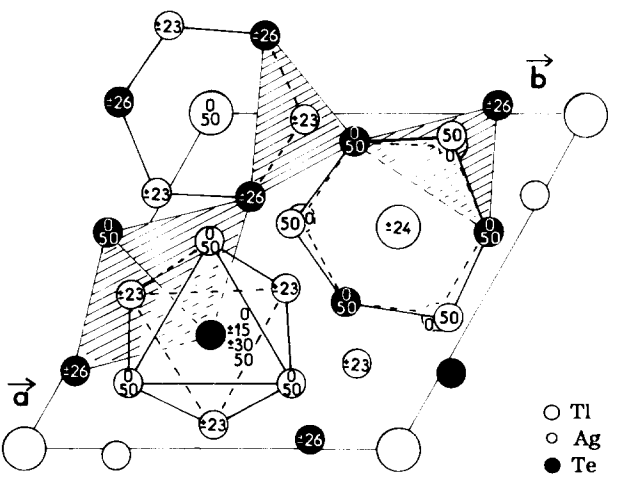

Fig. 1. Structure of $Tl_4Ag_{24-x}Te_{15-y}$ in projection along [001]. The numbers indicate the positional z parameters multiplied by 100. The channels centred by thallium atoms in hexagonal prisms are shown at (0,0,0) and (1/3,2/3,z) and the channel hosting tellurium atoms in silver octahedra is shown at (2/3,1/3,z). Te_4 tetrahedra centred by silver atoms are stripped.

Because of the too-small interatomic distances between them, the tellurium sites Te(4) and Te(5), Te(5) and Te(6), Te(6) and Te(7) cannot be occupied simultaneously. The occupation factors obtained by crystallographic refinement can be interpreted by an arrangement of possible tellurium positions. The different configurations with their rates of occurrence are given in Fig. 2. We can verify each occupation factor: Te(4), $0.12+0.5=0.62$; Te(5), 0.38; Te(6), 0.5; Te(7), $0.12+0.38=0.5$. According to the B or C configuration, the maximum number of tellurium atoms in these four sites is 3, and the value found in this work was 2.9.

Moreover, the Ag(5) site belonging to the octahedra is partially occupied (0.67). All the silver atoms are located at the centres of tetrahedra built up with the tellurium atoms (Fig. 1). The high values of the thermal parameters of Ag(1) and Ag(6) result from a high B_{33} factor, meaning a strong thermal agitation along the c axis.

The interatomic distances are reported in Table 2. The Ag–Te distances varying from 2.7 Å to 3.2 Å, it is difficult to decide whether the bonds are covalent (2.8 Å according to Van Vechten and Philips [10]) or ionic (3.2 Å according to Shannon [11]). In hexagonal prisms, all the Tl–Te and Te–Ag distances are larger than 3.5 Å, indicating an ionic bonding as found by Ayral-Marin *et al.* in AgTlTe [12].

The atomic formula $TlAg_{5.5}Te_{3.7}$ is very close to the compound $TlAg_{5.4}S_{3.5}$ reported by Klepp, with a half-size hexagonal cell and space group $P6_3/m$ [7]. These two structures contain channels formed by silver and sulphur (or tellurium) atoms centred by thallium atoms, and octahedral chains of silver atoms whose centres are statistically occupied by sulphur (or tellurium) atoms. Lastly, our crystallographic structure can be compared with $Tl_2Ag_{16}Te_{11}$ also described as a stacking of hexagonal prisms and octahedra but where each column contains these two types of polyhedra [13]. The hexagonal prism size is the same in both compounds.

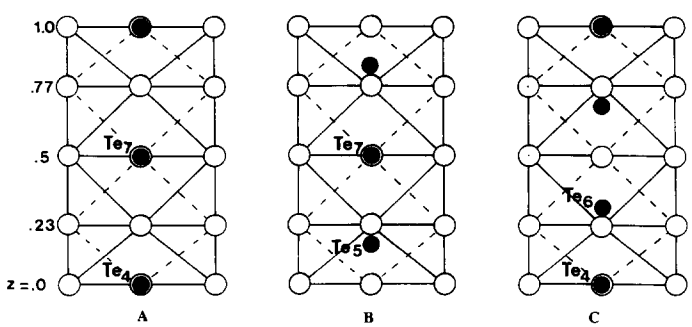

Fig. 2. The three possible arrangements A, B and C of tellurium atoms at $(2/3,1/3,z)$ in silver octahedra in projection on the b–c plane. The rates R_A, R_B and R_C of occurrence are as follows: $R_A=0.12$; $R_B=0.38$; $R_C=0.5$.

TABLE 2

Interatomic distances in $Tl_4Ag_{24-x}Te_{15-y}$ (space group $P\bar{6}$) up to 4 Å

Tl(1)	–6Ag(1)	3.6 (h)	Ag(4)	–Te(4)	2.8 (t)	Te(2)	–2Ag(1)	2.7
	–6Te(1)	3.6 (h)		–Te(2)	2.9 (t)		–Ag(2)	2.8
	–3Ag(4)	3.8		–2Ag(1)	2.9		–Ag(2)	2.9
				–Ag(2)	3.0		–Ag(4)	2.9
				–2Te(1)	3.1 (t)		–2Ag(6)	2.9
Tl(2)	–6Te(1)	3.5 (h)		–2Te(5)	3.2		–2Tl(3)	3.5
	–6Ag(1)	3.8 (h)		–2Ag(6)	3.5			
	–3Ag(5)	3.8		–2Ag(6)	3.5	Te(3)	–Ag(3)	2.7
				–Tl(1)	3.8		–Ag(5)	3.0
Tl(3)	–3Te(2)	3.5 (h)					–2Ag(1)	3.1
	–3Te(3)	3.6 (h)	Ag(5)	–Ag(3)	2.7		–Ag(3)	3.2
	–3Ag(2)	3.7 (h)		–2Te(1)	2.8 (t)		–2Ag(6)	3.2
	–3Ag(3)	3.9 (h)		–Te(7)	2.8 (t)		–2Tl(3)	3.6
	–3Ag(6)	3.9		–Te(3)	3.0 (t)			
				–2Te(6)	3.3	Te(4)	–2Te(6)	2.8
				–2Ag(1)	3.3		–3Ag(4)	2.8
Ag(1)	–Te(2)	2.7 (t)		–2Ag(6)	3.7		–6Ag(6)	3.4
	–Te(1)	2.8 (t)		–2Ag(6)	3.8			
	–Te(1)	2.8 (t)		–Tl(2)	3.8	Te(5)	–Te(5)	2.8
	–Ag(4)	2.9					–3Ag(6)	2.8
	–Ag(6)	3.0					–3Ag(4)	3.2
	–Te(3)	3.1 (t)	Ag(6)	–Te(5)	2.8 } (t)[a]		–Te(7)	3.2
	–Ag(5)	3.3		–Te(6)	2.8 }			
	–Ag(2)	3.6		–Te(1)	2.9 (t)	Te(6)	–Te(4)	2.8
	–Tl(1)	3.6		–Te(2)	2.9 (t)		–3Ag(6)	2.8
	–Tl(2)	3.8		–Ag(2)	2.9		–3Ag(5)	3.4
				–Ag(1)	3.0		–Te(6)	3.6
Ag(2)	–Te(2)	2.8 (t)		–Ag(3)	3.1			
	–Te(2)	2.9 (t)		–Te(3)	3.2 (t)	Te(7)	–3Ag(5)	2.8
	–2Ag(6)	2.9		–Te(4)	3.4		–2Te(5)	3.2
	–2Te(1)	3.0 (t)		–Ag(4)	3.5		–6Ag(6)	3.7
	–Ag(4)	3.0		–Ag(4)	3.5			
	–Ag(1)	3.6		–Te(7)	3.7			
	–2Tl(3)	3.7		–Ag(5)	3.7			
				–Ag(5)	3.8			
Ag(3)	–2Te(1)	2.7 (t)						
	–Te(3)	2.7 (t)	Te(1)	–Ag(3)	2.7			
	–Ag(5)	2.7		–Ag(1)	2.8			
	–2Ag(6)	3.1		–Ag(1)	2.8			
	–Te(3)	3.2 (t)		–Ag(5)	2.8			
	–Tl(3)	3.9		–Ag(6)	2.9			
				–Ag(2)	3.0			
				–Ag(4)	3.1			
				–Tl(2)	3.5			
				–Tl(1)	3.6			

h, hexagonal prism; t, tetrahedron.

[a]Te(5) and Te(6) cannot be present simultaneously.

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