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$CsAg_5Te_3$: a new metal-rich telluride with a unique tunnel structure

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Abstract

The synthesis and structure of a new ternary silver telluride, $CsAg_5Te_3$, is described. The compound was prepared from a Cs_2Te–CaTe–Te flux but it can also be prepared from a direct combination of Cs_2Te and Ag_2Te under vacuum at 600 °C. The crystal data for $CsAg_5Te_3$ at 20 °C (Mo $K\alpha$ radiation) are as follows: $a = 14.672(2)$ Å and $c = 4.601(3)$ Å; $V = 990.5(8)$ Å^3; $Z = 4$; $D_{calc} = 7.075$ g cm^{-3}; space group, $P4_2/mnm$ (No. 136); $2\theta_{max} = 50°$; number of independent data collected, 572; number of data observed with $I > 3\sigma(I)$, 267; number of variables, 32; $\mu = 218.51$ cm^{-1}; extinction coefficient, 0.585×10^{-7}; final $R = 0.040$; $R_w = 0.046$; goodness of fit, 1.42. The compound features a new structure type with Cs^+-filled, relatively large tunnels running through the lattice. The material is a semiconductor with a band gap of about 0.65 eV.

Keywords: Tunnel structure; Ternary silver telluride; Semiconductors

Recently, we have demonstrated that the dissolution of late transition metals in alkali metal chalcogenide fluxes can lead to exciting new materials. In particular, we have worked on a number of compounds containing copper or silver metals [1,2]. Most known silver-containing alkali metal chalcogenides can be classified in terms of A_2Q–$n(Ag_2Q)$, where A stands for an alkali metal, and Q a chalcogen atom (mostly S or Se). The lower n series has long been studied, and this includes the KAgSe ($n = 1$) type [3], the $K_2Ag_4Q_3$ (Q ≡ S or Se; $n = 2$) type [4], and the AAg_3Q_2 (A ≡ Rb or Cs; Q ≡ S, Se or Te; $n = 3$) type [5] structures; the recently synthesized $RbAg_5S_3$ ($n = 5$) [6], the title compound $CsAg_5Te_3$ ($n = 5$), $K_2Ag_{12}Se_7$ ($n = 6$) [7] and $CsAg_7S_4$ ($n = 7$) [6] cover the intermediate range of n. The only missing member in this range is $A_2Ag_8Q_5$, which belongs to the $n = 4$ group. Such a trend certainly provides us with some helpful hints on other possible phases of alkali metal silver chalcogenides. Several compositions of the higher n series are therefore postulated: $A_2Ag_{16}Q_9$ ($n = 8$), AAg_9Q_5 ($n = 9$) and $A_2Ag_{20}Q_{11}$ ($n = 10$). We believe that these phases and phases with an even higher n value could also be synthesized.

In this communication, we report the synthesis, structure and some properties of $CsAg_5Te_3$ (**I**), an $n = 5$ member of the A_2Q–$n(Ag_2Q)$ series. Together with AAg_3Te_2 (A ≡ Rb or Cs) [5c], it is the first example of a ternary alkali metal siver telluride known to date. The compound was crystallized in a Cs_2Te–CaTe–Te flux. The black thin needle-like crystals of **I** were obtained in a reaction containing 0.197 g (0.5 mmol) of Cs_2Te, 0.084 g (0.5 mmol) of CaTe, 0.054 g (0.5 mmol) of Ag and 0.510 g (4 mmol) of Te. The reaction was carried out in a sealed Pyrex tube of about 6 in length and 9 mm inner diameter at 420 °C for 4 days followed by slow cooling (4 °C h^{-1}) to 120 °C. The excess flux was removed from the final product using dimethylformamide (DMF). Crystal of both the title compound **I** and $CsAg_3Te_2$ [8], whose structure is isotypic to the known AAg_3Q_2 (A ≡ Rb or Cs; Q ≡ S or Se) type [5a,b], were found in the product. The structure of $CsAg_5Te_3$ was solved by single-crystal X-ray diffraction methods [9]. Atomic coordinates are given in Table 1. A pure powder sample of **I** was prepared by direct synthesis at 600 °C [10].

$CsAg_5Te_3$ is an extended solid with a novel structure type. It consists of an (Ag_5Te_3)-three-dimensional tunnel network filled with Cs^+ counterions. Structurally, the network is rather complex as are most other silver

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Table 1
Fractional atomic coordinates with average isotropic temperature factors for $CsAg_5Te_3$

Atom	x	y	z	B_{eq} ($Å^2$)
Cs	0.8867(2)	−0.8867	$-\frac{1}{2}$	2.05(9)
Te(1)	0.6721(2)	0.1154(2)	0	1.5(1)
Te(2)	0.9003(2)	0.9003	0	1.3(1)
Ag(1)	0.5816(3)	0.2142(3)	$-\frac{1}{2}$	3.2(2)
Ag(2)	0.6045(3)	0.0177(2)	$-\frac{1}{2}$	2.1(2)
Ag(3)	0.6762(3)	−0.6762	0	3.2(1)

sulfides. It is constructed in such a way that large open channels are formed and oriented parallel to the crystallographic c axis. Pairs of Cs^+ cations are accommodated in the center of the 12-member ring formed by equal number of silver and tellurium atoms bonded alternately together, which in turn gives rise to the infinite open channel (Fig. 1). Inspection of the three-dimensional structure, shown in Fig. 1(a), reveals the presence of $[AgTe]_n^{n-}$ columns. These columns, shown in Fig. 1(b), are in fact a common structural feature that is encountered in a number of other silver and copper ternary chalcogenides, including AAg_3Q_2 [5], ACu_3Q_2 [11] and $Na_3Cu_4S_4$ [12]. Unlike many chalcogenides synthesized in a molten polychalcogenide flux, $CsAg_5Te_3$ is a metal-rich compound (metal-to-chalcogen ratio, 6 to 3) containing only monotelluride. The shortest Te–Te contact in this compound is a nonbonding 4.139(4) Å. Atom Te(1) displays an unusual seven coordination with the silver atoms (Ag(1)×4; Ag(2)×1; Ag(3)×2). There are three crystallographically distinct silver atoms in this structure. Ag(1) and Ag(3) have a typical (distorted) tetrahedral coordination, whereas Ag(2) is trigonally bonded to three Te, a less common coordination for silver. The shortest Ag–Ag distance in this structure is 2.902(5) Å, slightly longer than the value of 2.836 Å in $RbAg_3Te_2$ [5c] but shorter than the value of 2.961 Å in $RbAg_5S_3$ [6]. The Ag–Te interatomic distances are, on the contrary, similar to those found in $RbAg_3Te_2$ [5c].

In the context of this paper it is worth discussing $RbAg_5S_3$, an interesting compound prepared by Kolis and coworkers [6] using a different approach involving supercritical ethylenediamine. This hexagonal sulfide compound has a different structure type from tetragonal $CsAg_5Te_3$. The infinite straight tunnels of $RbAg_5S_3$ have a differently shaped cross-section and are smaller (approximately 6 Å × 6 Å) compared with those in $CsAg_5Te_3$ (4 Å × 13 Å). Only one row of alkali-metal counterion, Rb^+, fills the center of the tunnel, while a double row of Cs^+ atoms fills the tunnels of our compound. The coordination environments of both silver and chalcogen atoms in the two structures are also rather different.

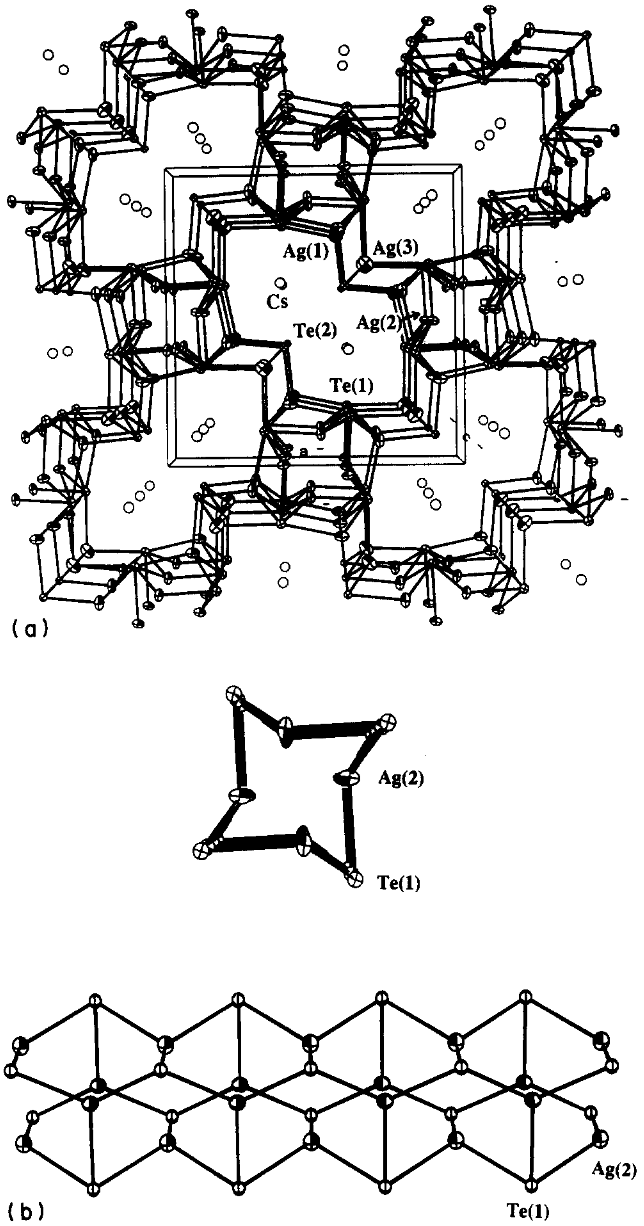

Fig. 1. (a) The three-dimensional structure of $CsAg_5Te_3$ with labeling. Selected bond distances and angles are as follows: Ag(1)–Te(1), 2.954(5) Å; Ag(1)–Te(1), 3.026(3) Å; Ag(1)–Te(2), 2.743(4) Å; Ag(2)–Te(1), 2.789(4) Å; Ag(2)–Te(1), 2.886(3) Å; Ag(3)–Te(1), 3.060(3) Å; Ag(3)–Te(2), 2.794(2) Å; Cs–Te(1), 3.899(2) Å; Cs–Te(2), 3.887(3) Å; Te(1)–Ag(1)–Te(1), 109.2(1)°; Te(1)–Ag(1)–Te(1), 99.0(1)°; Te(1)–Ag(1)–Te(2), 107.6(1)°; Te(1)–Ag(1)–Te(2), 115.7(1)°; Te(1)–Ag(2)–Te(1), 105.7(1)°; Te(1)–Ag(1)–Te(1), 118.44(8)°; Te(1)–Ag(3)–Te(1), 92.2(1)°; Te(1)–Ag(3)–Te(2), 113.17(9)°; Te(2)–Ag(3)–Te(2), 110.9(1)°. (b) The structure of the $[AgTe]_n^{n-}$ columns excised from the $[Ag_5Te_3]^-$ lattice. The closest Ag–Ag distance within these columns is 3.183(4) Å.

$CsAg_5Te_3$ is an electron-precise material and it is expected to be a semiconductor. Indeed, UV–visible–near-IR optical reflectance spectroscopy [13] revealed a direct band gap of 0.65 eV (Fig. 2). Our extended Hückel tight-binding electronic band calculations [14] on the (Ag_5Te_3)-three-dimensional net-

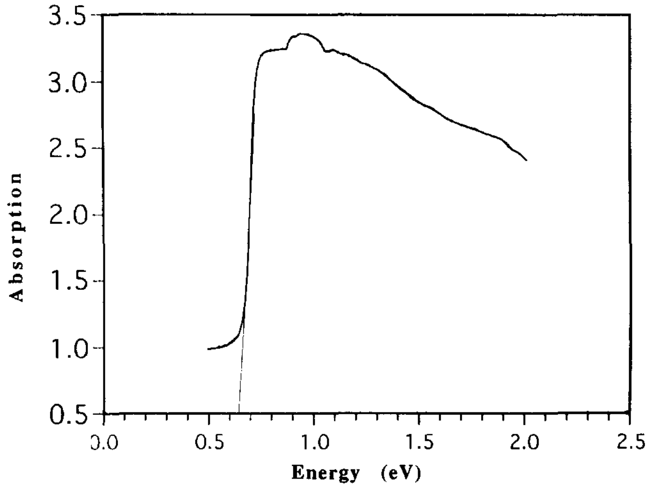

Fig. 2. The near-IR–visible optical absorption spectrum of $CsAg_5Te_3$.

work confirmed this observation [15]. A band gap is clearly present between the filled valence bands and the unoccupied conduction bands.

Supplementary material

Tables of calculated and observed X-ray powder diffraction patterns, positional and anisotropic thermal parameters of all atoms, and a listing of calculated and observed structure factors (6 pages) are available.

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[8] The following crystal data and unit-cell parameters were obtained for $CsAg_3Te_2$: monoclinic system; space group, *C2/m* (No. 12); $a=17.662(6)$ Å, $b=4.646(3)$ Å and $c=9.391(4)$ Å; $\beta=111.96(4)°$. The compound is isostructural to $RbAg_3Te_2$ [5c] and KAg_3S_2.

[9] (a) The crystal data for $CsAg_5Te_3$ at 20 °C (Mo Kα radiation) are as follows: $a=14.672(2)$ Å and $c=4.601(3)$ Å; $V=990.5(8)$ Å^3; $Z=4$; $d_{calc}=7.075$ g cm^{-3}; space group, $P4_2/mnm$ (No. 136); $2\theta_{max}=50°$; number of independent data collected, 572; number of data observed with $I>3\sigma(I)$, 267; number of variables, 32; $\mu=218.51$ cm^{-1}; extinction coefficient, 0.585×10^{-7}; final $R=0.040$; $R_w=0.046$; goodness of fit, 1.42. The crystal structure was solved by direct methods using SHELXS-86 [9b] and refined with the TEXSAN [9c] package of crystallographic programs. A DIFABS [9d] absorption correction was applied to the isotropically refined data. All atoms were then refined anisotropically.
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[10] A mixture containing 0.197 g (0.5 mmol) of Cs_2Te, 0.540 g (5.0 mmol) of Ag and 0.319 g (2.5 mmol) of Te was weighed and transferred to an alumina ceramics tube. The tube was then placed in a carbon-coated quartz tube (inside diameter, 14 mm) and sealed off under vacuum. The mixture was heated to 600 °C within 12 h and was kept at this temperature for 5 days. It was then slowly cooled to 300 °C (4 °C h^{-1}) and to 50 °C (10 °C h^{-1}). The product was finally washed with DMF and ethanol and dried with anhydrous ether.

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[15] Band calculation was carried out along the following symmetry lines: G–X–M–G–Z–A–R. A 108 *k*-point set was used in the calculations of the average properties.