Synthesis and Structure of the Layered Thorium Telluride $CsTh_2Te_6$

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The compound $CsTh_2Te_6$ has been synthesized at 800 °C by the reaction of Th with a Cs_2Te_3/Te melt as a reactive flux. The compound crystallizes in the space group D_{2h}^{17}-*Cmcm* of the orthorhombic system with two formula units in a cell of dimensions $a = 4.367(2)$ Å, $b = 25.119(10)$ Å, $c = 6.140(3)$ Å, and $V = 673.5(5)$ Å^3 at $T = 113$ K. The structure of $CsTh_2Te_6$ has been determined from single-crystal X-ray data. The structure comprises infinite, two-dimensional double layers of $ThTe_8$-bicapped trigonal prisms. The structural motif of the trigonal prisms resembles that found in UTe_2. Cs^+ cations, disordered equally over two crystallographically equivalent sites, separate the layers and are coordinated by eight Te atoms at the corners of a rectangular parallelepiped. Short Te−Te distances of 3.052(3) and 3.088(3) Å form linear, infinite, one-dimensional chains within the layers. Simple formalisms describe neither the Te−Te bonding in the chain nor the oxidation state of Th. The compound shows weak semiconducting behavior along the Th/Te layers perpendicular to the Te−Te chain.

Introduction

Because of their interesting magnetic properties and because of the accessibility of several oxidation states, solid-state compounds of actinide metals have been studied extensively.[1,2] The number of known uranium chalcogenide compounds greatly exceeds the number of known thorium chalcogenides. Binary thorium tellurides, characterized structurally only by X-ray powder patterns, include ThTe,[3] $ThTe_3$,[4] and Th_2Te_3.[4] Powder patterns for the ternary compounds ThNTe,[5] ThSbTe,[6] and ThBiTe[6] have also been reported. The ternary compound ThAsTe[6] has been characterized by a single-crystal X-ray diffraction study.

Often, analogous structures occur in compounds of uranium and thorium.[5,6] It is far more interesting, however, when the composition or structure or both change in going from uranium to thorium. In this extension to thorium, the new compound $CsTh_2Te_6$ has been synthesized and characterized. It has no analogues among cesium/uranium/tellurium compounds.

$CsTh_2Te_6$ was synthesized by the use of the reactive-flux method.[7] This technique has afforded an amazing variety of low-dimensional metal polychalcogenides with novel structures.[8−19] This synthetic approach exploits molten salts of the type A_2Q_x/Q (A = alkali metal or Cu; Q = S, Se, or Te; x = 1−5) as both a flux and a reactant. The resultant compounds typically exhibit unusual chalcogen−chalcogen bonding and novel structure types.

Experimental Section

Synthesis. The starting material Cs_2Te_3 was synthesized at −79 °C from reaction of stoichiometric amounts of elemental Cs (Aldrich, 99.5%) and Te (Aldrich, 99.8%) in liquid ammonia under an Ar atmosphere. The composition Cs_2Te_3 was confirmed by X-ray powder diffraction methods.[20,21] In an attempt to prepare $CsHfThTe_5$, the thorium and hafnium analogue of $CsTiUTe_5$,[22] $CsTh_2Te_6$ was prepared instead. The elements Th (36 mg, 0.15 mmol; Alfa, 99.9%), Hf (27 mg, 0.15 mmol; Aesar, 99.9%), and Te (97 mg, 0.76 mmol) were combined with Cs_2Te_3 (99 mg, 0.15 mmol). The reaction mixture was loaded into a fused-silica tube in a drybox under an Ar atmosphere; the tube was evacuated to ∼10^{-4} Torr and sealed. The contents were kept at 650 °C for 1 day and then at 800 °C for 5 days, before being cooled at 3 °C/h to room temperature. A few lustrous, black crystals formed at the surface and within uncharacterized, amorphous byproducts. The compound reacts slowly with air. Crystals suitable for X-ray structure determination and conductivity measurements were manually extracted from the essentially homogeneous melt under oil. An alternative synthetic route in which Hf was omitted also afforded crystals of $CsTh_2Te_6$ in low yield.

Analysis of several crystals with an EDX-equipped Hitachi S570 SEM confirmed the presence of Cs, Th, and Te in the approximate ratio 1:2:4; no Hf was detected. The exact composition of the compound was established from the X-ray structure determination.

Electrical Conductivity Measurements. Single crystals of $CsTh_2Te_6$ ranging in length from 0.4 to 0.6 mm were mounted with Ag paint

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Table 1. Crystal Data and Intensity Collection Details for $CsTh_2Te_6$

formula	$CsTh_2Te_6$	Z	2
fw	1362.59	T of data collcn (K)[b]	113(2)
space group	D_{2h}^{17}-$Cmcm$	d_{calcd} (g cm^{-3})	6.719
a (Å)	4.367(2)[a]	linear abs coeff (cm^{-1})	374
b (Å)	25.119(10)	transm factors[c]	0.369−0.710
c (Å)	6.140(3)	$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$	0.049
V (Å^3)	673.5(5)	$R_w(F_o^2)$ (all data)	0.102

[a] Obtained from a refinement with the constraints $\alpha = \beta = \gamma = 90°$. [b] The low-temperature system is based on a design by Huffman.[23] [c] The analytical method, as employed in the Northwestern absorption program AGNOST, was used for the absorption correction.[24]

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for $CsTh_2Te_6$

atom	x	y	z	U_{eq} (Å^2)[a]	occ
Cs	0	0.4967(2)	$^1/_4$	0.0155(8)	0.50
Th	0	0.68235(5)	$^1/_4$	0.0071(3)	1
Te(1)	0	0.27349(8)	$^1/_4$	0.0069(4)	1
Te(2)	0	0.11170(5)	0.0015(2)	0.0095(3)	1

[a] U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

on Au wires with graphite extensions. Two-probe dc resistivity measurements along the needle axis [100] were made at room temperature.

Structure Determination. Initial cell parameters were determined from well-exposed Weissenberg photographs taken at room temperature. A crystal was mounted directly in the cold stream of a Picker diffractometer;[23] final cell parameters were determined from 31 reflections automatically centered at 113 K in the range 34.18° ≤ 2θ(Mo) ≤ 35.96°. Six standards from diverse regions of reciprocal space were monitored every 100 reflections and exhibited no significant variation in intensity throughout data collection. The data were processed and corrected for absorption effects.[24] Additional experimental details are given in Table 1.

The initial positions for the Th and Te atoms were determined with the direct-methods program SHELXS[25] in the noncentrosymmetric space group $Cmc2_1$. The Cs atom was located from subsequent electron density maps. An unreasonably large thermal parameter was observed for Cs. After the constraint on the occupancy of Cs was lifted, the occupancy refined to a value of 0.47. The Cs atom occupancy was held at 0.50 for subsequent refinements. The structure was refined by full-matrix, least-squares techniques with the use of the program SHELXL-93.[26] Examination of the structure solution with the use of the MISSYM algorithm[27] in the PLATON program package[28] revealed a center of inversion in the structure. Hence, the correct space group is $Cmcm$. A refinement that included the occupancy of the Cs atom converged to an $R_w(F_o^2)$ value of 0.101 and to an occupancy of 0.474(9). Since refinement of site occupancies is a risky way to determine chemical compositions[29] and since the occupancy of the Cs atom did not differ significantly from 0.5, that value was adopted in the final refinement. This refinement on F_o^2 in space group $Cmcm$ converged to an $R_w(F_o^2)$ value of 0.102 and for those 450 reflections having $F_o^2 > 2\sigma(F_o^2)$ to a conventional R index $R(F)$ of 0.049. The final difference electron density map shows no peaks of height greater than 2.5% that of a Te atom. Table 2 gives the final values of the positional parameters and equivalent isotropic displacement parameters.

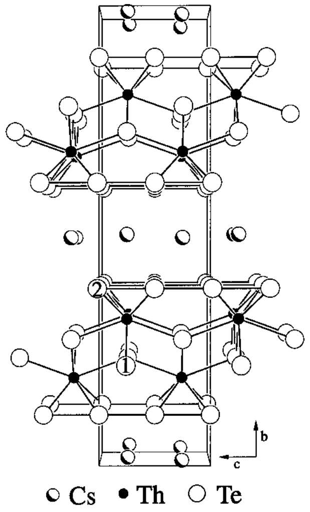

Figure 1. Unit cell of $CsTh_2Te_6$ as viewed down [100]. The atom-labeling scheme is given.

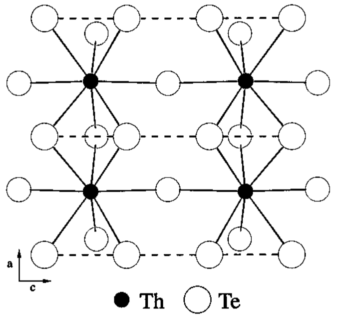

Figure 2. View of one half of the $^2_\infty[Th_2Te_6^-]$ layer of $CsTh_2Te_6$ showing the infinite, linear Te−Te chains that run along [001].

Table 3. Selected Bond Lengths (Å) for $CsTh_2Te_6$

Cs−Te(2)	4×	3.817(4)	Th−Te(1)	2×	3.264(2)
Cs−Te(2)	4×	3.929(4)	Te(2)−Te(2)		3.052(3)
Th−Te(1)	2×	3.164(2)	Te(2)−Te(2)		3.088(3)
Th−Te(2)	4×	3.201(2)			

Results and Discussion

A view of the unit cell of $CsTh_2Te_6$ is shown in Figure 1, and Table 3 gives important distances. Unlike the linked chains of the one-dimensional uranium ternary compound $CsUTe_6$,[22] the structure of $CsTh_2Te_6$ is two-dimensional. It contains $^2_\infty[Th_2Te_6^-]$ layers (Figure 2) that lie perpendicular to the [010] direction. The Cs^+ cations that separate the layers are coordinated by eight Te atoms at the corners of a rectangular parallelepiped. Cs···Te distances range from 3.817(4) to 3.929(4) Å. The Cs^+ cations are equally disordered over two crystallographically equivalent sites; if the Cs atom position were fully occupied, the Cs atoms would only be 3.075(1) Å apart.

The one crystallographically unique Th atom in the $CsTh_2Te_6$ structure is coordinated to eight Te atoms in a bicapped trigonal-prismatic geometry. The $ThTe_8$ polyhedra share triangular faces of two Te(2) atoms and one Te(1) atom in the [100] direction, and Te(1) capping atoms in the [001] direction. All Th−Te distances fall within the range 3.164(2)−3.264(2) Å, and all Te−Th−Te angles range from 56.94(6) to 150.70(3)°. These bond distances must be compared to uranium tellurides because of the paucity of geometrical data for thorium tellurides. The Th−Te distances in $CsTh_2Te_6$ agree with the U−Te distances found in $CsUTe_6$ (3.013(5)−3.263(5) Å).[22]

The structural motif of the bicapped trigonal prism in $CsTh_2Te_6$ is also seen in the structure of UTe_2.[30] The layered structure

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of $CsTh_2Te_6$ can be transformed into the three-dimensional structure of UTe_2 by removal of the interlamellar Cs atoms and condensation of the layers.

In both $CsTh_2Te_6$ and UTe_2, one edge of the triangular face of the trigonal prisms is shortened. Te−Te interactions of 3.052(3) Å result in $CsTh_2Te_6$. These Te−Te pairs combine to form infinite, linear Te−Te chains through the close interaction (3.088(3) Å) of two adjacent trigonal prisms. These Te chains line the ${}^{2}_{\infty}[Th_2Te_6{}^{-}]$ layers of $CsTh_2Te_6$ along the [001] axis (perpendicular to the needle axis).

The assignment of formal oxidation states in $CsTh_2Te_6$ is somewhat arbitrary. In the discussion of the oxidation state of the U atom in UTe_2, Beck and Dausch[30] formulated the compound as $U^{3+\delta}\,Te(1)^{2-}\,{}^{1}_{\infty}[Te(2)^{-(1+\delta)}]$. This description allows for partial reduction of the Te(2) atoms in the chain and subsequent oxidation of the U^{3+} ion but does not define a value for the oxidation state for the U atom. Specific elements of this formalism can be applied to $CsTh_2Te_6$. Atom Te(1) has no short Te−Te interactions and can be described as a discrete Te^{2-} anion; the infinite chain that contains atom Te(2) can be described as ${}^{1}_{\infty}[Te(2)^{-(1+\delta)}]$. If the short Te−Te interactions in $CsTh_2Te_6$ formed along the needle axis, high conductivity could result. However, whereas the ${}^{2}_{\infty}[Th_2Te_6{}^{-}]$ layers lie along the needle axis [100], the ${}^{1}_{\infty}[Te(2)^{-(1+\delta)}]$ chains extend in the [001] direction. As seen for several low-dimensional cesium tellurides,[22,31,32] the electrical conductivity is low. The conductivity of $CsTh_2Te_6$ measured along [100] is below the detection limits of the instrument ($<1 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$) (295 K). The material is a weak semiconductor or insulator.

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Supporting Information Available: Additional crystallographic details (Table SI), anisotropic displacement parameters (Table SII), and bond lengths and angles (Table SIII) (6 pages). Ordering information is given on any current masthead page.

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