Articles

Synthesis and Structure of the One-Dimensional Telluride $Cs_4Zr_3Te_{16}$

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The compound $Cs_4Zr_3Te_{16}$ has been synthesized at 900 °C through the reaction of Zr with a Cs_2Te_3/Te melt as a reactive flux. The compound crystallizes in the space group C_{2h}^5-$P2_1/n$ of the monoclinic system with four formula units in a cell of dimensions $a = 12.012(3)$ Å, $b = 18.999(7)$ Å, $c = 15.264(5)$ Å, $\beta = 101.71(2)°$, and $V = 3411(2)$ Å^3 ($T = 113$ K). The structure of $Cs_4Zr_3Te_{16}$ has been determined from single-crystal X-ray data. The structure comprises infinite, one-dimensional chains of Zr-centered polyhedra that extend along [100] and are separated from each other by Cs^+ cations. Each Zr atom is eight-coordinate. There are four unambiguous Te–Te single bonds in the range 2.754(1)–2.768(1) Å and six more Te–Te interactions in the range 2.930(1)–2.966(1) Å. Because of the wide range of Te–Te interactions, simple formalisms do not describe the bonding in the chain. The compound shows weak semiconducting behavior along the Zr/Te chains.

Introduction

The reactive flux technique[1] has proven to be widely applicable[2–7] to the preparation of ternary and quaternary metal chalcogenides and polychalcogenides. This technique exploits molten salts of the type A_2Q_x/Q (A = alkali metal, Cu; Q = S, Se, Te; x = 1–5) as a flux *and* as a reactant. The resultant compounds typically exhibit unusual chalcogen–chalcogen bonding and novel structure types. In the initial demonstration of this method,[1] a K_2S/S flux was reacted with Ti to afford crystals of the new one-dimensional material $K_4Ti_3S_{14}$. The Ti/S chain in this compound may be described as ${}^1_\infty[Ti_3(S_2)_6(S)_2{}^{4-}]$. The first extension of this technique to the tellurides[8] employed a K_2Te/Te flux in the synthesis of the one-dimensional compounds $K_4M_3Te_{17}$ (M = Zr, Hf). Here we present the synthesis and characterization of the new, closely related, one-dimensional telluride $Cs_4Zr_3Te_{16}$.

Experimental Section

Synthesis. The binary starting material Cs_2Te_3 was synthesized at −79 °C from the reaction of stoichiometric amounts of elemental Cs (Aldrich, 99.5%) and Te (Aldrich, 99.8%) in liquid ammonia under an Ar atmosphere. $Cs_4Zr_3Te_{16}$ was prepared by combining the elements Cu (15 mg, 0.25 mmol; Aldrich, 99.999%), Zr (13 mg, 0.12 mmol; Aesar, 99.9%), and Te (61 mg, 0.48 mmol) with Cs_2Te_3 (160 mg, 0.25 mmol).[9] 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 sample was kept at 600 °C for 2.5 days and then 900 °C for 6 days, before being cooled at 3 °C/h to room temperature. The product contained air-stable, lustrous black crystals at the surface and within the melt. Crystals suitable for X-ray structure determination and conductivity measurements were manually extracted from the essentially homogeneous melt.

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

Electrical Conductivity. Single crystals of $Cs_4Zr_3Te_{16}$ ranging in length from 0.4 to 0.6 mm were mounted with Ag paint on Au wires with graphite extensions. Two-probe dc resistivity measurements along the needle axis (a) were made at room and liquid nitrogen temperatures.

Crystallography. Initial cell parameters and the space group C_{2h}^5-$P2_1/n$ were determined from Weissenberg photographs taken at room temperature. Final cell parameters of a single crystal were determined by a least-squares analysis of 44 reflections automatically centered at 113 K on a Picker diffractometer.[10] The intensities of 12 531 reflections were recorded. The refined cell constants and some experimental details are listed in Table 1; more information is available in Table SI.[11] Six standards from diverse regions of reciprocal space were monitored every 100 reflections and exhibited no significant variation in intensity throughout data collection.

Table 1. Crystallographic Details for $Cs_4Zr_3Te_{16}$

formula	$Cs_4Zr_3Te_{16}$	Z	4
fw	2846.90	T, K[a]	113
space group	C_{2h}^5-$P2_1/n$	d(calcd), g cm^{-3}	5.544
a, Å	12.012(3)	abs coeff, cm^{-1}	185.15
b, Å	18.999(7)	transm factors	0.071–0.411
c, Å	15.264(5)	$R(F)$ for $F_o > 4\sigma(F_o)$[b]	0.0378
β, deg	101.71(2)	$R_w(F_o^2)$[b]	0.0876
V, Å^3	3411(2)		

[a] The low-temperature system is based on a design by Huffman.[10]
[b] $R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w(F_o^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum wF_o^4\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (0.04F_o^2)^2$; $w^{-1} = \sigma^2(F_o^2)$, $F_o^2 < 0$.

The data were processed and corrected for absorption effects.[12] The initial positions for the Cs, Zr, and Te atoms were determined with the direct-methods program SHELXS.[13] The structure was refined in a

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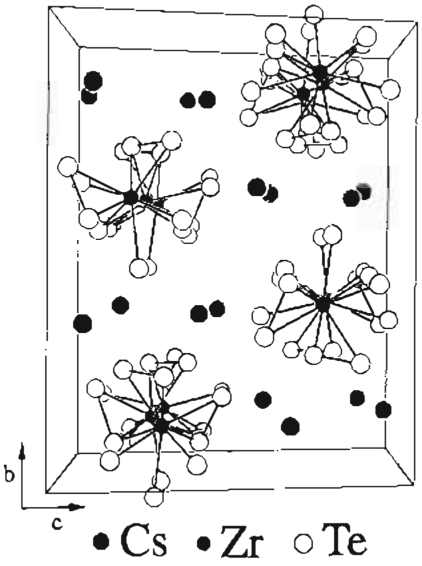

Figure 1. Crystal structure of $Cs_4Zr_3Te_{16}$ as viewed down [100]. The atoms are of arbitrary size.

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for $Cs_4Zr_3Te_{16}$

	x	*y*	*z*	$U_{eq}{}^a$
Cs(1)	0.419 43(4)	−0.153 91(3)	0.587 03(3)	0.012 07(10)
Cs(2)	0.364 46(5)	0.140 21(3)	1.058 24(3)	0.017 27(11)
Cs(3)	−0.077 07(5)	−0.126 42(3)	0.656 32(3)	0.013 96(10)
Cs(4)	0.147 16(5)	−0.139 47(3)	0.894 04(3)	0.014 94(10)
Zr(1)	−0.348 93(6)	0.114 52(4)	0.751 48(5)	0.008 21(14)
Zr(2)	−0.029 56(7)	0.114 33(4)	0.730 50(5)	0.007 84(13)
Zr(3)	0.292 71(6)	0.115 88(4)	0.707 60(5)	0.007 73(14)
Te(1)	−0.516 41(5)	0.064 95(3)	0.854 59(3)	0.009 87(10)
Te(2)	−0.387 60(5)	0.181 96(3)	0.916 62(3)	0.011 95(10)
Te(3)	−0.539 67(4)	0.065 93(3)	0.604 54(3)	0.009 03(10)
Te(4)	−0.380 96(5)	0.241 30(3)	0.644 23(3)	0.010 71(10)
Te(5)	−0.335 09(5)	−0.040 00(3)	0.724 62(3)	0.010 54(10)
Te(6)	−0.179 63(4)	0.230 97(3)	0.768 70(3)	0.009 17(10)
Te(7)	−0.148 19(5)	0.038 53(3)	0.855 32(3)	0.010 19(10)
Te(8)	−0.225 76(4)	0.052 00(3)	0.610 41(3)	0.009 12(10)
Te(9)	0.022 00(5)	0.148 33(3)	0.923 18(3)	0.010 06(10)
Te(10)	−0.081 07(5)	0.154 92(3)	0.540 55(3)	0.010 36(10)
Te(11)	0.123 51(4)	0.232 87(3)	0.697 55(3)	0.008 82(10)
Te(12)	0.168 68(4)	0.050 78(3)	0.845 48(3)	0.009 12(10)
Te(13)	0.090 31(4)	0.045 23(3)	0.603 11(3)	0.009 55(10)
Te(14)	0.328 05(5)	0.239 07(3)	0.819 52(3)	0.010 20(10)
Te(15)	0.273 54(5)	−0.038 49(3)	0.728 20(3)	0.011 64(10)
Te(16)	0.322 91(5)	0.177 51(3)	0.537 21(3)	0.010 99(10)

^{a} $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$.

Table 3. Selected Bond Lengths (Å) for $Cs_4Zr_3Te_{16}$

Zr(1)–Te(4)	2.894(1)	Zr(3)–Te(13)	2.947(1)
Zr(1)–Te(2)	2.947(1)	Zr(3)–Te(3)	2.952(1)
Zr(1)–Te(1)	2.949(1)	Zr(3)–Te(15)	2.964(1)
Zr(1)–Te(5)	2.973(1)	Zr(3)–Te(11)	2.995(1)
Zr(1)–Te(7)	2.977(1)	Zr(3)–Te(1)	3.023(1)
Zr(1)–Te(6)	2.981(1)	Zr(3)–Te(12)	3.074(1)
Zr(1)–Te(3)	3.008(1)	Te(1)–Te(2)	2.764(1)
Zr(1)–Te(8)	3.087(1)	Te(3)–Te(16)	2.754(1)
Zr(2)–Te(12)	2.918(1)	Te(4)–Te(6)	2.763(1)
Zr(2)–Te(8)	2.926(1)	Te(5)–Te(8)	2.958(1)
Zr(2)–Te(10)	2.942(1)	Te(5)–Te(7)	3.071(1)
Zr(2)–Te(9)	2.952(1)	Te(7)–Te(9)	2.957(1)
Zr(2)–Te(13)	2.952(1)	Te(8)–Te(10)	2.955(1)
Zr(2)–Te(7)	2.973(1)	Te(9)–Te(12)	2.966(1)
Zr(2)–Te(6)	2.988(1)	Te(10)–Te(13)	2.949(1)
Zr(2)–Te(11)	3.014(1)	Te(11)–Te(14)	2.768(1)
Zr(3)–Te(14)	2.878(1)	Te(12)–Te(15)	2.930(1)
Zr(3)–Te(16)	2.941(1)	Te(13)–Te(15)	3.052(1)

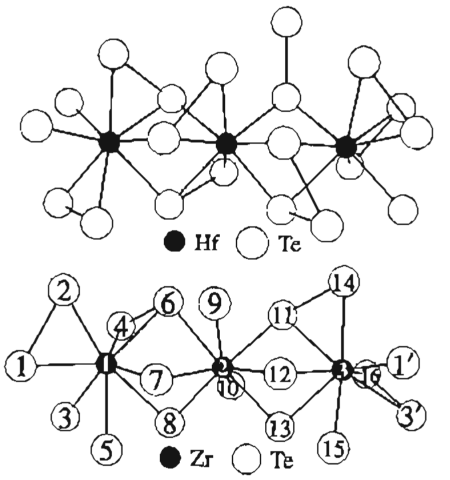

Figure 2. Comparison of the one-dimensional M/Te chains of $K_4Hf_3Te_{17}$[8] (top) and $Cs_4Zr_3Te_{16}$ (bottom). The atom-numbering scheme for $Cs_4Zr_3Te_{16}$ is given.

straightforward manner with the use of the program SHELXL-93.[14] The final refinement on F_o^2 involved 208 variables and 10 952 unique data, including those for which $0 \geq F_o^2 \geq -3\sigma(F_o^2)$. It converged to a value of $R_w(F_o^2)$ of 0.088 and for reflections having $F_o > 4\sigma(F_o)$ to a conventional *R* index $R(F)$ of 0.038. The final difference electron density map shows no peaks of height greater than 12% that of a Zr atom. Final values of the positional parameters and equivalent isotropic displacement parameters are presented in Table 2; anisotropic displacement parameters are presented in Table SII.[11]

Results

A view of the unit cell of $Cs_4Zr_3Te_{16}$ is shown in Figure 1, and selected distances are given in Table 3. Complete metrical data are given in Table SIII.[11] The structure is very similar to that of $K_4M_3Te_{17}$ (M = Zr, Hf); both consist of one-dimensional M/Te chains separated by asymmetrically coordinated alkali metal cations. In the $Cs_4Zr_3Te_{16}$ structure, Zr/Te chains extend along the [100] direction. The Cs^+ cations that separate these chains exhibit coordination numbers 12 (Cs(1)), 11 (Cs(2), Cs(3)), and 9 (Cs(4)). Cs⋯Te distances range from 3.629(1) to 4.456(1) Å.

The $Cs_4Zr_3Te_{16}$ structure contains three crystallographically unique Zr atoms that are bridged by Te atoms (Figure 2). Atom Zr(1) is bridged to atom Zr(2) through atoms Te(6), Te(7), and Te(8); atom Zr(2) is bridged to atom Zr(3) through atoms Te(11), Te(12), and Te(13); and atom Zr(3') is bridged to atom Zr(1) through atoms Te(1) and Te(3). If we take a maximum Zr–Te bond distance to be 3.09 Å, all three Zr atoms are eight-coordinate, all Zr–Te distances range from 2.878(1) to 3.087(1) Å, and all Te–Zr–Te angles range from 55.73(3) to 160.89(3)°. These Zr–Te distances agree well with those found in $ZrTe_3$ (2.921(3)–3.182(4) Å).[15]

The structures of both $K_4Hf_3Te_{17}$ and $Cs_4Zr_3Te_{16}$ bear some resemblance to that of MTe_5 (M = Hf, Zr).[16] The MTe_5 structure consists of an M atom at the center of a bicapped trigonal prism of Te atoms. The trigonal prisms share a triangular face to form a one-dimensional chain; the chains are connected by zigzag Te–Te linkages that join capping atoms. The M/Te chains of $K_4Hf_3Te_{17}$ and $Cs_4Zr_3Te_{16}$ are compared in Figure 2, where the subtle structural differences may be seen. The difference in the number of Te atoms between the two structures is the result of the substitution of a single Te atom in $Cs_4Zr_3Te_{16}$ for the μ_2-η^1-$Te_2{}^{2-}$ ligand in $K_4Hf_3Te_{17}$. Since $K_4M_3Te_{17}$ (M = Zr, Hf) are isostructural, the structural differences between $K_4Hf_3Te_{17}$ and $Cs_4Zr_3Te_{16}$ presumably do not arise from the change in group

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IV metal, but rather from the change in the alkali metal cation (A). This is surprising, for generally substitution of Cs^+ for K^+, for example in $AFeS_2$,[17,18] $ASbS_2$,[19,20] and $ANbUO_6$,[21,22] leaves the anion intact, although the crystal structure may change.

Solid-state tellurides have a propensity[23,24] for exhibiting Te–Te interactions intermediate between a Te–Te single bond (2.76 Å[25]) and a Te···Te van der Waals contact (4.10 Å[26]). MTe_3 (M = Zr, Hf),[15] UTe_2,[27] and Cs_2Te_5[28] are just a few of many compounds that exhibit intermediate Te–Te distances. $K_4M_3Te_{17}$ (M = Zr, Hf) exhibit a multitude of Te–Te interactions. An arbitrary maximum distance for a Te–Te single bond of 2.94 Å for the Hf compound gives the chain composition $^{1}_{\infty}[Hf_3(Te_3)(Te_2)_7{}^{4-}]$, with each of the Hf atoms in the +4 oxidation state. The subtle changes in the M/Te chain structure that result from substitution of Cs^+ for K^+ give a range of Te–Te interactions that defy simple descriptions of formal charge and electron counting. In $Cs_4Zr_3Te_{16}$ there are four unambiguous Te–Te single bonds with distances of 2.754(1)–2.768(1) Å. It is not possible to describe the longer Te–Te interactions in a straightforward way. For example, there are six Te–Te interactions within the range 2.930(1)–2.966(1) Å (Table 3). If we consider these interactions to be single bonds, the compound would possess in addition two $Te_4{}^{2-}$ ligands, and the Zr atoms would have a formal charge of +2.67! With the multitude of Te–Te interactions, we expected $Cs_4Zr_3Te_{16}$ to show metallic conductivity. However, the electrical conductivities along the [100] direction (Zr/Te chain direction) of $Cs_4Zr_3Te_{16}$ are $\approx 1 \times 10^{-4}$ Ω^{-1} cm^{-1} (77 K) and $\approx 5 \times 10^{-4}$ Ω^{-1} cm^{-1} (295 K). The material is thus a weak semiconductor.

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Supplementary Material Available: Additional crystallographic details (Table SI), anisotropic displacement parameters (Table SII), and bond lengths and angles (Table SIII) (10 pages). Ordering information is given on any current masthead page.

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