$Cs_2Ag_2ZrTe_4$: A New Layered Telluride Containing Tetrahedrally Coordinated Zirconium

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Abstract: The compound $Cs_2Ag_2ZrTe_4$ was synthesized through reaction of the elements in a Cs_2Te_3/Te flux at 900 °C. The compound crystallizes in the orthorhombic space group $D_2^6 - C222$ with two formula units in a cell of dimensions $a = 6.508(7)$ Å, $b = 15.164(16)$ Å, $c = 6.518(6)$ Å, $V = 643.2(11)$ Å^3 at 113 K. The structure has been refined to a value of $R_w(F_o^2)$ of 0.111 for 1138 data and 24 variables; the value of R_1 (on F) is 0.053. The $Cs_2Ag_2ZrTe_4$ structure comprises two-dimensional slabs of Ag- and Zr-centered tetrahedra separated by Cs^+ cations. This appears to be the first example of the tetrahedral coordination of Zr^{4+} by chalcogen anions in a solid-state compound.

Introduction

Knowledge of the coordination preferences of metal cations is valuable for predicting new solid-state structures and for developing strategies for their synthesis.[1] Accordingly, unusual coordination geometries of metal cations are of particular significance. Whereas Zr^{4+} clearly shows tetrahedral coordination in molecules, e.g., gaseous $ZrCl_4$,[2] its coordination number in solid-state compounds is 6 or greater. For example, Zr^{4+} is octahedrally coordinated in solid $ZrCl_4$[3] and in Rb_2ZrCl_6,[4] and it is eight-coordinate (bisdisphenoidal) in K_2ZrF_6.[5] In another example, Ti^{4+} is tetrahedrally coordinated in Ba_2TiS_4,[6,7] whereas Zr^{4+} is octahedrally coordinated in Ba_2ZrS_4.[8] Such high coordination numbers for Zr^{4+} are not surprising, since the cation is fairly large, is highly charged, and has an empty valence shell. There appears to be a single example of tetrahedral coordination of Zr^{4+} by the hard O^{2-} anion, namely the isolated ZrO_4^{4-} anion in Cs_4ZrO_4.[9] Among the chalcogenide anions Q^{2-} (Q = S, Se, Te), the softer, higher congeners of O^{2-}, tetrahedral coordination of Zr^{4+} was apparently unknown. The tetrahedral coordination of Zr^{4+} by Te^{2-} anions in $Cs_2Ag_2ZrTe_4$ reported here is a new, unique coordination geometry for Zr^{4+} in chalcogenide chemistry.

The A/M/Cu/Q family (A = alkali metal; M = group IV metal) contains both structurally and electronically interesting members. Use of the low-melting A_2Q_x fluxes[10] ($x = 1-5$) provides a good synthetic route for preparing these compounds. Structurally, the M cations are octahedrally coordinated in the layered ($KCuZrQ_3$,[11] $NaCuTiS_3$,[11] $NaCuZrQ_3$,[12] $Na_2Cu_2ZrS_4$[13]) or pseudolayered ($Cs_{0.68}CuTiTe_4$[14]) members and are seven-coordinate in the one-dimensional members (e.g., $Cs_3CuHf_2Te_{10}$[14]). Cu^+ cations invariably exhibit tetrahedral coordination in these structures. Whereas such tetrahedral coordination is the rule for Cu^+, the Ag^+ cation exhibits in addition other coordination preferences, including three- and five-coordinate. The substitution of Ag for Cu led to the synthesis of the present compound $Cs_2Ag_2ZrTe_4$ in which the Ag^+ cations *and* the Zr^{4+} cations are tetrahedrally coordinated. Amusingly, the Cu analogue of this compound is unknown.

Experimental Section

Synthesis. $Cs_2Ag_2ZrTe_4$ was prepared by the reactive flux method,[10] in which the elements Zr (Aesar, 99.9%), Ag (Aesar, 99.99%), and Te (Aldrich, 99.8%) were combined with Cs_2Te_3 in a 2:2:2:3 ratio. Cs_2Te_3 was sythesized at −79 °C from the reaction of stoichiometric amounts of elemental Cs (Aesar, 99.98%) with Te in liquid ammonia under an Ar atmosphere. The powders were ground together, sealed in a fused silica tube, heated at 900 °C for 4 days, then quenched to room temperature, next reheated to 900 °C, and finally cooled to room temperature at 4 °C/h. The preparation is repeatable. However, attempts to prepare $Cs_2Ag_2ZrTe_4$ in a rational stoichiometric synthesis were unsuccessful; powder diffraction and EDX (Energy Dispersive X-ray Analysis) studies indicate that invariably the known $CsAg_5Te_3$[15] and $Cs_4Zr_3Te_{16}$[16] phases predominate.

Structure Determination of $Cs_2Ag_2ZrTe_4$. Analysis of oscillation and Weissenberg photographs revealed Laue symmetry *mmm* and gave preliminary lattice constants. The systematic extinction (hkl, $h + k = 2n + 1$) is consistent with the orthorhombic space groups $D_2^6 - C222$, $C_{2v}^{11} - Cmm2$, $C_{2v}^{14} - Cm2m$, and $D_{2h}^{19} - Cmmm$. The final cell parameters were determined from a least-squares analysis of the setting angles of 33 reflections in the range of $28° < 2\theta$ (Mo Kα_1) $< 41°$ that were automatically centered at 113 K on a Picker diffractometer. Six standard reflections monitored at intervals of every 100 reflections showed no significant change during data collection. Crystal data and

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Table 1. Crystal Data and Intensity Collection for $Cs_2Ag_2ZrTe_4$

chemical formula	$Cs_2Ag_2ZrTe_4$
formula weight	1083.16
space group	$D_2^6 - C222$
a, Å	6.508(7)[a]
b, Å	15.164(16)
c, Å	6.518(6)
V, Å^3	643.2(11)
Z	2
D(calcd), g cm^{-3}	5.592
T of data collection, K[b]	113
radiation	graphite monochromated Mo Kα, $\lambda(K\alpha_1) = 0.7093$ Å
linear abs coeff, cm^{-1}	182
transmission factors[c]	0.556–0.624
R_w (F^2)	0.111
R_1	0.053

[a] The cell parameters were obtained from a refinement constrained so that $\alpha = \beta = \gamma = 90°$. [b] The low-temperature system is based on a design by Huffman.[28] The diffractometer was operated with the use of the Indiana University PCPS system.[29] [c] The analytical method as employed in the Northwestern absorption program AGNOST was used for the absorption correction.[19]

Table 2. Positional Parameters and Equivalent Isotropic Displacement Parameters for $Cs_2Ag_2ZrTe_4$

atom	x	y	z	U(eq)[a]
Cs(1)	1/4	1/4	0.73970(10)	0.0109(2)
Ag(1)	0	0	1/2	0.0094(2)
Ag(2)	0	1/2	0	0.0095(2)
Zr(1)	0	0	0	0.0064(3)
Te(1)	0.74239(7)	0.39379(3)	0.75902(8)	0.00800(14)

[a] U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

further details of data collection are given in Table 1 and Table S1.[17] The data were processed by programs standard for this laboratory.[18] EDX measurements on the crystal used for data collection indicated a Cs:Ag:Zr:Te ratio of 2:2:1:4. No other elements were detected.

After correction of the data for absorption[19] averages of the data were obtained for the various possible space groups. The data average slightly better in 222. Among the possible space groups only in $C222$ could a sensible solution be found. Initial atomic positions were determined with the direct methods program SHELXS.[20] The final full-matrix least-squares refinement[21] on F_o^2 involved 24 variables and 1138 independent reflections. It converged to values of $R_w(F_o^2)$ of 0.111 and R_1 (on F) for all data of 0.053. The final difference electron density map shows no features with a height greater than 1% that of a Zr atom. The MISSYM[22] algorithm in the PLATON suite of programs[23] detected no additional symmetry elements beyond those expected in $C222$. Table 2 lists positional and equivalent isotropic displacement parameters. Table S2[17] lists the anisotropic displacement parameters.

Results and Discussion

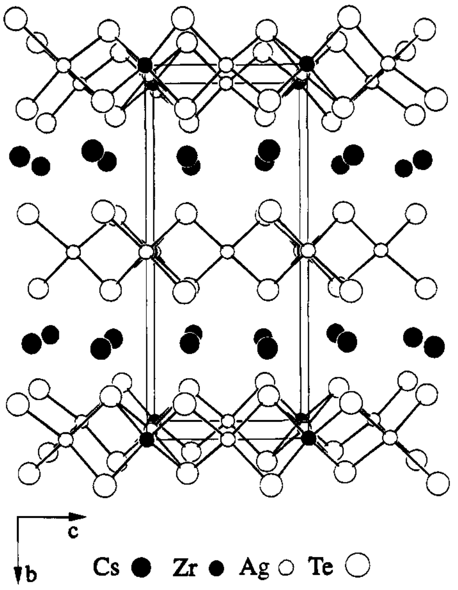

Figure 1. View down [100] of the structure of $Cs_2Ag_2ZrTe_4$. Atoms are shown as circles of arbitrary size.

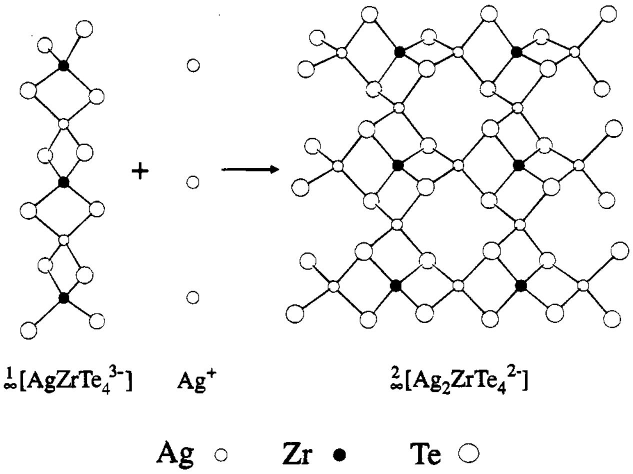

Figure 2. Diagram showing how the $^1_\infty[AgZrTe_4^{3-}]$ chains are stitched together by Ag^+ centers to form $^2_\infty[Ag_2ZrTe_4^{2-}]$ slabs. View is approximately down [010].

As it contains no Te–Te or metal–metal interactions, the structure of $Cs_2Ag_2ZrTe_4$ consists of Cs^+, Ag^+, and Zr^{4+} cations and Te^{2-} anions. It comprises $^2_\infty[Ag_2ZrTe_4^{2-}]$ slabs separated by square-prismatic Cs^+ cations (Figure 1). The Cs–Te interactions range from 3.878(3) to 3.960(3) Å (Table S3[17]). These distances are reasonable when compared with those found in the structure of Cs_2Te_5,[24] which has Cs–Te interactions ranging from 3.856(1) to 3.969(1) Å. The slabs (Figure 2) are constructed from the edge-sharing of $AgTe_4$ and $ZrTe_4$ tetrahedra. The $^1_\infty[AgZrTe_4^{3-}]$ chain in Figure 2 can be likened to the ordered $^1_\infty[CuNbSe_4^{2-}]$ chain of alternating edge-shared $CuSe_4$ and $NbSe_4$ tetrahedra in the $K_2CuNbSe_4$ structure.[25] But in the present structure these chains are "stitched together" into the $^2_\infty[Ag_2ZrTe_4^{2-}]$ slabs by the additional Ag^+ cations. In contrast, the $^2_\infty[Cu_2ZrS_4^{2-}]$ slabs of the $Na_2Cu_2ZrS_4$ structure[13] contain Cu tetrahedra bonded in pairs, which in turn are separated by Zr octahedra.

In the present structure the two crystallographically independent Ag^+ cations are in essentially tetrahedral $AgTe_4$ polyhedra of symmetry 222. For cation Ag(1) the Ag–Te distance is 2.817(2) Å and Te–Ag–Te angles are 106.34(7), 110.24(7), and 111.88(7)°; the corresponding values for cation Ag(2) are 2.806(2) Å and 106.61(7), 109.93(7), and 111.91(7)°. These distances compare well with the tetrahedral Ag–Te distances

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of 2.830(3) to 3.041(4) Å found in the structure of Tl_3AgTe_2.[26] As we noted above, most surprisingly the Zr^{4+} cation is in a tetrahedral $ZrTe_4$ polyhedron of symmetry 222 with a Zr−Te distance of 2.748(2) Å and Te−Zr−Te angles of 108.23(7), 109.92(7), and 110.27(7)°. As this $ZrTe_4$ tetrahedron is unique, no comparisons of bond lengths to known structures may be made. Octahedral Zr−Te distances in the $KCuZrTe_3$[11] structure are 2.656(1) to 3.180(1) Å.

The Hf analogue of the present compound has not yet been prepared. The tellurides of U^{4+} have shown some interesting contrasts with those of Zr^{4+} and Hf^{4+}.[15,27] However, a reaction of Ag, U, Te, and Cs_2Te_3, analogous to the present one, afforded no quaternary compound related to $Cs_2Ag_2ZrTe_4$, but rather produced the ternaries $CsUTe_6$ and $CsAg_5Te_3$.[15]

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Supplementary Material Available: Tables of crystal and structure refinement data, anisotropic displacement parameters, and interatomic distances and angles for $Cs_2Ag_2ZrTe_4$ (7 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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