

# Synthesis and structure of $\text{CsTi}_5\text{Te}_8$ : Relation to the $\text{TlV}_5\text{S}_8$ , $\text{TiCr}_3\text{S}_5$ , and similar channel structures

Danielle L. Gray, James A. Ibers\*

Department of Chemistry, Northwestern University, 2145 Sheridan Rd., Evanston, IL 60208-3113, USA

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## Abstract

The compound  $\text{CsTi}_5\text{Te}_8$  was obtained as a crystalline product by an “U-assisted” reaction of Cs, Ti, U, and  $\text{Cs}_2\text{Te}_3$  in a CsCl flux at 1173 K. The structure of  $\text{CsTi}_5\text{Te}_8$  contains a three-dimensional network of face-sharing and edge-sharing  $\text{TiTe}_6$  octahedra that form one-dimensional channels. The  $\text{Cs}^+$  cations reside in channels that propagate in the [0 1 0] direction. The structure is closely related to several other types of channel structures including those of the minerals of the hollandite and psilomelane families, and those of the  $\text{TlV}_5\text{S}_8$  and  $\text{TiCr}_3\text{S}_5$  structure types.

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**Keywords:** Channel structure; Synthesis; X-ray diffraction; Alkali-metal transition-metal telluride

## 1. Introduction

A series of compounds of formula  $M'M_5Q_8$  ( $M' = \text{Li, Na, K, Rb, Cs, Cd, Sn, Pb, Tl}$ ;  $M = \text{Cr, Ti, V}$ ;  $Q = \text{S, Se, Te}$ ) [1–4] have been synthesized over the last 30–40 years. These compounds are useful as models for one-dimensional ionic conductivity because they contain one-dimensional channels filled with cations that are relatively mobile at room temperature. However, traditional high-temperature solid-state syntheses of these compounds were frequently unsuccessful, and when they were successful the yields were often very low. Subsequently, low-temperature ion exchange reactions were developed to expand this unusual series of compounds. Such reactions afforded compounds involving many other  $M'$  metals as well as expanded the series for the selenides and tellurides [2].

Despite the large family of known  $M'M_5Q_8$  compounds,  $\text{CsTi}_5\text{Te}_8$  has apparently never been isolated. While re-synthesizing  $\text{CsTiUTe}_5$  [5], we isolated  $\text{CsTi}_5\text{Te}_8$  as well. It turns out that  $\text{CsTi}_5\text{Te}_8$  is not isostructural to any other  $M'M_5Q_8$  compound, but is a new structure type. Owing to interest in  $M'M_5Q_8$  compounds, we report here the synthesis of  $\text{CsTi}_5\text{Te}_8$  and discuss the structural relationships among  $\text{CsTi}_5\text{Te}_8$  and other closely related one-dimensional channel structures.

## 2. Experimental

### 2.1. Synthesis

Cs (Aldrich, 99.9%), Ti (Aldrich, 99.9%), Te (Aldrich, 99.8%), and CsCl (Aldrich 99%) were used as obtained.  $\text{Cs}_2\text{Te}_3$  was prepared from the reaction of the elements in liquid  $\text{NH}_3$  at 194 K. Depleted U turnings (ORNL) were cleaned in a concentrated  $\text{HNO}_3$  solution to remove the uranium oxide surface layer. The turnings were then quickly rinsed in deionized water and dried with acetone for immediate use.  $\text{CsTi}_5\text{Te}_8$  was obtained initially from the reaction of 0.10 mmol of Ti, 0.075 mmol of Te, 0.010 mmol of  $\text{Cs}_2\text{Te}_3$ , 0.125 mmol of CsCl, and 0.025 mmol of U. The reactants were loaded into a fused-silica tube under an Ar atmosphere in a glove box. The tube was sealed under a  $10^{-4}$  Torr atmosphere and then placed in a computer-controlled furnace. The furnace was heated to 1173 K in 12 h, kept at 1173 K for 144 h, and then cooled at 5 K/h to 298 K. The resultant reaction product was opened into paratone oil to prevent decomposition from air and moisture. As determined by the examination of selected single crystals with an EDX-equipped Hitachi S-3500 SEM, the product consisted of black crystals of several different habits; these included  $\text{U}_2\text{Te}_3$ ,  $\text{CsTiUTe}_5$ , and about a 2% yield of the new material  $\text{CsTi}_5\text{Te}_8$ .

Next, rational syntheses of  $\text{CsTi}_5\text{Te}_8$  were attempted from stoichiometric reactions of  $\text{Cs}_2\text{Te}_3$ , Ti, and Te under a variety of heating profiles with and without the addition of different  $\text{CsX}$  ( $X = \text{Cl, Br, I}$ ) salt fluxes. The only crystalline material isolated from any of these reactions was  $\text{TiTe}_2$ , although some of these reactions afforded detectable amounts of  $\text{CsTi}_5\text{Te}_8$  powder.

Ultimately, we returned to the “U-assisted” route with a loading designed to yield a 1:4 ratio of  $\text{CsTiUTe}_5$ : $\text{CsTi}_5\text{Te}_8$ . This loading consisted of 0.626 mmol of Ti, 0.880 mmol of Te, 0.075 mmol of  $\text{Cs}_2\text{Te}_3$ , 0.9 mmol of CsCl, and 0.030 mmol of U. The furnace was heated to 1173 K in 12 h, kept at 1173 K for 72 h, cooled at 5 K/h to 540 K, and then it was turned off. Analysis of an array of crystals from the product mixture showed that approximately 43% of the crystalline products was  $\text{CsTi}_5\text{Te}_8$ . This compound is moderately stable in air.

\* Corresponding author. Fax: +1 847 491 2976.

E-mail address: [ibers@chem.northwestern.edu](mailto:ibers@chem.northwestern.edu) (J.A. Ibers).

Table 1  
Crystallographic details for CsTi<sub>5</sub>Te<sub>8</sub>

fw	1393.21
<i>a</i> (Å)	13.414(2)
<i>b</i> (Å)	3.8912(5)
<i>c</i> (Å)	14.552(3)
$\beta$ (°)	93.135(1)
<i>V</i> (Å <sup>3</sup> )	758.4(2)
<i>T</i> (K)	153(2)
<i>Z</i>	2
Space group	<i>I</i> 2/ <i>m</i>
$\rho_c$ (g cm <sup>-3</sup> )	6.101
$\mu$ (cm <sup>-1</sup> )	199.26
<i>R</i> ( <i>F</i> ) <sup>a</sup>	0.0282
<i>R</i> <sub>w</sub> ( <i>F</i> <sup>2</sup> ) <sup>b</sup>	0.0747

$$^a R(F) = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \text{ for } F_o^2 > 2\sigma(F_o^2).$$

$$^b R_w(F_o^2) = \left[ \frac{\sum w(F_o^2 - F_c^2)^2}{\sum wF_o^4} \right]^{1/2}, w^{-1} = \sigma^2(F_o^2) + (0.04 \times F_o^2)^2 \text{ for } F_o^2 \geq 0; w^{-1} = \sigma^2(F_o^2) \text{ for } F_o^2 < 0.$$

## 2.2. Crystallography

Single-crystal X-ray diffraction data were collected with the use of graphite-monochromatized Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 153 K on a Bruker Smart-1000 CCD diffractometer [6]. The crystal-to-detector distance was 5.023 cm. Crystal decay was monitored by re-collecting 50 initial frames at the end of data collection. Data were collected by a scan of 0.3° in  $\omega$  in groups of 606 frames at  $\varphi$  settings of 0°, 90°, 180°, and 270°. The exposure time was 15 s/frame. The collection of intensity data was carried out with the program SMART [6]. Cell refinement and data reduction were carried out with the use of the program SAINT [6], and a face-indexed absorption correction was performed numerically with the use of the program XPREP [7]. A Leitz microscope with a calibrated traveling micrometer eyepiece was employed to measure the crystal dimensions for the face-indexed absorption correction. The program SADABS [7] was employed to make incident beam and decay corrections.

The structure was solved with the direct methods program SHELXS and refined with the full-matrix least-squares program SHELXL of the SHELXTL suite of programs [7]. Space group *I*2/*m*, rather than the standard setting of *C*2/*m*, was chosen because the resultant  $\beta$  angle is closer to 90°. This facilitates the description of the structure and its comparison with related channel structures. Additional experimental details are given in Table 1 and in Section Supporting information. Selected bond distances are presented in Table 2.

Table 2  
Selected bond distances (Å) for CsTi<sub>5</sub>Te<sub>8</sub>

Ti(1)–Te(1) $\times$ 2	2.7961(5)
Ti(1)–Te(3) $\times$ 4	2.8323(4)
Ti(2)–Te(1) $\times$ 2	2.7893(7)
Ti(2)–Te(3)	2.8147(9)
Ti(2)–Te(4) $\times$ 2	2.7681(7)
Ti(2)–Te(4)	2.7777(9)
Ti(3)–Te(1)	2.807(1)
Ti(3)–Te(2) $\times$ 2	2.7676(7)
Ti(3)–Te(2)	2.730(1)
Ti(3)–Te(3) $\times$ 2	2.8374(7)
Cs(1)–Te(2) $\times$ 4	3.8059(5)
Cs(1)–Te(4) $\times$ 4	3.7911(5)
Cs(1)–Te(1) $\times$ 2	3.9942(6)

## 3. Results and discussion

### 3.1. Synthesis

The synthesis of CsTi<sub>5</sub>Te<sub>8</sub> proceeded most efficiently from the “U-assisted” reaction of Ti, Te, Cs<sub>2</sub>Te<sub>3</sub>, CsCl, and U at 1173 K. The yield of single crystals of CsTi<sub>5</sub>Te<sub>8</sub> was approximately 43%. Rational syntheses of the product were attempted from stoichiometric reactions of Cs<sub>2</sub>Te<sub>3</sub>, Ti, and Te under a variety of heating profiles with and without the addition of different CsX (X = Cl, Br, I) salt fluxes. Some of these reactions afforded detectable amounts of CsTi<sub>5</sub>Te<sub>8</sub> powder but no single crystals.

### 3.2. Structure

The structure of CsTi<sub>5</sub>Te<sub>8</sub>, a new structure type, is shown in Fig. 1. It contains a three-dimensional network of face- and edge-sharing TiTe<sub>6</sub> octahedra that form one-dimensional channels in the [0 1 0] direction. The Cs<sup>+</sup> cations reside in these channels. Each Cs, which has 2/*m* symmetry, is coordinated by 10 Te atoms at the corners of a rectangular bicapped prism. There are three crystallographically independent Ti atoms in the structure. The site symmetries of Ti(1), Ti(2), and Ti(3) are 2/*m*, *m*, and *m*, respectively. Each Ti atom is coordinated octahedrally by six Te atoms. Like TiTe<sub>6</sub> octahedra edge share in the [0 1 0] direction to form infinite chains. In the [1 0  $\bar{1}$ ] direction Ti(1) and Ti(2) octahedral chains edge share octahedra to form flat sheets with an *abbabb* pattern, where Ti(1) chains are *a* and Ti(2) chains are *b*. In the [1 0 1] direction Ti(1) and Ti(3) octahedral chains edge and face share to form slightly puckered sheets with an *accacc* pattern, where Ti(3) chains are *c*. Each Ti(1) chain links to two Ti(3) chains by face-sharing octahedra, and each Ti(3) chain links to one Ti(1) chain by face sharing and one Ti(3) chain by edge sharing. The *abbabb* and *accacc* sheets intersect at the Ti(1) chain where each Ti(1) face shares with two Ti(3)Te<sub>6</sub>

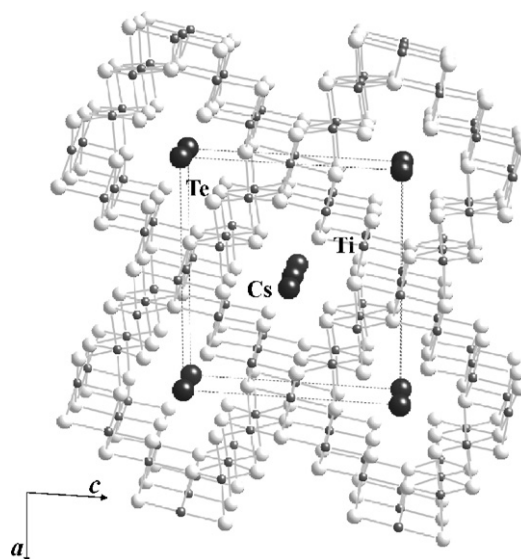


Fig. 1. The structure of CsTi<sub>5</sub>Te<sub>8</sub> as viewed down [0 1 0].

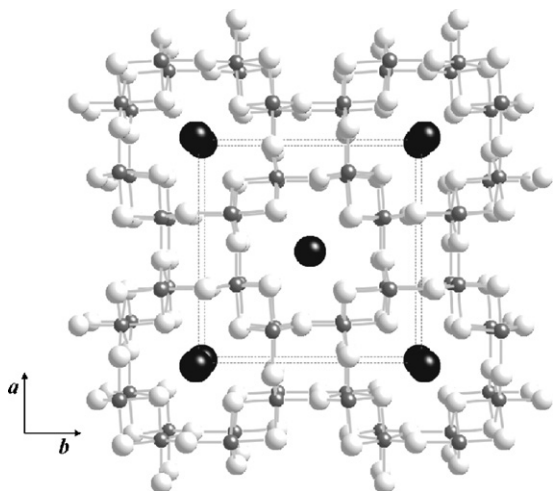


Fig. 2. The structure of  $\text{Ba}_{1.12}\text{Al}_{2.24}\text{Ti}_{5.76}\text{O}_{16}$  (hollandite) as viewed down  $[001]$ .

octahedra and edge shares with four  $\text{Ti}(2)\text{Te}_6$  octahedra to form the open channel network for the  $\text{Cs}^+$  ions.

The bond lengths (Table 2) in  $\text{CsTi}_5\text{Te}_8$  are normal. The Ti–Te bond distances range from 2.730(1) to 2.8374(7) Å, consistent with those of 2.678(4) to 2.838(4) Å in the structure of  $\text{TiCuTiTe}_3$  [8]. Cs–Te distances range from 3.7911(5) to 3.9942(6) Å, in agreement with those of 3.740(1) to 4.039(1) Å in the structure of  $\text{CsTiUTe}_3$  [5]. Because there are no Te–Te bonds in the structure, oxidation states of 1+, 3+, and 2– can be assigned to Cs, Ti, and Te, respectively.

The structure of  $\text{CsTi}_5\text{Te}_8$  is closely related to several other types of channel structures, including the hollandites ( $\text{A}_{2-y}\text{B}_{8-z}\text{X}_{16}$ : A = Ba, Pb, K; B = Al, Fe, Mg, Mn, Ti; X = O, OH) [9–11], compounds of the  $\text{TIV}_5\text{S}_8$  structure type [12], compounds of the  $\text{TiCr}_3\text{S}_5$  structure type [13], and psilomelane ( $(\text{Ba}, \text{H}_2\text{O})_2\text{Mn}_5\text{O}_{10}$ ) [14]. In each of these channel structures octahedral chains are packed in different ways. The structure of  $\text{Ba}_{1.12}\text{Al}_{2.24}\text{Ti}_{5.76}\text{O}_{16}$  [11], a representative hollandite, is shown in Fig. 2. The compound crystallizes in space group  $I4/m$ . In hollandites the  $\text{MO}_6$  octahedra edge share with four adjacent octahedra to form double strands. These double strands interconnect to form channels by corner-sharing O atoms. Channels are typically filled with alkali-metal or alkaline-earth cations. The hollandite structure type can distort or hinge at the corner-sharing O atom, as in  $\text{Ba}_{1.2}\text{Ti}_{6.8}\text{Mg}_{1.2}\text{O}_{16}$  [15] with concomitant reduction of the space group symmetry from  $I4/m$  to  $I2/m$ . In both the hollandites and the distorted hollandites an empty space is left where the four double strands connect, but it is not large enough to accommodate another metal ion. In contrast, because Ti–Te bonds are longer than M–O bonds and because of distortions at the hinges, in  $\text{CsTi}_5\text{Te}_8$  the space is large enough to accommodate a  $\text{Ti}^{3+}$  cation.

Most  $\text{AM}_5\text{Q}_8$  (A = Ti, Li, Na, K, Rb, Cs, Cd, Sn, Pb; M = Ti, V, Cr; Q = S, Se, Te) [1–4] compounds crystallize in space group  $C2/m$  in the  $\text{TIV}_5\text{S}_8$  [12] structure type, shown in Fig. 3. Although these compounds have the same stoichiometry as does  $\text{CsTi}_5\text{Te}_8$ , the connectivity of the  $\text{MQ}_6$  octahedra differs. The  $\text{TIV}_5\text{S}_8$  structure is also composed of edge- and face-sharing

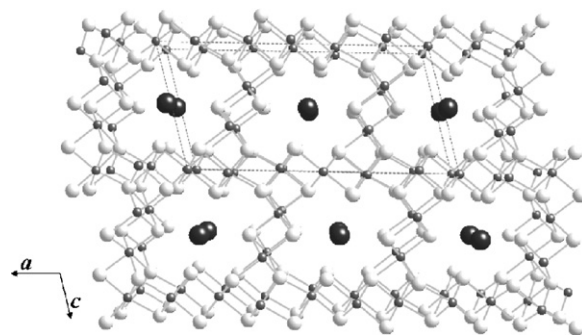


Fig. 3. The structure of  $\text{TIV}_5\text{S}_8$  as viewed down  $[010]$ .

octahedra with three distinct crystallographic sites for the transition metal M. M(1) and M(3) octahedral chains form sheets in the  $[100]$  direction in the same fashion as do the Ti(1) and Ti(2) octahedral chains in the  $[10\bar{1}]$  direction in  $\text{CsTi}_5\text{Te}_8$ . The difference in the structures arises in the way in which the sheets are connected. In  $\text{CsTi}_5\text{Te}_8$ , the structure is cross connected by sheets that intersect at atom Ti(1), but in the  $\text{TIV}_5\text{S}_8$  structure type the M(3) atom shares one face with an octahedral face of an M(2) double strand octahedral chain but the other face is exposed to the ion channel. In the structures of the present compound, the hollandites, and compounds with the  $\text{TIV}_5\text{S}_8$  structure type there are straight chains of cations in the channels. In contrast, compounds with the  $\text{TiCr}_3\text{S}_5$  structure type (Fig. 4a) [13] and psilomelane ( $(\text{Ba}, \text{H}_2\text{O})_2\text{Mn}_5\text{O}_{10}$ ) (Fig. 4b) [14] have channels that are wide enough to accommodate zigzag chains of cations (Fig. 4c). Nevertheless, these two structure types are closely related to the present one and to the parent structures of  $\text{TIV}_5\text{S}_8$  and hollandite. The  $\text{TiCr}_3\text{S}_5$  structure type is a variant of the  $\text{TIV}_5\text{S}_8$  structure type; both crystallize in space group  $C2/m$ . In  $\text{TiCr}_3\text{S}_5$  the layers only connect every fourth octahedron, thus expanding the channel from the eight exposed octahedra seen in  $\text{TIV}_5\text{S}_8$  to 10. Psilomelane ( $(\text{Ba}, \text{H}_2\text{O})_2\text{Mn}_5\text{O}_{10}$ ) [14], a variant of the hollandite structure, crystallizes in the space group  $A2/m$  (another non-standard setting of  $C2/m$ ). Instead of double strands, a double strand and an adjacent triple strand of edge-shared  $\text{MnO}_6$  octahedral chains interconnect at corner-shared O atoms.

Hollandite ( $\text{A}_{2-y}\text{B}_{8-z}\text{X}_{16}$ ) and other related channel minerals are a “catch all” in geological settings. The A and B sites can undergo a variety of chemical substitutions without affecting the overall structure. Because of this the hollandites have been incorporated into SYNROC, a composite used to immobilize alkali-metal cations in radioactive wastes [16]. Although the possibility of  $^{137}\text{Cs}$  mobility has been raised, the highly polar M–O bond in hollandites and the chemical composition of the framework in different formulations of SYNROC have helped to prevent high leaching rates under extreme conditions. Stability of the alkali-metals in the channels is greater than in other waste fixation processes [16,17].

Near complete replacement of the  $\text{Ti}^+$  ions in  $\text{TiM}_5\text{Q}_8$  compounds (M = Cr, Ti; Q = Se, Te) has been carried out between 150 and 400 °C with the use of ion-exchange reactions involving Li, Na, K, Rb, Cd, Sn, Pb, or Cs ions [2], although the present

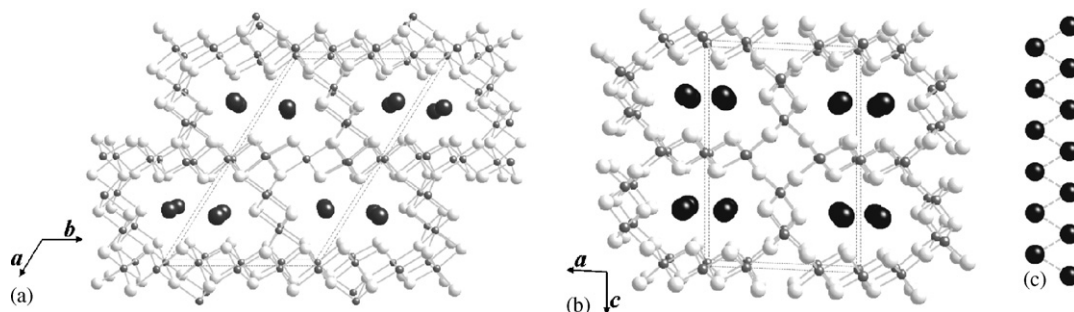


Fig. 4. (a) The structure of  $\text{TiCr}_3\text{S}_5$  as viewed down  $[001]$ . (b) The structure of  $(\text{Ba}, \text{H}_2\text{O})_2\text{Mn}_5\text{O}_{10}$  (psilomelane) as viewed down  $[010]$ . (c) Zigzag chain of cations that runs down an ion channel in both the  $\text{TiCr}_3\text{S}_5$  structure type and psilomelane.

compound  $\text{CsTi}_5\text{Te}_8$  was not obtained in this manner. We would thus expect that with the use of  $\text{CsTi}_5\text{Te}_8$  as the parent, a number of new  $M'\text{Ti}_5\text{Te}_8$  compounds with the  $\text{CsTi}_5\text{Te}_8$  structure type could be synthesized by ion exchange.

#### 4. Supporting information

The crystallographic file in cif format for  $\text{CsTi}_5\text{Te}_8$  has been deposited with FIZ Karlsruhe as CSD number 416704. These data may be obtained free of charge by contacting FIZ Karlsruhe at fax: +49 7247 808 666 or email [crysdta@fiz-karlsruhe.de](mailto:crysdta@fiz-karlsruhe.de).

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