Synthesis and structure of CsTi$_5$Te$_8$: Relation to the TlV$_5$S$_8$, TlCr$_3$S$_5$, and similar channel structures

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Abstract

The compound CsTi$_5$Te$_8$ was obtained as a crystalline product by an “U-assisted” reaction of Cs, Ti, U, and Cs$_2$Te$_3$ in a CsCl flux at 1173 K. The structure of CsTi$_5$Te$_8$ contains a three-dimensional network of face-sharing and edge-sharing TiTe$_6$ octahedra that form one-dimensional channels. The 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 TlV$_5$S$_8$ and TlCr$_3$S$_5$ structure types.

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1. Introduction

A series of compounds of formula $M'M_5Q_8$ ($M' = Li, Na, K, Rb, Cs, Cd, Sn, Pb, Ti; M = Cr, Ti, V; Q = S, Se, Te$) [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, CsTi$_5$Te$_8$ has apparently never been isolated. While resynthesizing CsTiUTe$_5$ [5], we isolated CsTi$_5$Te$_8$ as well. It turns out that CsTi$_5$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 CsTi$_5$Te$_8$ and discuss the structural relationships among CsTi$_5$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. Cs$_2$Te$_3$ was prepared from the reaction of the elements in liquid NH$_3$ at 194 K. Depleted U turnings (ORNL) were cleaned in a concentrated 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. CsTi$_5$Te$_8$ was obtained initially from the reaction of 0.10 mmol of Ti, 0.075 mmol of Te, 0.010 mmol of Cs$_2$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 U$_2$Te$_3$, CsTiUTe$_5$, and about a 2% yield of the new material CsTi$_5$Te$_8$.

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

Ultimately, we returned to the “U-assisted” route with a loading designed to yield a 1:4 ratio of CsTiUTe$_5$:CsTi$_5$Te$_8$. This loading consisted of 0.626 mmol of Ti, 0.880 mmol of Te, 0.075 mmol of Cs$_2$Te$_3$, 0.9 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 U$_2$Te$_3$, CsTiUTe$_5$, and about a 2% yield of the new material CsTi$_5$Te$_8$.
Table 1
Crystallographic details for CsTi5Te8

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<th>Parameter</th>
<th>Value</th>
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<tr>
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<td>I2/m</td>
</tr>
<tr>
<td>µ (cm⁻¹)</td>
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</tr>
<tr>
<td>F(001)</td>
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<tr>
<td>R(2θ)</td>
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Table 2
Selected bond distances (Å) for CsTi5Te8

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<tr>
<th>Bond</th>
<th>Distance (Å)</th>
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<tr>
<td>Ti(1)−Te(3)</td>
<td>2.8323(4)</td>
</tr>
<tr>
<td>Ti(2)−Te(1)</td>
<td>2.7893(7)</td>
</tr>
<tr>
<td>Ti(2)−Te(3)</td>
<td>2.8147(9)</td>
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<td>Ti(2)−Te(4)</td>
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<td>2.7777(9)</td>
</tr>
<tr>
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<td>2.807(1)</td>
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<tr>
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<td>Ti(3)−Te(3)</td>
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<td>Cs(1)−Te(2)</td>
<td>3.8059(5)</td>
</tr>
<tr>
<td>Cs(1)−Te(4)</td>
<td>3.7911(5)</td>
</tr>
<tr>
<td>Cs(1)−Te(1)</td>
<td>3.9942(6)</td>
</tr>
</tbody>
</table>

3. Results and discussion

3.1. Synthesis

The synthesis of CsTi5Te8 proceeded most efficiently from the “U-assisted” reaction of Ti, Te, Cs2Te3, CsCl, and U at 1173 K. The yield of single crystals of CsTi5Te8 was approximately 43%. Rational syntheses of the product were attempted from stoichiometric reactions of Cs5Te3, 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 CsTi5Te8 powder but no single crystals.

3.2. Structure

The structure of CsTi5Te8, a new structure type, is shown in Fig. 1. It contains a three-dimensional network of face- and edge-sharing TiTe6 octahedra that form one-dimensional channels in the [0 1 0] direction. The Cs⁺ 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 TiTe6 octahedra edge share in the [0 1 0] direction to form infinite chains. In the [0 0 1] direction Ti(1) and Ti(2) octahedral chains edge share octahedra to form flat sheets with an ababab pattern, where Ti(1) chains are a and Ti(2) chains are b. In the [0 1 0] 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 ababab and accacc sheets intersect at the Ti(1) chain where each Ti(1) face shares with two Ti(3)Te₆...
octahedra and edge shares with four Ti(2)Te₆ octahedra to form the open channel network for the Cs⁺ ions.

The bond lengths (Table 2) in CsTi₅Te₈ 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 TlCuTi₄Te₃ [8]. Cs–Te bond 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 CsTiUTe₃ [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 CsTi₅Te₈ is closely related to several other types of channel structures, including the hollandites (A₂₋₆B₆₋₆X₁₆; A = Ba, Pb, K; B = Al, Fe, Mg, Mn, Ti; X = O, OH) [9–11], compounds of the TIV₅S₈ structure type [12], compounds of the TICr₃S₅ structure type [13], and psilomelane ((Ba, H₂O)₂Mn₅O₁₀) [14]. In each of these channel structures octahedral chains are packed in different ways. The structure of Ba₁₂Al₂₂Ti₅₇O₁₆ [11], a representative hollandite, is shown in Fig. 2. The compound crystallizes in space group I4/m. In hollandites the MO₆ 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 Ba₁₂Al₆Mg₁₂O₁₆ [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 CsTi₅Te₈ the space is large enough to accommodate a Ti¹⁻⁺ cation.

Most AM₃Q₈ (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 TIV₅S₈ [12] structure type, shown in Fig. 3. Although these compounds have the same stoichiometry as does CsTi₅Te₈, the connectivity of the MQ₆ octahedra differs. The TIV₅S₈ structure is also composed of edge- and face-sharing octahedra with three distinct crystallographic sites for the transition metal M. M(1) and M(3) octahedral chains form sheets in the [1 0 0] direction in the same fashion as do the Ti(1) and Ti(2) octahedral chains in the [1 0 1] direction in CsTi₅Te₈. The difference in the structures arises in the way in which the sheets are connected. In CsTi₅Te₈, the structure is cross connected by sheets that intersect at atom Ti(1), but in the TIV₅S₈ 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 TIV₅S₈ structure type there are straight chains of cations in the channels. In contrast, compounds with the TICr₃S₅ structure type (Fig. 4a) [13] and psilomelane ((Ba, H₂O)₂Mn₅O₁₀) (Fig. 4b) [14] have channels that are wide enough to accommodate zigzag chains of cations (%e related to the present one and to the parent structures of TIV₅S₈ and hollandite. TheTICr₃S₅ structure type is a variant of the TIV₅S₈ structure type; both crystallize in space group C2/m. In TICr₃S₅ the layers only connect every fourth octahedron, thus expanding the channel from the eight exposed octahedra seen in TIV₅S₈ to 10. Psilomelane ((Ba, H₂O)₂Mn₅O₁₀) [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 MnO₆ octahedral chains interconnect at corner-shared O atoms.

Hollandite (A₂₋₆B₆₋₆X₁₆) 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 ¹³⁷Cs mobility has been raised, the strongly 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 Ti⁺ ions in TIM₃Q₈ 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
compound CsTi$_5$Te$_8$ was not obtained in this manner. We would thus expect that with the use of CsTi$_5$Te$_8$ as the parent, a number of new M$'$Ti$_5$Te$_8$ compounds with the CsTi$_5$Te$_8$ structure type could be synthesized by ion exchange.

4. Supporting information

The crystallographic file in cif format for CsTi$_5$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 crysdata@fix-karlsruhe.de.

Acknowledgment

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References