

# Synthesis and structure of CsCu<sub>3</sub>TiSe<sub>4</sub>

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## Abstract

The compound CsCu<sub>3</sub>TiSe<sub>4</sub> has been synthesized by the reaction of the elements in a Cs<sub>2</sub>Se<sub>3</sub> flux at 923 K. CsCu<sub>3</sub>TiSe<sub>4</sub> crystallizes in a new structure type with two formula units in space group *P*2<sub>1</sub>/*m* of the monoclinic system. The structure comprises two-dimensional  $\infty^2$ [Cu<sub>3</sub>TiSe<sub>4</sub><sup>-</sup>] layers separated by Cs atoms. Each  $\infty^2$ [Cu<sub>3</sub>TiSe<sub>4</sub><sup>-</sup>] layer is built from CuSe<sub>4</sub> and TiSe<sub>4</sub> tetrahedra.

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## 1. Introduction

Although a number of compounds of the type A<sup>1+</sup>/M<sup>1+</sup>/M'<sup>4+</sup>/Q<sup>2-</sup> (A = alkali metal; M = Ag or Cu; M' = Ti or Zr; Q = S, Se, or Te) are known there are only five compounds of formula A<sub>*m*</sub>M<sub>4-*m*</sub>M'Q<sub>4</sub> (*m* = 1, 2, 3) whose structures are known, and these are restricted to *m* = 2. These compounds are Na<sub>2</sub>Cu<sub>2</sub>ZrS<sub>4</sub> [1], Cs<sub>2</sub>Ag<sub>2</sub>ZrTe<sub>4</sub> [2], Cs<sub>2</sub>Cu<sub>2</sub>TiSe<sub>4</sub> [3], Cs<sub>2</sub>Ag<sub>2</sub>TiS<sub>4</sub> [3], and Rb<sub>2</sub>Cu<sub>2</sub>TiS<sub>4</sub> [3]. Here we report the synthesis and crystal structure of CsCu<sub>3</sub>TiSe<sub>4</sub>, the first example of an *m* = 1 compound in the A<sub>*m*</sub>M<sub>4-*m*</sub>M'Q<sub>4</sub> series, and contrast its structure with those with *m* = 2.

## 2. Experimental details

### 2.1. Synthesis

The following reagents were used as obtained: Cs (Aldrich, 99.5%), Ti (Aldrich, 99.7%), Cu (Alfa Aesar, 99.5%), and Se (Alfa Aesar, 99.5%). Cs<sub>2</sub>Se<sub>3</sub>, the reactive flux [4] employed in the synthesis, was prepared by the stoichiometric reaction of the elements in liquid NH<sub>3</sub>. CsCu<sub>3</sub>TiSe<sub>4</sub> was synthesized from the reaction of 3.0 mmol Cu, 1.0 mmol Ti, 4.0 mmol Se, and 1.2 mmol Cs<sub>2</sub>Se<sub>3</sub>. A reaction mixture was loaded into a fused-silica tube under an Ar atmosphere in a glove box. The tube was sealed under a 10<sup>-4</sup> Torr atmosphere and then placed in a computer-controlled furnace. The sample was heated to 923 K in 24 h, kept at 923 K for 72 h, cooled at 5.5 K/h to 373 K, and then the furnace was turned off. The reaction mixture was washed with *N,N*-dimethylformamide and then dried

with acetone. Red crystals of CsCu<sub>3</sub>TiSe<sub>4</sub> were obtained in approximately 85% yield (based on Ti). Examination of selected crystals with an EDX-equipped Hitachi S-3500 SEM led to results consistent with the stated composition. The compound is stable in air for several weeks.

### 2.2. Structure determination

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 [5]. The crystal-to-detector distance was 5.023 cm. Crystal decay was monitored by recollecting 50 initial frames at the end of the data collection. Data were collected by a scan of 0.3° in  $\omega$  in four groups of 606 frames at  $\phi$  settings of 0°, 90°, 180°, and 270°. The exposure time was 15 s/frame. The collection of the intensity data was carried out with the program SMART [5]. Cell refinement and data reduction were carried out with the use of the program SAINT [5] and a face-indexed absorption correction was performed numerically with the use of the program XPREP [6]. Then the program SADABS [5] 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 [6]. The program STRUCTURE TIDY [7] was then employed to standardize the atomic coordinates. Additional experimental details are shown in Table 1 and in Supporting information.

## 3. Results

### 3.1. Synthesis

The new compound CsCu<sub>3</sub>TiSe<sub>4</sub> has been synthesized in greater than 85% yield from Cu, Ti, Se, and Cs<sub>2</sub>Se<sub>3</sub> in the molar ratio 3:1:4:1.2 at 923 K. Earlier [3] the compound Cs<sub>2</sub>Cu<sub>2</sub>TiSe<sub>4</sub>

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Table 1  
Crystal data and structure refinement for CsCu<sub>3</sub>TiSe<sub>4</sub>

fw	687.27
Space group	<i>P</i> 2 <sub>1</sub> / <i>m</i>
<i>a</i> (Å)	5.7864 (4)
<i>b</i> (Å)	7.7671 (6)
<i>c</i> (Å)	10.1851 (8)
$\beta$ (deg)	106.517 (1)
<i>V</i> (Å <sup>3</sup> )	438.86 (6)
<i>Z</i>	2
<i>T</i> (K)	153 (2)
$\lambda$ (Å)	0.71073
$\rho_c$ (g/cm <sup>3</sup> )	5.201
$\mu$ (cm <sup>-1</sup> )	286.28
<i>R</i> ( <i>F</i> ) <sup>a</sup>	0.0304
<i>R</i> <sub>w</sub> ( <i>F</i> <sub>o</sub> <sup>2</sup> ) <sup>b</sup>	0.1084

<sup>a</sup>  $R(F) = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$  for  $F_o^2 > 2\sigma(F_o^2)$ .

<sup>b</sup>  $R_w(F_o^2) = \{\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma w F_o^4\}^{1/2}$ ;  $w^{-1} = \sigma^2(F_o^2) + (0.04 \times F_o^2)^2$  for  $F_o^2 \geq 0$  and  $w^{-1} = \sigma^2(F_o^2)$  for  $F_o^2 < 0$ .

was synthesized in about 90% yield from the same components in the molar ratio 2:1:3:1.5 at 823 K. Without further exploration it is impossible to ascertain whether the larger Cu/Cs ratio or the higher temperature or some other factor is responsible for the new composition.

### 3.2. Crystal structure

There are no metal–metal or Se–Se bonds in the structure. Accordingly, the formal oxidation states of Cs, Cu, Ti, and Se may be assigned as 1+, 1+, 4+, and 2–, respectively.

CsCu<sub>3</sub>TiSe<sub>4</sub> crystallizes in a new structure type with two formula units in space group *P*2<sub>1</sub>/*m*. Its structure is illustrated in Fig. 1. The structure is composed of  $\frac{2}{\infty}[\text{Cu}_3\text{TiSe}_4^-]$  layers separated by nine-coordinate Cs atoms. The resultant CsSe<sub>9</sub> polyhedra are tricapped trigonal prisms. In the structure there are two crystallographically unique Cu atoms. The  $\frac{2}{\infty}[\text{Cu}_3\text{TiSe}_4^-]$  layer, built from CuSe<sub>4</sub> and TiSe<sub>4</sub> tetrahedra, consists of the three fragments  $\frac{1}{\infty}[\text{Cu}_2\text{TiSe}_4^{3-}]$ ,  $\frac{2}{\infty}[\text{Cu}_1\text{TiSe}_4^{3-}]$  and  $\frac{1}{\infty}[\text{Cu}_2\text{TiSe}_4^{3-}]$ , as shown in Figs. 1, 2, and 3. Fig. 2 displays the middle fragment  $\frac{2}{\infty}[\text{Cu}_1\text{TiSe}_4^{3-}]$  with solid lines standing for Cu1–Se bonds, the upper fragment  $\frac{1}{\infty}[\text{Cu}_2\text{TiSe}_4^{3-}]$  with bold solid lines, and the lower fragment  $\frac{1}{\infty}[\text{Cu}_2\text{TiSe}_4^{3-}]$  with dashed lines. The  $\frac{1}{\infty}[\text{Cu}_2\text{TiSe}_4^{3-}]$  fragment, displayed in Fig. 3, is a chain along [100] built by edge-sharing Cu<sub>2</sub>Se<sub>4</sub> and TiSe<sub>4</sub> tetrahedra. The  $\frac{2}{\infty}[\text{Cu}_1\text{TiSe}_4^{3-}]$  fragment consists of  $\frac{1}{\infty}[\text{Cu}_1\text{Se}_2^{3-}]$  chains, and these chains are linked together by Se<sub>2</sub> atoms. The  $\frac{1}{\infty}[\text{Cu}_1\text{Se}_2^{3-}]$  chain can be derived from the  $\frac{1}{\infty}[\text{Cu}_2\text{TiSe}_4^{3-}]$  chain by the substitution of Ti with Cu.

Selected metrical data for the CsCu<sub>3</sub>TiSe<sub>4</sub> structure are listed in Table 2. In CsCu<sub>3</sub>TiSe<sub>4</sub> the Cs–Se distances (3.601(1)–3.8911(3) Å), the Cu–Se distances (2.421(1)–2.551(1) Å), and the Ti–Se distances (2.337(2)–2.462(2) Å) are reasonable when compared to those in Cs<sub>2</sub>Cu<sub>2</sub>TiSe<sub>4</sub> (Cs–Se: 3.666(1)–3.6667(1) Å, Cu–Se: 2.4732(9) Å, and Ti–Se: 2.3994(4) Å) [3]. The Se–M–Se angles range from 109.25(5)° to 110.07(7)° for Ti, 101.08(3)° to 116.65(4)° for Cu1, and

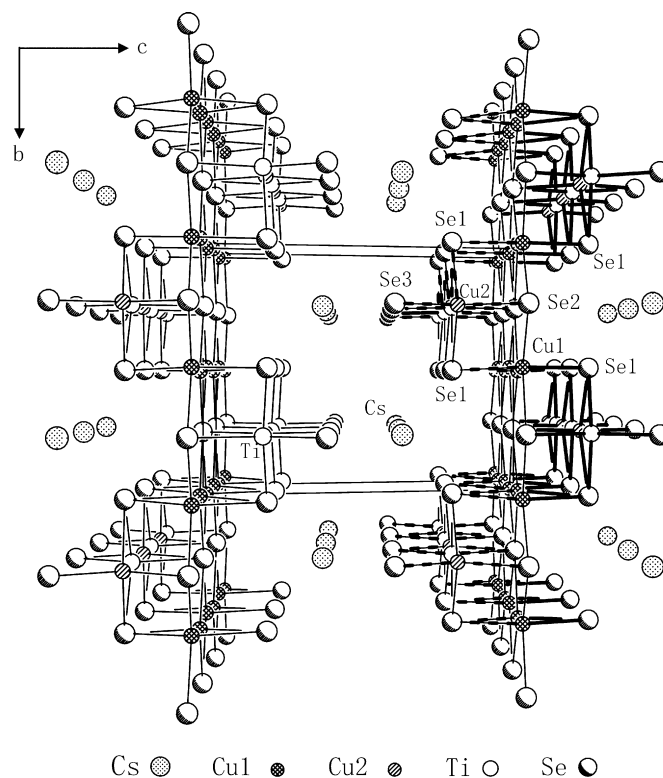


Fig. 1. The structure of CsCu<sub>3</sub>TiSe<sub>4</sub> viewed down [100].

104.55(5)° to 113.71(3)° for Cu<sub>2</sub>. The CuSe<sub>4</sub> tetrahedra are more distorted than is the TiSe<sub>4</sub> tetrahedron.

Table 3 presents some structural results for CsCu<sub>3</sub>TiSe<sub>4</sub> and for the *m*=2 compounds in the *A<sub>m</sub>M<sub>4–m</sub>M'Q<sub>4</sub>* series. These are all layered structures with the A atoms between the layers.

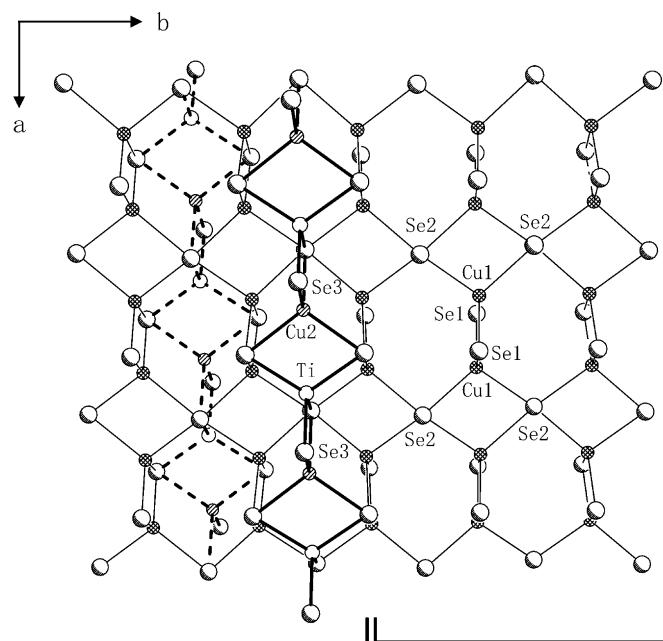
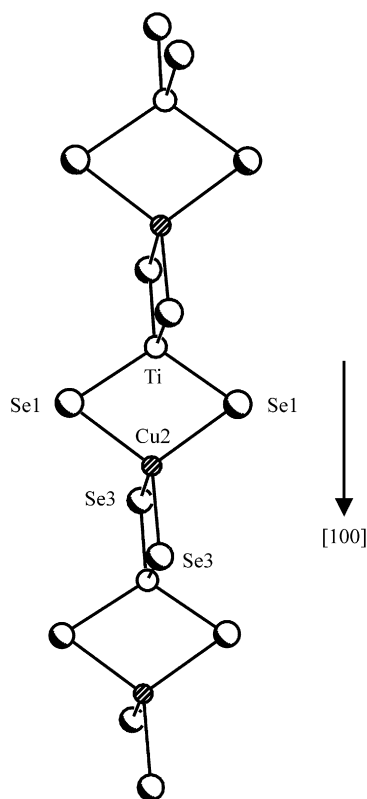


Fig. 2. Two-dimensional  $\frac{2}{\infty}[\text{Cu}_3\text{TiSe}_4^-]$  layer of CsCu<sub>3</sub>TiSe<sub>4</sub> from the Cu/Ti/Se portion on the right side of Fig. 1. The bold solid/dashed lines build the upper/lower  $\frac{1}{\infty}[\text{Cu}_2\text{TiSe}_4^{3-}]$  chains. For the sake of clarity, the right half shows only the middle  $\frac{2}{\infty}[\text{Cu}_1\text{TiSe}_4^{3-}]$  fragment.

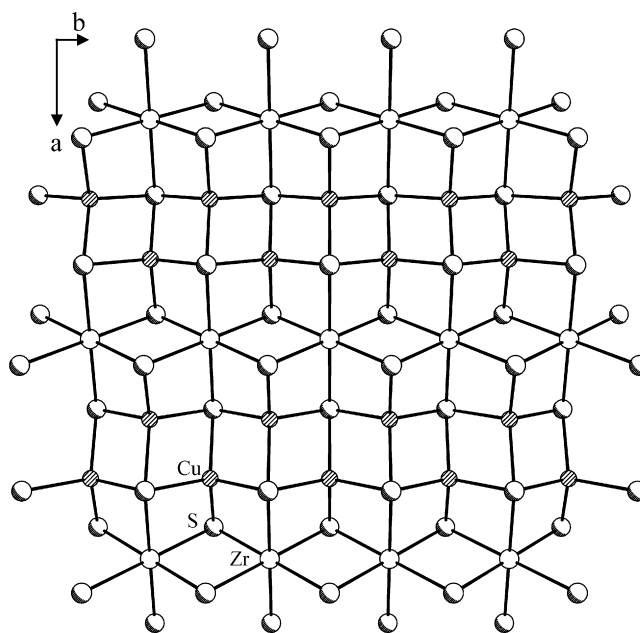
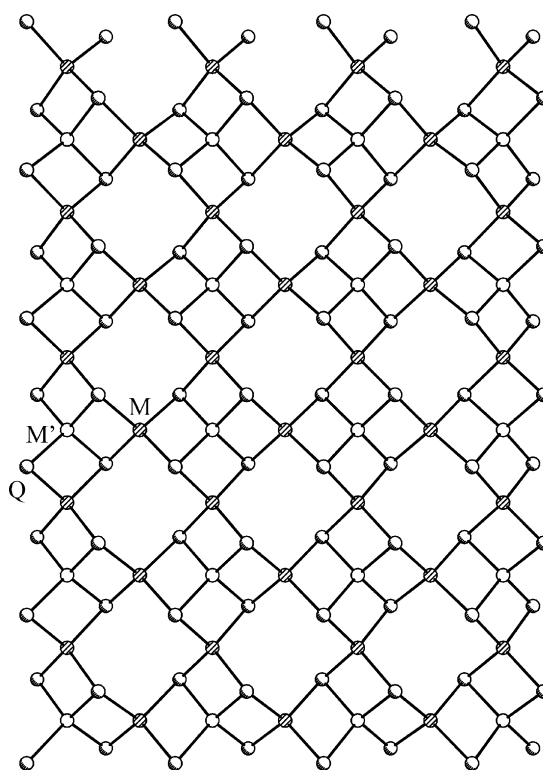
Fig. 3. The  $\frac{1}{\infty}[\text{Cu}_2\text{TiSe}_4^{3-}]$  chain.Table 2  
Selected distances (Å) in  $\text{CsCu}_3\text{TiSe}_4$ 

Cs-Se1 x2	3.7994 (8)	Ti-Se3	2.337 (2)
Cs-Se1 x2	3.8185 (8)	Cu1-Se1	2.458 (1)
Cs-Se2	3.656 (1)	Cu1-Se1	2.473 (1)
Cs-Se3	3.601 (1)	Cu1-Se2	2.4913 (9)
Cs-Se3	3.640 (1)	Cu1-Se2	2.548 (1)
Cs-Se3 x 2	3.8911 (3)	Cu2-Se1 x 2	2.4843 (9)
Ti-Se1 x 2	2.424 (1)	Cu2-Se2	2.551 (1)
Ti-Se2	2.462 (2)	Cu2-Se3	2.421 (1)

The layer in the  $\text{Na}_2\text{Cu}_2\text{ZrS}_4$  structure comprises edge-shared  $\text{CuS}_4$  tetrahedra and  $\text{ZrS}_6$  octahedra (Fig. 4). The layer in the other  $m=2$  compounds comprises edge-shared  $\text{MQ}_4$  and  $\text{M}'\text{Q}_4$  tetrahedra (Fig. 5). Obviously, the layer in the present compound is more complicated than are those in the  $m=2$  compounds. That this is true for  $\text{CsCu}_3\text{TiSe}_4$  versus  $\text{Cs}_2\text{Cu}_2\text{TiSe}_4$  argues against invoking arguments involving differing ionic radii as the explanation.

Table 3  
Some structural results for the known  $A_m\text{M}_{4-m}\text{M}'\text{Q}_4$  compounds

Compound	Space group	Z	Asymmetric unit	Building blocks			Layer figure
$\text{CsCu}_3\text{TiSe}_4$	$P2_1/m$	2	1Cs, 1Ti, 2Cu, 3Se	CsSe <sub>9</sub>	CuSe <sub>4</sub>	TiSe <sub>4</sub>	2
$\text{Na}_2\text{Cu}_2\text{ZrS}_4$	$C2/m$	2	1Na, 1Cu, 1Zr, 2S	NaS <sub>7</sub>	CuS <sub>4</sub>	ZrS <sub>6</sub>	4
$\text{Cs}_2\text{Ag}_2\text{ZrTe}_4$	$C222$	2	1Cs, 2Ag, 1Zr, 1Te	CsTe <sub>8</sub>	AgTe <sub>4</sub>	ZrTe <sub>4</sub>	5
$\text{Cs}_2\text{Cu}_2\text{TiSe}_4^a$	$P4_2/mcm$	2	1Cs, 1Ti, 1Cu, 1Se	CsSe <sub>8</sub>	CuSe <sub>4</sub>	TiSe <sub>4</sub>	5

<sup>a</sup>  $\text{Cs}_2\text{Ag}_2\text{TiS}_4$  and  $\text{Rb}_2\text{Cu}_2\text{TiS}_4$  are isostructural.Fig. 4. Two-dimensional  $\frac{2}{\infty}[\text{Cu}_2\text{ZrS}_4^{2-}]$  layer of  $\text{Na}_2\text{Cu}_2\text{ZrS}_4$ .Fig. 5. Two-dimensional  $\frac{2}{\infty}[\text{M}_2\text{M}'\text{Q}_4^{2-}]$  layer in  $\text{Cs}_2\text{Ag}_2\text{ZrTe}_4$ ,  $\text{Cs}_2\text{Cu}_2\text{TiSe}_4$ ,  $\text{Cs}_2\text{Ag}_2\text{TiS}_4$ , and  $\text{Rb}_2\text{Cu}_2\text{TiS}_4$ .

### Supporting information

Crystallographic data in CIF format have been deposited with FIZ Karlsruhe as CSD 391259. These data may be obtained free of charge by contacting FIZ Karlsruhe at +49 7247 808 666 (fax) or [crysdata@fiz-karlsruhe.de](mailto:crysdata@fiz-karlsruhe.de) (email).

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