The compound Cs₂U₃Se₇ has been synthesized at 1273 K by the reaction of U, Se, As, and Cs₂Se₃. The compound crystallizes in a new structure type in the orthorhombic space group $D_{16}^{16} \text{Pnma}$ with four formula units in a cell of dimensions $a = 22.847(1)$ Å, $b = 4.172(1)$ Å, $c = 16.639(1)$ Å. In the asymmetric unit there are three independent U atoms, each octahedrally coordinated by six Se atoms. These USe₆ octahedra are connected to form a channel structure with the channels running in the [010] direction. Within the unit cell the channel comprises twelve U centers.

1. Introduction

The actinide chalcogenides display a variety of interesting structures as well as magnetic, electronic, and optical properties [1,2]. In the ternary A/U/Q compounds (A = alkali metal; Q = S or Se or Te) among the compounds known are Li₂US₃ [3], Na₂US₃ [3], K₂UTe₃ [4], Rb₂UTe₃ [4], and KUS₂ [5]. None of these compounds show any Q–Q bonding interactions. In contrast, other actinide compounds do contain Q–Q bonds in their structures, and most of those known belong to the AAn₂Q₆ family (An = U, Th, Np; Q = S, Se, Te) [6–13], but Cs₂U₆Q₆ [14] and K₄USe₈ [15] are also known.

Because the actinide chalcogenides are little studied compared to other metal chalcogenides, exploratory syntheses frequently reveal previously unknown compounds and structures. Such is the case here where we report the synthesis and structural characterization of the new compound Cs₂U₃Se₇. This compound crystallizes in a new structure type but shows some similarities to the structures of Cr₂Sn₃Se₇ [16] and CaFe₂O₄ [17].

2. Experimental

2.1. Syntheses

Black needles of Cs₂U₃Se₇ have been obtained by the reaction of U (30 mg, 0.126 mmol), Se (13 mg, 0.164 mmol), As (6 mg, 0.080 mmol), and Cs₂Se₃ (34 mg, 0.038 mmol). The $^{238}$U powder was prepared from depleted turnings (Oak Ridge National Laboratory) by hydridization and decomposition under heat and vacuum [18], in a modification of a previous literature method [19]. The Cs₂Se₃ flux was synthesized by the stoichiometric reaction of Cs (Aldrich 99.5%) and Se (Cerac, 99.999%) in liquid NH₃ at 194 K [20]. The other reactants, Se (Cerac, 99.999%) and As (Strem, 2 N), were used as received. The starting mixture was loaded into a fused-silica tube under an Ar atmosphere in a glove box. The tube was then evacuated to 10⁻⁴ Torr, and flame sealed. It was then placed in a computer-controlled furnace, heated to 1273 K in 48 h, held there for 4 h, cooled to 1223 K in 12 h, held there for 192 h, then cooled to 298 K at 3 K/h. A few needles were selected and analyzed by EDX. These showed the presence of only Cs, U, and Se in the approximate atomic ratio 2:3:7.

2.2. Structure determination

Single-crystal X-ray diffraction data were collected at 100(2) K on a Bruker APEX II Kappa diffractometer equipped with graphite monochromatized MoKα radiation ($\lambda = 0.71073$ Å). A collection strategy of $\omega$ and $\phi$ scans was obtained by use of an algorithm in COSMO in the APEX II software [21]. The exposure time was 10 s/frame; the step size was 0.5°. Data were indexed, refined, and integrated by SAINT in the APEX II package [21]. Numerical face-indexed absorption corrections were carried out in the program SADABS [22]. The structure was solved and refined with the use of the SHELXTL package [23]. The program STRUCTURE TIDY [24] in...
3.1. Syntheses

Material.

3. Results

3.2. Structure

The compound Cs$_2$U$_3$Se$_7$ crystallizes in a new structure type in the orthorhombic space group $D_{2h}^{16}$ = Pnma, with four formula units in a cell of dimensions $a = 22.847(1)$ Å, $b = 4.172(1)$ Å, $c = 16.639(1)$ Å. In the structure there are three U, two Cs, and seven Se atoms in crystallographically independent sites all with site symmetry $m..$

A general view of the structure approximately down [010] is presented in Fig. 1 and selected metrical data are given in Table 2. Each U atom is octahedrally coordinated to six Se atoms. Each U1 atom is surrounded by three Se7, two Se5, and one Se6 atom; each U2 atom is coordinated by two Se3, two Se4, one Se5, and one Se2 atom; each U3 atom is coordinated by two Se1, two Se2, one Se6, and one Se4 atom. There are no Se–Se bonds in the structure. Therefore, formal oxidation states $+1, +4,$ and $-2$ may be assigned to Cs, U, and Se, respectively.

Fig. 2 shows the connectivity of the structure along [001]. Fig. 3 shows that Cs$_2$U$_3$Se$_7$ is a channel structure with the channels running along [010]. The channels are filled with seven-coordinate Cs atoms with Cs–Se interatomic distances ranging between 3.555(1) Å and 3.740(2) Å.

With the exception of the U1–S6 distance of 2.685(2) Å, the U–Se distances are typical for six-coordinate U$^{4+}$: they range from 2.837(1) Å to 2.896(2) Å. The U1–S6 distance is unexpectedly short. Given that the EDX analysis did not reveal the presence of oxygen and that the displacement ellipsoids of atom Se6 are not unusual, it seems very unlikely that the atom “Se6” is an admixture of Se and O. Even if the compound were actually Cs$_2$U$_3$Se$_7$.xO$_x$ we would expect that the admixture of O would be spread over multiple sites, and not just the Se6 site. Thus, we believe that the short U1–Se6 distance must arise from steric interactions. With a Se–Cs limit of 4.0 Å, the coordination

PLATON [25] was used to standardize the atomic positions. Crystal data and refinement details are given in Table 1 and in Supporting material.

3.1. Syntheses

Black needles of Cs$_2$U$_3$Se$_7$ were obtained in a high yield at 1273 K. An X-ray powder diffraction pattern did not show the presence of other elements or impurities despite the presence of As as a starting reactant. Nevertheless, susceptibility measurements (ZFC = 500 Oe) showed two possible antiferromagnetic transitions at 90 K and 51 K. The transition at 90 K was field dependent (FC = 500 Oe). There was also a field dependence at 298 K that is typical of the presence of ferromagnetic impurities. For these reasons the true magnetic behavior of Cs$_2$U$_3$Se$_7$ remains to be determined. Unfortunately, all further attempts to synthesize the compound with or without As led to the formation of the ternary compound Cs$_2$U$_3$Se$_6$ [7].

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3.2. Structure

The compound Cs$_2$U$_3$Se$_7$ crystallizes in a new structure type in the orthorhombic space group $D_{2h}^{16}$ = Pnma, with four formula units

### Table 1

Crystallographic data and structure refinement for Cs$_2$U$_3$Se$_7$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>$D_{2h}^{16}$ = Pnma</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>22.847(1)</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>4.172(1)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>16.639(1)</td>
</tr>
<tr>
<td>$V$ (Å$^3$)</td>
<td>1586.0(2)</td>
</tr>
<tr>
<td>$Z$</td>
<td>4</td>
</tr>
<tr>
<td>$T$</td>
<td>100(2) K</td>
</tr>
<tr>
<td>$\mu$ (g cm$^{-3}$)</td>
<td>6.419</td>
</tr>
<tr>
<td>$\beta$ (mm$^{-1}$)</td>
<td>51.11</td>
</tr>
<tr>
<td>$R(F)/R_w$</td>
<td>0.0378</td>
</tr>
<tr>
<td>$R_w$</td>
<td>0.071073</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>113.111 (1)</td>
</tr>
<tr>
<td>$\beta$</td>
<td>113.111 (1)</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>113.111 (1)</td>
</tr>
</tbody>
</table>

### Table 2

Selected interatomic bond lengths (Å) for Cs$_2$U$_3$Se$_7$.

<table>
<thead>
<tr>
<th>Atom–atom</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U1–Se6</td>
<td>2.686(2)</td>
</tr>
<tr>
<td>U1–Se5</td>
<td>2.837(1) × 2</td>
</tr>
<tr>
<td>U1–Se7</td>
<td>2.861(1) × 2</td>
</tr>
<tr>
<td>U1–Se1</td>
<td>2.889(1) × 2</td>
</tr>
<tr>
<td>U2–Se3</td>
<td>2.774(1) × 2</td>
</tr>
<tr>
<td>U2–Se5</td>
<td>2.856(2)</td>
</tr>
<tr>
<td>U2–Se6</td>
<td>2.881(1) × 2</td>
</tr>
</tbody>
</table>

* $R(F) = \sum|F_o|^2 - (\sum|F_i|^2)/|F_o|^2$ for $F_o > 2\sigma(F_o)$.
* $R_w = (\sum w F_o^2 - (\sum w F_i^2)^{1/2})^2/\sum w F_i^2$. For $F_o < 0$, $w^{-1} = \sigma(F_o) + (q F_o)^2$.
* where $q = 0.0452$. 

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![Fig. 1. General view down [010] of the structure of Cs$_2$U$_3$Se$_7$.](image1)

![Fig. 2. The connections of USe$_6$ octahedra viewed down [001] in the Cs$_2$U$_3$Se$_7$ structure.](image2)
numbers of atoms Se1 through Se7 are 5, 5, 5, 5, 4, 4, 5, respectively. In general, lower coordination numbers lead to shorter distances. Of the two four-coordinate Se atoms, atom Se5 is connected to two U2 atoms, one U3 atom, and one Cs1 atom with the Se5...Cs1 interaction being 3.740 Å. In contrast, four-coordinate atom Se6 is surrounded by atoms U1 and U2 and two Cs2 atoms with the Se6...Cs2 distance being 3.555(2) Å, the shortest Se...Cs interaction in the structure. We do not offer these observations as a definitive explanation of the short U1– Se6 distance.

Although the structure of Cs2U3Se7 represents a new structure type, it shows some similarities to the structures of Cr2Sn3Se7 [16] and CaFe2O4 [17]. All three crystallize in the orthorhombic space group D_{16}^h Pnma with all the atoms having site symmetry m. All three are channel structures with the channels running in the [010] direction and formed by the connections of USe6, (Cr/Sn)Se6, or FeO6 octahedra, respectively. However, within the unit cells the channel in Cs2U3Se7 comprises twelve metal centers (Fig. 3), whereas that in Cr2Sn3Se7 (Fig. 4) comprises thirteen, and that in CaFe2O4 (Fig. 5) comprises six.
4. Conclusions

The new compound Cs₂U₃Se₇ was synthesized at 1273 K. It crystallizes in the space group \( D_{16}^{12} \) of the orthorhombic system in a new structure type. The crystal structure is composed of channels along the [010] direction that are formed by the connection of USe₆ units. The channels are filled by Cs atoms. The structure of Cs₂U₃Se₇ shows similarities to those of Cr₂Sn₃Se₇ and CaFe₂O₄ but within the unit cells of each the number of metal centers in the channels differs.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.solidstatesciences.2013.01.008 and CSD No. 425462.

References