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Syntheses and crystal structures of the Ba$_7$UM$_2$S$_{12.5}$O$_{0.5}$ (M = Ti, Si/Fe) compounds

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Abstract

Black single crystals of the Ba$_7$UM$_2$S$_{12.5}$O$_{0.5}$ (M = Ti, Si/Fe) compounds were obtained by standard solid-state chemistry method at 1123 K. Both compounds crystallize at 100 K in the Ba$_7$UV$_2$S$_{12.5}$O$_{0.5}$ structure type in space group I4/mcm of the tetragonal system with $a = 16.1451(3)$ Å and $c = 9.5310(2)$ Å (Ba$_7$UTi$_2$S$_{12.5}$O$_{0.5}$) and $a = 16.1218(16)$ Å and $c = 9.4103(11)$ Å (Ba$_7$USi$_{1.7}$Fe$_{0.3}$S$_{12.5}$O$_{0.5}$). The crystal structures consist of infinite chains of U atoms octahedrally coordinated through the sharing of O/S corners along the c axis. The M atoms form isolated MS$_4$ tetrahedra aligned also along the c axis. The space between US$_5$O and MS$_4$ polyhedra is filled by Ba atoms.

Keywords:
- Solid state chemistry; Crystal structure; X-ray techniques; Ba$_7$UV$_2$S$_{12.5}$O$_{0.5}$ structure type

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1. **Introduction.**

Actinide chalcogenides (An = Th, U, Np; Q = S, Se, Te) form the basis for the study of interactions between the actinides (5f) and transition metals (3d). Although such An systems are well studied, those with Ak (Ak = alkaline-earth metal) are not. Examples of the latter were reported in a recent review [1]. Among them, the compounds Ba₇UM₂S₁₂.₅O₀.₅ (M = Fe, V) [2] are particularly relevant to the present study. These show remarkable flexibility that allows the accommodation of two transition metals having different oxidation states in the structure. In fact V⁴⁺ atoms are positioned in isolated VS₄ tetrahedra in the V compound, but in the Fe compound a short S−S bond leads to the formation of a Fe₂S₈ species and charge balance of the compound. The V compound crystallizes in space group I₄/mcm, whereas the Fe compound crystallizes in space group P₄/mbm of the tetragonal system. Here we describe the syntheses and structural characterization of the two new compounds, Ba₇UTi₂S₁₂.₅O₀.₅ and Ba₇USi₁.₅Fe₀.₃S₁₂.₅O₀.₅. Both crystallize in space group I₄/mcm in the Ba₇UV₂S₁₂.₅O₀.₅ structure type.

2. **Experimental section**

2.1 **Syntheses**

The starting reactants were used as supplied: Ba (Johnson Matthey, 99.5%), S (Mallinckrodt, 99.6%), Ti (Aldrich, 99.7%), and Si (Aldrich, 99.9%). Depleted U chips (IBI laboratories) were powdered by hydridization in a modification [3] of a previous literature protocol [4].

For each reaction, the weighed amounts of powders were loaded into a carbon-coated fused-silica 6 mm tube inside an Ar-filled dry box. The tube had been pre-baked and dried at 500 K. The tube was transferred with a special adapter to minimize oxygen or moisture contamination, then evacuated to 10⁻⁴ Torr, and flame sealed. Finally the tube was placed in a computer-controlled furnace, heated to 1123 K in 48 h, held at that temperature for 96 h, then cooled to 673 K at 2.5 K/h before the furnace was turned off. Some crystals were selected and analyzed with an EDX-equipped Hitachi S-3400 SEM.
**Ba$_7$UTi$_2$S$_{12.5}$O$_{0.5}$**. Black blocks of Ba$_7$UTi$_2$S$_{12.5}$O$_{0.5}$ were obtained (yield ≥ 70%) in an attempt to synthesize the eventual quaternary compound Ba$_3$TiUS$_6$ that crystallizes as a 2H hexagonal perovskite [5]. Therefore, the mixture consisted of U (20.23 mg, 0.084 mmol), Ti (14.00 mg, 0.255 mmol), Ba (35.01 mg, 0.255 mmol), and S (16.35 mg, 0.51 mmol). EDX analysis on black crystals revealed a molar ratio close to Ba:Ti:U:S ≈ 8:2:1:13. UOS [6] was detected as a byproduct. Other attempts were performed that led to the formation of a black powder.

**Ba$_7$USi$_{1.7}$Fe$_{0.3}$S$_{12.5}$O$_{0.5}$**. This compound was obtained (yield ≥ 70%) in an attempt to synthesize the Ba$_7$USi$_2$S$_{12.5}$O$_{0.5}$ compounds. The reaction mixture consisted of U (20 mg, 0.084 mmol), Ba (81.69 mg, 0.59 mmol), Si (4.76, 0.16 mmol), and S (35.43 mg, 1.11 mmol). Black blocks were analyzed by EDX to reveal Ba:U:Si:Fe:S ≈ 7:1:1.7:0.3:13. The presence of Fe is probably a contamination from an earlier reaction that led to another compound (Ba$_8$UFeSiS$_{14}$ [7]). A secondary phase was also detected with a U:S ratio of 1:1 and considered as UOS [6].

### 2.2 Structure determinations

Single-crystal X-ray diffraction data for the compounds Ba$_7$UTi$_2$S$_{12.5}$O$_{0.5}$ and Ba$_7$USi$_{1.7}$Fe$_{0.3}$S$_{12.5}$O$_{0.5}$ were collected at 100(2) K with the use of the Bruker APEX2 diffractometer equipped with graphite-monochromatized MoKα radiation (λ = 0.71073 Å) [8]. The data collection strategy used the algorithm COSMO implemented in the APEX2 package with a series of 0.3 scans in ω and φ. The exposure time was 10 s/frame. The collection of intensity data as well as cell refinement and data reduction were carried out with the use of the program APEX2 [8]. Face-indexed absorption, incident beam, and decay corrections were performed with the use of the program SADABS [9]. Both structures were solved and refined with the use of the SHELX14 programs [10]. As found previously, both structures contain oxygen; the O atoms were refined successfully. In addition the crystal structure of Ba$_7$USi$_{1.7}$Fe$_{0.3}$S$_{12.5}$O$_{0.5}$ was refined with Fe and Si occupying the same positions and having the same displacement parameters. Additional information is given in Table 1 and in Supplementary Material.
3. Results and discussion

3.1 Structure of Ba$_7$UM$_2$S$_{12.5}$O$_{0.5}$

The compounds Ba$_7$UTi$_2$S$_{12.5}$O$_{0.5}$ and Ba$_7$USi$_{1.7}$Fe$_{0.3}$S$_{12.5}$O$_{0.5}$ crystallize in the Ba$_7$V$_2$S$_{12.5}$O$_{0.5}$ [2] structure type in space group I4/mcm of the tetragonal system with four formula units in unit cells of dimensions $a = 16.1451(3)$ Å and $c = 9.5310(2)$ Å and $a = 16.1218(16)$ Å and $c = 9.4103(11)$ Å at 100 K, respectively. The asymmetric unit contains one disordered U1 atom (site symmetry 4..), one M (Ti or (0.85 Si + 0.15 Fe)) atom (m.2m), three Ba atoms Ba1, Ba2, Ba3 (.2., m.2m,−42m, respectively), three S positions S1, S2, S3 (..m, m.., and m.., respectively), and also an O1/S4 mixed site (422). A general drawing of the structure is viewed in Fig. 1 along the c axis; metrical values are reported in Table 2. Each U atom is octahedrally coordinated to five S atoms and one O atom. These octahedra are connected through the sharing of O/S corners along the c axis to form infinite chains, as viewed in Fig. 2. The presence of the -U-S-U-O- sequence leads to a 50% disorder of the U atoms along the c direction (Fig. 2). The Ti or (Si/Fe) site is coordinated to four S atoms to form isolated tetrahedra aligned along the c axis. The space between US$_5$O infinite chains and isolated MS$_4$ tetrahedra is filled by Ba atoms leading to the one-dimensional structure.

The U−S distances are 2.648(1) Å and 2.667(2) Å (Ba$_7$UTi$_2$S$_{12.5}$O$_{0.5}$) and 2.604(1) Å and 2.690(1) Å (Ba$_7$USi$_{1.7}$Fe$_{0.3}$S$_{12.5}$O$_{0.5}$). Similar U−S distances occur (2.627(1) Å and 2.679(1) Å) for Ba$_7$V$_2$US$_{12.5}$O$_{0.5}$ and 2.596(1)−2.667(2) Å (U1), 2.598(1)−2.640(2) Å (U2) for Ba$_7$UFe$_2$S$_{12.5}$O$_{0.5}$ [2]. Compare these distances with those of BaUS$_3$ [11] 2.668(1) to 2.696(1) Å, Ba$_2$Cu$_2$US$_5$ [12] 2.673(2) to 2.770(1) Å, and Li$_2$US$_3$ [13] 2.603 to 2.677 Å.

The U1−O distances are 2.118(1) Å and 2.101(1) Å for Ba$_7$UTi$_2$S$_{12.5}$O$_{0.5}$ and Ba$_7$USi$_{1.7}$Fe$_{0.3}$S$_{12.5}$O$_{0.5}$, respectively. In UP$_4$O$_{12}$ distance is 2.136(1) Å [14]. In Ba$_7$UTi$_2$S$_{12.5}$O$_{0.5}$ the Ti−S distances are 2.177(3) Å and 2.190(3) Å; these are 2.24(2) and 2.29(1) in Ti$_4$TiS$_4$ [15]. In Ba$_7$USi$_{1.7}$Fe$_{0.3}$S$_{12.5}$O$_{0.5}$ the Si/Fe distances are 2.111(1) Å and 2.139(1) Å. The Si−S distances in Ba$_8$USi$_2$S$_{14}$ are 2.105(3)−2.127(2) Å and the Fe−S distances in Ba$_8$USi$_2$FeS$_{14}$ are 2.154(1)−2.182 (1) Å [7].

The bond angles reported in Table 2 are typical for a US$_5$O octahedra and MS$_4$ tetrahedra. The Ba1 and Ba2 atoms are coordinated to eight S atoms whereas each Ba3 atom is nine coordinated. Those values are reported in Table 2 and may be compared with those
found in similar compounds, such as BaUS$_3$ [11], Ba$_5$US$_6$ [16], Ba$_{3.69}$US$_6$ [11], and BaU$_2$S$_5$ [11].

### 3.2 Oxidation states

Because there are no short S–S distances, the assignment of formal oxidation states in the Ba$_7$UTi$_2$S$_{12.5}$O$_{0.5}$ compound is straightforward with 7 Ba$^{2+}$, 2 Ti$^{4+}$, 1 U$^{4+}$, 12.5 S$^{2-}$, 0.5 O$^{2-}$. In the Ba$_7$USi$_{1.7}$Fe$_{0.3}$S$_{12.5}$O$_{0.5}$ the assumption of Fe$^{3+}$ with 7 Ba$^{2+}$, 1.7 Si$^{4+}$, 12.5 S$^{2-}$, 0.5 O$^{2-}$, leads to a mixed charge balance of U$^{4/5+}$. U$^{4/5+}$ has previously been conjectured in the compounds Ba$_{3.69}$US$_6$ [11], Ba$_{3.3}$Rb$_{0.7}$US$_6$ [17], and Ba$_{3.2}$K$_{0.8}$US$_6$ [17].

### 4. Conclusions

The Ba$_7$UM$_2$S$_{12.5}$O$_{0.5}$ ($M = Ti, Si/Fe$) compounds crystallize in Ba$_7$V$_2$US$_{12.5}$O$_{0.5}$ structure type in space group I4/mcm of the tetragonal system. The crystal structure consists of US$_5$O octahedra connected through the sharing of S/O corners to form infinite chains and isolated MS$_4$ tetrahedra, both aligned down the c axis. Ba atoms fill the space between US$_5$O and MS$_4$ polyhedra.

**Conflict of Interest**
None

**Declaration of Interest**
None

**Acknowledgments**
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**Appendix. Supplementary data**
Data for Ba$_7$UTi$_2$S$_{12.5}$O$_{0.5}$ (CCDC#1898481) and Ba$_7$USi$_{1.7}$Fe$_{0.3}$S$_{12.5}$O$_{0.5}$ (CCDC#1898480) may be obtained free of charge by contacting CCDC at (https://www.ccdc.cam.ac.uk).

**References**

Table 1. Crystal data and structure refinements for \( \text{Ba}_7\text{UTi}_2\text{S}_{12.5}\text{O}_{0.5} \) and \( \text{Ba}_7\text{USi}_{1.7}\text{Fe}_{0.3}\text{S}_{12.5}\text{O}_{0.5} \)

<table>
<thead>
<tr>
<th></th>
<th>( \text{Ba}<em>7\text{UTi}<em>2\text{S}</em>{12.5}\text{O}</em>{0.5} )</th>
<th>( \text{Ba}<em>7\text{USi}</em>{1.7}\text{Fe}<em>{0.3}\text{S}</em>{12.5}\text{O}_{0.5} )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>fw (g mol(^{-1}))</strong></td>
<td>1703.96</td>
<td>1720.19</td>
</tr>
<tr>
<td><strong>( a ) (Å)</strong></td>
<td>16.1451(3)</td>
<td>16.1218(16)</td>
</tr>
<tr>
<td><strong>( c ) (Å)</strong></td>
<td>9.5310(2)</td>
<td>9.4103(11)</td>
</tr>
<tr>
<td><strong>( V ) (Å(^3))</strong></td>
<td>2484.4(1)</td>
<td>2445.9(6)</td>
</tr>
<tr>
<td><strong>( \rho ) (g cm(^{-3}))</strong></td>
<td>4.556</td>
<td>4.671</td>
</tr>
<tr>
<td><strong>( \mu ) (mm(^{-1}))</strong></td>
<td>19.037</td>
<td>19.400</td>
</tr>
<tr>
<td><strong>( R(F) )(^d)</strong></td>
<td>0.0321</td>
<td>0.0148</td>
</tr>
<tr>
<td><strong>( R_w(F_o^2) )(^e)</strong></td>
<td>0.0704</td>
<td>0.0375</td>
</tr>
</tbody>
</table>

\(^a\) Space group = I4/mcm, \( T = 100(2) \) K, \( Z = 4 \), \( \lambda = 0.71073 \) Å.

\(^b\) CCDC\#1898481

\(^c\) CCDC\#1898480

\(^d\) \( R(F) = \sum \left| \frac{\left| F_o - F_c \right|}{\sum \left| F_o \right|} \right| \) for \( F_o^2 > 2\sigma(F_o^2) \).

\(^e\) \( R_w(F_o^2) = \left\{ \sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4 \right\}^{1/2} \). For \( F_o^2 < 0 \), \( w^{-1} = \sigma^2(F_o^2) \); for \( F_o^2 \geq 0 \), \( w^{-1} = \sigma^2(F_o^2) + (qF_o^2)^2 \) where \( q = 0.0178 \) for \( \text{Ba}_7\text{UTi}_2\text{S}_{12.5}\text{O}_{0.5} \), \( 0.0091 \) for \( \text{Ba}_7\text{USi}_{1.7}\text{Fe}_{0.3}\text{S}_{12.5}\text{O}_{0.5} \).
Table 2 Selected Interatomic Distances (Å) and bond angles (deg) for Ba$_7$UTi$_2$S$_{12.5}$O$_{0.5}$ and Ba$_7$UTi$_{1.7}$Fe$_{0.3}$S$_{12.5}$O$_{0.5}$.

<table>
<thead>
<tr>
<th></th>
<th>Ba$<em>7$UTi$<em>2$S$</em>{12.5}$O$</em>{0.5}$</th>
<th>Ba$<em>7$UTi$</em>{1.7}$Fe$<em>{0.3}$S$</em>{12.5}$O$_{0.5}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>U1−S4 × 4</td>
<td>2.667(2)</td>
<td>2.690(1)</td>
</tr>
<tr>
<td>U1−S1</td>
<td>2.648(1)</td>
<td>2.604(1)</td>
</tr>
<tr>
<td>U1−O1</td>
<td>2.118(1)</td>
<td>2.101(1)</td>
</tr>
<tr>
<td>M1−S2 × 2</td>
<td>2.177(3)</td>
<td>2.111(1)</td>
</tr>
<tr>
<td>M1−S3 × 2</td>
<td>2.190(3)</td>
<td>2.139(1)</td>
</tr>
<tr>
<td>Ba1−S</td>
<td>3.032(2)−3.421(2)</td>
<td>3.027(1)−3.502(1)</td>
</tr>
<tr>
<td>Ba2−S3 × 8</td>
<td>3.436(2)</td>
<td>3.378(1)</td>
</tr>
<tr>
<td>Ba3−S</td>
<td>3.262(2)−3.461(2)</td>
<td>3.2628(7)−3.441(1)</td>
</tr>
<tr>
<td>S1−U1−S1</td>
<td>180.0</td>
<td>180.0</td>
</tr>
<tr>
<td>S1−U1−S4</td>
<td>95.71(2)</td>
<td>95.37(1)</td>
</tr>
<tr>
<td>S2−Si1−S2</td>
<td>116.29(17)</td>
<td>117.57(7)</td>
</tr>
<tr>
<td>S2−Si1−S3</td>
<td>106.67(4)</td>
<td>107.05(1)</td>
</tr>
<tr>
<td>S3−Si1−S3</td>
<td>114.14(17)</td>
<td>111.08(8)</td>
</tr>
</tbody>
</table>
Fig. 1: View of the crystal structure of the Ba$_7$UM$_2$S$_{12.5}$O$_{0.5}$ down the c axis.
Figure 2: The alignment of the US₃O octahedra to form the infinite linear chains in the Ba₇UM₂S₁₂.₅O₀.₅ compounds.