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

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### Abstract

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

Keywords:

- Solid state chemistry; Crystal structure; X-ray techniques;  $\text{Ba}_7\text{UV}_2\text{S}_{12.5}\text{O}_{0.5}$  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  $Ba_7UM_2S_{12.5}O_{0.5}$  ( $M = Fe, V$ ) [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  $V^{4+}$  atoms are positioned in isolated  $VS_4$  tetrahedra in the V compound, but in the Fe compound a short S–S bond leads to the formation of a  $Fe_2S_8$  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,  $Ba_7UTi_2S_{12.5}O_{0.5}$  and  $Ba_7USi_{1.7}Fe_{0.3}S_{12.5}O_{0.5}$ . Both crystallize in space group  $I4/mcm$  in the  $Ba_7UV_2S_{12.5}O_{0.5}$  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, 99.99 %). 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<sub>7</sub>UTi<sub>2</sub>S<sub>12.5</sub>O<sub>0.5</sub>.** Black blocks of Ba<sub>7</sub>UTi<sub>2</sub>S<sub>12.5</sub>O<sub>0.5</sub> were obtained (yield ≥ 70%) in an attempt to synthesize the eventual quaternary compound Ba<sub>3</sub>TiUS<sub>6</sub> 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<sub>7</sub>USi<sub>1.7</sub>Fe<sub>0.3</sub>S<sub>12.5</sub>O<sub>0.5</sub>.** This compound was obtained (yield ≥ 70%) in an attempt to synthesize the Ba<sub>7</sub>USi<sub>2</sub>S<sub>12.5</sub>O<sub>0.5</sub> 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<sub>8</sub>UFeSi<sub>14</sub> [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<sub>7</sub>UTi<sub>2</sub>S<sub>12.5</sub>O<sub>0.5</sub> and Ba<sub>7</sub>USi<sub>1.7</sub>Fe<sub>0.3</sub>S<sub>12.5</sub>O<sub>0.5</sub> were collected at 100(2) K with the use of the Bruker APEX2 diffractometer equipped with graphite-monochromatized MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) [8]. The data collection strategy used the algorithm COSMO implemented in the APEX2 package with a series of 0.3 scans in  $\omega$  and  $\varphi$ . 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<sub>7</sub>USi<sub>1.7</sub>Fe<sub>0.3</sub>S<sub>12.5</sub>O<sub>0.5</sub> 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<sub>7</sub>UM<sub>2</sub>S<sub>12.5</sub>O<sub>0.5</sub>

The compounds Ba<sub>7</sub>UTi<sub>2</sub>S<sub>12.5</sub>O<sub>0.5</sub> and Ba<sub>7</sub>USi<sub>1.7</sub>Fe<sub>0.3</sub>S<sub>12.5</sub>O<sub>0.5</sub> crystallize in the Ba<sub>7</sub>UV<sub>2</sub>S<sub>12.5</sub>O<sub>0.5</sub> [2] structure type in space group I4/mcm of the tetragonal system with four formula units in unit cells of dimensions  $a = 16.1451(3) \text{ \AA}$  and  $c = 9.5310(2) \text{ \AA}$  and  $a = 16.1218(16) \text{ \AA}$  and  $c = 9.4103(11) \text{ \AA}$  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<sub>5</sub>O infinite chains and isolated MS<sub>4</sub> 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<sub>7</sub>UTi<sub>2</sub>S<sub>12.5</sub>O<sub>0.5</sub>) and 2.604(1) Å and 2.690(1) Å (Ba<sub>7</sub>USi<sub>1.7</sub>Fe<sub>0.3</sub>S<sub>12.5</sub>O<sub>0.5</sub>). Similar U–S distances occur (2.627(1) Å and 2.679(1) Å) for Ba<sub>7</sub>V<sub>2</sub>US<sub>12.5</sub>O<sub>0.5</sub> and 2.596(1)–2.667(2) Å (U1), 2.598(1)–2.640(2) Å (U2) for Ba<sub>7</sub>UFe<sub>2</sub>S<sub>12.5</sub>O<sub>0.5</sub> [2]. Compare these distances with those of BaUS<sub>3</sub> [11] 2.668(1) to 2.696(1) Å, Ba<sub>2</sub>Cu<sub>2</sub>US<sub>5</sub> [12] 2.673(2) to 2.770(1) Å, and Li<sub>2</sub>US<sub>3</sub> [13] 2.603 to 2.677 Å.

The U1–O distances are 2.118(1) Å and 2.101(1) Å for Ba<sub>7</sub>UTi<sub>2</sub>S<sub>12.5</sub>O<sub>0.5</sub> and Ba<sub>7</sub>USi<sub>1.7</sub>Fe<sub>0.3</sub>S<sub>12.5</sub>O<sub>0.5</sub>, respectively. In UP<sub>4</sub>O<sub>12</sub> distance is 2.136(1) Å [14]. In Ba<sub>7</sub>UTi<sub>2</sub>S<sub>12.5</sub>O<sub>0.5</sub> 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<sub>4</sub>TiS<sub>4</sub> [15]. In Ba<sub>7</sub>USi<sub>1.7</sub>Fe<sub>0.3</sub>S<sub>12.5</sub>O<sub>0.5</sub> the Si/Fe distances are 2.111(1) Å and 2.139(1) Å. The Si–S distances in Ba<sub>8</sub>USi<sub>2</sub>S<sub>14</sub> are 2.105(3)–2.127(2) Å and the Fe–S distances in Ba<sub>8</sub>USiFeS<sub>14</sub> are 2.154(1)–2.182 (1) Å [7].

The bond angles reported in Table 2 are typical for a US<sub>5</sub>O octahedra and MS<sub>4</sub> 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<sub>3</sub> [11], Ba<sub>2</sub>US<sub>6</sub> [16], Ba<sub>3.69</sub>US<sub>6</sub> [11], and BaU<sub>2</sub>S<sub>5</sub> [11].

### 3.2 Oxidation states

Because there are no short S–S distances, the assignment of formal oxidation states in the Ba<sub>7</sub>UTi<sub>2</sub>S<sub>12.5</sub>O<sub>0.5</sub> compound is straightforward with 7 Ba<sup>2+</sup>, 2 Ti<sup>4+</sup>, 1 U<sup>4+</sup>, 12.5 S<sup>2-</sup>, 0.5 O<sup>2-</sup>. In the Ba<sub>7</sub>USi<sub>1.7</sub>Fe<sub>0.3</sub>S<sub>12.5</sub>O<sub>0.5</sub> the assumption of Fe<sup>3+</sup> with 7 Ba<sup>2+</sup>, 1.7 Si<sup>4+</sup>, 12.5 S<sup>2-</sup>, 0.5 O<sup>2-</sup>, leads to a mixed charge balance of U<sup>4/5+</sup>. U<sup>4/5+</sup> has previously been conjectured in the compounds Ba<sub>3.69</sub>US<sub>6</sub> [11], Ba<sub>3.3</sub>Rb<sub>0.7</sub>US<sub>6</sub> [17], and Ba<sub>3.2</sub>K<sub>0.8</sub>US<sub>6</sub> [17].

## 4. Conclusions

The Ba<sub>7</sub>UM<sub>2</sub>S<sub>12.5</sub>O<sub>0.5</sub> (M = Ti, Si/Fe) compounds crystallize in Ba<sub>7</sub>V<sub>2</sub>US<sub>12.5</sub>O<sub>0.5</sub> structure type in space group I4/mcm of the tetragonal system. The crystal structure consists of US<sub>5</sub>O octahedra connected through the sharing of S/O corners to form infinite chains and isolated MS<sub>4</sub> tetrahedra, both aligned down the c axis. Ba atoms fill the space between US<sub>5</sub>O and MS<sub>4</sub> polyhedra.

### Conflict of Interest

None

### Declaration of Interest

None

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### Appendix. Supplementary data

Data for Ba<sub>7</sub>UTi<sub>2</sub>S<sub>12.5</sub>O<sub>0.5</sub> (CCDC#1898481) and Ba<sub>7</sub>USi<sub>1.7</sub>Fe<sub>0.3</sub>S<sub>12.5</sub>O<sub>0.5</sub> (CCDC#1898480) may be obtained free of charge by contacting CCDC at (<https://www.ccdc.cam.ac.uk>).

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**Table 1. Crystal data and structure refinements for Ba<sub>7</sub>UTi<sub>2</sub>S<sub>12.5</sub>O<sub>0.5</sub> and Ba<sub>7</sub>USi<sub>1.7</sub>Fe<sub>0.3</sub>S<sub>12.5</sub>O<sub>0.5</sub><sup>a</sup>**

	Ba <sub>7</sub> UTi <sub>2</sub> S <sub>12.5</sub> O <sub>0.5</sub> <sup>b</sup>	Ba <sub>7</sub> USi <sub>1.7</sub> Fe <sub>0.3</sub> S <sub>12.5</sub> O <sub>0.5</sub> <sup>c</sup>
fw (g mol <sup>-1</sup> )	1703.96	1720.19
<i>a</i> (Å)	16.1451(3)	16.1218(16)
<i>c</i> (Å)	9.5310(2)	9.4103(11)
<i>V</i> (Å <sup>3</sup> )	2484.4(1)	2445.9(6)
$\rho$ (g cm <sup>-3</sup> )	4.556	4.671
$\mu$ (mm <sup>-1</sup> )	19.037	19.400
<i>R</i> ( <i>F</i> ) <sup>d</sup>	0.0321	0.0148
<i>R</i> <sub>w</sub> ( <i>F</i> <sub>o</sub> <sup>2</sup> ) <sup>e</sup>	0.0704	0.0375

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

<sup>b</sup> CCDC#1898481

<sup>c</sup> CCDC#1898480

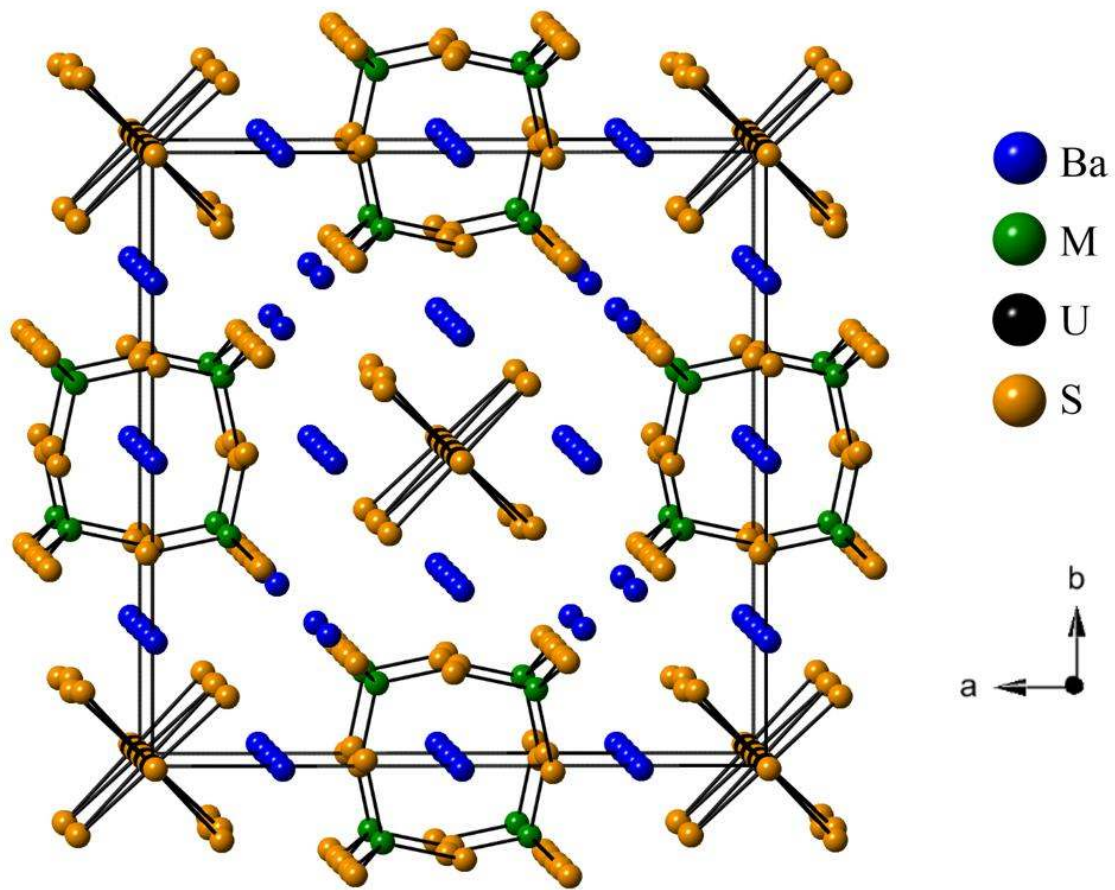
<sup>d</sup>  $R(F) = \Sigma | | F_o - F_c | | / \Sigma | F_o |$  for  $F_o^2 > 2\sigma(F_o^2)$ .

<sup>e</sup>  $R_w(F_o^2) = \{ \Sigma w(F_o^2 - F_c^2)^2 / \Sigma wF_o^4 \}^{1/2}$ . 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 Ba<sub>7</sub>UTi<sub>2</sub>S<sub>12.5</sub>O<sub>0.5</sub>, 0.0091 for Ba<sub>7</sub>USi<sub>1.7</sub>Fe<sub>0.3</sub>S<sub>12.5</sub>O<sub>0.5</sub>



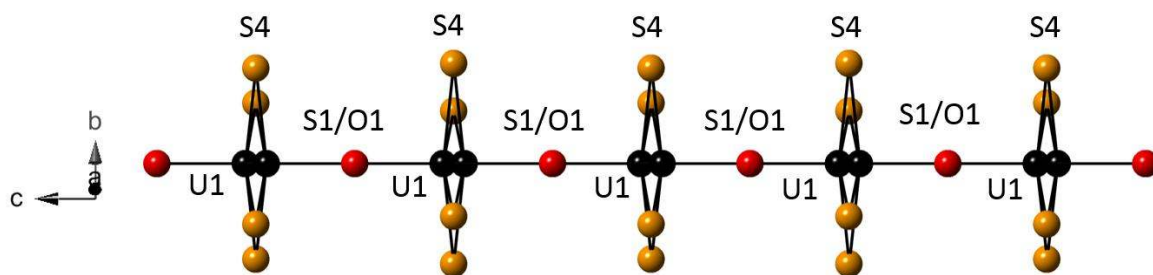
Table 2 Selected Interatomic Distances (Å) and bond angles (deg) for Ba<sub>7</sub>UTi<sub>2</sub>S<sub>12.5</sub>O<sub>0.5</sub> and Ba<sub>7</sub>UTi<sub>1.7</sub>Fe<sub>0.3</sub>S<sub>12.5</sub>O<sub>0.5</sub>.

	Ba <sub>7</sub> UTi <sub>2</sub> S <sub>12.5</sub> O <sub>0.5</sub>	Ba <sub>7</sub> UTi <sub>1.7</sub> Fe <sub>0.3</sub> S <sub>12.5</sub> O <sub>0.5</sub>
U1–S4 × 4	2.667(2)	2.690(1)
U1–S1	2.648(1)	2.604(1)
U1–O1	2.118(1)	2.101(1)
M1–S2 × 2	2.177(3)	2.111(1)
M1–S3 × 2	2.190(3)	2.139(1)
Ba1–S	3.032(2)–3.421(2)	3.027(1)–3.502(1)
Ba2–S3 × 8	3.436(2)	3.378(1)
Ba3–S	3.262(2)–3.461(2)	3.2628(7)–3.441(1)
S1–U1–S1	180.0	180.0
S1–U1–S4	95.71(2)	95.37(1)
S2–Si1–S2	116.29(17)	117.57(7)
S2–Si1–S3	106.67(4)	107.05(1)
S3–Si1–S3	114.14(17)	111.08(8)



**Fig. 1:** View of the crystal structure of the  $\text{Ba}_7\text{UM}_2\text{S}_{12.5}\text{O}_{0.5}$  down the  $c$  axis.

**Figure 2:**



**Fig 2:** The alignment of the  $US_5O$  octahedra to form the infinite linear chains in the  $Ba_7UM_2S_{12.5}O_{0.5}$  compounds.