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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 $a = 16.1451(3)$ Å and $c = 9.5310(2)$ Å ($\text{Ba}_7\text{UTi}_2\text{S}_{12.5}\text{O}_{0.5}$) and $a = 16.1218(16)$ Å and $c = 9.4103(11)$ Å ($\text{Ba}_7\text{USi}_{1.7}\text{Fe}_{0.3}\text{S}_{12.5}\text{O}_{0.5}$). 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 MS_4 tetrahedra aligned also along the c axis. The space between US_5O and 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.

Ba₇UTi₂S_{12.5}O_{0.5}. Black blocks of Ba₇UTi₂S_{12.5}O_{0.5} were obtained (yield ≥ 70%) in an attempt to synthesize the eventual quaternary compound Ba₃TiUS₆ 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.

Ba₇USi_{1.7}Fe_{0.3}S_{12.5}O_{0.5}. This compound was obtained (yield ≥ 70%) in an attempt to synthesize the Ba₇USi₂S_{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 (Ba₈UFeSiS₁₄ [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 Ba₇UTi₂S_{12.5}O_{0.5} and Ba₇USi_{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 MoK α 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 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 Ba₇USi_{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 Ba₇UM₂S_{12.5}O_{0.5}

The compounds Ba₇UTi₂S_{12.5}O_{0.5} and Ba₇USi_{1.7}Fe_{0.3}S_{12.5}O_{0.5} crystallize in the Ba₇UV₂S_{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 US₅O infinite chains and isolated MS₄ 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 (Ba₇UTi₂S_{12.5}O_{0.5}) and 2.604(1) Å and 2.690(1) Å (Ba₇USi_{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 Ba₇V₂US_{12.5}O_{0.5} and 2.596(1)–2.667(2) Å (U1), 2.598(1)–2.640(2) Å (U2) for Ba₇UFe₂S_{12.5}O_{0.5} [2]. Compare these distances with those of BaUS₃ [11] 2.668(1) to 2.696(1) Å, Ba₂Cu₂US₅ [12] 2.673(2) to 2.770(1) Å, and Li₂US₃ [13] 2.603 to 2.677 Å.

The U1–O distances are 2.118(1) Å and 2.101(1) Å for Ba₇UTi₂S_{12.5}O_{0.5} and Ba₇USi_{1.7}Fe_{0.3}S_{12.5}O_{0.5}, respectively. In UP₄O₁₂ distance is 2.136(1) Å [14]. In Ba₇UTi₂S_{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 Ti₄TiS₄ [15]. In Ba₇USi_{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 Ba₈USi₂S₁₄ are 2.105(3)–2.127(2) Å and the Fe–S distances in Ba₈USiFeS₁₄ are 2.154(1)–2.182(1) Å [7].

The bond angles reported in Table 2 are typical for a US₅O octahedra and MS₄ 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 BaUS₃ [11], Ba₂US₆ [16], Ba_{3.69}US₆ [11], and BaU₂S₅ [11].

3.2 Oxidation states

Because there are no short S–S distances, the assignment of formal oxidation states in the Ba₇UTi₂S_{12.5}O_{0.5} compound is straightforward with 7 Ba²⁺, 2 Ti⁴⁺, 1 U⁴⁺, 12.5 S²⁻, 0.5 O²⁻. In the Ba₇USi_{1.7}Fe_{0.3}S_{12.5}O_{0.5} the assumption of Fe³⁺ with 7 Ba²⁺, 1.7 Si⁴⁺, 12.5 S²⁻, 0.5 O²⁻, leads to a mixed charge balance of U^{4/5+}. U^{4/5+} has previously been conjectured in the compounds Ba_{3.69}US₆ [11], Ba_{3.3}Rb_{0.7}US₆ [17], and Ba_{3.2}K_{0.8}US₆ [17].

4. Conclusions

The Ba₇UM₂S_{12.5}O_{0.5} (M = Ti, Si/Fe) compounds crystallize in Ba₇V₂US_{12.5}O_{0.5} structure type in space group I4/mcm of the tetragonal system. The crystal structure consists of US₅O octahedra connected through the sharing of S/O corners to form infinite chains and isolated MS₄ tetrahedra, both aligned down the c axis. Ba atoms fill the space between US₅O and MS₄ polyhedra.

Conflict of Interest

None

Declaration of Interest

None

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Appendix. Supplementary data

Data for Ba₇UTi₂S_{12.5}O_{0.5} (CCDC#1898481) and Ba₇USi_{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>).

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Table 1. Crystal data and structure refinements for Ba₇UTi₂S_{12.5}O_{0.5} and Ba₇USi_{1.7}Fe_{0.3}S_{12.5}O_{0.5}^a

	Ba ₇ UTi ₂ S _{12.5} O _{0.5} ^b	Ba ₇ USi _{1.7} Fe _{0.3} S _{12.5} O _{0.5} ^c
fw (g mol ⁻¹)	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 ³)	2484.4(1)	2445.9(6)
ρ (g cm ⁻³)	4.556	4.671
μ (mm ⁻¹)	19.037	19.400
<i>R</i> (<i>F</i>) ^d	0.0321	0.0148
<i>R</i> _w (<i>F</i> _o ²) ^e	0.0704	0.0375

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

^b CCDC#1898481

^c CCDC#1898480

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

^e $R_w(F_o^2) = \{ \Sigma w(F_o^2 - F_c^2)^2 / \Sigma wF_o^4 \}^{1/2}$. 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 Ba₇UTi₂S_{12.5}O_{0.5}, 0.0091 for Ba₇USi_{1.7}Fe_{0.3}S_{12.5}O_{0.5}

Table 2 Selected Interatomic Distances (Å) and bond angles (deg) for Ba₇UTi₂S_{12.5}O_{0.5} and Ba₇UTi_{1.7}Fe_{0.3}S_{12.5}O_{0.5}.

	Ba ₇ UTi ₂ S _{12.5} O _{0.5}	Ba ₇ UTi _{1.7} Fe _{0.3} S _{12.5} O _{0.5}
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)

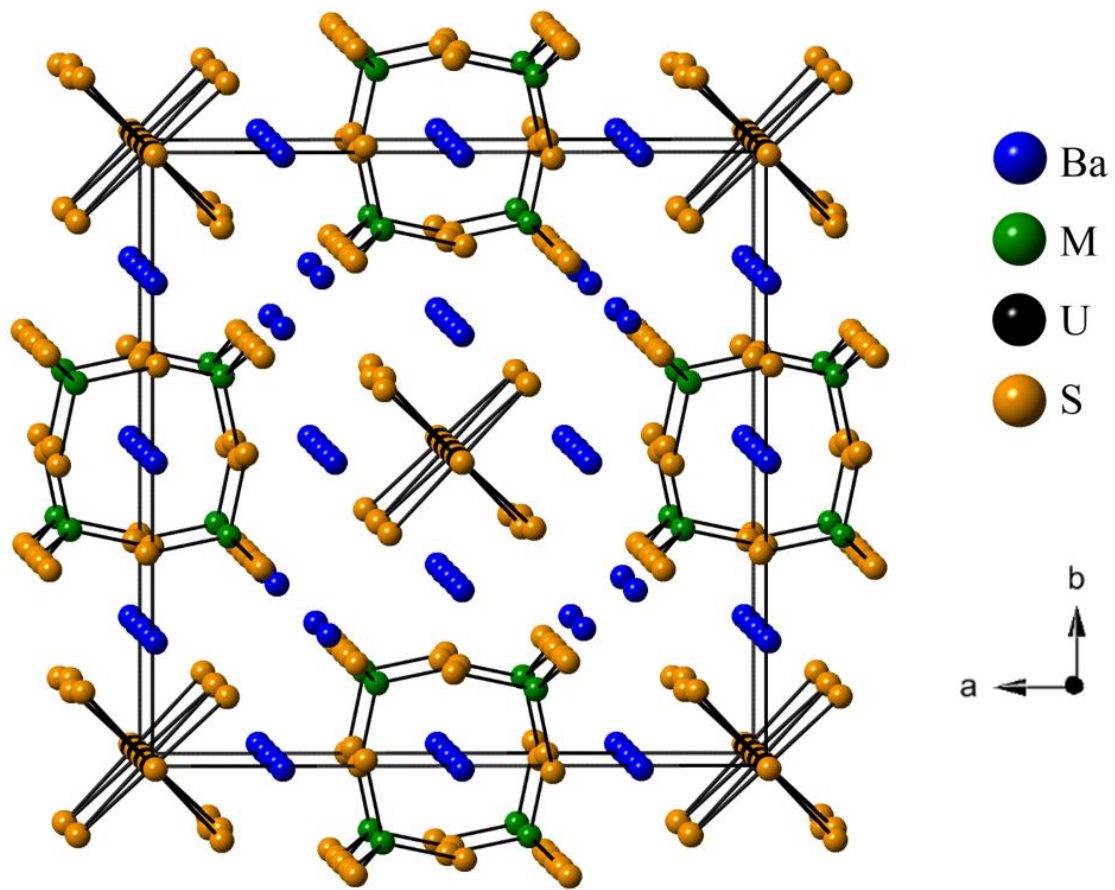


Fig. 1: View of the crystal structure of the $\text{Ba}_7\text{UM}_2\text{S}_{12.5}\text{O}_{0.5}$ down the c axis.

Figure 2:

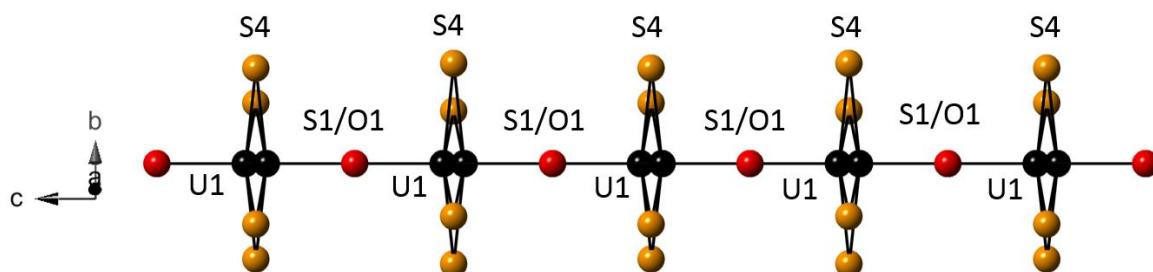


Fig 2: The alignment of the US_5O octahedra to form the infinite linear chains in the $Ba_7UM_2S_{12.5}O_{0.5}$ compounds.