



HAL
open science

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

Adel Mesbah, Jai Prakash, Jessica Beard, Christos Malliakas, James Ibers

► **To cite this version:**

Adel Mesbah, Jai Prakash, Jessica Beard, Christos Malliakas, James Ibers. Syntheses and crystal structures of the $\text{Ba}_7\text{UM}_2\text{S}_{12.5}\text{O}_{0.5}$ ($\text{M} = \text{Ti}, \text{Si}/\text{Fe}$) compounds. *Materials Letters*, 2019, 252, pp.293-295. 10.1016/j.matlet.2019.05.092 . hal-02349662

HAL Id: hal-02349662

<https://hal.umontpellier.fr/hal-02349662>

Submitted on 14 Nov 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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

Adel Mesbah,^{a,b} Jai Prakash,^{a,c} Jessica C. Beard,^a Christos. D. Malliakas,^a and James A. Ibers^{a,*}

^aDepartment of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208-3113, United States.

^bICSM, UMR 5257 CEA, CNRS, ENSCM, Univ Montpellier, Site de Marcoule - Bât. 426, BP 17171, 30207 Bagnols-sur-Cèze, France.

^cDepartment of Chemistry, Indian Institute of Technology Hyderabad, Kandi 502 285, Sangareddy, Telangana, India.

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

* Corresponding author.

E-mail address: ibers@chem.northwestern.edu

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 $\text{Ba}_7\text{UM}_2\text{S}_{12.5}\text{O}_{0.5}$ (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, $\text{Ba}_7\text{UTi}_2\text{S}_{12.5}\text{O}_{0.5}$ and $\text{Ba}_7\text{USi}_{1.7}\text{Fe}_{0.3}\text{S}_{12.5}\text{O}_{0.5}$. Both crystallize in space group I4/mcm in the $\text{Ba}_7\text{UV}_2\text{S}_{12.5}\text{O}_{0.5}$ 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

Acknowledgments

Use was made of the IMSERC X-ray Facility at Northwestern University, which has received support from the Soft and Hybrid Nanotechnology Experimental (SHyNE) Resource (NSF ECCS-1542205); the State of Illinois, and International Institute for Nanotechnology (IIN).

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>).

References

- [1] A. Mesbah, J. Prakash, J.A. Ibers, Dalton Trans. 45 (2016) 16067-16080.

- [2] J. Prakash, M.S. Tarasenko, A. Mesbah, S. Lebègue, C.D. Malliakas, J.A. Ibers, *Inorg. Chem.* 53 (2014) 11626-11632.
- [3] D.E. Bugaris, J.A. Ibers, *J. Solid State Chem.* 181 (2008) 3189-3193.
- [4] A.J.K. Haneveld, F. Jellinek, *J. Less-Common Met.* 18 (1969) 123-129.
- [5] A. Mesbah, C.D. Malliakas, S. Lebègue, A.A. Sarjeant, W. Stojko, L.A. Koscielski, J.A. Ibers, *Inorg. Chem.* 53 (2014) 2899-2903.
- [6] N. Sato, H. Masuda, M. Wakeshima, K. Yamada, T. Fujino, *J. Alloys Compd.* 265 (1998) 115-120.
- [7] A. Mesbah, J. Prakash, S. Lebègue, W. Stojko, J.A. Ibers, *Solid State Sci.* 48 (2015) 120-124.
- [8] Bruker APEX2 Version 2009.5-1 Data Collection and Processing Software,, Bruker Analytical X-Ray Instruments, Inc., Madison, WI, USA, 2009.
- [9] Bruker SMART Version 5.054 Data Collection and SAINT-Plus Version 6.45a Data Processing Software for the SMART System, Bruker Analytical X-Ray Instruments, Inc., Madison, WI, USA, 2003.
- [10] G.M. Sheldrick, *Acta Crystallogr. Sect. A: Found. Crystallogr.* 64 (2008) 112-122.
- [11] A. Mesbah, J.A. Ibers, *J. Solid State Chem.* 199 (2013) 253-257.
- [12] H.-yi Zeng, J. Yao, J.A. Ibers, *J. Solid State Chem.* 181 (2008) 552-555.
- [13] H. Masuda, T. Fujino, N. Sato, K. Yamada, M. Wakeshima, *J. Alloys Compd.* 284 (1999) 117-123.
- [14] S.A. Linde, Y.E. Gorbunova, A.V. Lavrov, *Zh. Neorg. Khim.* 28 (1983) 1391-1395.
- [15] K.O. Klepp, G. Eulenberger, *Z. Naturforsch. B: Anorg. Chem. Org. Chem.* 39 (1984) 705-712.
- [16] A. Mesbah, E. Ringe, S. Lebègue, R.P. Van Duyne, J.A. Ibers, *Inorg. Chem.* 51 (2012) 13390-13395.
- [17] A. Mesbah, J. Prakash, J.C. Beard, E.A. Pozzi, M.S. Tarasenko, S. Lebegue, C.D. Malliakas, R.P. Van Duyne, J.A. Ibers, *Inorg. Chem.* 54 (2015) 2851-2857.

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)

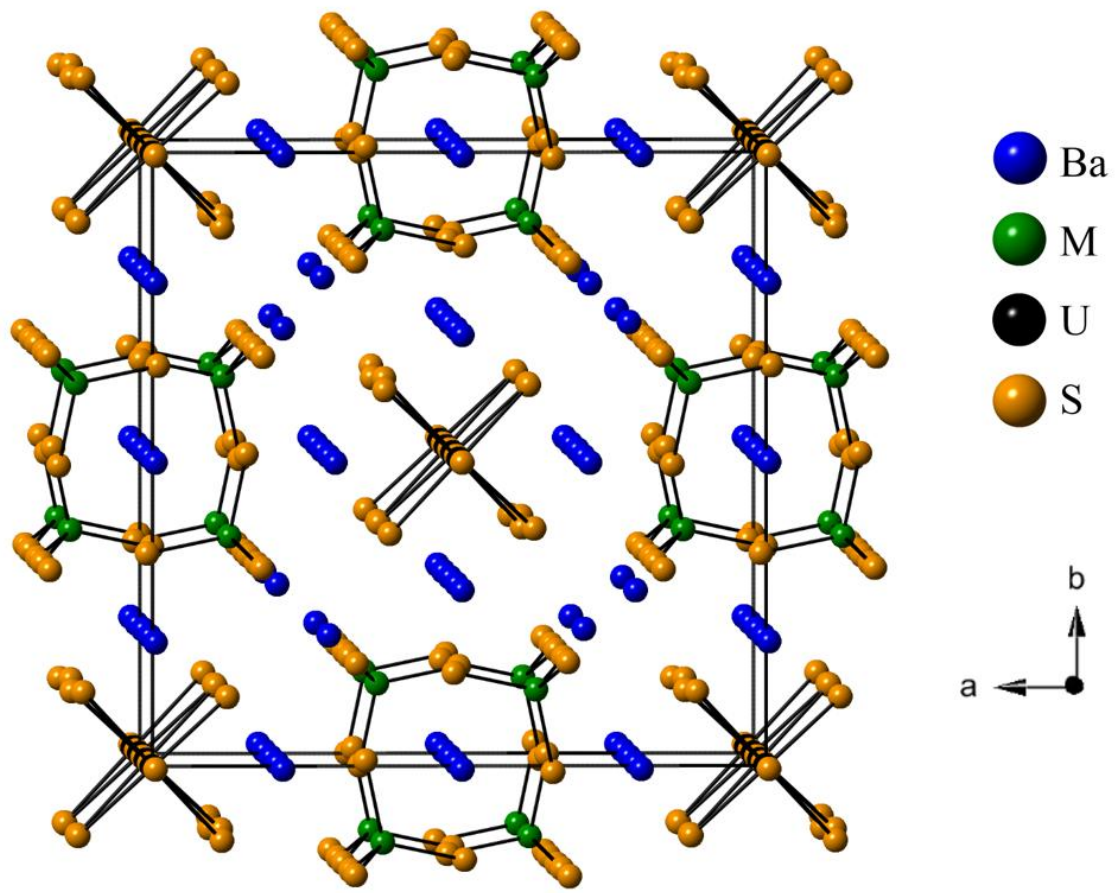


Fig. 1: View of the crystal structure of the $\text{Ba}_7\text{UM}_2\text{S}_{12.5}\text{O}_{0.5}$ down the c axis.

Figure 2:

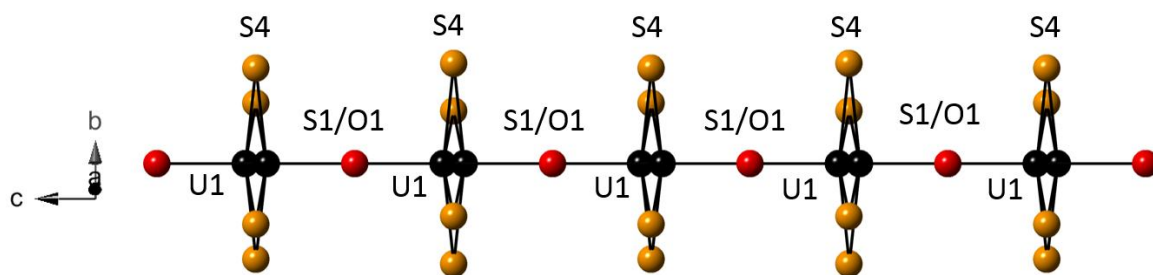


Fig 2: The alignment of the US_5O octahedra to form the infinite linear chains in the $Ba_7UM_2S_{12.5}O_{0.5}$ compounds.