# Syntheses and crystal structures of three barium uranium sulfides

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## ARTICLE INFO

## ABSTRACT

The barium uranium sulfides $Ba_{3.69}US_6$, $BaUS_3$, and $BaU_2S_5$ have been synthesized at 1273, 1323, and 1323 K, respectively. The structures of these compounds have been determined by single-crystal X-ray diffraction methods. They crystallize in space groups $D_{3d}^6-R\bar{3}c$, $D_{2h}^{16}-Pnma$, and $C_{2h}^5-P2_1/c$, respectively. Among these three ternaries and $Ba_2US_6$ the coordination geometries about the U atoms vary considerably. $Ba_{3.69}US_6$ is a mixed $U^{4+}/U^{5+}$ compound whereas the others are $U^{4+}$ compounds. The decreasing dimensionality of the four compounds with increasing Ba–to–U content shows the expected trend.

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## 1. Introduction

In our continued interest in actinide chalcogenides with potentially interesting physical properties we have turned to the syntheses of Ak/U/Q compounds (Ak=Ca, Sr, or Ba; Q=S, Se, or Te) because few structures of such compounds are known. These include $BaUS_3$ [1,2], $AkU_2S_5$ (Ak=Ca, Sr, and Ba) [3,4], and $SrTh_2Se_5$ [5]. The crystal structure of $SrTh_2Se_5$ was determined from single-crystal X-ray diffraction data. The structure of $BaUS_3$ was reported from X-ray powder diffraction data and refined by the Rietveld method from neutron powder diffraction data recorded at 300 K. Owing to the similarity of its X-ray diffraction powder pattern to that of the $U_3S_5$ structure the compound $BaU_2S_5$ was thought to be orthorhombic, space group $P2_122_1$ [3,4].

Here we present the syntheses and structures from single-crystal X-ray diffraction data of $Ba_{3.69}US_6$, $BaUS_3$, and $BaU_2S_5$. $Ba_{3.69}US_6$ is a new compound; the structure of the $BaUS_3$ was refined from single-crystal X-ray diffraction data collected at 100 K to obtain a more accurate structure than that determined earlier from X-ray powder diffraction data; and the earlier structure of the $BaU_2S_5$ was revised and corrected. These three structures are described and compared to the structure of the $Ba_2An(S_2)_2S_2$ (An=U, Th) [6]. They display varied coordination geometries about uranium, the expected dependence of U–S distances on the formal oxidation state of uranium, and the dependence of dimensionality on Ba–to–U content.

## 2. Experimental

### 2.1. Syntheses

The following reactants were used as starting materials: $^{238}$U powder obtained by hydridization and decomposition of turnings (Oak Ridge National Laboratory) in a modification [7] of a previous literature method [8]. The other reagents were used as obtained: BaS (Alfa, 99.7%), Ag (Aldrich, 99.99%), V (Johnson Matthey Electronics, 99.51%), Co (Thiokol, unknown purity), Sb (Aldrich, 99.5%), and S (Mallinckrodt, 99.6%). The antimony sulfide ($Sb_2S_3$) used as a flux was prepared by direct reaction of S and Sb at 1273 K for 24 h. All the reactions were performed in sealed carbon-coated fused-silica 6 mm tubes. The starting mixtures were loaded into tubes under an argon atmosphere in a glove box. Then the tubes were evacuated to $10^{-4}$ Torr, flame sealed, and placed in a computer-controlled furnace.

$Ba_{3.69}US_6$: A few black blocks were isolated from the reaction of BaS (42.7 mg, 0.25 mmol), U (20.23 mg, 0.085 mmol), V (4.3 mg, 0.085 mmol), and S (8 mg, 0.25 mmol). The mixture was heated to 1273 K in 48 h, held there for 8 d, cooled to 673 K at 2 K h$^{-1}$, and then the oven was turned off. The major reaction product contained V. A few black crystals did not, but instead analyzed for Ba:U:S close to 3.5:1:6, as determined with an EDX-equipped Hitachi S-3400 SEM.

$BaUS_3$: In a search for new Ba/U/Ag/S quaternaries a mixture of BaS (28.8 mg, 0.17 mmol), U (20.23 mg, 0.085 mmol), Ag (18.33 mg, 0.17 mmol), and S (8.18 mg, 0.255 mmol) was heated to 1323 K in 26 h, held there for 5 d, cooled to 473 K at 5 K h$^{-1}$, and then the furnace was turned off. Small black blocks were obtained in a yield about 90 wt% based on U. Ba:U:S ≈ 1:1:3 (SEM).

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$BaU_2S_5$: In a search for new Ba/U/Co/S quaternaries a mixture of BaS (44.04 mg, 0.26 mmol), Co (7.66 mg, 0.13 mmol), U (30.94 mg, 0.13 mmol), and S (12.5 mg, 0.39 mmol) was heated to 1323 K in 26 h, held there for 5 d, cooled to 473 K at 5 K h$^{-1}$, and then the furnace was turned off. The reaction resulted in the formation of a black powder. EDX analysis showed the presence of a compound with Ba:U:S=1:2:5, as well as some Co-containing materials. 50 mg of this powder was mixed and ground with 50 mg of $Sb_2S_3$ and reloaded in a carbon-coated fused silica tube. The mixture was heated to 1273 K in 48 h, kept there 8 d, cooled to 473 K at 3 K h$^{-1}$, and then the furnace was turned off. In addition to black columnar crystals of $Sb_2S_3$, black plates with Ba:U:S=1:2:5 (SEM) were found in a yield of about 15 wt% based on U.

## 2.2. Structure determinations

Single-crystal X-ray diffraction data were collected on a bruker APEX II Kappa diffractometer equipped with a graphite mono-chromatized MoK$_\alpha$ radiation ($\lambda$=0.71073 Å) at 100(2) K. Data collection strategies composed of $\omega$ and $\varphi$ scans were obtained from an algorithm in the program COSMO in the APEX II software [9]. The step size was 0.3° and the exposure time was 10 s/frame. Data were indexed, refined, and integrated with the program SAINT in the APEXII package [9]. Numerical face-indexed absorption corrections were applied with the use of the

program SADABS [10]. The structures were solved and refined with the use of the programs in the SHELXTL package [11]. The refinements of $BaUS_3$ and $BaU_2S_5$ were straightforward. That of $Ba_{3.69}US_6$ involved the complication that placement of the atoms at full occupancy led to the composition $Ba_4US_6$ and to a poor refinement ($R(F)$=0.06). When the site occupancy of the Ba2 atom was refined the composition became $Ba_{3.69(2)}US_6$, in better agreement with the EDX results, and the refinement improved
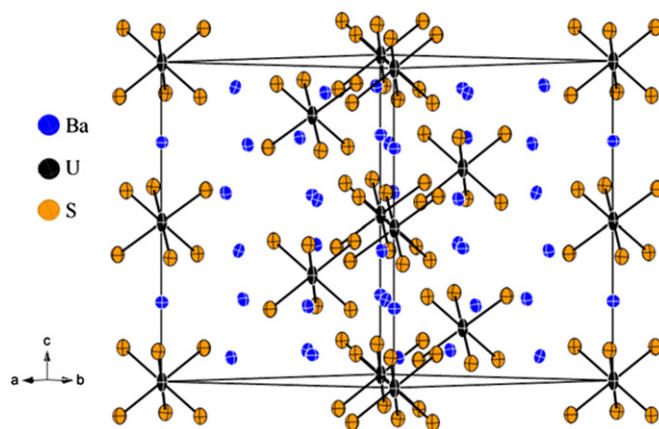


**Fig. 1.** General view of the structure of $Ba_{3.69}US_6$ down [1 0 1].

**Table 1**
Crystallographic data and structure refinements for $Ba_{3.69}US_6$, $BaUS_3$, and $BaU_2S_5$[a].

|  | $Ba_{3.69}US_6$ | $BaUS_3$ | $BaU_2S_5$ |
|---|---|---|---|
| Space group | $D_{3d}^6 - R\bar{3}c$ | $D_{2h}^{16} - Pnma$ | $D_{2h}^5 - P2_1/c$ |
| $a$ (Å) | 12.1193(11) | 7.4791(6) | 8.4335(4) |
| $b$ (Å) | – | 10.326(1) | 7.5037(3) |
| $c$ (Å) | 14.8934(17) | 7.1722(6) | 11.7695(5) |
| $\beta$ (deg) |  |  | 90.613(2) |
| $\gamma$ (deg) | 120 |  |  |
| $V$ (Å$^3$) | 1894.4(3) | 553.90(8) | 744.76(6) |
| $Z$ | 6 | 4 | 4 |
| $\rho$ (g cm$^{-3}$) | 4.932 | 5.655 | 6.900 |
| $\mu$ (mm$^{-1}$) | 25.065 | 37.224 | 49.900 |
| $R(F)$[b] | 0.0157 | 0.0242 | 0.0236 |
| $R_w(F_0^2)$[c] | 0.0320 | 0.0565 | 0.0463 |

[a] For all structures, $\lambda$=0.71073 Å, $T$=100(2) K.

[b] $R(F)=\Sigma||F_0|-|F_c||/\Sigma|F_0|$ for $F_0^2 > 2\sigma(F_0^2)$.

[c] $R_w(F_0^2)=\left\{\Sigma\left[w\left(F_0^2-F_c^2\right)^2\right]/\Sigma wF_0^4\right\}^{1/2}$. For $F_0^2 < 0$, $w^{-1}=\sigma^2\left(F_0^2\right)$; for $F_0^2 \geq 0, w^{-1}=\sigma^2\left(F_0^2\right)+\left(qF_0^2\right)^2$ where $q$=0.0130 for $Ba_{3.69}US_6$, 0.0256 for $BaUS_3$, and 0.0159 for $BaU_2S_5$.

**Table 2**
Selected interatomic distances (Å) [a].

| Distance | $Ba_{3.69}US_3$ | $BaUS_3$ | $Ba_2US_6$[b] | $BaU_2S_5$ |
|---|---|---|---|---|
| U1–S1 | 6 × 2.658(1) | 2 × 2.677(1) | 4 × 2.820(1) | U1–S:2.731(1) to 2.989(1) |
| U1–S1 |  | 2 × 2.696(1) |  | U2–S:2. 683(1) to 2.897(1) |
| U1–S2 |  | 2 × 2.668(1) | 4 × 2.734(2) |  |
| Ba1–S1 | 2 × 3.218 (1) | 2 × 3.162(2) | 4 × 3.219(1) | Ba–S:3.066(1) to 3.475(1) |
| Ba1–S1 | 2 × 3.240(1) | 2 × 3.409(1) | 2 × 3.298(1) |  |
| Ba1–S1 | 2 × 3.280(1) | 2 × 3.589(2) |  |  |
| Ba1–S1 | 2 × 3.404(1) |  |  |  |
| Ba1–S2 |  | 3.127(2) | 2 × 3.217(1) |  |
| Ba1–S2 |  | 3.186(2) |  |  |
| Ba2–S1 | 6 × 3.079(1) |  |  |  |
| S1–S1 |  |  | 2.082 (1) |  |

[a] To facilitate comparisons in this table distances from the cif files in supporting information, where necessary, have been rounded to three significant figures.

[b] Ref. [6].

markedly ($R(F)$=0.0157). The program STRUCTURE TIDY [12] in PLATON [13] was used to standardize the atomic positions. Crystal structure data and refinement details are given in Table 1 and in Supporting material.

## 3. Results

### 3.1. Syntheses

The compound $Ba_{3.69}US_6$ was obtained in a very low yield in a reaction at 1273 K that led mainly to a Ba/U/V/S quaternary and UOS (from the silica tube). Attempts to synthesize the pure compound led to the formation of $Ba_2US_6$ [6] and UOS.

$BaUS_3$ was obtained in high yield at 1323 K from a BaS/U/Ag/S mixture. UOS was also produced.

Single crystals of $BaU_2S_5$ were obtained in a two-step reaction. First, black powder of $BaU_2S_5$ was obtained by the reaction of BaS, U, Co and S. This powder was ground, mixed with $Sb_2S_3$, and heated to 1273 K. Black plates of $BaU_2S_5$ were obtained in an estimated yield of 15 wt% based on U.

### 3.2. Structures

Metrical data are given in Table 2.

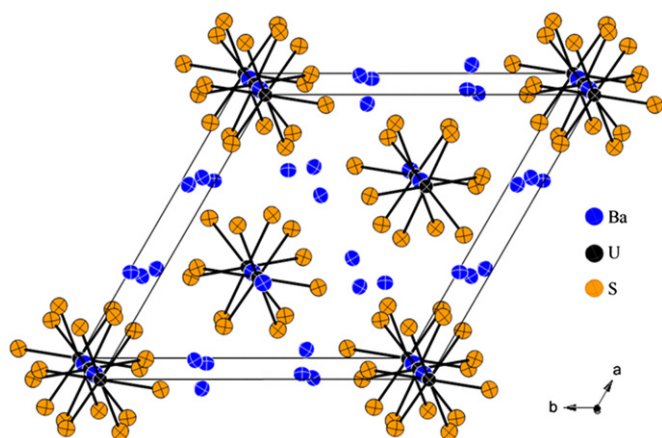$Ba_{3.69}US_6$: This compound crystallizes in the $K_4CdCl_6$ structure type [14] in space group $D_{3d}^6-R\bar{3}c$ with six formula units in a trigonal cell with $a$=12.1193(11) Å, $c$=14.8934(17) Å. The asymmetric unit contains one U atom (site symmetry $\bar{3}$), one S atom in a general position (1) and two Ba atoms Ba1 (.2) and Ba2 (32). A general view of the structure along [1 0 1] is shown in Fig. 1. The U atom is octahedrally coordinated by six S atoms, the U–S distance being 2.6580(8) Å. The Ba1 atom is surrounded by eight S atoms with Ba–S distances ranging between 3.2178(9) and 3.4038(8) Å; the Ba2 atom is trigonal-prismatically coordinated by six S atoms with Ba–S=3.0790(8) Å. The Ba2 site is 69.4(2)% occupied. The structure consists of the $US_6$ octahedra sharing triangular faces with $BaS_6$ trigonal prisms along the $c$ axis. The Ba1 atoms are positioned between the chains (Fig. 2).

$BaUS_3$: The compound crystallizes in the $GdFeO_3$ structure type in orthorhombic space group $D_{2h}^{16}-Pnma$ with four formula units in a cell with $a$=7.4791(6) Å, $b$=10.326(1), $c$=7.1722(6) Å. It was refined first from X-ray powder data [1] and later refined from neutron powder diffraction data recorded at 300 K [2].
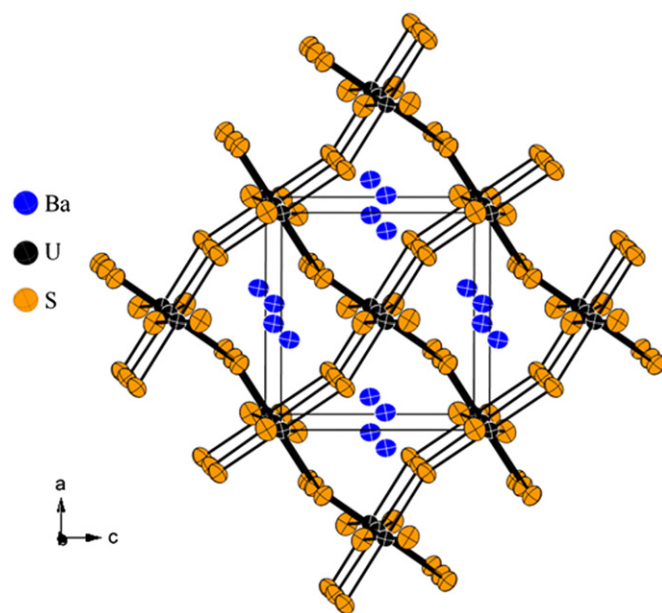


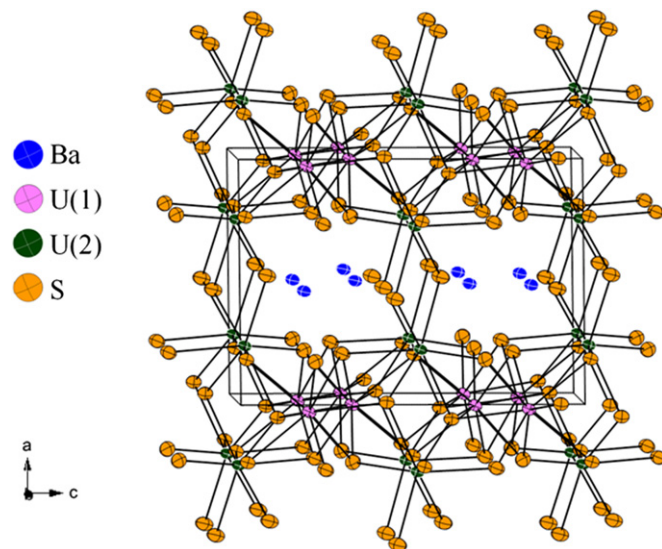Fig. 4. The structure of $BaUS_3$ projected down the $b$ axis.



Fig. 2. General view of the structure of $Ba_{3.69}US_6$ down the $c$ axis.
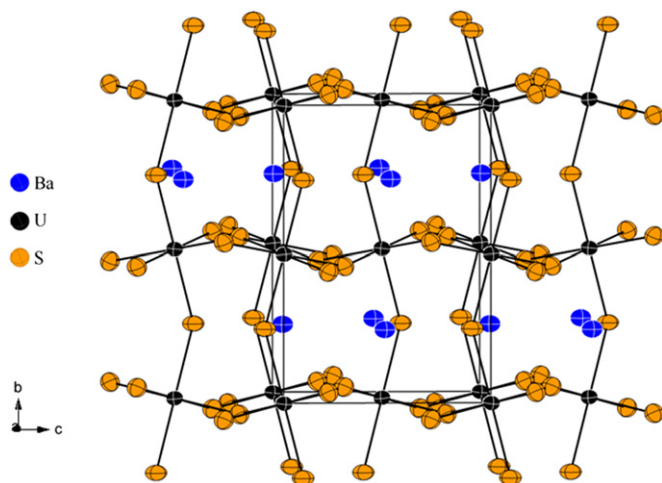


Fig. 3. General view of the structure of $BaUS_3$ down the $a$ axis.



Fig. 5. General view of the unit cell of $BaU_2S_5$ down the $b$ axis.

A general view of the structure projected down $a$ is shown in Fig. 3. As reported previously [1,2], the structure may be described as that of a distorted perovskite. The asymmetric unit contains one U atom (site symmetry $\bar{1}$), one Ba atom ($\bar{1}$), two S atoms, S1 (1) and S2 (.$m$.). The U atom is octahdrally coordinated to six S atoms with U–S distances of 2.668(1), 2.677(1),and 2.696(1) Å. The Ba atom is in a bicapped trigonal prism of S atoms with Ba–S distances ranging from 3.127(2) to 3.589(2) Å. The structure consists of $US_6$ octahedra stacked three dimensionally by sharing corners. The Ba atoms are situated in the channels (Fig. 4).

$BaU_2S_5$: Earlier X-ray powder diffraction results collected at 293 K structure were taken to suggest that the compound $BaU_2S_5$ was orthorhombic, space group $P2_122_1$ [3,4]. However, we find that at 100 K the material crystallizes in the $PbU_2Se_5$ structure type [15] in the monoclinic space group $C_{2h}^5$–$P2_1/c$. This difference is presumably due either to the different temperatures at which data were collected or to the inability from powder data to detect a monoclinic $\beta$ angle differing very slightly from 90°(Table 1). A view of the present structure of $BaU_2S_5$ is shown in Fig. 5. The asymmetric unit contains two U atoms, one Ba atom, and five S atoms, all in general positions. The U1 atom is coordinated by eight S atoms in bicaped trigonal prism, whereas the U2 atom is coordinated by seven Se atoms in a distorted face-capped octahedron. Each U1 atom shares all three edges of a trigonal prism face with three U1 neighbors; two of the neighboring atoms share caps as well (Fig. 6). The U–S distances vary between 2.730 (1) and 2.989(1) Å. The U2 polyhedra form chains by sharing edges along the $a$ axis (Fig. 7). U2–S distances vary between 2.638(1) and 2.897(1) Å. The Ba atoms are coordinated to nine S atoms in channels along [0 1 0].



**Fig. 6.** View along [1 0 0] showing the coordination of the U1 atoms in $BaU_2S_5$.



**Fig. 7.** View of the U2 chains in $BaU_2S_5$ along [1 0 0].

## 4. Discussion

Metrical data for U–S interatomic distances in selected, known ternary and quaternary uranium sulfides are presented in Table 3. Among the four ternaries, namely $Ba_{3.69}US_6$, $BaUS_3$, $Ba_2US_6$, and $BaU_2S_5$, the coordination geometries about the U atoms vary considerably. These are octahedral in the structures of $Ba_{3.69}US_6$ and $BaUS_3$; pseudo-octahedral in the structure of $Ba_2US_6$ (i.e., $Ba_2U(S_2)_2(S)_2$) if one considers the four $S^{2-}$ anions and centers of the two $S_2^{2-}$ pairs or alternatively a distorted $US_8$ polyhedron if one considers all eight S centers; and both a bicapped trigonal prism and highly distorted face-capped octahedron in the structure of $BaU_2S_5$. Despite these differences there is a discernible trend in the range of U–S distances versus the assigned formal oxidation states of U. On the basis of charge balance all but $Ba_{3.69}US_6$ are compounds of $U^{4+}$. The average oxidation state of U in $Ba_{3.69}US_6$ is +4.62, intermediate between $U^{4+}$ and $U^{5+}$. However, if $U^{5+}$:$U^{4+}$ were 2:1 then the oxidation state of U would be 4.66. This value is in remarkable agreement with the experimental value of 4.62(2), given the pitfalls in the way of the determination of chemical composition from crystal structure refinements [16].

The general observation [17] that successive insertion of an alkali metal into a metal chalcogenide lowers the dimensionality of the resultant structure also applies here for insertion of an alkali-earth metal into a metal chalcogenide. In $BaU_2S_5$ with Ba:U=0.5:1, the $US_x$ polyhedra are connected in three directions and the structure may be described as three dimensional (3-D). In $BaUS_3$ with Ba:U=1:1, the $US_6$ octahedra are connected in three directions by corner sharing. The structure may also be described
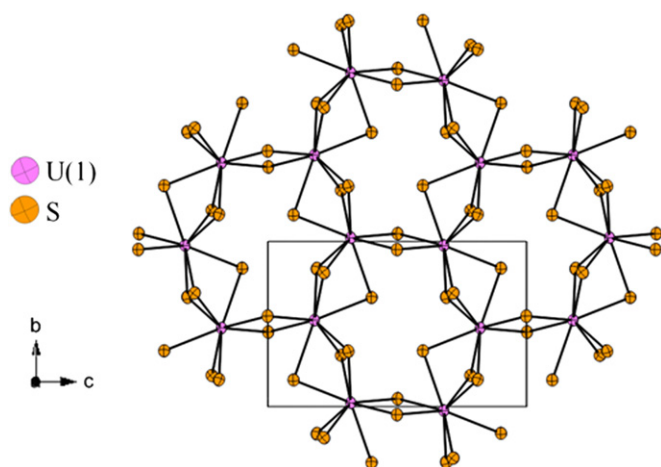
**Table 3**
U–S interatomic distances in selected ternary and quaternary uranium sulfides.

| Compound | U coord number | U–S range (Å)[a] | U oxidation state | Ref. |
|---|---|---|---|---|
| $K_2Cu_3US_5$ | 6 | 2.651(6) | +5 | [18] |
| $Ba_8Hg_3U_3S_{18}$ | 6 | 2.571(4)–2.743(3) | mixed +4/+5 | [19] |
| | 6 | 2.595(4)–2.758(3) | | |
| | 6 | 2.602(4)–2.745(3) | | |
| $Ba_{3.69}US_6$ | 6 | 2.6580(9) | mixed +4/+5 | This work |
| $BaUS_3$ | 6 | 2.668(1)–2.696(1) | +4 | This work |
| $Ba_2Cu_2US_5$ | 6 | 2.673(2)–2.770(1) | +4 | [20] |
| $BaU_2S_5$ | 7 | 2.683(1)–2.897(1) | +4 | this work |
| | 8 | 2.730(1)–2.989(1) | +4 | |
| $Ba_2US_6$[b] | 8 | 2.734(1)–2.820(1) | +4 | [6] |
| $Rb_{0.85}U_{1.74}S_6$ | 8 | 2.775(3)–2.847(2) | +4 | [21] |
| $K_{0.91}U_{1.79}S_6$ | 8 | 2.761(2)–2.846(2) | +4 | [22] |

[a] To facilitate comparisons in this table distances from the original cif files, where necessary, have been rounded to three significant figures.
[b] The U center in this compound is surrounded by four S atoms and two $S_2$ pairs. Here we consider the latter to be four separate S atoms.
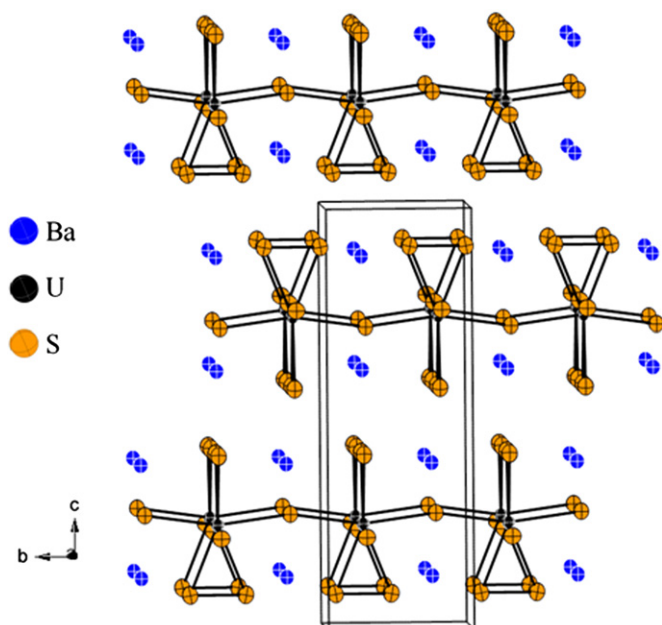
**Fig. 8.** General view of the $Ba_2US_6$ structure down the $a$ axis.

as three dimensional. In $Ba_2US_6$ [6] with Ba:U=2:1, the U polyhedra are connected to each other by sharing corners to form an infinite $^2_\infty[An(S_2)_2(S)_2^{4-}]$ layers separated by $Ba^{2+}$ cations (Fig. 8). The structure may be described as two dimensional (2-D). In $Ba_{3.69}US_6$ with Ba:U=3.59:1, the structure comprises $US_6$ octahedra separated from one another by $Ba^{2+}$ cations. The structure may be described as isolated (*iso*) ([17]).

Note, finally, that the different ways of stacking affect directly the U concentration in the compounds, with the U densities of 1.25 g cm$^{-3}$ (*iso*, $Ba_{3.69}US_6$), 1.71 g cm$^{-3}$ (2-D, $Ba_2US_6$), 2.85 and 4.24 g cm$^{-3}$ (3-D for $BaUS_3$ and $BaU_2S_5$), respectively.

## 5. Conclusions

The barium uranium sulfides $Ba_{3.69}US_6$, $BaUS_3$, and $BaU_2S_5$ have been synthesized at 1273, 1323, and 1323 K, respectively. The structures of these compounds have been determined by single-crystal X-ray diffraction methods. They crystallize in space groups $D_{3d}^6 - R\bar{3}c$, $D_{2h}^{16} - Pnma$, and $C_{2h}^5 - P2_1/c$, respectively. Among these three ternaries and $Ba_2US_6$ the coordination geometries about the U atoms vary considerably. $Ba_{3.69}US_6$ is a mixed $U^{4+}/U^{5+}$ compound whereas the others are $U^{4+}$ compounds. The dimensionality of the four compounds shows the expected trend of decreasing with increasing Ba–to–U content.

## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.jssc.2012.12.023.

The crystallographic data in cif format for $Ba_{3.69}US_6$, $BaUS_3$, and $BaU_2S_5$ have also been deposited with FIZ Karlsruhe as CSD numbers 425334, 425333, and 425332, respectively. These data may be obtained free of charge by contacting FIZ Karlsruhe at +497247808666 (fax) or crysdata@fiz-karlsruhe.de (e-mail). Data for $Ba_2US_6$ may be found in Reference [6].

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