Positional Flexibility: Syntheses and Characterization of Six Uranium Chalcogenides Related to the 2H Hexagonal Perovskite Family

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Supporting Information

ABSTRACT: Six new uranium chalcogenides, Ba4USe6, Ba3FeUSe6, Ba3MnUSe6, Ba3Rb0.7US6, and Ba3.2K0.8US6, related to the 2H hexagonal perovskite family have been synthesized by solid-state methods at 1173 K. These isostructural compounds crystallize in the K2CdCl6 structure type in space group D3d-R3c of the trigonal system with six formula units per cell. This structure type is remarkably flexible. The structures of Ba3FeUSe6, Ba3MnUSe6, and Ba3Rb0.7US6 consist of infinite [MUQ6]+ chains (M = Fe or Mn; Q = S or Se) oriented along the c axis that are separated by Ba atoms. These chains are composed of alternating M-centered octahedra and U-centered trigonal prisms sharing triangular faces; in contrast, in the structures of Ba4USe6, Ba3Rb0.7US6, and Ba3.2K0.8US6, there are U-centered octahedra alternating with Ba2, Rb+, or K−centered trigonal prisms. Moreover, the Ba4USe6, Ba3FeUSe6, Ba3MnUSe6, and Ba3Rb0.7US6 and Ba3.2K0.8US6 compounds contain U4+, whereas Ba3Rb0.7US6 and Ba3.2K0.8US6 are mixed U4+/5+ compounds. Resistivity and μ-Raman spectroscopic measurements and DFT calculations provide additional insight into these interesting subtle structural variations.

INTRODUCTION

Perovskites are among the most studied inorganic solid-state compounds as they show a variety of interesting physical properties, including intriguing magnetic behavior, superconductivity, thermoelectricity, and ionic conductivity. The crystal structure of the prototype perovskite of formula ABO3 has cubic symmetry and is three-dimensional. Here, A and B are cations of very different sizes. The O atoms bond to both. The B atoms are octahedrally coordinated, and the A atoms are 12-fold coordinated in a cuboctahedron. From this cubic structure, there are numerous derivatives arising from diverse combinations of not only the cations but also the anions. Some differences in the sizes of the A and B elements lead to a change in the crystal system and stabilization of the hexagonal form. The resultant hexagonal structures range from three-dimensional to zero-dimensional salts. Among these are the 2H hexagonal perovskite-related structures that exhibit one-dimensional infinite chains separated in general by alkaline-earth elements. These and other low-dimensional inorganic compounds are of particular interest as they exhibit a wide range of structures and physical properties.

A general formula for the 2H hexagonal perovskite-related compounds is \( A_3A'O_6 \). The structure consists of stacking sequences of BO6 octahedra and A’O6 trigonal prisms, where \( n/m \) is the ratio between [A3A’O6] and [A3O6] layers. Here, A’ is usually an alkaline-earth element; B is the element filling the octahedral site, and A’ is the element positioned in the trigonal prism. A’ can be A, B, or another element; hence, these structures are highly flexible in their compositions. The oxides and the halides are the most reported compounds in the perovskites family; however, there is increased interest in the chalcogenides. In fact, some of these have different applications, such as in photovoltaics. Recently, 2H perovskite-related structures have been reported that contain f elements. These show different sequences in the arrangement of the BO6 octahedra and the A’O6 trigonal prisms. An example is the structure of Ba3Cr2US9 with \( n = 3 \) and \( m = 1 \). Other examples are the few reported f-element structures of the K2CdCl6 structure type (\( n = 0, m = 0 \)) in which there are infinite chains composed of the equal alternation of A’ trigonal prisms and B octahedra. These include Ba3AgUS6, Ba3FeUS6, Ba3AgUS6, and Ba3LnInS6 (Ln = Pr, Sm, Gd, Yb).

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Table 1. Crystallographic Data and Structure Refinement Details for Six Uranium Chalcogenides

<table>
<thead>
<tr>
<th></th>
<th>Ba₄USe₆</th>
<th>Ba₂FeUSe₆</th>
<th>Ba₃MnUSe₆</th>
<th>Ba₃MnUS₆</th>
<th>Ba₃Rb₀.₇USe₆</th>
<th>Ba₃K₀.₈USe₆</th>
</tr>
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<tbody>
<tr>
<td>fw (g mol⁻¹)</td>
<td>1261.15</td>
<td>1179.66</td>
<td>1178.75</td>
<td>897.35</td>
<td>927.88</td>
<td>881.51</td>
</tr>
<tr>
<td>a (Å)</td>
<td>12.5997(2)</td>
<td>12.4842(10)</td>
<td>12.4561(2)</td>
<td>12.0200(5)</td>
<td>12.0875(3)</td>
<td>12.0798(2)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>15.6063(2)</td>
<td>13.9285(11)</td>
<td>14.1345(3)</td>
<td>13.6410(6)</td>
<td>15.1516(5)</td>
<td>15.0390(3)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>2145.61(7)</td>
<td>1879.63(3)</td>
<td>1899.34(7)</td>
<td>1707.38(16)</td>
<td>1917.18(11)</td>
<td>1899.48(7)</td>
</tr>
<tr>
<td>ρ (g cm⁻³)</td>
<td>5.856</td>
<td>6.253</td>
<td>6.183</td>
<td>5.236</td>
<td>4.823</td>
<td>4.726</td>
</tr>
<tr>
<td>γ (mm⁻¹)</td>
<td>37.349</td>
<td>40.668</td>
<td>40.097</td>
<td>26.519</td>
<td>26.458</td>
<td>23.752</td>
</tr>
<tr>
<td>R(Fo)</td>
<td>0.014</td>
<td>0.014</td>
<td>0.015</td>
<td>0.011</td>
<td>0.009</td>
<td>0.011</td>
</tr>
<tr>
<td>R(Fe)</td>
<td>0.030</td>
<td>0.028</td>
<td>0.029</td>
<td>0.023</td>
<td>0.019</td>
<td>0.019</td>
</tr>
<tr>
<td>R(wF)</td>
<td>0.030</td>
<td>0.028</td>
<td>0.029</td>
<td>0.023</td>
<td>0.019</td>
<td>0.019</td>
</tr>
</tbody>
</table>

*For all structures, space group D₆₃₋₋R₃c, λ = 0.10737 Å, T = 100(2) K, and Z = 6. R(Fo) = ∑|Fo| - |Fc|/∑|Fo| for Fo > 2σ(Fo). R(Fe) = (Fo - Fc)^2/∑Fo^2. For Fe^2 < 0, w'= w(Fo) + (σ(Fo))^2, where w = 0.0132 for Ba₄USe₆, 0.0091 for Ba₂FeUSe₆, 0.0065 for Ba₃MnUSe₆, 0.0066 for Ba₃MnUS₆, and 0.0043 for Ba₃K₀.₈USe₆.*

In this present work, we present the syntheses and characterizations of six new uranium chalcogenides of the 2H hexagonal pervoskite-related family that crystallize in the K₂CdCl₆ structure type (space group D₆₃₋₋R₃c). Their structures demonstrate remarkable flexibility in the position of the U atom in the structure and its resultant oxidation state. Characterization of these compounds includes μ-Raman and resistivity measurements and DFT calculations.

**EXPERIMENTAL METHODS**

**Syntheses.** The U powder was prepared by hydridization of depleted U turnings (IBI Laboratories) using a modified, previously published procedure. All other reactants were used as supplied: Ba (Johnson Matthey, 99.5%), Se (Cerac, 99.999%), S (Mallinckrodt, 99.6%), Mn (Johnson Matthey, 99.3%), Fe (Aesar, 99.99%), CsCl (Aldrich, 99.9%), RbCl (Alfa, 99.8%), and KCl (Aldrich, 99%).

**Synthesis of Ba₄USe₆.** Black crystals of Ba₄USe₆ were obtained from the reaction of Ba (35 mg, 0.255 mmol), Mn (4.7 mg, 0.085 mmol), and Se (40.3 mg, 0.510 mmol) with CsCl flux (200 mg). The reaction tube was heated to 773 K in 12 h, then held for 12 h, ramped to 1173 K in 24 h, and annealed for 96 h. The tube was then cooled to 673 K in 48 h and finally to 298 K in 12 h.

**Synthesis of Ba₂FeUSe₆.** Black crystals of Ba₂FeUSe₆ were obtained from the reaction of Ba (35 mg, 0.255 mmol), Fe (4.7 mg, 0.085 mmol), and Se (40.1 mg, 0.51 mmol) in 100 mg of CsCl used as flux. Three products were found: black crystals of Ba₂FeUSe₆, showing Ba:Fe:Se = 3:1:1, black blocks of a possible new quaternary with the composition Ba₆Fe:Se:Cl = 2:11:1, and UOSe₂.

**Synthesis of Ba₃MnUSe₆.** Black crystals of Ba₃MnUSe₆ were obtained by the reaction of Ba (35 mg, 0.255 mmol), Mn (4.7 mg, 0.085 mmol), and Se (40.1 mg, 0.51 mmol) in CsCl (50 mg) used as flux. Three different compounds were found: black blocks of Ba₃MnUSe₆, showing Ba:Mn:U:Se ≈ 3:1:1:6, square plates of UOSe₂, and orange plates of Ba₃MnSe₄.

**Synthesis of Ba₃MnUS₆.** Small black plates of Ba₃MnUS₆ were obtained in a direct combination of Ba (35 mg, 0.255 mmol), Mn (4.66 mg, 0.085 mmol), U (20 mg, 0.085 mmol), and S (16 mg, 0.51 mmol). Found was Ba₃Mn:U:S ≈ 3:1:6 with UOSe as a byproduct.

**Synthesis of Ba₃Rb₀.₇USe₆.** The reaction of Ba (35 mg, 0.255 mmol), U (20 mg, 0.085 mmol), and S (16 mg, 0.51 mmol) in 100 mg of RbCl flux produced black crystals of Ba₃Rb₀.₇USe₆, showing Ba:Rb:U:S = 33:0.7:1:6 as well as UOS and an excess of RbCl.

**Synthesis of Ba₃.₃Rb₀.₇USe₆.** The reaction of Ba (35 mg, 0.255 mmol), U (20 mg, 0.085 mmol), S (16 mg, 0.51 mmol) in a KCl flux (50 mg) produced small black plates of Ba₃.₃Rb₀.₇USe₆, showing Ba:Rb:U:S ≈ 3:0.8:1.6 as well as UOS.

**Structure Determinations.** The crystal structures of the six compounds, Ba₄USe₆, Ba₂FeUSe₆, Ba₃MnUSe₆, Ba₃MnUS₆, Ba₃Rb₀.₇USe₆, and Ba₃K₀.₈USe₆, were determined from single-crystal X-ray diffraction data collected with the use of graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) at 100(2) K on a Bruker APEX2 diffractometer. The algorithm COSMO implemented in the program APEX2 was used to establish the data collection strategy with a series of 0.3° scans in ω and φ. The exposure time was 10 s/frame, and the crystal-to-detector distance was 60 mm. The collection of intensity data as well as cell refinement and data reduction were carried out with the use of the program APEX2. Face-indexed absorption, incident beam, and decay corrections were performed with the use of the program SADABS. All the structures were solved and refined with the SHELXL14 program package. The structure refinements of Ba₄USe₆, Ba₂FeUSe₆, Ba₃MnUSe₆, Ba₃MnUS₆, Ba₃Rb₀.₇USe₆, and Ba₃K₀.₈USe₆ were straightforward. However, those for Ba₃.₃Rb₀.₇USe₆ and Ba₃K₀.₈USe₆ were not. The best solution for each of these structures involved placing at the crystallographic site 32 the composition (Ba/Rb or Ba/K) dictated by the EDX results. The program STRUCTURE TIDY was PLATON used to standardize the atomic positions. Further details are given in Table 1 and in the Supporting Information.

**μ-Raman Spectroscopy.** Raman spectroscopy was performed using a Nikon Eclipse Ti2000-U inverted microscope in a manner similar to that previously described. A stabilized 785 nm diode laser (Innovative Photonic Solutions) was aligned into the microscope through a 50X extra-long working distance objective (numerical aperture = 0.55), which focused the incident beam onto #2 glass coverslips supporting the synthesized single crystal. The objective collected the scattered light, which was then focused onto the 100 µm entrance slit of an Acton SP2300 imaging spectrometer. A 150 groove/mm grating dispersed the collected light onto a liquid N₂-cooled, back-illuminated CCD (Spec10:400BR, Princeton Instruments).

Crystals were irradiated with 830 µW, except for weakly scattering Ba₃MnUS₆ for which 6.8 mW was used. All spectra were collected for 10 s.

**Resistivity Studies.** Four-probe temperature-dependent resistivity data were collected using a homemade resistivity apparatus equipped with a Keithley 2182 nanovoltmeter, a Keithley 236 source-measure unit, and a high-temperature vacuum chamber controlled by a K-20 MMR system. An I−V curve from 1 × 10⁻² to −1 × 10⁻⁸ A with a step of 2 × 10⁻⁶ A was measured for each temperature point, and resistance was calculated from the slope of the I−V plot. Data acquisition was controlled by custom-written software. Graphite paint (PELCO isopropanol-based graphite paint) was used for electrical contacts with Cu of 0.025 mm thickness (Omega). Direct current was applied along an arbitrary direction.
DFT Calculations. Ab initio calculations were performed with the Vienna ab initio simulation package (VASP)\(^{31,32}\) using the Heyd, Scuseria, Ernzerhof (HSE)\(^{33-36}\) functional within density functional theory\(^{37,38}\) and the projector augmented wave method.\(^{39}\) Spin polarization was allowed. The cell and atom positions were taken identical to the experimental values. For a given compound, the various magnetic orders allowed in a crystallographic cell were calculated, and the one with the lowest total energy was retained as the ground state configuration. The default cutoff for the plane-wave part of the wave function and a \(k\)-point mesh of \(4 \times 4 \times 4\) to sample the Brillouin zone were used to reach numerical convergence.

RESULTS

Syntheses. The six compounds, \(\text{Ba}_4\text{USe}_6\), \(\text{Ba}_3\text{FeUSe}_6\), \(\text{Ba}_3\text{MnUSe}_6\), \(\text{Ba}_3\text{MnUS}_6\), \(\text{Ba}_3\text{.3Rb}_0\text{.7US}_6\), and \(\text{Ba}_3\text{.2K}_0\text{.8US}_6\), were obtained in >50 wt % yields by the reactions of the elements at 1173 K. The synthesis of \(\text{Ba}_3\text{MnUSe}_6\) did not involve a flux, whereas the syntheses of the other compounds involved an alkali-metal chloride as a flux. Inability to separate these compounds from diverse byproducts, including \(\text{UOS}\) and \(\text{UOSe}\), severely limits useful information that might have been obtained from magnetic studies. Regrettably, the actinide chalcogenides are highly oxyphilic and usually the products of our reactions are accompanied by \(\text{UOQ}\) phases that result from the etching of the carbon-coated fused-silica tubes. In some instances, interesting but surprising new O-containing compounds have resulted.\(^{40,41}\)

Table 2. Interatomic Distances (Å)\(^a\) in the Present and Related Compounds

<table>
<thead>
<tr>
<th>distance (Å)</th>
<th>(\text{Ba}_4\text{USe}_6)</th>
<th>(\text{Ba}_3\text{FeUSe}_6)</th>
<th>(\text{Ba}_3\text{MnUSe}_6)</th>
<th>(\text{Ba}_3\text{MnUS}_6)</th>
<th>(\text{Ba}_3\text{.3Rb}_0\text{.7US}_6)</th>
<th>(\text{Ba}_3\text{.2K}_0\text{.8US}_6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U1–Se1 × 6</td>
<td>2.825(1)(^c)</td>
<td>2.836(1)(^b)</td>
<td>2.842(1)(^b)</td>
<td>2.724(1)(^b)</td>
<td>2.655(1)(^c)</td>
<td>2.635(1)(^c)</td>
</tr>
<tr>
<td>M1–Se1 × 6</td>
<td>3.221(1)(^b)</td>
<td>2.676(1)(^c)</td>
<td>2.721(1)(^c)</td>
<td>2.607(1)(^c)</td>
<td>3.139(1)(^b)</td>
<td>3.115(1)(^b)</td>
</tr>
<tr>
<td>Ba1–Se1 × 2</td>
<td>3.348(1)</td>
<td>3.274(1)</td>
<td>3.261(1)</td>
<td>3.132(1)</td>
<td>3.242(1)</td>
<td>3.231(1)</td>
</tr>
<tr>
<td>Ba2–Se1 × 2</td>
<td>3.384(1)</td>
<td>3.282(1)</td>
<td>3.332(1)</td>
<td>3.237(1)</td>
<td>3.250(1)</td>
<td>3.241(1)</td>
</tr>
<tr>
<td>Ba3–Se1 × 2</td>
<td>3.413(1)</td>
<td>3.387(1)</td>
<td>3.397(1)</td>
<td>3.287(1)</td>
<td>3.264(1)</td>
<td>3.262(1)</td>
</tr>
<tr>
<td>Ba4–Se1 × 2</td>
<td>3.513(1)</td>
<td>3.417(1)</td>
<td>3.399(1)</td>
<td>3.294(1)</td>
<td>3.409(1)</td>
<td>3.407(1)</td>
</tr>
</tbody>
</table>

\(^a\)All distances have been rounded from CIF files in the Supporting Information to facilitate comparisons. \(^b\)Symmetry site 32 (trigonal prism). \(^c\)Symmetry site 3 (octahedral). \(^d\)Both Ba and the alkali metal are placed at the same site (trigonal prism). \(^e\)From ref 18. \(^f\)From ref 17.

Figure 1. General view of the structure of \(\text{Ba}_3\text{FeUSe}_6\), \(\text{Ba}_3\text{MnUSe}_6\), and \(\text{Ba}_3\text{MnUS}_6\) along \([110]\). Oct, tp, and dsap are abbreviations for octahedron, trigonal prism, and distorted square antiprism, respectively.

Figure 2. A view of the structure of \(\text{Ba}_3\text{FeUSe}_6\), \(\text{Ba}_3\text{MnUSe}_6\), and \(\text{Ba}_3\text{MnUS}_6\) along \([110]\). Oct, tp, and dsap are abbreviations for octahedron, trigonal prism, and distorted square antiprism, respectively.

Figure 3. Infinite chains along the \(c\) axis in the \(\text{Ba}_3\text{MUQ}_6\) family showing the evolution of structure dimensionality; oct and tp correspond to octahedra and trigonal prism, respectively.

Figure 4. Raman spectra of the synthesized compounds using 785 nm excitation. U–S/Se stretches are observed for U in trigonal prismatic coordination (upper three spectra) and in octahedral coordination (lower three spectra).
Crystal Structures. The compounds Ba₄USe₆, Ba₃FeUSe₆, Ba₃MnUSe₆, Ba₃MnUS₆, Ba₃.3Rb₀.7US₆, and Ba₃.2K₀.8US₆ are isostructural and crystallize in the K₄CdCl₆ structure type in space group D₃d⁻R̅₃c of the trigonal system with six formula units per cell (Table 1). Selected metrical data are reported in Table 2. Although the six compounds are isostructural in the classic sense, their structures differ in the distribution of the atoms between the 32 and 3̅ sites. Ba₃FeUSe₆, Ba₃MnUSe₆, and Ba₃MnUS₆. These structures have the same arrangement of atoms as in Ba₃FeUS₆. The asymmetric unit comprises one U atom (site symmetry 32), one M (Fe or Mn) atom (3̅), one Ba atom (3̅), and one Q (Se or S) atom (1). A general view of the structure is projected along [110] in Figure 1. In these three compounds, the U atom is connected to six Q atoms to form a trigonal prism, and the 3d element M is octahedrally coordinated to six Q atoms.

Ba₄USe₆, Ba₃Rb₀.7US₆, and Ba₃.3K₀.8US₆. These three compounds have the same arrangement of atoms as those in Ba₃.₆₉US₆ and Ba₃AgUS₆ with the U atom in the 3̅ symmetry site (Figures 2 and 3). Consequently, the other site with 32 symmetry is filled by 1 Ba, 0.3 Ba + 0.7 Rb, and 0.2 Ba + 0.8 K for Ba₄USe₆, Ba₃Rb₀.7US₆, and Ba₃.₃K₀.₈US₆, respectively. In these three compounds, the U atom is octahedrally coordinated, and the Ba or mixed Ba/A site is trigonal-prismatically coordinated.

Oxidation State and Structure Flexibility. In the Ba₄USe₆, Ba₃FeUSe₆, and Ba₃MnUSe₆ compounds, the U−Se distances are 2.8248(3), 2.8362(3), and 2.8422(3) Å, respectively. These compare favorably with those in the structures of the other six-coordinate U⁴⁺ compounds, for example, Rb₂Pd₃USe₆, 2.8331(5) to 2.8659(7) Å; RbAuUSe₃, 2.846(3) to 2.866(2) Å; and CsAuUSe₃, 2.863(1) to 2.893(2) Å. In the Ba₃FeUSe₆ structure, the Fe−Se distance of 2.6761(3) Å may be compared with those of 2.4968(7) to 2.6782(7) Å for the Fe²⁺Se₆ octahedra in FeUSe₃. In the Ba₃MnUSe₆ structure, the Mn−Se distance is 2.7212(3) Å, which is between those of 2.696(1) to 2.736(1) Å for the Mn²⁺−Se distance in the structure of Mn₂GeSe₄. In the Ba₃MnUS₆ structure, the Mn−Se distance is 2.7212(3) Å, which is between those of 2.696(1) to 2.736(1) Å for the Mn²⁺−Se distance in the structure of Mn₂GeSe₄. In the Ba₃MnUS₆ structure, the Mn−S distance of 2.7241(6) Å is typical for structures of 3d six-coordinate U⁴⁺ compounds, for example, 2.712(1) Å in the structure of Ba₃FeUS₆. The Mn−S distance of 2.6067(2) Å is in agreement with Mn²⁺ in octahedral coordination as found in the MnₓSnS₄ structure (2.604(1) to 2.620(2) Å). There are no Q−Q bonds in these structures. Thus, the compounds Ba₄USe₆, Ba₃FeUSe₆, Ba₃MnUSe₆, and Ba₃MnUS₆ contain U⁴⁺ and Mn²⁺ and are charge balanced.
The compounds Ba$_3$Rb$_0.7$US$_6$ and Ba$_3$K$_0.8$US$_6$ contain Ba$^{2+}$, Rb$^+$ or K$^+$, and S$^{2-}$. For charge balance of these two formulas, the average oxidation state of the U atoms must be +4.7 and +4.8, respectively. Thus, both of these compounds contain both...
U\textsuperscript{4+} and U\textsuperscript{5+} atoms in their structures. Indeed, the U–S distances of 2.655(1) and 2.636(1) Å compare well with that of 2.658(1) Å in Ba\textsubscript{3}AgSe\textsubscript{6},\textsuperscript{\textsuperscript{6}} another mixed U\textsuperscript{4+}/U\textsuperscript{5+} compound. Note that all of these distances, as expected, are shorter than typical U\textsuperscript{4+}–S distances.

As mentioned, the uranium chalcogenides crystallize in the K\textsubscript{2}CdCl\textsubscript{6} structure type display very interesting chemical flexibility in the position of the U atom (Figure 3). The tabulation in Table 2 indicates that this flexibility is driven by the nature of the second cation B or A. Thus, the 3d elements Fe and Mn prefer octahedral coordination, and the flexible U atom goes to the A’ position (trigonal prismatic). However, the larger atoms (Ag, Ba, K, and Rb) clearly prefer the A’ site such that the flexible U atom goes to the B position (octahedral coordination).

This family of compounds presents a rare example of the chemical and positional flexibility that U can display in inorganic materials. In principle, we can tune the oxidation state of the U atoms by judicious choice of the relative sizes of the A’ and B atoms in the 2H perovskite-related compounds. An interesting challenge is to stabilize this structure with U\textsuperscript{5+} by adding a trivalent element, such as Al, Sc, Y, or even a lanthanide (Ln), but the latter could readily produce a disordered Ln/U structure.

**Spectroscopic Properties.** Raman spectra of the six synthesized compounds provide additional insight into their structures (Figure 4). Spectra of the one-dimensional structures Ba\textsubscript{4}FeUSe\textsubscript{6}, Ba\textsubscript{3}MnUSe\textsubscript{6}, and Ba\textsubscript{3}MnUS\textsubscript{6} each exhibit a dominant low-wavenumber mode, likely owing to U–S/Se stretches within the trigonal prism. Both the Se-containing compounds exhibit this mode at 236 cm\textsuperscript{−1}, an unsurprising agreement given the similarity in U–Se interatomic distances in these compounds (Table 2). This mode is observed at 266 cm\textsuperscript{−1} for Ba\textsubscript{3}MnUS\textsubscript{6}. Symmetric U–S/Se stretching modes are observed at 336 and 338 cm\textsuperscript{−1} for Ba\textsubscript{3}AgSe\textsubscript{6} and Ba\textsubscript{3}K\textsubscript{0.3}Se\textsubscript{6}, which are comparable with a previously reported U–S symmetric mode.\textsuperscript{48} Whereas Ba\textsubscript{3}AgRb\textsubscript{2}Se\textsubscript{6} and Ba\textsubscript{3}K\textsubscript{0.3}Se\textsubscript{6} contain identical U octahedra, the higher stretching frequency in Ba\textsubscript{3}AgSe\textsubscript{6} is a result of shorter and stronger U–S interatomic distances in accordance with Badger’s rule.\textsuperscript{49} This mode is observed to lie substantially lower in frequency at 238 cm\textsuperscript{−1} for Ra\textsubscript{4}USe\textsubscript{6} compared with that of its S analogues, consistent with the ∼0.2 Å increase in the U–S/Se interatomic distance and the greater mass of Se. Appreciably higher signal intensities observed in spectra of the Se-containing compounds cannot be explained by the size of the crystals studied; the difference probably results from the greater polarizability of Se as well as potential resonance effects.

**Resistivity Studies.** The three compounds measured, namely Ba\textsubscript{4}USe\textsubscript{6}, Ba\textsubscript{3}FeUSe\textsubscript{6}, and Ba\textsubscript{3}MnUSe\textsubscript{6}, are narrow gap semiconductors (Figure 5). Resistivity drops from 2.3 Ω cm at 300 K to 0.66 Ω cm at 500 K for Ba\textsubscript{4}USe\textsubscript{6} from 85 Ω cm to 46 Ω cm for Ba\textsubscript{3}FeUSe\textsubscript{6} and from 128 Ω cm to 99 Ω cm for Ba\textsubscript{3}MnUSe\textsubscript{6}. The activation energy extracted from the corresponding Arrhenius plots is 0.08(1), 0.04(1), and 0.02(1) eV for Ba\textsubscript{4}USe\textsubscript{6}, Ba\textsubscript{3}FeUSe\textsubscript{6}, and Ba\textsubscript{3}MnUSe\textsubscript{6}, respectively.

**DFT Calculations.** Four compounds were studied with density functional theory. The total (upper plot) and partial (lower plots) density of states of Ba\textsubscript{4}USe\textsubscript{6}, Ba\textsubscript{3}FeUSe\textsubscript{6}, Ba\textsubscript{3}MnUSe\textsubscript{6}, and Ba\textsubscript{3}MnUS\textsubscript{6} are presented in Figures 6, 7, 8, and 9, respectively. They present some remarkable similarities in their electronic structure: all four compounds are found to be semiconducting with a band gap of 2.6 eV for Ba\textsubscript{4}USe\textsubscript{6}, 2.1 eV for Ba\textsubscript{3}FeUSe\textsubscript{6}, 1.8 eV for Ba\textsubscript{3}MnUSe\textsubscript{6}, and 2.1 eV Ba\textsubscript{3}MnUS\textsubscript{6}. The states just below the Fermi level (put at zero eV on the plots) are derived mainly from U-f states with some contribution from other atoms, mainly Fe-d and Mn-d states for the three compounds containing a transition metal. The U, Fe, and Mn atoms carry a magnetic moment, which is seen from the corresponding asymmetric partial density of states. These magnetic moments induce a small magnetic polarization on the other atoms (S, Se, and Ba), which is seen from their partial density of states.

**CONCLUSIONS**

The 2H hexagonal perovskite-related family exhibits remarkable chemical flexibility. We show that the 5f element U is very flexible with respect to its position within the structure and its oxidation state. The six new uranium chalcogenides, Ba\textsubscript{4}USe\textsubscript{6}, Ba\textsubscript{3}FeUSe\textsubscript{6}, Ba\textsubscript{3}MnUSe\textsubscript{6}, Ba\textsubscript{3}MnUS\textsubscript{6}, Ba\textsubscript{3}Rb\textsubscript{2}Se\textsubscript{6}, and Ba\textsubscript{3}K\textsubscript{0.7}Se\textsubscript{6}, represent an example of this flexibility. These compounds, synthesized by solid-state methods at 1173 K, are isostructural and crystallize in the K\textsubscript{2}CdCl\textsubscript{6} structure type in space group D\textsubscript{3h}\textsuperscript{−1}−R\textsubscript{3c} of the trigonal system with six formula units per cell. In Ba\textsubscript{3}FeUSe\textsubscript{6}, Ba\textsubscript{3}MnUSe\textsubscript{6}, and Ba\textsubscript{3}MnUS\textsubscript{6}, the structure consists of infinite \(\{\text{MUQ}_6\textsuperscript{6−}\}\) chains (M = Fe or Mn; Q = S or Se) oriented along the c axis that are separated by Ba atoms. These chains are composed of alternating M-centered octahedra and U-centered trigonal prisms sharing triangular faces; in contrast, in the structures of Ba\textsubscript{4}USe\textsubscript{6}, Ba\textsubscript{3}Rb\textsubscript{2}Se\textsubscript{6} and Ba\textsubscript{3}K\textsubscript{0.7}Se\textsubscript{6} are mixed U\textsuperscript{4+}/5+ compounds. Moreover, Ba\textsubscript{3}FeUSe\textsubscript{6}, Ba\textsubscript{3}MnUSe\textsubscript{6}, and Ba\textsubscript{3}MnUS\textsubscript{6} compounds contain U\textsuperscript{4+}, whereas Ba\textsubscript{3}AgRb\textsubscript{2}Se\textsubscript{6} and Ba\textsubscript{3}K\textsubscript{0.7}Se\textsubscript{6} are mixed U\textsuperscript{4+}/5+ compounds. Moreover, μ-Raman spectroscopic measurements provide additional insight into these interesting subtle structural variations. Resistivity measurements show that Ba\textsubscript{4}USe\textsubscript{6}, Ba\textsubscript{3}FeUSe\textsubscript{6}, and Ba\textsubscript{3}MnUSe\textsubscript{6} are semiconductors with activation energies of 0.08(1), 0.04(1), and 0.02(1) eV. Band gaps calculated using the HSE06 functional are 2.6, 2.1, and 1.8 eV, respectively, for these compounds and 2.1 eV for Ba\textsubscript{3}MnUS\textsubscript{6}.

**ASSOCIATED CONTENT**

Supporting Information
Crystallographic file in CIF format for Ba\textsubscript{4}USe\textsubscript{6}, Ba\textsubscript{3}FeUSe\textsubscript{6}, Ba\textsubscript{3}MnUSe\textsubscript{6}, Ba\textsubscript{3}Rb\textsubscript{2}Se\textsubscript{6}, and Ba\textsubscript{3}K\textsubscript{0.7}Se\textsubscript{6}. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
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