



Syntheses and crystal structures of the quaternary uranium lanthanide oxyselenides $\text{UYb}_2\text{O}_2\text{Se}_3$ and $\text{U}_2\text{Ln}_2\text{O}_4\text{Se}_3$ ($\text{Ln} = \text{Pr}, \text{Sm}, \text{Gd}$)

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ABSTRACT

Single crystals of the new uranium lanthanide oxyselenide compounds $\text{UYb}_2\text{O}_2\text{Se}_3$ and $\text{U}_2\text{Ln}_2\text{O}_4\text{Se}_3$ ($\text{Ln} = \text{Pr}, \text{Sm}, \text{Gd}$) have been synthesized from an Sb_2Se_3 flux. The structures have been determined from single-crystal X-ray diffraction data. $\text{UYb}_2\text{O}_2\text{Se}_3$ is isostructural to $\text{UYb}_2\text{O}_2\text{S}_3$. The structure comprises layers of edge-sharing YbSe_6 octahedra and double layers of disordered $(\text{U}/\text{Ln})\text{O}_4\text{Se}_4$ square antiprisms. The $\text{U}_2\text{Ln}_2\text{O}_4\text{Se}_3$ ($\text{Ln} = \text{Pr}, \text{Sm}, \text{Gd}$) compounds are isostructural to $\text{U}_2\text{Ln}_2\text{O}_4\text{S}_3$ ($\text{Ln} = \text{La} - \text{Gd}$) whose structure had been deduced previously from X-ray powder diffraction data. In the structure a dodecahedron of four O atoms and four Se atoms surrounds a site primarily occupied by U and a distorted bicapped octahedron of five Se atoms and three O atoms surrounds a site primarily occupied by the lanthanide. These compounds represent the first examples of quaternary uranium oxyselenides.

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1. Introduction

Although considerable attention has been paid to the effect of cation substitution on structure, mixed-anion compounds represent a relatively unexplored and exciting field of solid-state chemistry. Of particular interest is the role of multiple anions in quaternary or higher systems where the differences in cation–anion interactions can influence the crystal structure. Large differences in electronegativity or bonding affinity can lead to layered structures and result in interesting electrical and optical properties [1]. The mixed-anion compounds of the lanthanides with transition metals have a number of desirable electronic and magnetic properties [2,3]. Many of these properties are dependent on the anion, and changing anions within a group can greatly influence the physical properties of the compounds [4].

By comparison the mixed-anion compounds of the actinides have received little attention. Although there has been some interest in uranium oxysulfides, there has been little in mixed anion compounds with anions heavier than S [5–8]. Uranium lanthanide oxysulfides crystallize primarily in two structures. The larger lanthanides, La–Gd, form the compounds $\text{U}_2\text{Ln}_2\text{O}_4\text{S}_3$, an example of the $\text{Ce}_4\text{O}_4\text{S}_3$ structure type where the lanthanide and actinide polyhedra are connected throughout the structure [7]. The structure is the $n=2$ variant of a family of compounds $\text{U}_2\text{Ln}_{2n-2}\text{O}_{2n}\text{S}_{n+1}$ ($\text{Ln} = \text{La} - \text{Gd}$), where n ranges from 2 to 6 [7]. The cell parameters of the lanthanum analogues of these extended structures have been reported by X-ray powder diffraction measurements and their

layering determined by electron microscopy studies [7,8]. The unit cells of the lanthanide compounds, Ce–Gd, have also been reported by X-ray powder diffraction measurements [7]. In contrast, the smaller lanthanides, Gd–Lu and Y, form the compounds $\text{ULn}_2\text{O}_2\text{S}_3$ [5,9,10]; these were originally reported as $\text{U}_2\text{LnO}_2\text{S}_3$ [5,9]. In this structure there are layers of LnS_8 octahedra separating double layers of U/Ln sites bound to both O and S. Previously there had been no reported examples of quaternary uranium oxyselenides.

Inorganic structures with multiple cations are common; however, structures with multiple anions are often more difficult to synthesize. Whereas it is possible to combine most binary compounds of a single anion, the same bonding preferences that lead to interesting properties in mixed-anion compounds can also limit reactivity. If the preference of a cation for its starting anion is too high, then it is unlikely for a reaction to occur. Likewise, if the anions are introduced separately, then preferred coordination can lead to a mixture of binaries rather than to a quaternary product. Such challenges create the need for new synthetic approaches based on the compound being synthesized and the reactivity of the starting materials. We present here three methods for the syntheses of quaternary uranium lanthanide oxyselenides: the direct combination of ternary and binary starting materials, a pseudo-metathesis synthesis, and introduction of an external oxygen source.

2. Experimental

2.1. Syntheses

^{238}U turnings (Oak Ridge National Laboratory) were powdered according to a modification [11] of a previous literature procedure

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[12]. UO_2 was prepared from the reduction of UO_3 (Alfa Aesar, 99.8%) under flowing H_2 at 1173 K. All other reactions were conducted in carbon-coated fused-silica tubes evacuated to 10^{-4} Torr. Yb (Alfa, 99.9%), Sm (Aldrich, 99.9%), Sb (Aldrich, 99.5%), Se (Cerac, 99.999%), SeO_2 (Aldrich 99.8%), Gd_2O_3 (Aldrich 99.9%), and Pr_6O_{11} (Aldrich 99.999%) were used as received. Sb_2Se_3 was synthesized from the reaction of Sb and Se in a 2:3 ratio at 1273 K for 24 h. USe_2 was prepared by the reaction of stoichiometric amounts of the elements at 1273 K for 72 h.

2.1.1. $\text{UYb}_2\text{O}_2\text{Se}_3$

$\text{UYb}_2\text{O}_2\text{Se}_3$ was formed by the direct combination of the starting binary and ternary compounds. UOSe was formed by heating a mixture of equal molar amounts of UO_2 and USe_2 at 1073 K for 1 week and then cooling the reaction to 298 K over two weeks. 1.2 mmol (0.2 g) Yb and 1.7 mmol (0.137 g) Se were reacted at 1073 K for seven days to give a polycrystalline product that consisted mostly of YbSe with a small amount of unreacted Se, as determined by X-ray powder diffraction measurements. 0.09 mmol (0.03 g) UOSe and 0.026 g of the YbSe/Se mixture were ground along with 0.02 mmol (0.014 g) Se and the mixture was heated to 673 K in 4 h, then to 1323 K in 11 h, left at 1323 K for 168 h, and then cooled 2 K/h to 1123 K before being air quenched. The resultant powder was shown by diffraction measurements and the use of JADE-8 software [13] to comprise a structure similar to that of $\text{UYb}_2\text{O}_2\text{Se}_3$ along with some unreacted UOSe [10]. Crystals of $\text{UYb}_2\text{O}_2\text{Se}_3$ were formed by combining the resultant powder with 0.01 g Sb_2Se_3 and heating the mixture to 1223 K over 100 h, holding it at 1223 K for 1 week, and then cooling it to 923 K at 3 K/h. The resultant black plates, approximately 30 wt% yield based on U, could then be separated from the needles of Sb_2Se_3 and plates of UOSe .

2.1.2. $\text{U}_2\text{Pr}_2\text{O}_4\text{Se}_3$

$\text{U}_2\text{Pr}_2\text{O}_4\text{Se}_3$ was formed through a pseudo-metathesis synthesis involving the transition from O and Se coordinated exclusively to a single cation to a mixed anion coordination for both cations. A mixture of 0.08 mmol (0.03 g) USe_2 , 0.01 mmol (0.011 g) Pr_6O_{11} , and 0.15 mmol (0.012 g Se) was heated at 1273 K for 168 h and then air quenched. Examination of the resultant microcrystals on an EDX-equipped Hitachi 3400 SEM showed the presence of U, Pr, Se, and O. The powder was mixed with 0.02 g Sb_2Se_3 and heated to 1273 K in 24 h, held at 1273 K for 100 h, cooled to 1073 K at 2 K/h, held there for 72 h, cooled to 973 K in 36 h before cooling to 298 K in 12 h. The resulting black rectangular block crystals, approximately 5 wt% yield based on U,

were mechanically separated from the unreacted starting materials and the Sb_2Se_3 flux.

2.1.3. $\text{U}_2\text{Sm}_2\text{O}_4\text{Se}_3$

$\text{U}_2\text{Sm}_2\text{O}_4\text{Se}_3$ was formed with the use of SeO_2 as external oxygen source. Sm_2Se_3 was synthesized by the reaction of stoichiometric amounts of the elements at 1273 K over 1 week. 0.12 mmol (0.03 g) U, 0.09 mmol (0.048 g) Sm_2Se_3 , 0.06 mmol (0.0069 g) SeO_2 , and 0.25 mmol (0.02 g) Se were heated to 1223 K in 100 h, held there for 168 h, then cooled to 923 K at a rate of 3 K/h, and then air quenched. The resultant polycrystalline material comprised U, Sm, Se, and O, as determined by EDX analysis. In order to form single crystals the powder was mixed with 0.05 g Sb_2Se_3 and heated to 1273 K in 24 h, held at 1273 K for 168 h, cooled to 973 K at 3 K/h, and then air quenched. The resultant $\text{U}_2\text{Sm}_2\text{O}_4\text{Se}_3$ black square plates, approximately 20 wt% yield based on U, were mechanically separated from the unreacted starting materials and the Sb_2Se_3 flux.

2.1.4. $\text{U}_2\text{Gd}_2\text{O}_4\text{Se}_3$

$\text{U}_2\text{Gd}_2\text{O}_4\text{Se}_3$ was formed through a pseudo-metathesis synthesis involving the transition from O and Se coordinated exclusively to a single cation to a mixed anion coordination for both cations. A mixture of 0.08 mmol (0.03 g) USe_2 , 0.04 mmol (0.0137 g) Gd_2O_3 , and 0.28 mmol (0.022 g) Se was heated to 1273 K in 24 h, held there for 168 h, and then cooled to 297 K in 12 h. The resultant black micrometer-sized crystals showed the presence of U, Gd, Se, and O by EDX analysis. The crystals were mixed with 0.01 g Sb_2Se_3 and heated to 1273 K in 12 h, held at 1273 K for 168 h, cooled to 1073 K at 2 K/h, and then air quenched. The resultant black square plates of $\text{U}_2\text{Gd}_2\text{O}_4\text{Se}_3$, approximate yield 20 wt% based on U, were mechanically separated from the starting materials and Sb_2Se_3 flux.

2.2. Structure determinations

The structures of the above compounds were determined from single-crystal X-ray diffraction data collected on a Bruker SMART APEX CCD diffractometer [14,15]. Face-indexed absorption, incident beam, and decay corrections were performed with the use of the program SADABS [16]. Each structure was solved with the direct-methods program SHELXS and refined with the least-squares program SHELXL [17]. The program STRUCTURE TIDY was used to standardize the positional parameters [18].

Table 1
Crystallographic details of the uranium lanthanide oxyselenide compounds^a.

	$\text{U}_2\text{Pr}_2\text{O}_4\text{Se}_3$	$\text{U}_2\text{Sm}_2\text{O}_4\text{Se}_3$	$\text{U}_2\text{Gd}_2\text{O}_4\text{Se}_3$	$\text{UYb}_2\text{O}_2\text{Se}_3$
Space group	<i>Pbam</i>	<i>Pbam</i>	<i>Pbam</i>	<i>I4/mmm</i>
<i>a</i> (Å)	7.0466(3)	6.9873(2)	6.9724(4)	3.8534(9)
<i>b</i> (Å)	14.9241(5)	14.7923(4)	14.8052(7)	3.8534(9)
<i>c</i> (Å)	4.0235(1)	3.9854(1)	3.9678(2)	21.610(5)
<i>V</i> (Å ³)	423.13(3)	411.924(19)	409.59(4)	320.88(13)
ρ (g/cm ⁻³)	8.310	8.688	8.850	8.828
μ (cm ⁻¹)	62.33	66.45	68.68	70.989
% occupancy of U on 4 <i>h</i> site	93.5(1)	81.5(1)	80.5(1)	
% occupancy of Ln on 4 <i>g</i> site	93.5(1)	81.5(1)	80.5(1)	
<i>R</i> (<i>F</i>) ^b	0.0253	0.0182	0.0222	0.0317
<i>R</i> _w (<i>F</i> ²) ^c	0.0633	0.0436	0.0578	0.0945
<i>q</i> ^c	0.0232	0.0172	0.0196	0.0323

^a For all compounds *T* = 100 K, *Z* = 2.

^b $R(F) = \frac{\sum \|F_o\| - \|F_c\|}{\sum \|F_o\|}$ for $F_o^2 > 2\sigma(F_o^2)$.

^c $R_w(F_o^2) = \frac{[\sum (w(F_o^2 - F_c^2))^2]}{[\sum w(F_o^2)]^{1/2}}$. For $F_o^2 < 0$, $w^{-1} = \sigma^2(F_o^2)$; for $F_o^2 \geq 0$, $w^{-1} = \sigma^2(F_o^2) + (qF_o^2)^2$.

The structure of $\text{UYb}_2\text{O}_2\text{Se}_3$ was refined with 50% occupancy of Yb1 at the U site and full Yb occupancy at the octahedral lanthanide site, as was found for the S analogue $\text{UYb}_2\text{O}_2\text{S}_3$ [10].

Although the $\text{U}_2\text{Ln}_2\text{O}_4\text{Se}_3$ compounds formally charge balance (U^{4+} , Ln^{3+} , O^{2-} , Se^{2-}), refinements with pure U and pure lanthanide positions led to unrealistic oxygen displacement parameters and poor overall refinement quality. Far better refinements were obtained by imposing charge balance but allowing the U/Ln ratio at a given site to vary. Additional details of the refinements can be found in Table 1 and in the Supporting material.

3. Results and discussion

3.1. Syntheses

The synthetic method used for $\text{UYb}_2\text{O}_2\text{Se}_3$ is similar to that previously reported for the compound $\text{UYb}_2\text{O}_2\text{S}_3$ [10]. UOSE cannot be formed by the same method as UOS and this necessitated an additional synthetic step [19]. The change in color from red to black in going from $\text{UYb}_2\text{O}_2\text{S}_3$ to $\text{UYb}_2\text{O}_2\text{Se}_3$ is in keeping with the decrease in band gap expected from replacement of S with Se.

The syntheses of the $\text{U}_2\text{Ln}_2\text{O}_4\text{Se}_3$ compounds were all conducted at temperatures below that of 1673 K that was used in syntheses of the analogous oxysulfides [7]. This was accomplished through the use of Sb_2Se_3 as a low melting flux, which also allowed the formation of diffraction-quality single crystals. Several heating profiles and fluxes were tested for each composition in order to achieve the highest quality crystals, although the most successful profiles remained similar. However, under all synthetic conditions yields of diffraction-quality crystals were less than 30 wt%, based on U.

3.2. Structures

$\text{UYb}_2\text{O}_2\text{Se}_3$ crystallizes in the space group $I4/mmm$ with two formula units in the unit cell. The structure consists of two cation positions. In one, the disordered U/Yb1 cation (site symmetry $4mm$) is coordinated in a distorted square antiprism with one face consisting of four O atoms and the other of four Se atoms; in the other the ordered Yb2 cation (site symmetry $4/mmm$) is octahedrally coordinated by six Se atoms (Fig. 1). Selected interatomic distances can be found in Table 2. The U–O interatomic distance of 2.2966(7) Å is in good agreement with that of 2.28(2) Å in $\text{UYb}_2\text{O}_2\text{S}_3$ and the U–Se distance of 3.052(2) Å agrees with that of 3.012(5) for the shorter U–Se distance in UOSe [10,19]. The distances from the ordered Yb site of 2.7248(6) Å and 2.777(3) Å are also in good agreement with those of other octahedrally coordinated Yb^{3+} selenides, such as LaYbSe_3 with two Yb–Se distances of 2.7109(7) Å and four of 2.8258(8) Å [20].

The $\text{U}_2\text{Ln}_2\text{O}_4\text{Se}_3$ structure shown in Fig. 2 also has two crystallographically independent cation positions. However, owing to the similarities in coordination environment and oxophilicity of Ln and U there is disorder at both sites. The site primarily occupied by U (symmetry . . m) (Table 1) is surrounded by four O and four Se atoms arranged in a dodecahedron. The site primarily occupied by Ln (symmetry . . m) is surrounded by three O atoms and five Se atoms in a distorted bicapped octahedron. The relative occupancies (Table 1) conform to the expected trend where the more oxophilic U should preferentially occupy the site with greater oxygen coordination. The degree of disorder increases going from Pr to Gd because the difference in ionic radii between Ln^{3+} and U^{4+} decreases.

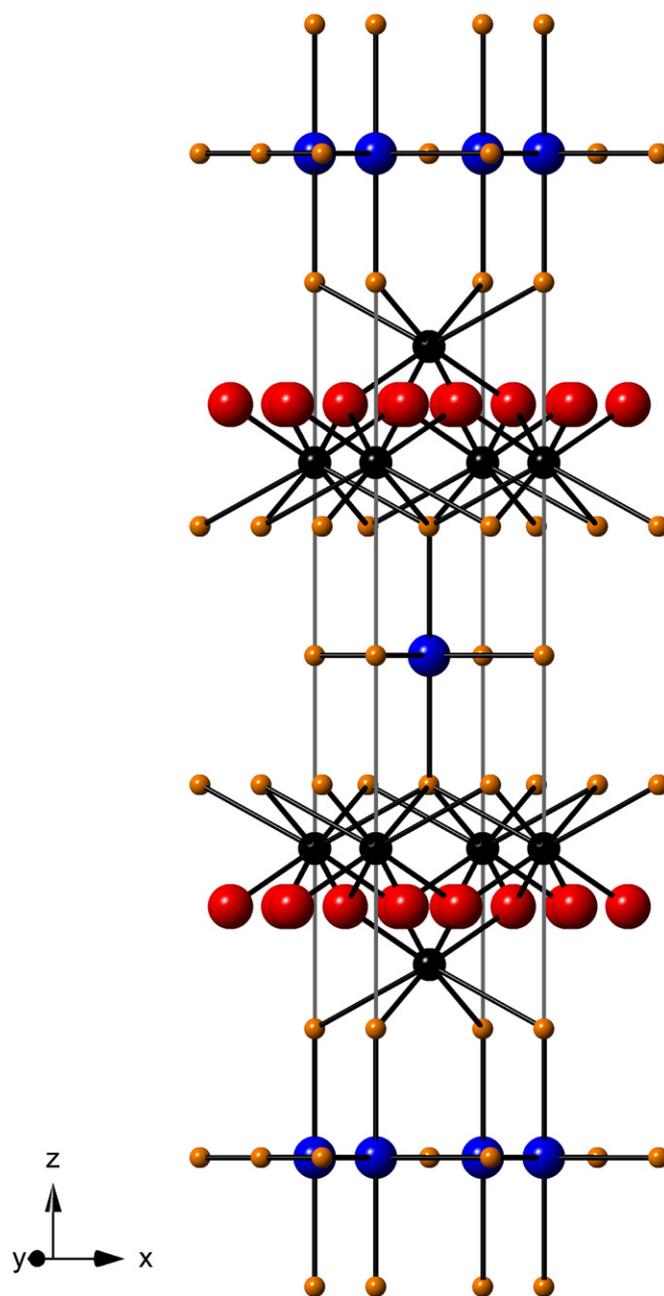


Fig. 1. The $\text{UYb}_2\text{O}_2\text{Se}_3$ structure: U/Yb sites in black, Yb sites in blue, O red, Se orange. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 2

Selected interatomic distances (Å) in $\text{UYb}_2\text{O}_2\text{Se}_3$.

(U/Yb1)–O × 4	2.2966(7)
(U/Yb1)–Se × 4	3.052(2)
Yb2–Se × 4	2.7248(6)
Yb2–Se × 2	2.777(3)

Table 3 provides details on interatomic distances. Because of the U/Ln disorder only general trends can be discussed. The U–O interatomic distances with an average length of 2.24 Å are in good agreement with those found in the mixed anion compound $\text{UY}_4\text{O}_3\text{S}_5$, which range from 2.196 (3) Å to 2.303 (6) Å [21]. The

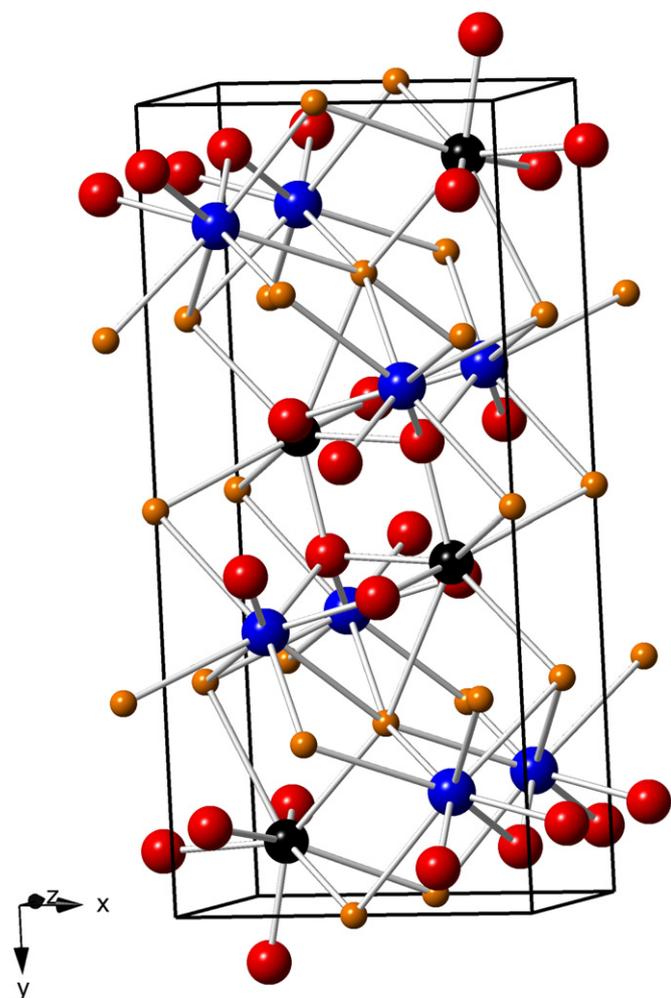


Fig. 2. The $U_2Ln_2O_4Se_3$ ($Ln=Pr, Sm, Gd$) structure: primarily U sites are in black, primarily Ln sites are in blue, O red, Se orange. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 3
Selected interatomic distances (Å) in $U_2Ln_2O_4Se_3$ ($Ln=Pr, Sm, Gd$).

Distance ^a	$U_2Pr_2O_4Se_3$	$U_2Sm_2O_4Se_3$	$U_2Gd_2O_4Se_3$
(Ln/U)–O1	2.367(4)	2.324(4)	2.298(5)
(Ln/U)–O2 × 2	2.425(3)	2.392(2)	2.367(3)
(Ln/U)–Se1	3.0486(3)	3.0161(3)	3.0143(4)
(Ln/U)–Se2 × 2	3.0694(5)	3.0392(5)	3.0412(6)
(Ln/U)–Se2 × 2	3.1104(5)	3.0925(5)	3.0912(7)
(U/Ln)–O1 × 2	2.162(2)	2.144(1)	2.141(2)
(U/Ln)–O2	2.245(4)	2.231(4)	2.246(6)
(U/Ln)–O2	2.420(5)	2.398(4)	2.417(6)
(U/Ln)–Se2	2.9871(7)	2.9604(6)	2.9547(8)
(U/Ln)–Se1 × 2	3.1259(2)	3.1053(2)	3.0873(3)
(U/Ln)–Se2	3.2898(7)	3.2541(7)	3.2562(8)

^a Sites are denoted with the element primarily occupying the site followed by the less prevalent element. Ln/U corresponds to the 4g site, U/Ln to the 4h site.

average U–Se distance, 3.08 Å, also conforms to the expected value with the exception of the one long distance ranging from 3.2562(8) Å in $U_2Gd_2O_4Se_3$ to 3.2898(7) Å in $U_2Pr_2O_4Se_3$. Overall the distances from the lanthanide site decrease in the order $Pr > Sm > Gd$ as would be expected from the lanthanide contraction.

4. Conclusions

We present the first examples of quaternary uranium oxyse- lenides. Unlike most previous syntheses of uranium oxychalcogenides, the reported compounds were formed at low temperatures, < 1373 K, with the use of a low melting flux to aid crystal growth. The three synthetic routes presented, namely, direct combination of binaries and ternaries, a pseudo-metathesis reaction between the binaries, and the introduction of a controlled amount of oxygen from an external source, show a flexibility that should prove useful in the syntheses of other mixed-anion compounds.

The compound $UYb_2O_2Se_3$ is isostructural with $UYb_2O_2S_3$ with 50% Yb1/U occupancy on the square antiprismatic site [10]. The compounds $U_2Ln_2O_4Se_3$ ($Ln=Pr, Sm, Gd$) are isostructural and possess the structure deduced earlier from X-ray powder diffraction data for $U_2La_2O_4S_3$ [7]. Disorder of the U/Ln sites in $U_2Ln_2O_4Se_3$ follows the trends expected for the relative oxophilicities of U and Ln and for the relative ionic radii.

Supporting material

The crystallographic data for $UYb_2O_2Se_3$, $U_2Pr_2O_4Se_3$, $U_2Sm_2O_4Se_3$, and $U_2Gd_2O_4Se_3$ have been deposited with FIZ Karlsruhe as CSD numbers 423731, 423730, 423729, and 423732, respectively. These data may be obtained free of charge by contacting FIZ Karlsruhe at +497247808666 (fax) or crysdata@fiz-karlsruhe.de (email).

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Appendix A. Supplementary Information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jssc.2011.12.002](https://doi.org/10.1016/j.jssc.2011.12.002).

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