Synthesis and structural characterization of the new compound $UEr_2O_2S_3$ and the evidence for the old compound $U_2ErO_2S_3$

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ABSTRACT

Black square plates of the new compound $UEr_2O_2S_3$ have been synthesized by the reaction of UOS, Er, and S with an Sb_2S_3 flux at 1273 K. The structure of $UEr_2O_2S_3$ has been solved and refined from single-crystal X-ray diffraction data. $UEr_2O_2S_3$ forms a layered structure with layers of edge-sharing ErS_6 octahedra and double layers of disordered $(U/Er)O_4S_4$ square antiprisms. Upon reexamination of the previously reported X-ray data for the $U^{3.5+}$ compound $U_2ErO_2S_3$ we conclude that it also may be characterized as the U^{4+} compound $UEr_2O_2S_3$.

1. Introduction

The chemistries of the lighter actinides, such as Th, resemble those of the transition metals whereas the chemistries of the heavier actinides, Am and beyond, resemble those of the lanthanides. In between are U, Np, and Pu. These three elements can show a wide variety of formal oxidation states, ranging from $3+$ to $7+$. Such formal oxidation states, comprising as they do various $5f^n$ configurations, are key to the chemical and structural nature of compounds of these elements.

The assignment of formal oxidation states on the basis of charge balance often leads to puzzling results. Consider U_3S_5 [1,2]. There are no S–S bonds in the structure so we assign the oxidation state of -2 to S. Hence it appears that the oxidation state of U is $+3.33$! However, the structure contains two crystallographically distinct sites, U(1) and U(2). U(1) is in a 7-coordinate site with U–S distances ranging from 2.863 to 3.026 Å; U(2) is in an 8-coordinate site with U–S distances ranging from 2.640 to 2.854 Å. There are twice as many U(1) atoms in the cell as U(2) atoms. This allows the compound to be formulated as $(U^{3+})_2(U^{4+})(S^{2-})_5$, which charge balances. This assignment is supported by U–S distances, magnetic susceptibility data, as well as by analogy to the rare-earth derivatives, i.e., Ln_2UQ_5 or $(Ln^{3+})_2(U^{4+})(Q^{2-})_5$ [3]. However, in other instances the formal oxidation state of a cation in a compound cannot be assigned so

readily and the issue of intermediate valence compounds arises. For example, in the lanthanide oxychalcogenide compound $La_5Cu_6O_4S_7$ there are no S–S bonds and hence charge balance leads to an oxidation state of $7/6+$ for Cu; yet there are only two crystallographically distinct Cu sites [4]. Intermediate valence compounds are of particular interest because of their potential for unusual electrical and magnetic properties [5,6]. Whereas such systems have been studied for transition metals, there are relatively few reports of actinides with intermediate oxidation states [7–9].

In comparison to the lanthanides, there have been relatively few reported actinide oxychalcogenide compounds. Of the previously reported quaternary actinide oxychalcogenides the compound $U_2ErO_2S_3$ [8,9] is of particular interest because on the basis of charge balance the formal oxidation state of U in the compound is $+3.5$. The problem here is that there is only one crystallographically distinct U site and hence U^{3+} and U^{4+} cations must occupy the same 8-coordinate site. Is this an instance of U in an intermediate valence state? Clearly, reexamination of this compound is in order. The compound was synthesized from the reaction of UOS and Er_2S_3 at 1773–2173 K under Ar. These conditions are above the tolerances of fused-silica ampules and instead require sealed refractory metal crucibles or specially designed furnaces. Thus we invoked a lower-temperature synthesis [10] and this led successfully to the new compound $UEr_2O_2S_3$, which charge balances with U^{4+} and Er^{3+}. Here we discuss that synthesis as well as the determination of the structure of $UEr_2O_2S_3$ and present evidence that it is indeed the compound previously formulated as $U_2ErO_2S_3$. Finally, we reexamine the

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data that led to the original formulation $U_2ErO_2S_3$ and show that it is equally consistent with the formulation $UEr_2O_2S_3$.

2. Experimental section

All reactions were performed in carbon-coated fused-silica tubes evacuated to 10^{-4} Torr. UOS was synthesized as previously described [11]. Er (Alfa, 99.9%), S (Alfa-Aesar 99.99%), and Sb (Aldrich, 99.5%) were used as received. Sb_2S_3 was formed from the reaction of Sb and S in a 2:3 ratio in an evacuated fused-silica tube. The compound $UEr_2O_2S_3$ was prepared through a two-step solid-state reaction. In the first step 0.03 g UOS (0.1 mmol), 0.017 g Er (0.12 mmol), and 0.005 g S (0.16 mmol) were combined in a fused-silica tube in an argon filled glove box. The tube was sealed and then heated at 1273 K for seven days and cooled at 4 K/h to 873 K where it was quenched in air. An X-ray diffraction pattern of the resultant powder was obtained with a Rigaku Geigerflex powder X-ray diffractometer with the use of Cu $K\alpha$ radiation ($\lambda=1.54056$ Å). The resulting polycrystalline sample was ground together with an equal mass of Sb_2S_3 and again heated at 1273 K for seven days, cooled at 2 K/h to 873 K, and then quenched in air to obtain suitable single crystals.

$UEr_2O_2S_3$ crystalized as large black square plates in 30 wt% yield. These were isolated from black needles of Sb_2S_3, a few orange needles Er_2S_3, and black polycrystalline UOS. EDX analysis of the black plates on a Hitachi S-3400 scanning electron microscope showed an approximate U:Er:S ratio of 1:2:3. Oxygen is below the detection limit of the instrument and so it could not be adequately measured by this method.

The structure of a square plate was determined from single-crystal X-ray diffraction data collected on a Bruker SMART APEX CCD diffractometer [12,13]. Face-indexed absorption, incident beam, and decay corrections were performed with the use of the program SADABS [14]. The structure was solved with the direct-methods program SHELXS and refined with the least-squares program SHELXL [15]. The models refined were those employed earlier for the Yb and Y analogues [10]. These are detailed in Table 1. The program STRUCTURE TIDY was used to standardize the positional parameters [16].

Re-analysis of the previously reported refinement of $U_2ErO_2S_3$ was conducted using the original structure factors (F_o) (deposited as SUP42948 of Reference [9]). These values were converted to F_o^2. Because the original weighting scheme was not available, we took $\sigma(F_o)$ to be F_o on the assumption of Poisson counting statistics. The original unit cell constants were used (Table 2). The models refined were those detailed above and the results are summarized in Table 1. Additional experimental details for the present refinement and for the re-refinement of the original data [9] are provided in Tables 1 and 2 and the supporting material.

Table 1
Refinement models of the original data and new data for $UEr_2O_2S_3$ and $U_2ErO_2S_3$.

Model	R_1[a]	R_w[b]	q_1	q_2
Original[c] $U_2ErO_2S_3$	0.0374	0.0865	0.0256	49.38
Original $UEr_2O_2S_3$	0.0367	0.087	0.0253	39.08
Original $U_{1.4(1)}Er_{1.6(1)}O_2S_3$	0.035	0.0833	0.0252	38.7
New[d] $U_2ErO_2S_3$	0.0176	0.0466	0.0117	21.05
New $UEr_2O_2S_3$	0.0141	0.035	0.0183	5.27
New $U_{1.24(3)}Er_{1.76(3)}O_2S_3$	0.0125	0.0319	0.0191	1.66

[a] $R_1(F)=\Sigma ||F_o|-|F_c||/\Sigma |F_o|$ for $F_o^2 > 2\sigma(F_o^2)$.
[b] $R_w(F_o^2)=\{\Sigma [w(F_o^2-F_c^2)^2]/\Sigma wF_o^4\}^{1/2}$. $w^{-1}=\sigma^2(F_o^2)$ for $F_o^2 < 0$; $w^{-1}=\sigma^2(F_o^2)+(q_1 \times P^2)^2+q_2P$ where $P=(F_o^2+2F_c^2)/3$.
[c] Reference [9].
[d] Present work.

Table 2
Crystallographic details for original and new structure determinations.[a]

	Original[b] $U_2ErO_2S_3$	New $UEr_2O_2S_3$
T (K)	293	100(2)
a (Å)	3.785(2)	3.7876(4)
c (Å)	20.83(1)	20.797(2)
V (Å^3)	298.4(5)	298.35(5)
ρ(g/cm^3)	8.59	7.8
μ(mm^{-1})	69.0[c]	55.88

[a] For both determinations $\lambda=0.71073$ Å, space group$=I4/mmm$, $Z=2$.
[b] Reference [9].
[c] Note that $\mu=83.26$ mm^{-1} was used in the original absorption correction.

3. Results

Synthesis. $UEr_2O_2S_3$ was synthesized in a similar fashion to the low-temperature method reported previously for $ULn_2O_2S_3$ (Ln=Y, Yb), where a low melting antimony sulfide flux was used to promote crystallization [10]. The reaction occurred at a lower temperature than the previously reported method for the preparation of $U_2ErO_2S_3$ which required heating the reactants to temperatures of 1773 K and 2173 K under argon [9]. Both synthetic routes led to black products.

Structure. The X-ray powder diffraction pattern of the present material, which was analyzed with the program JADE8 [17], compared well with one simulated from the single-crystal results originally reported for the compound $U_2ErO_2S_3$ [9].

Table 1 details the various refinement models for the present data for the new compound $UEr_2O_2S_3$. Although the model involving refined U/Er1 disorder gives slightly better agreement, we do not consider this significant. What is clear is that the model for the composition $UEr_2O_2S_3$ is significantly better than that for the earlier reported composition $U_2ErO_2S_3$, as judged both by the lower agreement indices and lower values of q_2. In our experience if the data have been properly corrected for absorption effects then values of q_2 above 10 indicate problems with the model. Table 1 also details the refinement models for the original data for $U_2ErO_2S_3$. As opposed to the present structure determination, the original data as re-refined do not distinguish between the compositions $UEr_2O_2S_3$ and $U_2ErO_2S_3$.

$UEr_2O_2S_3$ is isostructural to $UYb_2O_2S_3$ [10]. The structure consists of two cation positions. In one, the disordered U/Er1 cation (site symmetry 4 mm) is in a distorted square antiprism with one face consisting of four O atoms and the other of four S atoms; in the other the ordered Er2 cation (site symmetry 4/mmm) is octahedrally coordinated by six S atoms (Fig. 1). Selected interatomic distances for the composition $UEr_2O_2S_3$ can be found in Table 3. The differences between the two structure determinations are small. The present U/Er1-S distance of 2.960(1) Å is somewhat longer than those of 2.891 and 2.898 Å in the compound $CaHo_2S_4$ [18]. Presumably, this is not the result of the model of U/Er1 disorder that necessarily places both cations at the same crystallographic position because the ionic radii in 8-coordination of Er^{3+} and U^{4+} are identical [19]. More likely, it is the result of the presence of O atoms in the present U/Er1 coordination sphere. The Er2-S distances of 2.6782(3) and 2.662(3) Å may be compared with the Yb2-S distances of 2.6702(6) and 2.631(5) Å in $UYb_2O_2S_3$ [10].

4. Conclusion

The low-temperature synthetic route employed previously for the syntheses of the new compounds $UYb_2O_2S_3$ and $UY_2O_2S_3$

Fig. 1. The structure of $UEr_2O_2S_3$. The 99% probability ellipsoids are shown. U/Er, black; Er, blue; O, red; S, yellow. (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.

Distance	$UEr_2O_2S_3$ new	$UEr_2O_2S_3$ original[a]
(U/Er1)-O $\times$ 4	2.2839(3)	2.2953(7)
(U/Er1)-S $\times$ 4	2.960(1)	2.946(2)
Er2-S $\times$ 4	2.6782(3)	2.6764(7)
Er2-S $\times$ 2	2.662(3)	2.678(5)

[a] New refinement of the data of Reference [9].

the same problem of U/Lu disorder exists in that compound and that it too is a compound of U^{4+}.

Supporting material

The crystallographic files in CIF format for the present data and the re-refinement of the earlier data for $UEr_2O_2S_3$ have been deposited with FIZ Karlsruhe as CSD numbers 423537 and 423543, respectively. These data may be obtained free of charge by contacting FIZ Karlsruhe at $+497247808666$ (fax) or crysdata@fiz-karlsruhe.de (email).

Acknowledgments

Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2011.12.040.

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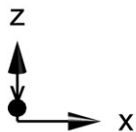
leads to the successful synthesis of the new compound $UEr_2O_2S_3$, a compound that is charge-balanced with U^{4+}. The compound synthesized in a higher-temperature different reaction was formulated as $U_2ErO_2S_3$ [9]. However, re-refinement of the original X-ray data indicates that the compound can equally well be formulated as $UEr_2O_2S_3$. Although we have not reexamined the compounds formulated as $(UOS)_4LuS$ [20], whose charge-balance also requires $U^{3.5+}$ in an eight-fold coordination we suspect that

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