

The Ternary $\text{UO}_2\text{-UO}_3\text{-EuO}_{1.5}(\text{EuO})$ System and Investigation of $\text{Eu(II)-Actinide(IV)-Perovskites}$

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At 1250°C, the following single-phase regions have been detected in the $\text{UO}_2\text{-UO}_3\text{-EuO}_{1.5}$ region of the ternary uranium-europium-oxygen system: (a) $\beta\text{-U}_3\text{O}_8$: no solubility for $\text{EuO}_{1.5}$ could be observed. (b) Fluorite phase: The oxygen limiting compositions are $(\text{U, Eu})\text{O}_{2.25}$ and $(\text{U, Eu})\text{O}_{1.79}$, respectively; the range of the stoichiometric composition MO_2 is between UO_2 and $(\text{U}_{0.36}, \text{Eu}_{0.64})\text{O}_2$, a fluorite phase with U(VI) is only obtainable for the substoichiometric region from $(\text{U}_{0.32}, \text{Eu}_{0.68})\text{O}_{1.98}$ to $(\text{U}_{0.24}, \text{Eu}_{0.76})\text{O}_{1.86}$. (c) Rhombohedral phase: It extends from $\text{UO}_3 \cdot 6\text{EuO}_{1.5}$ on the $\text{UO}_3\text{-EuO}_{1.5}$ side of the system to the $0.7\text{UO}_2 \cdot \text{O} \cdot 3\text{EuO}_{1.5} - 0.6\text{UO}_2 \cdot 0.4\text{EuO}_{1.5}$ line on the $\text{UO}_2\text{-EuO}_{1.5}$ side, showing an increased phase width with lowering of the uranium valency. (d) Monoclinic $B\text{-EuO}_{1.5}$: No solubility for UO_{2+x} could be observed. The first lanthanide-actinide perovskite compounds, orthorhombic EuUO_3 , and EuNpO_3 could be prepared by different methods; attempts to prepare similar ternary oxides containing Th(IV), Pu(IV), and Am(IV), however, failed. EMF measurements have proven that cubic $C\text{-EuO}_{1.5}$ is the thermodynamically stable $\text{EuO}_{1.5}$ -modification below $1050 \pm 20^\circ\text{C}$.

1. Introduction

Europium oxide is being considered as a thermal or epithermal "burnable" poison to control reactivity in UO_2 or mixed U-Pu-oxide fuels for nuclear reactors (1). For this purpose sintered $\text{UO}_2\text{-EuO}_{1.5}$ mixed oxides will be used as nuclear fuel; the $\text{EuO}_{1.5}$ addition, however, will not exceed a few percent. Because a large solubility for $\text{EuO}_{1.5}$ in UO_2 has been demonstrated (2), the fuel probably will consist of a single-phase solid solution of $\text{EuO}_{1.5}$ in UO_2 .

Phase equilibria diagrams between uranium and lanthanide oxides have been published for the systems $\text{UO}_2\text{-LaO}_{1.5}\text{-O}_2$ (3, 4), $\text{UO}_2\text{-NdO}_{1.5}\text{-O}_2$ (5), $\text{UO}_2\text{-HoO}_{1.5}\text{-O}_2$, and $\text{UO}_2\text{-LuO}_{1.5}\text{-O}_2$ (6) at 1250°C and for several pseudobinary $\text{UO}_{2+x}\text{-REO}_{1.5}$ -systems at $p(\text{O}_2) = 1 \text{ atm}$ (3, 5-7). The principal difference of the $\text{UO}_2\text{-EuO}_{1.5}\text{-O}_2$ -system compared to other uranium-rare earth-oxygen systems is

the occurrence of stable oxides containing divalent europium.

Investigations dealing with parts of this system have been published (2, 8). The binary $\text{UO}_2\text{-EuO}_{1.5}$ system is a simple eutectic one with an eutectic temperature of $2125 \pm 50^\circ\text{C}$ (2). Extensive solubility of $\text{EuO}_{1.5}$ in the fluorite phase exists, but no solubility of UO_2 in monoclinic $B\text{-EuO}_{1.5}$ was found—in agreement with this work. Contrary to that observation in this study, however, no stabilization of cubic $\text{EuO}_{1.5}$ by the incorporation of UO_2 was observed.

Investigations in (8) have demonstrated the existence of a fluorite phase between 38-64 mol % $\text{EuO}_{1.5}$ under oxidizing conditions at 1100°C. At higher $\text{EuO}_{1.5}$ contents a "lattice-distorted" fluorite phase ranging up to >90 mole % $\text{EuO}_{1.5}$ was observed.

The aim of this investigation was to clarify the phase relationship in the $\text{UO}_2\text{-EuO}_{1.5}\text{-O}_2$ system by using X-ray and high temperature

galvanic cell measurements. Because of the high volatility of europium monoxide at $>1100^{\circ}\text{C}$, no reliable phase equilibria could be established in the $\text{EuO}-\text{EuO}_{1.5}-\text{UO}_2$ part of the $\text{Eu}-\text{U}-\text{O}$ system.

2. Experimental Procedure

Most of the specimen were prepared by sintering coprecipitates " $(\text{NH}_4)_2\text{U}_2\text{O}_7 + \text{Eu}(\text{OH})_3$ " in air at temperatures between 1000 and 1550°C up to several days, the duration of heating depending on temperature and composition. Specimen in the oxygen-poor part of the system were obtained by mixing weighed amounts of UO_2 , U_3O_8 , and $\text{EuO}_{1.5}$ and sintering the mixtures at 1250°C ($\pm 20^{\circ}\text{C}$) for about 2 months in argon-filled quartz tubes. For most specimen preparations, iridium crucibles were used. After being heated, the samples were quenched in liquid nitrogen and analyzed for uranium and oxygen contents by

cerimetric methods. The analytical accuracy for x and y in $(\text{U}_{1-y}, \text{Eu}_y)\text{O}_{2+x}$ is ± 0.02 and ± 0.01 , respectively. The identification of the phases present was done by X-ray diffraction; the determination of the lattice constants was carried out by using computer programs.

The high-temperature galvanic cell measurements were done by using 15 mole% CaO -doped ZrO_2 (Fa. Coppers, Düsseldorf) as oxygen conductors in the form of crucibles. In most cases, the standard oxygen electrode was applied as the second half-cell. For a closer description of the high-temperature galvanic cell, details of the measurements and the evaluation of the measured EMF values, see (4).

3. Results and Discussion

3.1 The $\text{UO}_2-\text{UO}_3-\text{EuO}_{1.5}$ System

X-ray diffraction studies have shown that in the $\text{UO}_2-\text{UO}_3-\text{EuO}_{1.5}$ part of the $\text{U}-\text{Eu}-\text{O}$

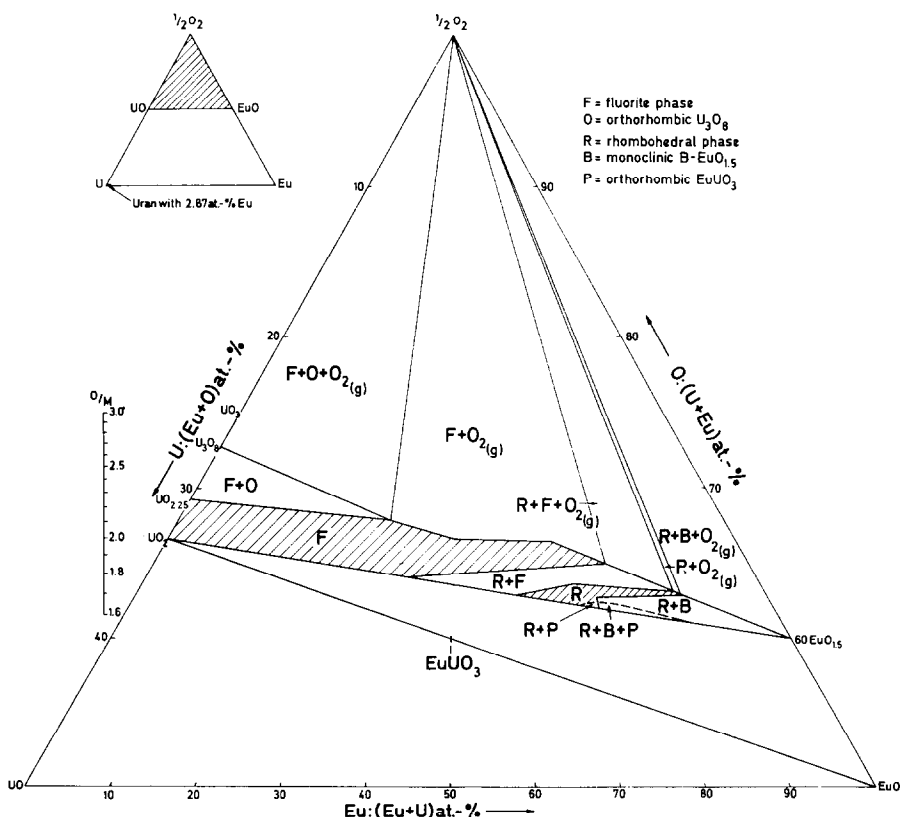


FIG. 1. Phase diagram of the $\text{UO}-\text{EuO}-\frac{1}{2}\text{O}_2$ part of the ternary $\text{U}-\text{Eu}-\frac{1}{2}\text{O}_2$ system at 1250°C .

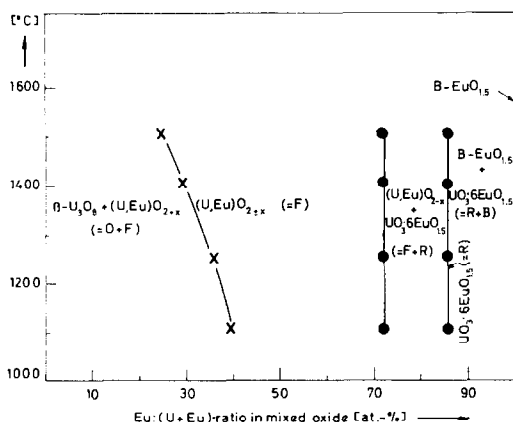


Fig. 2. The quasibinary $\text{UO}_{2+x}\text{-EuO}_{1.5}$ system for $p(\text{O}_2) = 1$ atm.

system at temperatures above 1100°C the following single phase regions exist: (a) $\beta\text{-U}_3\text{O}_8$; (b) a fluorite phase with large phase width; (c) a rhombohedral phase with $\text{UO}_3 \cdot 6\text{EuO}_{1.5}$ as the oxygen- and europium-richest composition; and (d) monoclinic $B\text{-EuO}_{1.5}$.

In contrast to a preliminary publication (9) and to observations in (2), no stabilization of cubic $C\text{-EuO}_{1.5}$ by the incorporation of $\text{UO}_{2(+x)}$ at high temperatures could be observed by closer examination. It was found, however, that solid-state reactions of specimens of $\text{UO}_2\text{-EuO}_{1.5}$, rich in $\text{EuO}_{1.5}$, give rise to the formation of $\text{Eu}^{\text{II}}\text{U}^{\text{IV}}\text{O}_3$, the first lanthanide-actinide perovskite compound to be reported.

Based on the experimental data obtained, the phase diagram of the $\text{UO}_2\text{-UO}_3\text{-EuO}_{1.5}$ part of the U-Eu-O system has been elaborated and is given in Fig. 1. Figure 2 shows the phase relationships in the pseudobinary $\text{UO}_{2+x}\text{-EuO}_{1.5}$ system ($0 \leq x \leq 1$) at an oxygen pressure of $p(\text{O}_2) = 1$ atm.

3.1.1. The $\beta\text{-U}_3\text{O}_8$ phase. No solubility of $\text{EuO}_{1.5}$ in $\beta\text{-U}_3\text{O}_8$ was observed for $1100^\circ\text{C} \leq T \leq 1550^\circ\text{C}$. This finding is based on two facts: (a) No change in lattice constants for $\beta\text{-U}_3\text{O}_8$ was observed in the presence of varying amounts of $\text{EuO}_{1.5}$. (b) The X-ray diagrams of the sintered specimen containing ≤ 0.3 mole % $\text{EuO}_{1.5}$ showed the reflections of monoclinic $B\text{-EuO}_{1.5}$. Based on these obser-

vations an upper solubility limit of 0.1–0.2 mole % $\text{EuO}_{1.5}$ in $\beta\text{-U}_3\text{O}_8$ can be estimated.

3.1.2. The fluorite phase. As may be seen from Figs. 1 and 2, most of the phase diagrams are filled by the cubic fluorite phase. In the pseudobinary system, $\text{UO}_{2+x}\text{-EuO}_{1.5}$, the fluorite phase extends from 39 mole % $\text{EuO}_{1.5}$ at 1100°C to 25 mole % $\text{EuO}_{1.5}$ at 1550°C on the uranium-rich side up to the temperature-independent ($1100\text{--}1550^\circ\text{C}$) value of 72 mole % $\text{EuO}_{1.5}$ on the europium-rich part.

In (8), a phase width of 38–64 mole % $\text{EuO}_{1.5}$ is postulated. While the value on the uranium-rich side of the system agrees well with our data, there is a considerable difference on the europium-rich side. This difference may be explained as follows: The width of the fluorite phase in (8) was elaborated from the linear part of the diagram, in which the lattice constants are plotted versus the composition. Our studies, in contrast, have shown that such an extrapolation is only conclusive for systems without valency changes, e.g., for the $\text{ThO}_2\text{-EuO}_{1.5}$ system, but not for systems in which there is a continuous change from a lattice with oxygen interstitials to a lattice with oxygen vacancies, partly due to changes in the valency states of uranium (10).

The change of lattice constants as a function of composition (Fig. 3) can be explained when

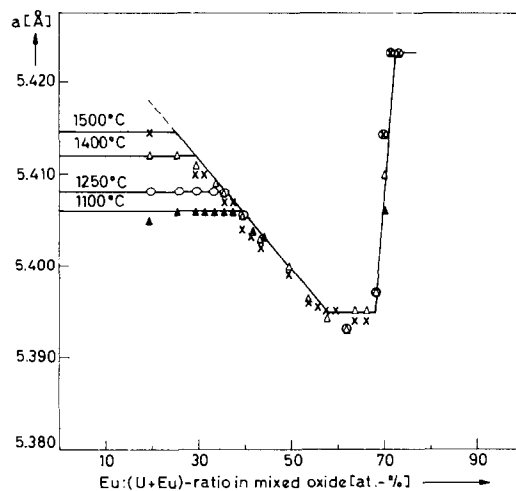


Fig. 3. Change of lattice constants as a function of composition for the $\text{UO}_{2+x}\text{-EuO}_{1.5}$ system at $p(\text{O}_2) = 1$ atm.

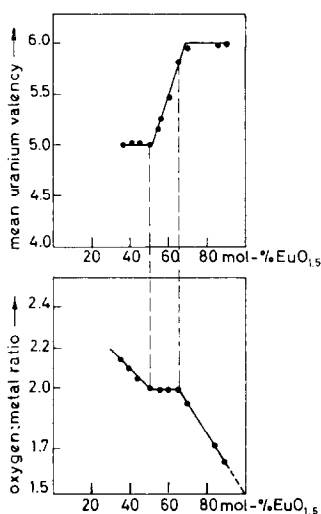


FIG. 4. Mean uranium valency and oxygen to-metal ratio for composition >30 mol% $\text{EuO}_{1.5}$ in the $\text{UO}_{2+x}\text{-EuO}_{1.5}$ -system at $p(\text{O}_2) = 1$ atm.

we also consider the mean valency of uranium and the oxygen-to-metal ratio of the specimen. Up to nearly 50 mol% $\text{EuO}_{1.5}$, the valency of uranium in the fluorite phase is U(V), continuously changing to U(VI), however, when increasing the $\text{EuO}_{1.5}$ content (Fig. 4). For $\text{EuO}_{1.5}$ -contents higher than about 64–67 mole% $\text{EuO}_{1.5}$, all uranium is U(VI). The replacement of the small U^{6+} ion ($r \approx 0.83$ Å for C.N. 6) by the large Eu^{3+} ion ($r = 0.950$ Å for C.N. 6) in this last-mentioned region must lead to an increase in the lattice constants of the specimen in question. (This increase was also observed in (8), but there it was ascribed to a lattice-distorted fluorite phase without closer description). In the region lower in $\text{EuO}_{1.5}$ content (around 60 mole% $\text{EuO}_{1.5}$) we have a replacement of 2U^{5+} by Eu^{3+} and U^{6+} . Because $r(\text{U}^{5+}) \approx \frac{1}{2}[r(\text{Eu}^{3+}) + r(\text{U}^{6+})]$, a change in lattice constants will occur only when the oxygen stoichiometry ($\text{O}:(\text{Eu} + \text{U})$) is changed, but not if there is a completely filled fluorite lattice.

The width of the fluorite phase on both the oxygen-rich and oxygen-poor compositions can be deduced from Fig. 1. The $\text{O}:(\text{U} + \text{Eu})$ value never exceeds 2.25, as in the binary $\text{UO}_{2.25}$. In the $\text{UO}_2\text{-EuO}_{1.5}$ part, the solubility at 1250°C extends to 42 mole% $\text{EuO}_{1.5}$,

corresponding to $(\text{U}_{0.58}, \text{Eu}_{0.42})\text{O}_{1.79}$, a value somewhat lower than that of about 53 mole% $\text{EuO}_{1.5}$ given in (2) for temperatures of about 1600°C . With increasing $\text{O}:\text{U}$ values, this limiting solubility varies as the $\text{EuO}_{1.5}$ content varies. In each case, however, a separation into two phases (fluorite + U_3O_8) occurs when $\text{O}:\text{U} > 2.25$ in the specimen. This led to a very small single-phase region at the $\text{UO}_3\text{-EuO}_{1.5}$ join from 68 to 76 mole% $\text{EuO}_{1.50}$, which excludes the stoichiometric fluorite phase $(\text{U}_{1/3}^{\text{VI}}, \text{Eu}_{2/3}^{\text{III}})\text{O}_2$, known for $RE = \text{La}$ (3) and Nd (5), but not for $RE = \text{Ho}$, Tm , and Lu (6, 11). The limiting stoichiometric composition of the fluorite phase is $(\text{U}_{0.36}, \text{Eu}_{0.64})\text{O}_{2.00}$. The stoichiometric composition $(\text{U}_{0.5}, \text{Eu}_{0.5})\text{O}_{2.00}$ ($a = 5.401$ Å) has been prepared previously (12). According to a neutron diffraction study (13), $(RE_{0.5}, \text{U}_{0.5})\text{O}_2$ ternary oxides ($RE = \text{La}, \text{Nd}, \text{Ho}, \text{Lu}, \text{Y}$) crystallize in the nondistorted cubic fluorite lattice with oxygen on the normal positions, the same must be assumed for $RE = \text{Eu}$. Heating $(\text{U}_{0.5}, \text{Eu}_{0.5})\text{O}_2$ in oxygen at 1 atm to 1250°C results in single-phase $(\text{U}_{0.5}, \text{Eu}_{0.5})\text{O}_{2.02}$ (mean uranium valency $\bar{W}(\text{U}) = 5.08$).

There is no phase change of stoichiometric $(\text{Eu}_{1/2}, \text{U}_{1/2})\text{O}_2 (= \text{EuUO}_4)$ between $1060^\circ\text{K} \leq T \leq 1660^\circ\text{K}$ (6). The molar free enthalpy for a solution of oxygen in EuUO_4 in this temperature region is given by

$$\Delta \bar{G}(\text{O}_2)(T)/\text{kcal} \cdot \text{mole}^{-1} = (-113.6 \pm 2.5) + (57.8 \pm 1.8) \cdot 10^{-3} \cdot T.$$

3.1.3. The rhombohedral phase. Heating $\text{U}:\text{RE} = 1:6$ mixtures ($RE = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Tb}, \text{Ho}, \text{Tm}, \text{Yb}, \text{Lu}, \text{Y}$) in air or oxygen at temperatures above 1000°C results in the formation of rhombohedral compounds $\text{UO}_3 \cdot 6\text{REO}_{1.5}$ (14), the structures of which are closely related to the fluorite type (15). A corresponding compound also could be prepared for $RE = \text{Eu}$ by heating powdered $\text{U}_3\text{O}_8/\text{EuO}_{1.5}$ mixtures (1:18) in flowing oxygen at $1000\text{--}1250^\circ\text{C}$. The lattice constant of the orange colored $\text{UO}_3 \cdot 6\text{EuO}_{1.5}$ (hexagonal parameters $(\pm 0.004$ Å), $a = 10.117$ Å, $c = 9.595$ Å) fits well in the series of isostructural rare-earth compounds.

$\text{UO}_3 \cdot 6\text{EuO}_{1.5}$ does not show any solubility (limit ± 1 mole%) for either UO_3 or $\text{EuO}_{1.5}$.

TABLE I

THERMODYNAMIC DATA FOR MONOPHASIC RHOMBOHEDRAL (U, Eu)O_x-COMPOUNDS (STANDARD VALUES, REFERRED TO THE STANDARD OXYGEN ELECTRODE)

Composition	<i>T</i> (°C)	<i>E</i> ^o (mV)	<i>dE/dT</i> (mV/K)	<i>p</i> (O ₂) (atm)	ΔG^o (kcal/mole)	ΔH^o (kcal/mole)
(U _{0.34} , Eu _{0.66})O _{1.67}	1005	470	-0.09	0.38 ex-07	-43.3	-94.0
	1050	451	-0.09	0.13 ex-06	-41.6	-94.1
	1100	430	-0.09	0.47 ex-06	-39.7	-94.1
	1145	410	-0.09	0.15 ex-05	-37.8	-94.1
	1200	385	-0.09	0.53 ex-05	-93.9	
(U _{0.25} , Eu _{0.75})O _{1.60}	1250	369	-0.09	0.13 ex-04	-34.0	-94.4
	850	490	-0.07	0.16 ex-08	-45.2	-87.3
	900	470	-0.07	0.81 ex-08	-43.3	-87.3
	950	450	-0.07	0.38 ex-07	-41.4	-87.3
	1004	429	-0.07	0.16 ex-06	-39.6	-87.4
	1048	413	-0.07	0.49 ex-06	-38.0	-87.6
	1100	390	-0.07	0.18 ex-05	-36.0	-87.4
	1145	370	-0.07	0.54 ex-05	-34.1	-87.3
	1200	347	-0.07	0.18 ex-04	-32.0	-78.2
UO ₃ ·6EuO _{1.5}	1243	328	-0.07	0.42 ex-04	-30.3	-87.1
	948	400	-0.08	0.28 ex-06	-36.9	-84.5
	1000	378	-0.08	0.10 ex-05	-34.8	-84.1
	1044	357	-0.08	0.34 ex-05	-32.9	-83.9
	1120	327	-0.08	0.19 ex-04	-30.1	-84.1
	1159	315	-0.08	0.36 ex-04	-29.1	-84.6
	1202	293	-0.08	0.97 ex-04	-27.0	-84.2
	1245	277	-0.08	0.21 ex-03	-25.5	-84.3

A phase width, however, is found in the region of lower uranium valency. In contrast to preliminary observations in (9), in which for 1250°C a phase width only has been stated along the composition line UO₃·6EuO_{1.5}-UO₂·2EuO_{1.5}, closer examination revealed a deviation in stoichiometry extending toward the UO₂-EuO_{1.5}-boundary. EMF measurements have proven the single-phase composition UO₃·6EuO_{1.5} for 958°C ≤ *T* ≤ 1245°C, (U_{0.34}, Eu_{0.66})O_{1.67} for 1005°C ≤ *T* ≤ 1250°C, and (U_{0.25}, Eu_{0.75})O_{1.60} for 850°C ≤ *T* ≤ 1243°C. Thermodynamic data calculated from the measured *E* values by using a galvanic cell of the type Pt/(U, Eu)O_x/ZrO₂(CaO)/Fe, FeO/Pt are given in Table I.

It is suggested that the lattice-distorted fluorite phase mentioned in (8) is in fact a not well-crystallized rhombohedral phase or a two-phase mixture of fluorite + rhombohedral phases, respectively.

3.1.4 The EuO_{1.5} phase. Monoclinic *B*-EuO_{1.5} does not take up into solid solution

uranium oxides (limit, 0.2 mole %). This is deduced from either the constancy of the lattice constants of *B*-EuO_{1.5} in the presence of UO_{2+x} (0 ≤ *x* ≤ 1) or from the appearance of the rhombohedral phase in the X-ray diffraction powder diagrams for >0.5 mole % UO_{2+x}.

EMF measurements with a galvanic cell of the type Pt/EuO_{1.5}/ZrO₂(CaO)/O₂ (1 atm)/Pt have clearly shown that cubic *C*-EuO_{1.5} is the thermodynamic stable EuO_{1.5}-modification in the region 800°C ≤ *T* ≤ 1050°C (Fig. 5; 16) and not a topochemically formed metastable modification (17). This is in agreement with data on the enthalpy of formation of europium sesquioxide at room temperature obtained by oxygen bomb and solution calorimetry (18):

$$\Delta H_{298.15K} (C\text{-Eu}_2\text{O}_3 \rightarrow B\text{-Eu}_2\text{O}_3) = - (2.7 \pm 0.3) \text{ kcal mole}^{-1}.$$

Therefore, 1050 ± 20°C is the true transformation temperature *C*-EuO_{1.5} → *B*-EuO_{1.5}. A back-transformation of *B*-EuO_{1.5} into

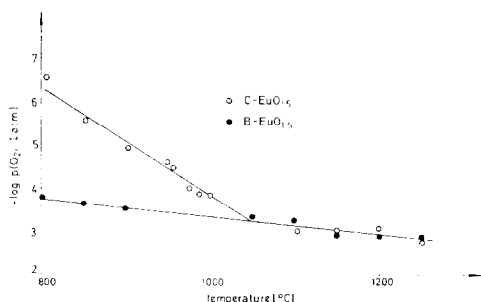
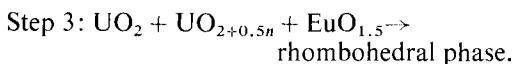
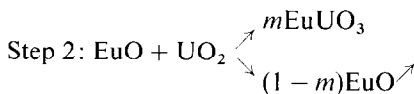
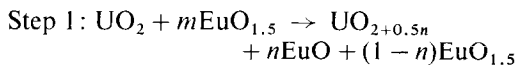


Fig. 5. Oxygen partial pressure of $B\text{-EuO}_{1.5}$ and $C\text{-EuO}_{1.5}$ as deduced from EMF measurements.

$C\text{-EuO}_{1.5}$ below this transformation temperature, however, could not be observed.

3.1.5. EuUO_3 . Indications for a perovskite compound were first obtained by heating $\text{UO}_2 + 70$ mole % $\text{EuO}_{1.5}$ mixtures in evacuated quartz ampoules at 1250°C : The resulting product was either a two-phase mixture of perovskite + rhombohedral phase or a three-phase mixture of perovskite + rhombohedral phase + $B\text{-EuO}_{1.5}$, depending on composition (23). It was also observed that part of the europium monoxide has volatilized to the somewhat cooler part of the ampoules, leading to an increased O:U ratio of the resulting reaction mixture. This observation and a closer examination of the composition of the result-

ing rhombohedral phase leads to the following reaction scheme:



The amount of formation of EuUO_3 or volatilization of EuO (step 2) depends on very specific reaction conditions and could not be kept constant in our experiments. Therefore, more detailed information on the $\text{UO}_2 + \text{EuO}_{1.5}$ reaction, leading in part to the perovskite formation, cannot be given. Furthermore, it is not clear whether EuUO_3 is formed as a thermodynamically stable compound in the $\text{UO}_2\text{-EuO}_{1.5}$ system or the multiphase regions containing EuUO_3 are metastable. However, deduced from the intensity of the X-ray diffraction powder diagrams a change with reaction time of the amount of EuUO_3 formed could not be observed.

Pure EuUO_3 could not be obtained by the earlier-mentioned reaction nor by the following reactions: $\text{UO}_2 + \text{EuO}$, $\text{UO}_2 + \text{EuO}_{1.5} +$

TABLE II

INDEXING OF THE FIRST DIFFRACTION LINES OF ORTHORHOMBIC EuO_3 AND EuNpO_3 ($\text{Cu}_{K\alpha}$ -RADIATION, Ni-FILTERED, Au AS STANDARD)

hkl	EuUO_3		EuNpO_3		Relative intensity
	d (observed)	d (calculated)	d (observed)	d (calculated)	
1 1 0	4.3078	4.3037			Weak
0 0 2	4.3078	4.3037			Weak
0 2 0	3.0805	3.0805	3.0847	3.0722	Medium
1 1 2	3.0435	3.0435	3.0455	3.0334	Very strong
2 0 0	3.0113	3.0074	3.0133	2.9975	Medium
2 2 0	2.1513	2.1522	2.1474	2.1454	Strong
2 2 1	2.0887	2.0878			Very weak
1 3 1	1.8944	1.8952			Very weak
1 3 2	1.7710	1.7710	1.7647	1.7659	Weak
0 2 4	1.7653	1.7640	1.7577	1.7577	Weak
2 0 4	1.7489	1.7502	1.7434	1.7434	Weak
3 1 2	1.7434	1.7434	1.7360	1.7378	Medium

Eu and $\text{UO}_2 + \text{EuO}_{1.5} + \text{U}$ (1000–1250°C, flowing hydrogen or evacuated quartz ampoules). In most cases a more or less large part of the EuO had volatilized at temperatures higher than 1100°C, whereas at lower temperatures only products with broad X-ray diffraction peaks have been obtained—even after a reaction time of several weeks. The best preparations consisted of about 75–90% of EuUO_3 .

The X-ray diffraction powder pattern of EuUO_3 could be indexed on the basis of an orthorhombic cell, corresponding to the orthorhombic interlanthanide $A^{III}B^{III}\text{O}_3$ perovskites (19) with lattice constants of $a = 6.020 \pm 0.003 \text{ \AA}$, $b = 6.165 \pm 0.003 \text{ \AA}$, and $c = 8.616 \pm 0.004 \text{ \AA}$. The indexing of the first 12 diffraction peaks of EuUO_3 is given in Table II. Because there is no change of lattice constants of EuUO_3 in the presence of $\text{UO}_{2(x)}$ and $\text{EuO}_{1.5}$, it is suggested that there is no solubility for these oxides in the perovskite. After having concluded this investigation, the preparation of EuUO_3 was published in (24). The authors of (24), however, also could not prepare pure EuUO_3 nor were they able to establish the structure and the lattice parameters of EuUO_3 .

3.2. Other Lanthanide-Actinide Perovskites

No $A^{III}B^{III}\text{O}_3$ lanthanide-actinide perovskites could be obtained, the only possible candidates being Ac^{3+} -compounds with the heavy lanthanides and La^{3+} (Ce^{3+} , Pr^{3+} . . .)-compounds with the heavy actinides which, at present, cannot be prepared in weighable amounts. Therefore, $A^{II}B^{IV}\text{O}_3$ compounds may be the only easily obtainable lanthanide-actinide perovskites, of which EuUO_3 is the first example.

Attempts to prepare the corresponding Th-compound by the previously mentioned reactions failed—in contrast to suggestions in (24). This may be expected because of the nonexistence of “ SrThO_3 ” (20) and the very similar crystallographic behavior of Eu(II) and Sr(II). The existence of “ SrThO_3 ” in (24) was based on data in (25), which could not be proved in later investigations. $\text{Eu}^{II}\text{Np}^{IV}\text{O}_3$ was obtained by solid-state reaction of $\text{EuO} + \text{NpO}_2$ in an evacuated quartz ampoule at

1200°C for 20d; at 1100°C only specimens with very broad diffraction lines were obtained. Attempts to prepare EuNpO_3 by reaction of Eu-metal, $\text{EuO}_{1.5}$, and NpO_2 resulted only in the formation of a fluorite phase (solid solution of $\text{EuO}_{1.5}$ in NpO_2) and some EuO, which volatilized. The brown EuNpO_3 crystallizes in the same orthorhombic structure, as does EuUO_3 , the lattice constants of EuNpO_3 being $a = 6.001 \pm 0.008 \text{ \AA}$, $b = 6.150 \pm 0.008 \text{ \AA}$, and $c = 8.579 \pm 0.012 \text{ \AA}$ (for indexing, see Table II).

The corresponding compounds of Pu(IV) and Am(IV) also could not be prepared. The reaction of EuO and PuO_2 at 1100/1250°C (3 weeks) in an evacuated ampoule led to the formation of two cubic phases with lattice constants of $a = 5.41 \text{ \AA}$ and $a = 10.98 \text{ \AA}$, respectively. The first one is believed to be a solid solution of EuO in PuO_2 ; similar to the SrO– ThO_2 system (20), the solubility of EuO in PuO_2 should not exceed a few mole percent. The second one is a solid solution of the $\text{PuO}_{1.5+x}$ – $\text{EuO}_{1.5}$ system (Pu_{1-y} , Eu_y) $\text{O}_{1.5+x}$ ($x \leq 0.5$). Such a solid-state redox reaction $\text{Eu}^{2+} + \text{Pu}^{4+} \rightleftharpoons \text{Eu}^{3+} + \text{Pu}^{3+}$ seems possible when considering the redox potentials (measured in solution, however: 21). A PuO_2 – $\text{EuO}_{1.5}$ solid solution can be excluded, however, because an oxidation of the probes was strictly avoided and the lattice constant of the samples is higher than those of PuO_2 ($a = 5.396 \text{ \AA}$; 10) and C– $\text{EuO}_{1.5}$ ($a = 10.866 \text{ \AA}$; 22), which is impossible for a system with lattice constants that probably follow Vegard's rule because no change in oxidation state occurs under the experimental conditions.

In the corresponding americium system, a solid solution of cubic C–($\text{Eu}_{0.5}$, $\text{Am}_{0.5}$) $\text{O}_{1.5}$ was also obtained instead of a perovskite compound.

The only further candidate for Eu(II)–actinide(IV) perovskites, therefore, is the Pa(IV)-compound, the preparation of which was not attempted during this study.

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