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Studies of the Europium–Oxygen–Fluorine and Samarium–Oxygen–Fluorine Systems*

R. G. BEDFORD AND E. CATALANO

Lawrence Radiation Laboratory, University of California, Livermore, California 94550

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A portion of the ternary system Eu–Eu_2O_3–EuF_3 has been investigated by equilibrating EuO–EuF_3 and EuO–EuF_2 mixtures at 1500°C and examining the products with a polarizing microscope and by X-ray diffraction. The composition at the liquid–solid boundary was not measured directly, but has been estimated. A phase diagram is presented for that part of the system studied. No ternary compounds are formed with europium in an oxidation state lower than +3 in samples cooled from 1500°C.

Several compositions of the Eu_2O_3–EuF_3 and Sm_2O_3–SmF_3 binary systems were examined using differential thermal analysis and X-ray powder diffraction. In these systems, at least one intermediate phase (and probably two or more) in addition to LnOF is stable. These additional phases all lie on the fluoride side of LnOF. At temperatures above 600°C, solid solutions extend from approximately $LnO_{0.8}F_{1.4}$ to $LnO_{0.6}F_{1.8}$.

1. Introduction

A few years ago we observed anomalous magnetic behavior in EuF_2 which was associated with trace impurities in the single crystals (*1*). The magnetic and optical properties of the inclusions in the EuF_2 crystals did not appear to correspond to any known europium compound. This prompted us to investigate the Eu–EuF_3–Eu_2O_3 system in an attempt to identify the impurity, since oxygen seemed to be the most probable contaminant. The EuF_2–EuF_3 and the EuO–Eu_2O_3 binary systems have been described in detail elsewhere (*2–5*).

Bevan et al. (*6*) have discussed the lanthanon oxyfluorides and reviewed the literature on these systems. Oxyfluorides have been reported for all the lanthanon (Ln) elements and yttrium, and the structure for the stoichiometric MOF compounds of these elements at room temperature for all but Ce, Tm, Yb, and Lu seems to be established as the rhombohedral LaOF-type described by Zachariasen (*7*) for LaOF and YOF (*6–15*). For La and Y, Zachariasen (*7*) found tetragonal solid solutions $MO_{1-x}F_{1+2x}$ $(0.0 < x < 0.3)$ in addition to the stoichiometric rhombohedral LaOF and YOF. Bevan et al. (*6*) have shown that for the Y, Sm, Gd, and Er oxyfluorides, the composition region between the stoichiometric MOF and the trifluoride is much more complicated than previously assumed. A report of the continuing investigation of the intermediate composition region and the transition of stoichiometric LnOF from rhombohedral to cubic (fluorite) for La, Nd, Sm, and Gd has been given by Brauer and Roether (*14*). Recently, Shinn and Eick (*15*) have published a paper on the rhombohedral-to-cubic transition for MOF compounds (M = La, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, and Y).

Detailed investigation of the phase relationships in the extremely complex oxyfluoride systems was not attempted here since we were primarily interested in the possible existence of a compound containing europium in the divalent state. However, differential thermal analysis (DTA) and Debye–Scherrer X-ray powder diffraction studies were made for several compositions in the EuF_3–Eu_2O_3 system. These studies provide evidence for previously unknown oxyfluoride phases of Eu(III), supporting the findings of Bevan, Brauer and co-workers (*6, 14*) that the region between stoichiometric MOF and the trifluorides for lanthanon elements contains a number of discrete phases which undergo transitions or disproportionation reactions on heating. Similar studies were attempted with the analogous samarium system, but useful quantitative information was obtained only for stoichiometric SmOF.

Our present study found no evidence for a ternary

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compound in the Eu–EuF_3–Eu_2O_3 system with europium in an oxidation state lower than +3. The only phase in this system which resembles in any respect the impurities in the EuF_2 crystals of Ref. (*1*) is Eu_3O_4. The color and structure of Eu_3O_4 are consistent but the magnetic properties do not correspond to those of the impurity material. Recently, Shafer and Kuptsis (*16*) have published convincing evidence that the impurity in EuF_2 which was responsible for the anomalous magnetic behavior observed in Ref. (*1*) and other work was a sulfide of europium, concluding that it was EuS. We had rejected EuS as a candidate because neither the optical nor the magnetic properties of ordinary EuS correspond to those of the magnetic inclusions. Ordinary EuS is isotropic (cubic, NaCl type), and the inclusions were birefringent. The magnetic ordering temperature of EuS is about 3°K, or 15% lower than that of the inclusion material.

2. The EuF_2–EuO System

EuF_2 was prepared by hydrogen reduction of EuF_3 in a molybdenum container. EuO was made by reduction of Eu_2O_3 by Eu in a sealed Mo capsule. These materials are more fully described in Refs. (*2*) and (*5*).

Mixtures of EuO and EuF_2* were sealed in molybdenum capsules by electron bombardment welding (EBW). The samples were heated to 1500°C in a vacuum induction furnace, held at that temperature for at least 2 hr and cooled quickly by turning off the power and introducing argon or helium. About 2 min were required for the temperature to fall below 750°C. The resulting products were examined by X-ray powder diffraction and optical microscopy.

All the EuF_2–EuO mixtures had completely melted. Microscopic examination of the products showed the composition 0.4 EuF_2–0.6 EuO to be very near the eutectic. Samples with larger proportions of EuF_2 showed the eutectic structure in a matrix of EuF_2. X-ray analysis showed the products of all of these runs to be EuO (cubic, NaCl type), $a = 5.14_4$ Å and EuF_2 (fcc, fluorite), $a = 5.84_3$ Å.

3. The EuF_3–Eu_2O_3 and SmF_3–Sm_2O_3 Systems

Mixtures of EuF_3 and Eu_2O_3 or SmF_3 and Sm_2O_3 were sealed in platinum–10% rhodium capsules by EBW and heated to 1500°C in an induction furnace. The products were crushed and resealed in Pt–10Rh capsules, again heated to 1500°C for 2 hr and rapidly cooled by turning off the furnace power. Starting materials were nominal 99.9% oxides and trifluorides which had been heated in air or under HF, respectively, to reduce contamination and stored in desiccators (*2*, *5*).

Samples from the above preparations were examined by X-ray powder diffraction, optical microscopy, and DTA. A description of the DTA apparatus and procedures is given in Ref. (*3*). Samples of approximately 0.4 g for DTA were encapsulated in Pt–10Rh containers by EBW at $\sim 10^{-5}$ Torr. Measurements were made at heating rates of 10°C min^{-1} from 200 to 1500°C.

Our observations on EuF_3–Eu_2O_3 and SmF_3–Sm_2O_3 are insufficient to provide a complete understanding of these systems. Seven compositions in each system were studied. Optical examination did not provide useful information because of the similarity of the appearance of all phases under either unpolarized or polarized light. Refractive index measurements would be required to distinguish between the various phases. Since DTA measurements were limited to temperatures below 1500°C, melting was observed only for compositions rich in trifluorides. However, we did observe a number of effects which may help to provide a better understanding of these systems. A summary of our observations and interpretations is given in Table I, and a tentative phase diagram for the Eu_2O_3–EuF_3 system is presented in Fig. 1. Other possible phase diagrams are consistent with the observations. The drawing is presented primarily to describe the general behavior of the binary system and to define assumptions used in interpreting the Eu–EuF_3–Eu_2O_3 ternary system.

Reversible thermal effects were observed beginning at 501°C for SmOF and at 503°C for EuOF (Table I). The temperatures for these effects are in good agreement with those reported by Brauer (*14*) for the rhombohedral-cubic transitions in oxyfluorides of La, Nd, Sm, and Gd. Brauer found these transitions in the range 450–550°C with the value for SmOF close to 500°C. Shinn and Eick (*15*) report rhombohedral-cubic transitions at 524°C. Shinn and Eick apparently reported peak maxima rather than temperatures corresponding to the initiation of transitions on heating, which may account for some of the discrepancy between our results and theirs. During the preparations and DTA experiments with the europium oxyfluorides, and to a lesser degree with the samarium oxyfluorides, our sealed platinum alloy capsules bulged slightly after being heated to 1500°C, indicating that partial decomposition occurred at high temperatures. The free volume in our containers was sufficient to contain an amount

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* The compositions are plotted in Fig. 2.

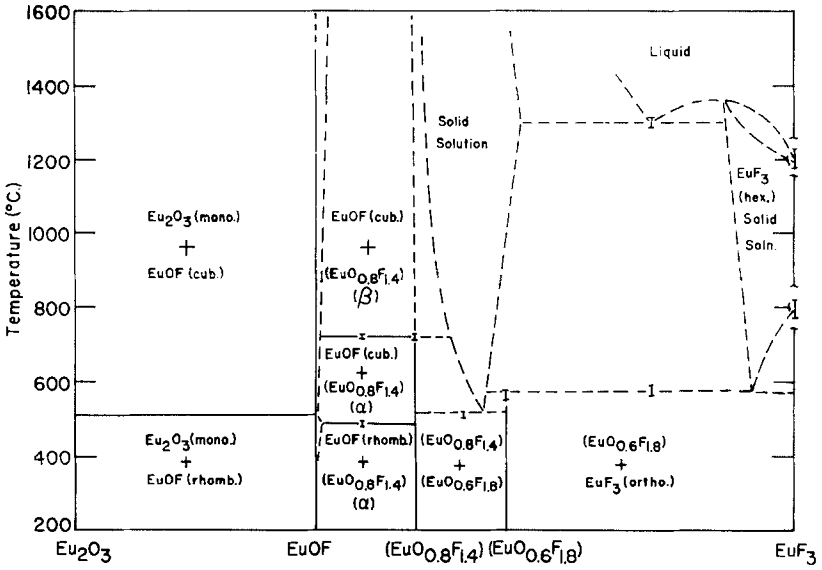

FIG. 1. A tentative phase diagram of the binary system Eu_2O_3–EuF_3.

of gaseous decomposition product at 10 atm that would correspond to about 1 mol% of the oxyfluoride sample. (The capsules would probably have developed leaks if the internal pressures exceeded 10 atm.) Small differences between the stoichiometries of the samples used, particularly regarding possible oxygen deficiency in our materials, also could contribute to the difference between our results and those of Shinn and Eick.

Despite the higher heating and cooling rates used in our experiments, the hysteresis we observed was only about 5° for SmOF and 10° for EuOF, compared with the 20° reported as typical by Shinn and Eick. The thermal effect beginning at 481°C in the sample with composition $EuO_{0.9}F_{1.2}$ is probably due to the rhombohedral-cubic transition in EuOF, lowered in temperature by solution of fluoride.

X-ray analyses indicated that except for the

TABLE I

X-RAY AND DTA RESULTS FOR THE Eu_2O_3–EuF_3 SYSTEM AND SmOF

Composition	X-ray powder diffraction analysis of products	DTA results	
		Temperature range (°C)	Peak height[a]
EuOF	EuOF (rhomb)	503–505	5.3
$EuO_{0.9}F_{1.2}$	EuOF (rhomb) + wk lines	481–498	1.8
		718–734	1.5
$Eu_{0.8}F_{1.4}$	EuOF (rhomb) + wk lines	721–734	4.1
$EuO_{0.7}F_{1.6}$	EuOF (rhomb) + EuF_3 (orth)	505–522	1.0
$EuO_{0.6}F_{1.8}$	EuOF (rhomb) + EuF_3 (orth) + wk lines	553–578	0.7
$EuO_{0.3}F_{2.4}$	EuF_3 (orth) + wk lines	568–588	(0.5)[b]
		1293–1315	8.8
EuF_3	EuF_3 (orth)	776–806	~3
		1180–1258	21.9
SmOF	SmOF (rhomb)	501–508	7.7

[a] Peak heights normalized to average sample size of 0.4 g, assuming peak height directly proportional to mass of sample.

[b] Peak detectable only on cooling.

sample of stoichiometric SmOF, the samarium oxyfluoride mixtures did not reach equilibrium. Samples with compositions $SmO_{0.9}F_{1.2}$, $SmO_{0.8}F_{1.4}$ and $SmO_{0.7}F_{1.6}$ appeared to be mixtures of SmOF (rhombohedral) + Sm_2O_3 (bcc) after heating at 1500°C as described above. Samples of $SmO_{0.6}F_{1.8}$, and $SmO_{0.3}F_{2.4}$ appeared to be mixtures of SmOF (rhombohedral) and SmF_3 (orthorhombic). We observed thermal effects in these samples which were similar to those seen in the europium oxyfluorides but with lower intensities, wider temperature ranges, and more hysteresis. In the samarium oxyfluoride mixtures, we did not observe an effect corresponding to the peaks at 720°C in $EuO_{0.9}F_{1.2}$ and $EuO_{0.8}F_{1.4}$. Failure to achieve equilibrium in the samarium oxyfluoride system is not surprising. Bevan et al. (*6*) found that several hours of annealing were needed to prepare the fluorine-rich phases they identified.

The europium oxyfluoride system was apparently better behaved than the corresponding samarium system, although it is possible that the effects observed in both systems correspond to metastable equilibria. Observation of the thermal effect at 720°C for $EuO_{0.9}F_{1.2}$ and $EuO_{0.8}F_{1.4}$ and the absence of the rhombohedral-cubic transition in $EuO_{0.8}F_{1.4}$ implies the existence of an intermediate compound such as that reported by Brauer (*14*) for the samarium oxyfluoride system. The thermal effect at 1293°C for $EuO_{0.3}F_{2.4}$ was due to melting, as confirmed by visual inspection of samples heated to 1500°C in sealed Pt–10Rh containers before being loaded into the DTA capsules. The $SmO_{0.3}F_{2.4}$ sample also was completely melted at 1500°C. None of the other samples showed any evidence of even partial melting after being heated to 1500°C. The small temperature range of the thermal effect indicates that the eutectic composition lies very close to $EuO_{0.3}F_{2.4}$.

The disappearance of the thermal effect corresponding to the rhombohedral-to-cubic transition of the stoichiometric oxyfluorides in samples of higher fluoride concentration is at variance with X-ray results indicating the presence of LnOF (rhombohedral) at room temperature for all compositions down to $LnO_{0.6}F_{1.8}$ in both the samarium and europium systems. A possible explanation for this discrepancy is that phases identified as SmOF (rhombohedral) and EuOF (rhombohedral) in the fluoride-rich samples were actually compounds with closely related structures in the composition range $LnO_{0.9}F_{1.2}$–$LnO_{0.6}F_{1.8}$. The structures of all of these phases reported by Brauer (*14*) are closely related to the fluorite structure. Our specimens could also be composed of phases quenched in from solid solution regions at higher temperatures.

An attempt to prepare an oxyfluoride Eu_3O_4F analogous to the phase Eu_3O_4Br reported by Bärnighausen (*4*) was unsuccessful. A sample of this composition prepared from EuF_3 plus Eu_2O_3 yielded EuOF (rhombohedral) plus Eu_2O_3 (bcc, $a = 10.86_9$ Å) when annealed at 1500°C and quickly cooled. In only four cases have we seen Eu_2O_3 in the cubic form after being heated above 1300°C: In this preparation, in a ternary mixture described in Table II, and in the products of two preliminary runs in which mixtures of EuO + EuF_3 and EuF_2 + EuF_3 + Eu_2O_3 were heated to 1800° in tantalum containers, cooled slowly to 1500°C, and then quenched. The products of the runs in tantalum were $EuF_{2.26}$ (fcc, $a = 5.80_5$ Å) + Eu_2O_3 (bcc). These results have not been included in the discussion of the ternary system because the samples reacted with the tantalum containers.

The similarity between the oxyfluoride systems and the reduced fluoride systems is worthy of some attention. Solid solutions and nonstoichiometric compounds in both the $LnO_{1-x}F_{1+2x}$ $(0 \leqslant x \leqslant 0.4)$ (*6, 7, 14*) and the LnF_{2+x} $(0 \leqslant x \leqslant 0.45)$ (*2, 3*) systems have structures based on an fcc fluorite lattice. The predominant lattice defects in a number of nonstoichiometric oxides, fluorides, and oxyfluorides based on the fluorite structures are interstitial anions or anion vacancies (*17*). Interstitial anions have been shown to be the primary lattice defect in several such solid solutions involving a lanthanon trifluoride in a difluoride or an oxyfluoride (*2, 17–20*). The cation sublattice in these systems is essentially ideal.

Because of the energy involved in anion–cation separation, it is unlikely that configurations which do not satisfy local charge compensation will be significant in these systems. In LnOF (fluorite), the oxide and fluoride ions are randomly distributed on the anion lattice sites, satisfying the condition that unit cells with excess oxide ions contain corresponding anion vacancies and cells with excess fluoride ions contain corresponding interstitial ions. For solid solutions containing excess LnF_3 which have either the fluorite or a closely related structure, the extra fluoride ions are introduced as pairs, one substituting for an oxide ion and the other as an associated interstitial ion. Changes in structure involving ordering of these "defects" require interdiffusion of the anions. As pointed out by Brauer (*14*), dimorphic transitions become more difficult in these systems as the interstitial sites are filled.

In the reduced fluoride systems with compositions

TABLE II

ANALYSIS OF COMPOSITIONS IN THE TENRARY SYSTEM Eu–Eu_2O_3–EuF_3 PREPARED BY EQUILIBRATING EuO–EuF_3 MIXTURES AT 1500°C

			X-ray powder pattern observations (with intensity and quality)*					
			fcc fluoride phase†			Additional phases‡		
Mol ratio EuO/EuF_3	Optical observations (transmitted light)	X-ray sample No.	Lattice parameter-Å	Pattern	Composition-EuF_{2+x}	Pattern	Composition	Comments
2.70§	1st phase dark red, transparent, and brightly birefringent **(Eu_3O_4)**	1	5.84_0	s, g	$EuF_{2.00}$	s, g m, f	EuO Eu_3O_4	—
	2nd phase colorless, transparent, and non-birefringent **(EuF_{2+x})**	2	5.80_5	m, p	$EuF_{2.26}$	s, g s, g	EuO Eu_3O_4	—
	3rd phase opaque **(EuO)** (1st phase is major component; 2nd phase minor; 3rd phase very small amounts.)							
2.33§	1st phase dark red, transparent, and brightly birefringent **(Eu_3O_4)** 2nd phase colorless, transparent, and non-birefringent **(EuF_{2+x})** 3rd phase colorless, transparent, and brightly birefringent (1st and 2nd phases about equal in amount; 3rd phase very small amounts.)	1	5.83_8	s, g	$EuF_{2.02}$	w, p	Eu_3O_4	—
1.86§	Same as previous sample	1	5.83_8	s, g	$EuF_{2.02}$	m, f	Eu_3O_4	—
1.50§	1st phase colorless, transparent, and non-birefringent **(EuF_{2+x})**	1	5.83_8	s, g	$EuF_{2.02}$	s, g	Eu_2O_3 (monoclinic) + additional weak lines, possibly EuOF	—
	2nd phase light tan, transparent, with mosaic-like birefringence (Both phases about equal in amount.)	2	5.84_0	s, g	$EuF_{2.00}$	s, g	Eu_2O_3 (monoclinic)	—
1.50§§	1st phase light tan, transparent, and non-birefringent **(EuF_{2+x})**	1	5.80_5	s, g	$EuF_{2.26}$	m, f	Eu_2O_3 (bcc)	Cooled slowly, see discussion under section 3.
	2nd phase colorless, transparent, and brightly birefringent							
1.22§	1st phase light tan, transparent, with mosaic-like birefringence	1	5.83_8	s, g	$EuF_{2.02}$	w, p	EuOF + several extra weak lines	
	2nd phase colorless, transparent, and non-birefringent **(EuF_{2+x})** (1st phase is major component.)	2	5.80_5	s, g	$EuF_{2.26}$	s, g	EuOF + several extra weak lines	

TABLE II (*continued*)

Mol ratio EuO/EuF$_3$	Optical observations (transmitted light)	X-ray sample No.	X-ray powder pattern observations (with intensity and quality)*					
			fcc fluoride phase†			Additional phases‡		
			Lattice parameter-Å	Pattern	Composition-EuF$_{2+x}$	Pattern	Composition	Comments
1.00§	1st phase tan, transparent, and none-birefringent **(EuF$_{2+x}$)** 2nd phase colorless, transparent, and birefringent	1	5.80$_5$	m, f	EuF$_{2.26}$	s, g	EuOF	—
		2	5.83$_0$	s, g	EuF$_{2.09}$	w, p	EuOF	—
		3	5.81$_4$	s, g	EuF$_{2.20}$	s, g	EuOF	—
0.825§§	1st phase colorless, transparent, and non-birefringent **(EuF$_{2+x}$)** 2nd phase light tan, transparent, and birefringent (Both phases about equal in amount.)	1	5.79$_5$	s, g	EuF$_{2.27}$	s, g	EuOF	—
0.818§	Same as previous sample but with opaque metallic inclusions (Mo contamination)	1	5.78$_3$	m, f	EuF$_{2.28-2.43}$	s, g	EuOF	Interior of crucible corroded
0.667§§	1st phase colorless, transparent, and brightly birefringent 2nd phase tan, transparent with some optical density, and birefringent	1	5.78$_3$	s, g	EuF$_{2.28-2.43}$	(Patterns very similar to EuOF)		
0.667§	Same as previous sample but with opaque metallic inclusions (Mo contamination)	1	5.78$_3$	m, f	EuF$_{2.28-2.43}$	m, f	EuOF	Interior of crucible corroded
0.400§§	At least two colorless, transparent phases, with some birefringence	1	5.78$_2$	s, g	EuF$_{2.28-2.43}$	(Patterns similar to EuOF but with different lattice parameters.)		(Sample perhaps not completely melted
0.389§§	1st phase brown, transparent, and weakly birefringent 2nd phase colorless, transparent, and and non-birefringent	1	5.78$_3$	s, g	EuF$_{2.28-2.43}$	(Several unidentified lines)		Cooled slowly

*Powder pattern observations rated as follows:
s - strong; m - medium; w - weak; g - good; f - fair; p - poor

†EuF$_{2+x}$ solid solution; compositions derived from lattice parameter, Ref. [2].

‡Phases identified from patterns corresponding to the following structures:

EuO (fcc)—a = 5.14$_5$ Å

Eu$_3$O$_4$ (orthorhombic)—a = 10.09 Å; b = 12.07 Å; c = 3.50 Å

Eu$_2$O$_3$ (monoclinic)—a = 14.04 Å; b = 3.68 Å; c = 8.74 Å; β = 100° 7'

Eu$_2$O$_3$ (bcc)—a = 10.86$_9$ Å

EuOF (rhombohedral, hexagonal representation)—a = 3.88$_4$ Å; c = 19.34$_5$ Å

§Container: Mo

§§Container: Pt-10%Rh

LnF_{2+x}, the excess F^- ions are introduced as associated pairs of interstitial F^- ions and trivalent cations. Phase changes in these systems should occur more readily because they require only local rearrangements of anions and electron transfers. In fact, the manifestation of this behavior is observed in the difference between DTA thermograms for the difluoride–trifluoride (*3*), and the oxide–fluoride systems. The hysteresis for nonstoichiometric samples is much more pronounced for the oxyfluoride material.

4. The Ternary System in the Region Bounded by the Composition EuF_2–EuF_3–Eu_2O_3–EuO

Compositions within the ternary field were prepared by equilibrating mixtures of EuF_3 and EuO. The mixtures were encapsulated in either Mo or Pt–10Rh crucibles and sealed by EBW. Starting materials were the EuF_3 and EuO already described. Molybdenum crucibles were used for mixtures for which the EuO/EuF_3 mole ratio exceeded 0.67 and Pt–10Rh crucibles for mixtures with EuO/EuF_3 mole ratios of 1.5 or less. Several intermediate compositions were heated in both kinds of containers. The samples were held at 1500°C in an induction furnace for at least 2 hr before being cooled rapidly. Two samples were cooled slowly after annealing at 1500°C.

The products of the equilibrated mixtures of EuF_3 and EuO were examined by X-ray powder diffraction and optical microscopic techniques. (See Table II).

Optical identification of EuO and Eu_3O_4 is unambiguous because no other phases in this system appear similar to either of these materials. Fluorides on the divalent side of $EuF_{2.1}$ are transparent, nearly colorless, and nonbirefringent. Fluorides from $EuF_{2.1}$ to $EuF_{2.3}$ are transparent, light brownish-yellow, and weakly birefringent. Compositions from $EuF_{2.3}$ to EuF_3 are transparent, nearly colorless, and brightly birefringent (*2*). It is difficult to detect small concentrations of EuO in Eu_3O_4 or of EuF_{2+x} in one of the other transparent colorless phases. It is not possible to distinguish between EuF_3, EuOF, and Eu_2O_3 without using more sophisticated techniques than those applied in this study. However, very small amounts of EuO can be detected in phases other than Eu_3O_4. It is also easy to detect very small amounts of one of the trivalent species or of Eu_3O_4 in any of the other phases.

The compositions of the fluorides found in the products were obtained from X-ray lattice parameters using data reported in Ref. (*2*). In a number of runs, microscopic examination indicated the presence of more than one fluoride composition. For these cases, X-ray powder diffraction patterns were taken for several samples. The X-ray data confirmed that two different fluoride compositions were present in some of the products, and three fluoride compositions were found in one sample. The composition of crystalline products in rapidly cooled samples depends upon the phase boundary surfaces in the system and the crystallization paths. Since our samples were cooled rapidly, equilibrium was not necessarily maintained, and more than three phases were found in some of the products.

The interpretation most consistent with the ternary equilibration data, the Eu_2O_3–EuF_3 pseudobinary shown in Fig. 1, and the EuO–Eu_2O_3 binary system (*4*, *5*) is illustrated in Fig. 2.

5. Conclusions

The ternary equilibria in the Eu–O–F systems are well-established at 1500°C, with the following exceptions. The number, compositions, and structures of the oxyfluoride phases in the range ~$EuO_{0.6}F_{1.8}$–

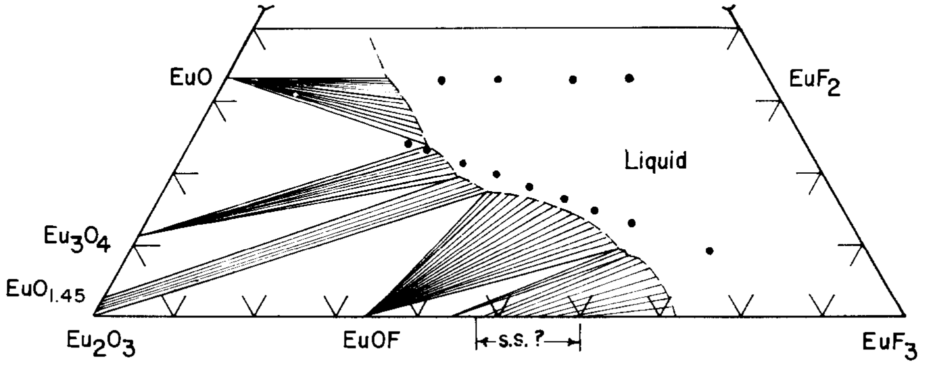

FIG. 2. A section of the ternary system Eu–Eu_2O_3–EuF_3 at 1500°C. Data points correspond to the compositions listed in Table II and sample EuO–EuF_2 mixtures.

$EuO_{0.8}F_{1.2}$ are uncertain. The phase diagram (Fig. 2) is drawn on the assumption that the EuF_3–Eu_2O_3 system is binary and correctly represented in Fig. 1. The liquidus points on the EuF_3–Eu_2O_3 and EuF_2–EuO joins can be estimated with fair reliability, but the liquid–solid phase boundaries in the intermediate region are pure speculation. The products of the EuF_3–EuO reactions all appeared to have been completely melted; but since the samples were not crushed and reheated nor analyzed by DTA, the possibility that some of these compositions could have been only partially liquid at 1500°C cannot be excluded. The diagram is drawn as if there were only one liquid phase, but there is no direct evidence for this interpretation. A miscibility gap may exist between anion-rich and metal-rich liquids similar to the gaps found in other lanthanon–lanthanon-halide systems (*21–27*). The region of the system on the metal-rich side of EuO–EuF_2 has not been investigated.

There is clearly no evidence for a ternary compound in this system other than those between EuF_3 and Eu_2O_3. It is possible that one or more other ternary compounds may exist, but we think this unlikely as no such phase was evidenced in any of the preparations—neither in those cooled rapidly nor in those cooled slowly.

The optical and X-ray properties of the three oxide phases prepared in the presence of fluorides are identical to those observed for samples in which no fluoride was present. Also, the properties of the fluorides formed in the presence of oxides or oxyfluorides are identical to those of fluorides for which analysis indicates negligible oxygen content. Therefore, we believe that the solubility of fluorides in any of the oxide phases or of oxide in the fluorides is very small in the crystalline state. Since there were no color changes in the oxyfluoride samples equilibrated with reduced fluorides similar to the color changes observed when lanthanon sesquioxides are partially reduced (*5*, *28*), partially reduced or anion-deficient lanthanon oxyfluorides may not be stable. One would have expected to observe partially reduced solid solutions based on the fluorite structure with anion vacancies, particularly in the europium oxyfluoride system.

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References

1. K. Lee, H. Muir, and E. Catalano, *J. Phys. Chem. Solids* **26**, 523 (1965).
2. E. Catalano, R. G. Bedford, V. G. Silveira, and H. H. Wickman, *J. Phys. Chem. Solids* **30**, 1613 (1969).
3. R. G. Bedford and E. Catalano, Phase diagrams of the SmF_2–SmF_3, EuF_2–EuF_3, and YbF_2–YbF_3 systems, *in* "Proc. 8th Rare Earth Research Conf.," Reno, Nev., 1970 (availability restricted to attendees).
4. H. Bärnighausen, *J. Prakt. Chem.* **34**, 1 (1966).
5. R. G. Bedford and E. Catalano, An Investigation of the Eu–Eu_2O_3 system and the equilibria between the europium oxides and the Eu–Pt system, with related studies of the Sm–Sm_2O_3 and the Yb–Yb_2O_3 systems, submitted for publication.
6. D. J. M. Bevan, R. S. Cameron, A. W. Mann, G. Brauer, and A. Roether, *Inorg. Nucl. Chem. Lett.* **4**, 241 (1968).
7. W. H. Zachariasen, *Acta Crystallogr.* **4**, 231 (1951).
8. N. C. Baenziger, J. R. Holden, G. E. Knudsen, and A. I. Popov, *J. Amer. Chem. Soc.* **76**, 4734 (1954).
9. D. H. Templeton and C. H. Dauben, *J. Amer. Chem. Soc.* **76**, 5237 (1954).
10. K. S. Vorres and R. Riviello, "Proc. 4th Rare Earth Research Conf.," Phoenix, Ariz., 1964 (L. Eyring, ed.). Gordon and Breach, New York, 1965, p. 521.
11. L. R. Batsonova and G. N. Kustova, *Russ. J. Inorg. Chem.* **9**, 181 (1964).
12. N. V. Podberezskaya, L. R. Batsonova, and L. S. Egorova, *J. Struct. Chem. USSR* **6**, 815 (1965).
13. W. Finkelnburg and A. Stein, *J. Chem. Phys.* **18**, 1296 (1950).
14. G. Brauer and U. Roether, "Proc. 7th Rare Earth Research Conf.," Coronado, Calif. p. 253, 1968 (availability restricted to attendees).
15. D. B. Shinn and H. A. Eick, *Inorg. Chem.* **8**, 232 (1969).
16. M. W. Shafer and J. D. Kuptsis, *J. Phys. Chem. Solids* **30**, 2325 (1969).
17. L. E. J. Roberts, *in* "Non-Stoichiometric Compounds" (R. F. Gould, Ed.), pp. 66–73. *Amer. Chem. Soc.*, Washington, D.C., 1963.
18. E. Zintl and A. Udgard, *Z. Anorg. Allg. Chem.* **240**, 150 (1939).
19. W. Klemm and H. A. Klein, *Z. Anorg. Allg. Chem.* **248**, 167 (1941).
20. J. Short and R. Roy, *J. Phys. Chem.* **67**, 1860 (1963).
21. L. F. Druding and J. D. Corbett, *J. Amer. Chem. Soc.* **83**, 2462 (1961).
22. R. A. Sallach and J. D. Corbett, *Inorg. Chem.* **2**, 457 (1963).
23. L. F. Druding, J. D. Corbett, and B. H. Ramsey, *Inorg. Chem.* **2**, 869 (1963).
24. J. E. Mee and J. D. Corbett, *Inorg. Chem.* **4**, 88 (1965).
25. J. D. Corbett and B. C. McCollum, *Inorg. Chem.* **5**, 938 (1966).
26. G. I. Novikov and O. G. Polyachenok, *Russ. J. Inorg. Chem.* **8**, 545 (1963).
27. O. G. Polyachenok and G. I. Novikov, *Russ. J. Inorg. Chem.* **8**, 1478 (1963).
28. A. E. Miller and A. H. Daane, *J. Inorg. Nucl. Chem.* **27**, 1955 (1965).