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The System Eu–Fe–O: Compound Formation and Its Implications for Systematic Crystal Chemistry

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Compound formation and phase relations at 1200°C have been studied for the $EuO–Eu_2O_3–Fe_2O_3–Fe$ portion of the system Eu–Fe–O. Only two ternary compounds, in both of which the europium was trivalent, could be prepared over the temperature range 1100–1400°C. The existence of seven ternary compounds containing divalent europium is predicted by the crystal chemical analogy of Eu^{2+} and Sr^{2+} compounds. None of these could be prepared. Divalent europium was found not to be stable in any phase assemblage with trivalent iron. This result is consistent with simple oxidation–reduction thermodynamics. The relevance of these results to systematic crystal chemistry is discussed.

Introduction

One of the significant accomplishments of systematic crystal chemistry has been the ability to predict the existence and probable structure of new compounds by crystal chemical analogy. When two ions with the same charge have approximately the same size, it is usually found that one may substitute for the other in a compound and that if a compound can be prepared containing one of the ions, an isostructural compound containing the other ion can also be prepared.

We recently described several instances from the Eu–Mo–O and Eu–W–O systems (*1*) which implied that when the conditions of the synthesis experiment were such that variable valences could exist for one or more cations, crystal chemical analogy was not always adequate to predict compound formation. For example, it was shown that although Eu^{2+} and Sr^{2+} have virtually identical size, there is no $Eu^{2+}Mo^{4+}O_3$ analog to the perovskite structure compound $Sr^{2+}Mo^{4+}O_3$.

In this report of the compound formation in a portion of the system Eu–Fe–O, we present further evidence that crystal chemical analogy alone is often not adequate to predict compound formation in variable valence mixed oxide systems.

Our interest in the system Eu–Fe–O was not confined to crystal chemistry, since any new compounds containing divalent europium and divalent or trivalent iron could have interesting magnetic properties. Shafer and co-workers (*2–4*) have studied the crystal chemistry and magnetic properties of binary and ternary compounds of divalent europium, but have not reported any studies of compounds in the system Eu–Fe–O. However, recently there have been a series of papers on the preparation and magneto-optic properties of Fe-doped EuO films (*5–7*). The results of these investigations indicated that Fe was not entering the EuO lattice as a substitutional solid solution to any significant extent. Except for this limited region around the compound EuO, the only other study of the system Eu–Fe–O was on the binary join $Eu_2O_3–Fe_2O_3$. Roth (*8*) found two intermediate compounds, $EuFeO_3$ with the $GdFeO_3$-type structure and $Eu_3Fe_5O_{12}$ with the garnet structure.

The binary systems Eu–O and Fe–O are well characterized. Studies of Eu–O by Bärnighausen (*9*), McCarthy and White (*10*), and Bedford and Catalano (*11*) have all shown that at 1200°C the only intermediate compounds are EuO, Eu_3O_4, and Eu_2O_3. The EuO and Eu_3O_4 show no significant range of stoichiometry, while Eu_2O_3 can have a slight oxygen deficiency. The system Fe–O has been extensively investigated (*12–15*). At

1200°C, it has the intermediate compounds $Fe_{1-x}O$ ($x \sim 0.05$–0.10), Fe_3O_4 (which can have a slight oxygen excess), and Fe_2O_3.

Only the portion of the system bounded by EuO–Eu_2O_3–Fe_2O_3–Fe will be described. In this region, all reactions at 1200°C could be performed in the solid state.

Experimental

Starting materials for this study were Eu_2O_3 (99.99%, Molycorp.), Fe_2O_3 (99.8%, Baker Chemicals), and Fe (99.99%, Hilger and Watts). The EuO was synthesized from Eu_2O_3 and Eu (99.9%, Research Chemicals) by the method of Shafer (*4*). Batches with the desired bulk compositions were prepared from the appropriate mixtures of EuO–Fe_2O_3 or EuO–Eu_2O_3–Fe_2O_3–Fe and ground in an agate mortar. Each mixture was pressed into a pellet and heated at 1200°C for 12–18 hr in a purified flowing argon atmosphere, followed by regrinding, repelletizing and reheating for an additional 6–12 hr. Phase identification was by X-ray powder diffraction supplemented by microscopic examination. In cases where one of the room-temperature magnetic phases (Fe, Fe_3O_4, $Eu_3Fe_5O_{12}$) was present in a phase assemblage in small amounts, it was identified and separated for X-ray analysis with a powerful magnet. The oxygen content of each run was checked by the gravimetric oxidation procedures described earlier (*16*, *17*). No significant loss or gain in oxygen was noted when the pellets were heated singly. If two or more pellets were heated in the same run, an oxygen exchange often took place with some pellets gaining and some losing oxygen. This phenomenon had been noted previously in the Eu–Ti–O system (*16*).

Results

Phase Relations

The phase relations in the portion of the system Eu–Fe–O bounded by EuO–Eu_2O_3–Fe_2O_3–Fe at 1200°C are given in Fig. 1. The runs used to determine the phase assemblages are labeled with Arabic numerals and listed in Table I. The phase assemblages are labeled with Roman numerals and listed in Table II. The EuO, Eu_3O_4, Eu_2O_3, and $EuFeO_3$ coexist with metallic Fe. The $EuFeO_3$ also coexists with the $Fe_{1-x}O$ and Fe_3O_4 solid solutions. The $Eu_3Fe_{12}O_{19}$ forms a compatibility triangle with Fe_3O_4 and Fe_2O_3.

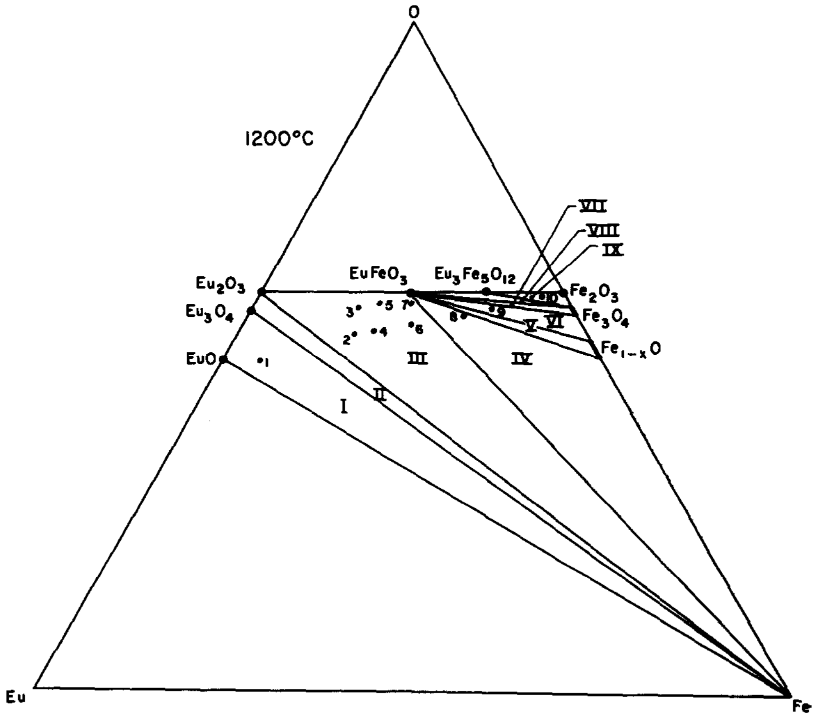

FIG. 1.

TABLE I

RUN TABLE

No.	Eu[a]	Fe[a]	O[a]	Phase assemblage (X-ray)[b]
1	0.450	0.050	0.500	S—EuO + M—Eu_3O_4 + W—Fe
2	0.308	0.154	0.538	S—Eu_2O_3 + W—$EuFeO_3$ + M—Fe
3	0.284	0.143	0.573	S—Eu_2O_3 + M—$EuFeO_3$ + W—Fe
4	0.272	0.182	0.546	S—Eu_2O_3 + S—$EuFeO_3$ + M—Fe
5	0.250	0.167	0.583	S—$EuFeO_3$ + W—Eu_2O_3 + W—Fe
6	0.222	0.222	0.556	S—$EuFeO_3$ + W—Eu_2O_3 + M—Fe
7	0.205	0.205	0.590	S—$EuFeO_3$ + W—Eu_2O_3 + W—Fe
8	0.143	0.284	0.573	S—$EuFeO_3$ + M—$Fe_{1-x}O$ + W—Fe
9	0.105	0.320	0.575	S—$EuFeO_3$ + M—$Fe_{1-x}O$ + W—Fe_3O_4
10	0.031	0.375	0.594	S—$Eu_3Fe_5O_{12}$ + S—Fe_2O_3 + M—Fe_3O_4

[a] Atomic fractions.

[b] Intensity of the phase in the X-ray diffractogram. S = strong, M = medium, W = weak.

Compound Formation

The only ternary compounds stable at 1200°C are the two previously reported Eu^{3+} iron oxides, $EuFeO_3$ and $Eu_3Fe_5O_{12}$. These were readily identified by comparison of their X-ray diffractograms to the tabulated patterns, 8-407 and 13-327, respectively, in the Powder Diffraction File (*18*). The cubic cell parameter determined for $Eu_3Fe_5O_{12}$ (12.496 ± 0.001 Å) was in excellent agreement with the value (12.498 Å) reported by Espinosa (*19*).

There are seven known Sr^{2+} iron oxides. According to crystal chemical analogy, there should also be seven Eu^{2+} iron oxides. Table III lists the Sr^{2+} compounds and references along with the corresponding hypothetical Eu^{2+} compounds and their run numbers in Fig. 1. Not included in Table III is the fact that $Sr_2FeO_{3.5}$, $Sr_3Fe_2O_6$, and $Sr_2Fe_2O_5$ all show intensive solid solution by substitution of Fe^{4+} for Fe^{3+} with a corresponding increase in oxygen content (*20*, *22*, *24*). It would not be likely to find Fe^{4+}, which is stable only under highly oxidizing conditions, coexisting in the same compound with Eu^{2+}, which is stable only under highly reducing conditions.

TABLE II

PHASE ASSEMBLAGES IN FIG. 1

No.	Assemblage
I	EuO + Eu_3O_4 + Fe
II	Eu_3O_4 + Eu_2O_3 + Fe
III	Eu_2O_3 + $EuFeO_3$ + Fe
IV	$EuFeO_3$ + Fe + $Fe_{1-x}O$
V	$EuFeO_3$ + $Fe_{1-x}O$
VI	$EuFeO_3$ + $Fe_{1-x}O$ + Fe_3O_4
VII	$EuFeO_3$ + Fe_3O_4
VIII	$EuFeO_3$ + Fe_3O_4 + $Eu_3Fe_5O_{12}$
IX	$Eu_3Fe_5O_{12}$ + Fe_3O_4 + Fe_2O_3

TABLE III

Sr^{2+} Iron Oxide	Reference	Hypothetical Eu^{2+} analog	Run number
$Sr_2FeO_{3.5}$	*20*	$Eu_2FeO_{3.5}$	2
$SrEu^{3+}FeO_4$	*21*	Eu_2FeO_4	3
$Sr_3Fe_2O_6$	*20*, *22*	$Eu_3Fe_2O_6$	4
$SrEu_2^{3+}Fe_2O_7$	*23*	$Eu_3Fe_2O_7$	5
$Sr_2Fe_2O_5$	*24*	$Eu_2Fe_2O_5$	6
$SrFe_2O_4$	*18*, #1-1027	$EuFe_2O_4$	8
$SrFe_{12}O_{19}$	*25*	$EuFe_{12}O_{19}$	10

None of the hypothetical Eu^{2+} compounds listed in Table III could be prepared. Mixtures corresponding to the bulk compositions $Eu_2FeO_{3.5}$, Eu_2FeO_4, $Eu_3Fe_2O_6$, $Eu_3Fe_2O_7$, and $Eu_2Fe_2O_5$ all gave the same phase assemblage (Eu_2O_3 + $EuFeO_3$ + Fe) after heating. Mixtures of the bulk compositions of $EuFe_2O_4$ and $EuFe_{12}O_{19}$ had the phase assemblages ($EuFeO_3$ + Fe + $Fe_{1-x}O$) and ($Eu_3Fe_5O_{12}$ + Fe_3O_4 + Fe_2O_3), respectively, after the 1200°C heating. Each of these seven bulk compositions was also heated at 1100, 1300, and 1400°C for 12 hr to check on the possibility that the Eu^{2+} compounds were stable at other temperatures. The results were the same as those at 1200°C except that most of the pellets showed evidence of partial melting at 1400°C.

We also examined the compound $EuFeO_3$ for nonstoichiometry due to oxygen deficiency and corresponding reduction in cation charge. Run 7 has an oxygen content slightly less than that of $EuFeO_3$. However, it yielded the phase assemblage (Eu_2O_3 + $EuFeO_3$ + Fe) after heating. Precision cell parameters were measured for $EuFeO_3$ prepared in air and $EuFeO_3$ from this phase assemblage.

	$EuFeO_3$ in air	$EuFeO_3$ in run 7	Geller and Wood (*26*)
a_0	5.371 ± 0.003 Å	5.373 ± 0.002 Å	5.371 Å
b_0	5.598 ± 0.003 Å	5.603 ± 0.002 Å	5.611 Å
c_0	7.681 ± 0.002 Å	7.687 ± 0.002 Å	7.686 Å
V	230.9 ± 0.1 Å^3	231.4 ± 0.06 Å^3	231.6 Å^3

There are slightly larger cell parameters for the $EuFeO_3$ from run 7, which may indicate a small amount of nonstoichiometry for $EuFeO_3$. The substitution of the larger Eu^{2+} or Fe^{2+} for Eu^{3+} or Fe^{3+} could have a greater effect than the corresponding oxygen deficiency on cell volume. The cell parameters of $EuFeO_3$ as determined by Geller and Wood (*26*) were also listed for comparison. Actually, they correspond more closely with the parameters of $EuFeO_3$ from run 7. These results, plus the fact that run 7 was distinctly in a three-phase assemblage, indicated that the reduction in $EuFeO_3$ was slight. Also, there was no way of distinguishing whether this small amount of reduction was due to substitution of Eu^{2+} for Eu^{3+} or Fe^{2+} for Fe^{3+}.

We conclude from these results that Eu^{2+} cannot coexist with Fe^{3+} in a mixed oxide compound. In the hypothetical compound $EuFe_{12}O_{19}$, the concentration of Eu^{2+} would be about 3 mole %. Yet even this small amount of Eu^{2+} reduces a corresponding amount of Fe^{3+} to yield the phase assemblage of run 10. Throughout the Eu–Fe–O region studied, any Eu^{2+} present in the initial mixture reduced a corresponding amount of Fe^{3+} to a lower oxidation state. If sufficient Eu^{2+} was present, some of the Fe^{3+} was reduced all the way to metallic iron. This was the case in runs 1–8.

Discussion

The results of this study are in marked contrast to compound formation in the system Eu–Ti–O (*16*). In that system, there is a Eu^{2+} analog for each of the known Sr^{2+} compounds (Eu_2TiO_4/Sr_2TiO_4, $Eu_3Ti_2O_7/Sr_3Ti_2O_7$, $EuTiO_{2.5-3}/SrTiO_{2.5-3}$, $EuFe_{12}O_{19}/SrFe_{12}O_{19}$). Recently, isostructural $SrTi_2O_4$* and $EuTi_2O_4$* compounds have also been reported (*27*). It should be noted that $Sr_2FeO_{3.5}$ and $SrEuFeO_4$ are isostructural with Eu_2TiO_4 and that a $Sr_3Fe_2O_6$ and $SrEu_2Fe_2O_7$† are isostructural with $Eu_3Ti_2O_7$. Also, $SrFeO_{2.5}$ ($Sr_2Fe_2O_5$) has the brownmillerite structure, an orthorhombic distortion of the cubic perovskite structure of $Eu^{2+}Ti^{3+}O_{2.5}$. Thus, Eu^{2+} is known to form oxide compounds with Ti^{4+} and Ti^{3+} in many of the same structure types as the Sr^{2+}-iron oxides. Since the radii of Sr^{2+} and Eu^{2+} are virtually identical (*28*), isostructural Eu^{2+}-iron oxides would be expected.

Clearly another parameter must be considered when variable valence cations are involved. The obvious choice is a thermodynamic parameter. Consider the free energy necessary to reduce $Fe^{3+}O_{1.5}$, $Ti^{3+}O_{1.5}$, and $Ti^{4+}O_2$ to the metal at 1200°C (*29*).

$$\begin{array}{lr} FeO_{1.5} \rightarrow Fe + 3/4\ O_2 & 53.2\ \text{kcal/mole,} \\ TiO_{1.5} \rightarrow Ti + 3/4\ O_2 & 133.9\ \text{kcal/mole,} \\ TiO_2 \rightarrow Ti + O_2 & 162.3\ \text{kcal/mole.} \end{array}$$

Much more energy is required to reduce Ti^{3+} or Ti^{4+} to Ti^0 than to reduce Fe^{3+} to Fe^0. Reduction of Fe^{3+} to ($0.5\ Fe^{2+}/0.5\ Fe^{3+}$) as in Fe_3O_4 or to Fe^{2+} requires even less energy.

$$\begin{array}{lr} FeO_{1.5} \rightarrow FeO_{1.33} + 1/12O_2 & 1.1\ \text{kcal/mole,} \\ FeO_{1.5} \rightarrow FeO + 1/4O_2‡ & 12.7\ \text{kcal/mole‡.} \end{array}$$

Thus, considering, for example, the isostructural A_2BO_4 compounds, the energy available from the oxidation of Eu^{2+} to Eu^{3+} is not enough to reduce Ti^{4+} to Ti^0 in Eu_2TiO_4, while in the hypothetical $Eu^{2+}Eu^{3+}FeO_4$ it is enough to reduce Fe^{3+} to Fe^0, as evidenced by run 3. This simple oxidation–reduction treatment is not adequate to describe all of the energy changes involved in a particular run, since the free energy of formation of $EuFeO_3$ must also be included. It does illustrate the need for consideration of oxidation–reduction thermodynamics when predicting compound formation in oxide systems with variable valence cations. A more complete thermodynamic discussion will be the subject of a later report.

We conclude that predictions of compound formation in oxide systems based on crystal chemical analogy alone are generally valid when each of the cations involved has only a single possible valency (e.g., Na^+, Sr^{2+}, Al^{3+}) or, if multiple valences are possible, when the syntheses are performed in air and each of the cations has its usual air-stable valence. If the cations have several possible valences and the oxygen fugacity maintained in the synthesis is such that more than one of these valences may be stable, then oxidation–reduction thermodynamics must also be considered.

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* These compounds were not encountered by McCarthy et al. (*16, 17*) in their studies of the systems Sr–Ti–O and Eu–Ti–O at 1400°C. Apparently, $SrTi_2O_4$ and $EuTi_2O_4$ undergo subsolidus dissociation between 1100°C [the preparation temperature reported by Sieler and Kaiser (*27*)] and 1400°C.

† The $SrEu_2Fe_2O_7$ is not strictly isostructural with $Sr_3Ti_2O_7$ and $Eu_3Ti_2O_7$, since ordering of the Sr and Eu^{3+} on the $Sr(Eu^{2+})$ site causes a change in space group from $I4/mmm$ to $P4_2/mnm$, $P4_2nm$ or $P\bar{4}n2$ (*23*).

‡ This is actually the data for $Fe_{0.947}O$. Stoichiometric FeO does not exist.

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