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Complex Oxides Containing Divalent Europium. I. Guidelines for the Prediction of New Phases. Application to Phases of the Type $EuMO_3$

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The problem of the stability of complex europium(II) oxides is considered in detail. A set of guidelines suitable for both the understanding of existing complex europium(II) oxide phases and the prediction of new phases is developed. These guidelines are applied to compounds of the type $EuMO_3$, most of which have some form of the perovskite structure. $EuNbO_3$ and $EuUO_3$ are reported for the first time.

This paper is both a brief review of all known mixed europium(II) oxides and a discussion of guidelines for predicting new phases of this type. Such oxides are those found in ternary (Eu–M–O), quaternary (Eu–M–M′–O), and more complex systems where M is a metal. Such phases as $EuSO_4$ and $EuCO_3$ are not considered "mixed oxides" for the purpose of this discussion because of the high degree of covalent bonding in the anion radical.

Our interest in europium(II) oxides stems from their interesting magnetic and magnetooptic properties. The monoxide, EuO, is ferromagnetic at low temperatures[1] and several ternary europium(II) oxides have unusual magnetic and magnetooptic properties.[2]

The first report of a mixed europium(II) oxide was of $EuTiO_3$ by Brous, *et al.*[3] They noted that it was isostructural with $SrTiO_3$ and had an almost identical unit cell parameter. This implied that the oxidation states were II and IV rather than III and III and that the ionic radii of Sr^{2+} and Eu^{2+} were nearly identical. After the discovery of ferromagnetism in EuO, Shafer[4] studied a number of oxide systems which might contain Eu^{2+} using the existence of a known Sr^{2+} analog as a guide. He recognized that this did not guarantee the stability of a Eu^{2+} phase since he was unable to prepare several phases for which Sr^{2+} analogs were known. Table I lists the compositions of these and all of the subsequently reported Eu^{2+} phases known to us. References are given to reports of synthesis, crystal chemistry, and properties measurements. For our purposes we assume that these reports are correct in the stoichiometry of the phase and the assignment of divalence to Eu.

Table I. Complex Oxides Containing Eu^{2+}

M in Eu–M–O	Phase	Ref
Ti	$EuTiO_3$	2–9
	Eu_2TiO_4	5, 6, 10, 11
	$Eu_3Ti_2O_7$	5, 6, 11
	$Eu_4Ti_3O_{10}$	5
	$EuTi_2O_4$	10
	$EuTi_{12}O_{19}$	5
Zr	$EuZrO_3$	4, 7, 13
	Eu_2ZrO_4	4
Hf	$EuHfO_3$	13
Nb	$EuNbO_3$	This study
Ta	$EuTa_2O_6$	14
Cr	$Eu_3Cr_2O_6$	15
Mo	$EuMoO_4$	16, 17
W	$EuWO_4$	4, 14, 16–18
B	EuB_2O_4	21
Al	$EuAl_2O_4$	4, 22
	$Eu_3Al_2O_6$	4, 15
	$Eu_5Al_2O_8$	4
	$EuAl_{12}O_{19}$	22
U	$EuUO_3$	This study
Si	$EuSiO_3$	4
	Eu_2SiO_4	2, 4, 23–26
	Eu_3SiO_5	4
RE	$Eu(RE^{III})_2O_4$ RE = Sm, Eu, Gd–Lu, Y, Sc	15, 27–30
	$EuNd_4O_7$	30
	$Eu_3Nd_4O_9$	30
Eu^{3+}, Al	$Eu^{II}Eu^{III}AlO_4$	31
	$Eu^{II}{}_2Eu^{III}AlO_5$	31
	$Eu^{II}Eu^{III}{}_2Al_2O_7$	31
RE–Al	$Eu(RE)AlO_4$ RE = La, Ce, Pr, Nd, Sm, Gd	31
Ca, W	Eu_2CaWO_6	4
Sr, W	Eu_2SrWO_6	4
Li, Eu^{3+}	$LiEu^{II}{}_2Eu^{III}O_4$	50
	$Li_2Eu^{II}Eu^{III}{}_4O_8$	51

Prediction of New Oxide Phases Containing Eu^{2+}

Consideration of known europium(II) oxides and our experience in experimental studies aimed at preparing new Eu^{2+} phases[5,16,20,32] have suggested three guidelines for the prediction of new europium(II) oxide phases. In this paper discussion will be confined to compound formation between EuO and MO_2 phases where M is any metal. For the most part these phases will have some form of the perovskite structure type. The guidelines are applied to prediction of new $Eu^{II}(M,M')O_3$ phases in the following paper hereafter referred to as part II.

Every known europium(II) oxide phase has an Sr^{2+} analog. The latest compilation of effective ionic radii in oxides[33] gives essentially the same value for Sr^{2+} and Eu^{2+} in both six- and eightfold coordination. From a crystal chemical standpoint it is very unlikely that a europium(II) oxide phase will be stable if the corresponding Sr^{2+} phase is not. For example, we have found that in the Eu–Mo–O system there is no "$Eu^{II}{}_2MoO_4$" phase. When a study was made of the Sr–Mo–O system, it was found that the Sr analog of "Eu_2MoO_4," "Sr_2MoO_4," was also not a stable phase over the temperature range 900–1400°.[34] Similarly, in a study of the Eu–W–O system, no "$Eu^{II}W^{IV}O_3$" phase was expected or found, since there is no "$SrWO_3$" phase in the Sr–W–O system.[35] These observations lead to the first guideline, which follows.

i. The Proposed Europium(II) Oxide Phase Should Have an Sr^{2+} Analog. Although every Eu^{2+} phase should have an Sr^{2+} analog, the reverse is frequently not valid. This is demonstrated emphatically in the system Eu–Fe–O,[32] where seven europium(II) iron oxides would be predicted on the basis of known strontium(II) iron oxide analogs. However, none was found, and it was suggested that Eu^{2+} was a much too powerful reducing agent to coexist with the relatively easily reduced iron oxides. This leads to our second guideline, which will be discussed more quantitatively in the next section.

ii. The Other Cation(s) Which Would Coexist with Eu^{2+} in the Oxide Must Not Be Too Easily Reduced. These two guidelines are sufficient to explain the existence or nonexistence of most europium(II) oxides. However, there are a few cases where they are inadequate. For example, Eu^{2+} is known to coexist with W^{6+} in $EuWO_4$, but the analog of Sr_3WO_6, "Eu_3WO_6," is not a stable phase.[4,20] If it did exist it would have the ordered perovskite $(NH_4)_3FeF_6$ structure type and

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Table II. Free Energy Change for Reduction Reactions Per Mole of O_2 at 1500°K[a]

Reaction	Oxide	$\Delta G°$(1500°K), kcal
A. $MO_2 \rightarrow M + O_2$	ThO_2	228
	UO_2	194
	HfO_2	192
	ZrO_2	190
	SiO_2	153
	NbO_2	136
	....	
	MoO_2	80
	SnO_2	63
	GeO_2	59
	RuO_2	<0
	IrO_2	<0
	OsO_2	<0
B. $4MO_2 \rightarrow 2M_2O_3 + O_2$		
	PuO_2	139
	....	
	TiO_2	115
	CeO_2	91
	VO_2	49
	MnO_2	<0
	CrO_2	<0

[a] The dotted line gives the position of the reaction $4EuO + O_2 \rightarrow 2Eu_2O_3$.

one Eu^{2+} would have to share the octahedral sites with W^{6+}. In virtually every phase in Table I, Eu^{2+} occupies a site with coordination higher than 6 and this suggests that Eu^{2+} prefers a higher coordination than 6 in complex oxides. Requiring Eu^{2+} to occupy an octahedral site apparently adds a destabilizing effect. Indeed, if one of the three Eu^{2+} ions is replaced by a Sr^{2+}, which presumably goes into the octahedral site, then a Eu_2SrWO_6 phase is stable.[4] The third guideline relates to this observation:

iii. The New Europium(II) Oxide Should Not Fall near the Boundary of the Structure Stability Field. For perovskites, the structure field can be defined with some success by the familiar Goldschmidt tolerance factor which is discussed more fully in II. For other structure types many "structure field diagrams" are available; see a recent publication by Muller and Roy.[37]

Redox Thermodynamics

The redox thermodynamics for the oxides EuO, Eu_3O_4, and Eu_2O_3 have been discussed in detail by McCarthy and White.[38] Following the same approach but with the more recent thermodynamic data estimates for EuO and Eu_2O_3 of Gschneidner, *et al.*,[39] we derive the free energy change for EuO oxidizing to Eu_2O_3. (It is not necessary for the purposes of this discussion to consider the intermediate step oxidation to Eu_3O_4.)

$$4EuO + O_2 \rightarrow 2Eu_2O_3$$

$$\Delta G°(1500°K) = -137 \text{ kcal/mol}$$

We have chosen 1500°K as our reference temperature because it is a typical synthesis temperature (1227°) and is the approximate upper long-term-use temperature of evacuated silica ampoules.

To make the second rule more quantitative this free energy of oxidation will be compared to free energy of reduction of metal oxides with which EuO might combine. Table II lists free energy of reduction per mole of O_2 at 1500°K for two groups of reactions with tetravalent binary oxides. A similar table is presented in the second paper of this series covering monovalent, divalent, trivalent, pentavalent, and hexavalent ions. The values listed were derived from the compilations of Reed,[40] Coughlin,[41] and Gschneidner.[39] Every oxide listed in Table II forms a complex oxide with SrO and thus, by our first guideline, is a candidate for forming complex oxides with EuO. With the exceptions of compounds with SiO_2 and GeO_2 all $SrMO_3$ analogs have some form of the perovskite structure. The existence of a strontium(II) oxide phase has been ascertained by reference to Galasso,[42,43] Wells,[44] Muller and Roy[37] and to the index to the "Powder Diffraction File."[45]

A few of the oxides listed in Table II have been included only for completeness and should not be considered as candidates for forming europium(II) complex oxides. The large divalent Sr^{2+} (with Ba^{2+} and Pb^{2+}) has the ability to stabilize unusual high oxidation states such as Mn^{4+}, Cr^{4+}, Pb^{4+}, Fe^{4+}, and Co^{4+}. Such species could not be expected to coexist with Eu^{2+}.

Experimental Section

All attempted preparations were carried out in the solid state. The details are given in Table III. The general preparative and characterization procedures are described in part II and will not be repeated here. Results of each synthesis attempt are included in column 4 of Table III.

Discussion

It is pertinent to compare our second guideline with experiment, including previously known results and those reported here for the first time. Table I lists $EuHfO_3$, $EuZrO_3$, and $EuSiO_3$ as known phases. In this study we report $EuUO_3$ although the solid-state reaction is apparently not complete at the temperatures used here. Possibly this reflects the fact that U^{4+} is a relatively large ion for the B-site in perovskites giving a somewhat unfavorable tolerance factor. $EuThO_3$ and $EuPuO_3$ should also be stable at high temperatures. Single-phase $EuNbO_3$ could readily be prepared with a cell constant, $a_0 = 4.008 \pm 0.002$ Å. All of these results are in accord with the guidelines implicit in Table II.

The compositions reported for the two new phases, $EuNbO_3$ and $EuUO_3$, are idealized as no analytical data are yet available. A detailed study of the Eu^{2+}–Nb–O system is in progress.

Concerning the phases which should not exist, McCarthy[16] was unable to prepare $EuMoO_3$. In $EuVO_3$, $EuCrO_3$, and $EuMnO_3$ all cations are known to be trivalent.[36] We report here unsuccessful attempts to prepare $EuSnO_3$ and $EuRuO_3$ finding instead a two-phase mixture of the pyrochlore phase,

Table III. Detailed Experimental Procedure

M in $EuMO_3$	Reaction mix	Firing schedule	Phases detected in product
Sn	$Eu_2O_3 + {}^3/_2SnO_2 + {}^1/_2Sn$	1050°, 2 days	$Eu_2Sn_2O_7$
Sn	$Eu_2O_3 + SnO_2 + SnO$	800–1000°, 2 days	$Eu_2Sn_2O_7$
Sn	$EuO + SnO_2$	1000°, 72 hr	Eu_2SnO_7 + Sn Metallic mirror of Sn develops in pumped system
Ru	$Eu_2O_3 + {}^3/_2RuO_2 + {}^1/_2Ru$	1100°, 30 hr	$Eu_2Ru_2O_7$ + Ru
Ru	$EuO + RuO_2$	1250°, 1 day	$Eu_2Ru_2O_7$ + Ru
U	$EuO + UO_2$	1100–1150°, 2 days	$EuUO_3$[a] + fcc phase (UO_2); impossible to eliminate fcc phase at these temperatures
Nb	$Eu_2O_3 + {}^3/_2NbO_2 + Nb$	1150°, days	$EuNbO_3$
Nb	$EuO + NbO_2$	1100°, 1 day	$EuNbO_3$

[a] Precision cell constants are not reported for $EuUO_3$ because single-phase material could not be prepared. Diffraction lines for this phase corresponded closely to $SrUO_3$: R. S. Roth, *J. Res. Nat. Bur. Stand.*, **58**, 75 (1957).

Table IV. Relevant Ionization Potentials and Differences (kcal mol^{-1})

M	I_4(M)[a]	I_3(Eu or Sm)[b]	I_4(M) − I_3(Eu)	I_4(M) − I_3(Sm)
Ti	997	575 ± 9 (Eu)	422	451
V	1100	546 ± 9 (Sm)	525	554

[a] C. E. Moore, "Atomic Energy Levels," National Bureau of Standards, Washington, D.C., 1949, 1952. [b] Estimated: D. A. Johnson, *J. Chem. Soc. A*, 1525 (1969).

$Eu_2Sn_2O_7$ or $Eu_2Ru_2O_7$, and the respective metal. $EuGeO_3$ also should not exist. However, our guidelines predict that TiO_2 should be reduced to Ti_2O_3 whereas $Eu^{II}Ti^{IV}O_3$ is a well-known ternary phase. In fact one method of preparing $EuTiO_3$ is by reaction of Eu_2O_3 and Ti_2O_3. Clearly, our simple half-reaction scheme underestimates the extra lattice energy stabilization which accompanies the formation of a ternary phase. Further examples will occur in the following paper covering the Eu(M,M')O_3 phases. The existence of $Eu^{II}Ce^{IV}O_3$ is less likely than that of $EuTiO_3$ but cannot be ruled out on this basis.

Energetics of Formation of Perovskites of Eu^{2+} and Sm^{2+} with Ti and V. In certain favorable cases it is possible to gain a more detailed understanding of the energetics than afforded by the half-reaction approach. One such circumstance is represented by perovskite systems of the type $EuMO_3$ where M = Ti and V. Because of structural similarities the question of the stability of samarium(II) perovskites arises naturally and will be treated here as well. These compounds could exist either as $Eu^{II}M^{IV}O_3$ ($Sm^{II}M^{IV}O_3$) abbreviated as (II,IV) or as $Eu^{III}M^{III}O_3$ ($Sm^{III}M^{III}O_3$) abbreviated as (III,III). Cubic perovskite Sr^{2+} analogs are reported[47] for M = Ti and V. The trivalent rare earth elements form $Ln^{III}M^{III}O_3$ phases with structures related to $GdFeO_3$, an orthorhombically distorted perovskite.

To provide a basis for choosing between these two possibilities, we analyze the free energy of formation for both structure types by means of a Born–Haber cycle and an ionic model for the lattice energy. Expressions for the free energy of formation, ΔG_f, for both cases can be written as

$$\begin{aligned}\Delta G_f(\text{II,IV}) = {} & \Delta G_f[\text{Eu(g)}] + I_1(\text{Eu}) + I_2(\text{Eu}) + \\ & 3\Delta G_f(\text{O}^{2-}(\text{g})) + \Delta G_f(\text{M(g)}) + I_1(\text{M}) + I_2(\text{M}) + \\ & I_3(\text{M}) + I_4(\text{M}) + \Delta G_{\text{latt}}(\text{Eu}^{\text{II}}\text{M}^{\text{IV}}\text{O}_3) \qquad (1)\end{aligned}$$

and

$$\begin{aligned}\Delta G_f(\text{III,III}) = {} & \Delta G_f(\text{Eu(g)}) + I_1(\text{Eu}) + I_2(\text{Eu}) + I_3(\text{Eu}) + \\ & 3\Delta G_f(\text{O}^{2-}(\text{g})) + \Delta G_f(\text{M(g)}) + I_1(\text{M}) + I_2(\text{M}) + \\ & I_3(\text{M}) + \Delta G_{\text{latt}}(\text{Eu}^{\text{III}}\text{M}^{\text{III}}\text{O}_3) \qquad (2)\end{aligned}$$

where the I_i(M) are the ith ionization potentials and Sm can be substituted for Eu.

The difference in formation free energies is then

$$\begin{aligned}\Delta G_f(\text{II,IV}) - \Delta G_f(\text{III,III}) = {} & [I_4(\text{M}) - I_3(\text{Eu})] + \\ & [\Delta G_{\text{latt}}(\text{II,IV}) - \Delta G_{\text{latt}}(\text{III,III})] \qquad (3)\end{aligned}$$

As entropy differences are likely to be small, lattice enthalpies or internal energies can be substituted for free energies in the second bracketed term.

From the information in Table IV, the first term can easily be computed and these values are found in the third column. It is clear, given these numbers, that the first term in the expression for the free energy difference favors the formation of the (III,III) perovskite by greater than 400 kcal mol^{-1} in all cases. In order for a (II,IV) perovskite to be stable, the lattice energy difference must contribute at least this amount.

Let us assume an ionic model for the lattice energy and further that the major contribution is from the Madelung term, $E_M = -Me^2/a_0$, where M is the Madelung constant, a_0 is the cubic cell edge, and e is the electronic charge. Johnson and Templeton[48] and Templeton[49] have determined Madelung constants for *cubic* perovskites with ions of various charges on the 12-fold and 6-fold sites. For a (II,IV) perovskite $M = 49.5100$ and for the (III,III) case $M = 44.5549$. Clearly the Madelung term favors the formation of the (II,IV) perovskite for similar a_0 but it is important to estimate the magnitude of this energy difference.

Table V. Madelung Energies for $EuTiO_3$ and $SmTiO_3$ (kcal mol^{-1})

	$EuTiO_3$		$SmTiO_3$	
a_0, Å	3.904	3.90[a]	3.91[b]	3.914[c]
E_M	−4215	−3793	−4215	−3783
E_M(II,IV) − E_M(III,III)	−422		−432	
ΔG_f(II,IV) − ΔG_f(III,III)	~0		+19	

[a] Pseudo-cubic cell parameter.[46] [b] It has been estimated that $r(Sm^{2+}) = r(Eu^{2+})$ to within 1%: D. A. Johnson, *J. Chem. Soc. A*, 2578 (1969). [c] Pseudo-cubic cell parameter.[46]

Table V lists calculated Madelung energies of $EuTiO_3$ and $SmTiO_3$ for both (II,IV) and (III,III) cubic perovskites. Note the nearly identical cell constants of all four compounds being considered here. The numbers in Table V should not be regarded as accurate given the sort of approximations involved. In particular we have ignored the orthorhombic distortion expected for the (III,III) perovskites and have calculated the Madelung energies for a cubic structure. It is difficult to assess *a priori* the effect of such an approximation, but our simple analysis allows for the expectation of a (II,IV) perovskite for $EuTiO_3$ and a (III,III) perovskite for $SmTiO_3$ in good agreement with experiment.

For M = V the data of Tables IV and V are pessimistic regarding the stability of (II,IV) perovskites for either Eu^{2+} or Sm^{2+}. The first term in expression 3 favors the (III,III) perovskite by at least 100 kcal mol^{-1} over those cases where M = Ti. It is difficult to imagine that lattice energy could provide stabilization of the (II,IV) perovskite by this amount and indeed both $EuVO_3$ and $SmVO_3$ are (III,III) perovskites.

Finally, although only "pure" (II,IV) or (III,III) perovskites have been considered, it is clear that our redox analysis helps to identify those phases for which mixed-valence perovskites might be possible. For example, $EuTiO_3$ is clearly of marginal stability as a (II,IV) perovskite and should contain some Eu^{3+}–Ti^{3+} substitution. Such behavior is known for $EuTiO_3$ in the form of variations in lattice parameters and magnetic susceptibility.[4]

Summary

We have presented a set of three guidelines which aid in understanding the existence of complex Eu^{2+} oxides and should be useful for the prediction of new Eu^{2+} oxides. First, an Sr^{2+} analog of the complex phase should exist; second, any other metal ion in the complex phase should not be easily reduced by Eu^{2+}, and, third, the new phase must have a favorable lattice energy.

The second guideline is defined by a redox scheme involving half-reactions of the relevant binary oxides. By comparison of the second guideline with experimental information on $EuMO_3$ phases we find that binary oxides fall roughly into three classes: those oxides which are very stable to reduction and form Eu^{2+} phases (ZrO_2 and $EuZrO_3$), those which are quite easily reduced to the element or lower oxidation state and hence do not form Eu^{2+} phases (SnO_2), and those borderline cases which are apparently stabilized by lattice energy (TiO_2 and $EuTiO_3$). The role of the lattice energy is examined in detail by use of a Born–Haber cycle for Eu(Sm)MO_3 where M = Ti and V. These guidelines are extended in II and applied to many metal oxides in varying oxidation states.

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Registry No. $EuNbO_3$, 53809-82-8; $EuTiO_3$, 12020-61-0; $SmTiO_3$, 12210-42-3; Eu, 7440-53-1.

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Complex Oxides Containing Divalent Europium. II. Eu(M,M')O_3 Phases

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The redox guidelines developed previously for the prediction of new complex europium(II) oxides are extended to Eu(M,M')O_3 perovskites. Attempts to prepare nearly 40 new europium oxides are described in a systematic experimental test of the guidelines. Fourteen compounds are actually found to be stable under the conditions of preparation. In terms of the combination of ions occupying the sixfold site these are (Mg^{II},W^{VI}), (Mn^{II},W^{VI}), (A^{III},Ta^{V}), (Ti^{III},Ta^{V}), (V^{III},Ta^{V}), (Cr^{III},Ta^{V}), (Eu^{III},Ta^{V}), (Ti^{III},Nb^{V}), (V^{III},Nb^{V}), (Cr^{III},Nb^{V}) (Mg^{II},Ta^{V}), (Mn^{II},Ta^{V}), (Mg^{II},Nb^{V}), (Mn^{II},Nb^{V}). Precision cell constants are reported for all of these phases. Agreement between the redox guidelines and experiment is discussed as are the implications of these results for the existence of new nonperovskite oxides of Eu^{2+}.

Introduction

As emphasized in the first paper of this series hereafter referred to as I, studies of divalent europium compounds have been numerous over the past few years owing largely to the remarkable magnetic, transport, and magnetooptical properties found in relatively simple systems such as EuO and the other monochalcogenides. Recently, we have undertaken to prepare more complex oxides containing divalent europium and a wide variety of metal ions in various oxidation states. The impetus for these efforts was twofold: (1) to prepare a set of materials suitable for a systematic study of magnetic and optical interactions between Eu^{2+} and various paramagnetic metal ions from the 3d, 4d, 5d, and 5f transition series and (2) to investigate in a systematic way the redox properties of the Eu^{2+} ion in oxide lattices according to the principles discussed in I.

The perovskite structure seemed a convenient choice because its high symmetry is favorable to the interpretation of magnetic and optical properties and because there is an availability of

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