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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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Contribution from the Chemistry Department, Dalhousie University, Halifax, Nova Scotia, Canada,
and the Materials Research Laboratory, The Pennsylvania State University, University Park, Pennsylvania 16802

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

J. E. GREEDAN,* GREGORY J. McCARTHY, and CAROL SIPE

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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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* To whom correspondence should be addressed at the Institute for Materials Research and Department of Chemistry, McMaster University, Hamilton, Ontario L8S HM1, Canada.

Table I. Detailed Experimental Procedures and Results

M	Reaction mix	Firing schedule	Phases detected in product
		$Eu(M_{0.5}W_{0.5})O_3$	
Mg	$Eu_2O_3 + MgO + {}^2/_3WO_3 + {}^1/_3W$	1100°, 3 days	$EuWO_4$ (major) + W + $Eu(Mg_{0.5}W_{0.5})O_3$ (minor)
Mg	$EuO + {}^1/_2MgWO_4$[a]	1100°, 24 hr; regrind; 1200°, 18 hr	$Eu(Mg_{0.5}W_{0.5})O_3$ (brown-black)
Mn	$Eu_2O_3 + MnO + {}^2/_3WO_3 + {}^1/_3W$	1100°, 3 days	$EuWO_4$ (major) + W + MnO[b]
Mn	$EuO + MnWO_4$	1100°, 48 hr	$Eu(Mn_{0.5}W_{0.5})O_3 + EuWO_4$ (trace)
Zn	$Eu_2O_3 + ZnO + {}^2/_3WO_3 + {}^1/_3W$	1100°, 3 days	$EuWO_4$ (major) + Eu_6WO_{12} (minor) + W + ZnO
Zn	$EuO + {}^1/_2ZnWO_4$	1000°, 24 hr	$EuWO_4 + Eu_6WO_{12}$ + Zn[c]
Co,Ni	$EuO + ({}^1/_2CoWO_4, {}^1/_2NiWO_4)$	1000°, 24 hr	$EuWO_4 + Eu_6WO_{12} + W$
Cu	$Eu_2O_3 + CuO + {}^2/_3WO_3 + {}^1/_3W$	700–750°, 12 hr; 1000°, 24 hr	$EuWO_4 + W + Eu_6WO_{12}$
		$Eu(M_{0.5}M_{0.5})O_3$	
Mg	$EuO + {}^1/_2MgO + {}^1/_2MoO_3$	1100°, 3 days	"Eu_2MoO_5"
Mn	$EuO + {}^1/_2MnO + {}^1/_2MoO_3$	1100°, 3 days	"Eu_2MoO_5"
Mg	$EuO + {}^1/_2MgO + UO_3$	1200°, 2 days	fcc phase, UO_2–Eu_2O_3, solid soln
		$Eu(M_{0.5}Re_{0.5})O_3$	
Mg	$EuO + {}^1/_2MgO + ReO_3$	1200°, 2 days	Eu_2ReO_5
		$Eu(M_{0.5}Ta_{0.5})O_3$	
Ti	$Eu_2O_3 + {}^1/_2Ti_2O_3 + {}^3/_{10}Ta_2O_5 + {}^2/_5Ta$	1200°, 2 days	$Eu(Ti_{0.5}Ta_{0.5})O_3$ (blue-black), $EuTiO_3$; several regrinding and refiring steps necessary to eliminate $EuTiO_3$
Ti	$EuO + TiTaO_4$	1100°, 2 days	$Eu(Ti_{0.5}Ta_{0.5})O_3$
V	$Eu_2O_3 + {}^1/_2V_2O_3 + {}^3/_{10}Ta_2O_5 + {}^2/_5Ta$	1200°, 2 days	$Eu(V_{0.5}Ta_{0.5})O_3$ (black) + several other phases
V	$EuO + VTaO_4$	1150–1200°, 20 hr	$Eu(V_{0.5}Ta_{0.5})O_3$ + trace fcc phase, Eu_3TaO_7
Cr	$Eu_2O_3 + {}^1/_2Cr_2O_3 + {}^3/_{10}Ta_2O_5 + {}^2/_5Ta$	1150°, 3 days	$Eu(Cr_{0.5}Ta_{0.5})O_3$, $EuCrO_3$ (trace); difficult to eliminate
Cr	$EuO + {}^1/_2CrTaO_4$	1150°, 2 days	$Eu(Cr_{0.5}Ta_{0.5})O_3$ (orange-brown)
Mn	$Eu_2O_3 + {}^1/_2Mn_2O_3 + {}^3/_{10}Ta_2O_5 + {}^2/_5Ta$	1200°, 2 days	$Eu(Mn_{0.33}Ta_{0.67})O_3$ (major) + Eu_3TaO_7 (minor)
Mn	$EuO + {}^1/_4Mn_2O_3 + {}^1/_4Ta_2O_5$	1100°, 1 day	$Eu(Mn_{0.33}Ta_{0.67})O_3$ (major) + Eu_3TaO_7 (minor)
Fe	$Eu_2O_3 + {}^1/_2Fe_2O_3 + {}^3/_{10}Ta_2O_5 + {}^2/_5Ta$	1200°, 1 day	$EuFeO_3 + Eu_3TaO_7$
Ga	$EuO + {}^1/_4Ga_2O_3 + {}^1/_4Ta_2O_5$	1100°, 1 day	Eu_3TaO_7 (major) + weak, unidentified lines
Al	$EuO + {}^1/_2AlTaO_4$	1200°, 4 days; refire and regrind twice	$Eu(Al_{0.5}Ta_{0.5})O_3$ (yellow)
Eu	$EuO + {}^1/_4EuTaO_4$	1150°, 24 hr	$Eu(Eu_{0.5}Ta_{0.5})O_3 + Eu_3TaO_7$; prolonged firing does not eliminate Eu_3TaO_7
		$Eu(M_{0.5}Nb_{0.5})O_3$	
Ti	$Eu_2O_3 + {}^1/_2Ti_2O_3 + {}^3/_{10}Nb_2O_5 + {}^2/_5Nb$	1200°, 2 days	$Eu(Ti_{0.5}Nb_{0.5})O_3$ (major) + $EuTiO_3$ (minor)
Ti	$EuO + {}^1/_4TiNbO_4$	1100°, 2 days	$Eu(Ti_{0.5}Nb_{0.5})O_3$ (blue-black)
V	$Eu_2O_3 + {}^1/_2V_2O_3 + {}^3/_{10}Nb_2O_5 + {}^2/_5Nb$	1200°, 2 days	$Eu(V_{0.5}Nb_{0.5})O_3$ (black) + other trace phases
V	$EuO + {}^1/_2VNbO_4$	1100°, 2 days	$EuVO_3$ (major phase)
Cr	$Eu_2O_3 + {}^1/_2Cr_2O_3 + {}^3/_{10}Ta_2O_5 + {}^2/_5Ta$	1150°, 4 days	$Eu(Cr_{0.5}Nb_{0.5})O_3$ (dark gray) Eu_3NbO_7 (trace)
Cr	$EuO + {}^1/_4Cr_2O_3 + {}^1/_4Nb_2O_5$	1100°, 4 days	$Eu(Cr_{0.5}Nb_{0.5})O_3 + Eu_3NbO_7$ (trace)
		$Eu(M_{0.33}Ta_{0.67})O_3$	
Mg	$Eu_2O_3 + MgO + Ta_2O_5 + Ta$	1200°, 1 day	$Eu(Mg_{0.33}Ta_{0.67})O_3 + Eu_3TaO_7$ (trace)
Mg	$EuO + {}^1/_3MgTa_2O_6$	1100°, 1 day	$Eu(Mg_{0.33}Ta_{0.67})O_3$ + (yellow–yellow-green)
Mn	$EuO + {}^1/_3MnO + {}^1/_3Ta_2O_5$	1200°, 2 days	$Eu(Mn_{0.33}Ta_{0.67})O_3 + Eu_3TaO_7$ (trace)
Mn	$EuO + {}^1/_3MnTa_2O_6$	1100°, 1 day	$Eu(Mn_{0.33}Ta_{0.67})O_3$ (yellow)
Ni	$EuO + {}^1/_3NiO + {}^1/_3Ta_2O_5$	900°, 1 day; 1200°, 1 day	Eu_3TaO_7 (major) + unidentified phases
		$Eu(M_{0.33}Nb_{0.67})O_3$	
Mg	${}^1/_2Eu_2O_3 + {}^1/_3MgO + {}^7/_{30}Nb_2O_5 + {}^1/_5Nb$	1200°, 1 day; required refire; 1200°, 2 days	$Eu(Mg_{0.33}Nb_{0.67})O_3$ (dark gray)
Mg	$EuO + {}^1/_3MgO + {}^1/_3Nb_2O_5$	1100°, 2 days	$Eu(Mg_{0.33}Nb_{0.67})O_3$
Mn	$EuO + {}^1/_3MnO + {}^1/_3Nb_2O_5$	1200°, 2 days	$Eu(Mn_{0.33}Nb_{0.67})O_3 + Eu_3NbO_7$ (trace)
		$Eu(Cr_{0.67}M_{0.33})O_3$	
W	$EuO + {}^1/_3Cr_2WO_6$	1200°, 1 day	$EuCrO_3$ (major) + $EuWO_4 + Eu_6WO_{12}$ + W
U	$EuO + {}^1/_3Cr_2O_3 + {}^1/_3UO_3$	1200°, 1 day	$EuCrO_3$ (major) + UO_2–Eu_2O_3 solid soln
Re	$EuO + {}^2/_3Cr_2O_3 + {}^1/_3ReO_3$	960°, 2 days	$EuCrO_3$ (major)

[a] Prepared by firing $MgO + WO_3 \cdot H_2O$ at 1000°, 12 hr. Use of commercial $MgWO_4$ (Ventron) resulted in substantial $EuWO_4$ impurity under the same reaction conditions. [b] Green crystals of MnO were found in the cool end of the tube after completion of the run under these conditions. [c] Metallic Zn mirror appeared upon flaming of the tube prior to sealing under vacuum.

Table II. Existence of Perovskite Phases of the Type $Eu(M,M')O_3$

Perovskite

$(M^{II}_{0.5},M^{II}_{0.5})$ = (Mg,W), (Mn,W), (Ca,W),[a] (Sr,W)[a]
$(M^{III}_{0.5},M^{V}_{0.5})$ = (Al,Ta), (Ti,Ta), (V,Ta), (Cr,Ta), (Eu,Ta), (Ti,Nb), (V,Nb), (Cr,Nb)
$(M^{II}_{0.33},M^{V}_{0.67})$ = (Mg,Ta), (Mn,Ta), (Mg,Nb), (Mn,Nb)

No Perovskite

$(M^{II}_{0.5},M^{VI}_{0.5})$ = (Mg,Mo), (Mn,Mo), (Ni,W), (Co,W), (Cu,W), (Zn,W), (Mg,U), (Mg,Re), (Eu,W)[a,b]
$(M^{III}_{0.5},M^{V}_{0.5})$ = (Mn,Ta), (Fe,Ta), (Ga,Ta), (Mn,Nb), (Fe,Nb), (Cr,W), (Cr,Re), (Cr,Mo)
$(M^{II}_{0.33},M^{V}_{0.67})$ = (Co,Ta), (Ni,Ta), (Mg,Sb)
$(M^{III}_{0.67},M^{VI}_{0.33})$ = (Cr,W), (Cr,U), (Cr,Re)

[a] Reported by Shafer.[1] [b] McCarthy, *et al.*[2]

a large number of Sr^{2+} analogs of the type $Sr(M,M')O_3$ where (M,M') represents various combinations of metal ions, the average charge of which is 4+.

Experimental Section

General Preparative Procedure. All products were prepared by solid-state reaction. The components were weighed (typical total mass was 0.5 g) and thoroughly mixed using a high-speed mill. Pellets were pressed and loaded into a quartz tube. If EuO was a part of the reaction mixture, the tube was fitted with a liner of Mo foil to prevent reaction between EuO and the silica wall. In a few instances Ta foil was used but its high reactivity was usually found to be detrimental in most cases. Pt foil was also found to be unsatisfactory under these nonoxidizing conditions. The quartz tube and contents were carefully outgassed on a vacuum line by gently heating to red heat until a pressure of 10^{-5} Torr could be maintained and then the tube was sealed. Details of the heat treatment including actual temperature and duration for each preparation are given in a following section. After heating, the ampoules and contents were water-quenched. EuO was prepared according to Shafer[1] using an excess of Eu metal (Research Chemicals 99.9%) and 99.9 or 99.99% Eu_2O_3 (also Research Chemicals) in a Ta crucible. All other starting materials were either reagent grade or better.

The phase purity and structure type of the products were characterized by X-ray powder data, using a Siemens diffractometer with a scintillation detector and Cu Kα radiation (λ 1.54178 Å). Calibration was done with high-purity Si (a_0 = 5.4301 Å), Ag (a_0 = 4.086 Å), W (a_0 = 3.1652 Å), and CdO (a_0 = 4.6958 Å) obtained from the National Bureau of Standards. Precision cell constants were determined by a least-squares computer refinement of unambiguously indexed reflections. See Table I for experimental procedures and results.

Results

The existence or nonexistence of the perovskite phases $Eu(M,M')O_3$ is charted in Table II *vs.* the (M,M') combination which occupies the small cation site. All results are from this work except those indicated. Some remarks should be made here regarding what is meant by the nonexistence of an $Eu(M,M')O_3$ perovskite phase. Indirect evidence that a europium(II) perovskite exists is obtained if the powder pattern is essentially identical with that of the Sr^{2+} analog. In several cases magnetic[3] and Mössbauer[4] evidences have confirmed the assignments based on X-ray inference. When we report that an europium(II) perovskite does not exist, we mean simply that no perovskite phase can be detected by X-ray analysis when an appropriate reaction mixture is fired under conditions sufficient to prepare the Sr^{2+} analog. This operational definition does not preclude the possibility that under some other set of conditions, perhaps extreme pressure or higher temperatures, the europium(II) perovskite phase might be stabilized. The firing temperatures for these preparations were limited by the use of quartz ampoules.

Precision cell parameters for most of the $Eu(M,M')O_3$ here are given in Table III. For comparison we have also included cell parameters for the Sr^{2+} analogs when available.

Table III. Precision Cell Parameters for $Eu(M,M')O_3$ and $Sr(M,M')O_3$ Phases

$Eu(M,M')O_3$	Cell parameter,[c] Å	$Sr(M,M')O_3$	Cell parameter, Å
$Eu(Mg_{0.5}W_{0.5})O_3$	7.901 (2)[a]	$Sr(Mg_{0.5}W_{0.5})O_3$[a]	7.9[d]
$Eu(Mn_{0.5}W_{0.5})O_3$	8.071 (3)[a]	$Sr(Mn_{0.5}W_{0.5})O_3$[a]	8.01[e]
$Eu(Mg_{0.33}Ta_{0.67})O_3$	3.991 (2)[b]	$Sr(Mg_{0.33}Ta_{0.67})O_3$[b]	4.00[f]
$Eu(Mg_{0.33}Nb_{0.67})O_3$	3.992 (2)[b]	$Sr(Mg_{0.33}Nb_{0.67})O_3$[b]	4.00[f]
$Eu(Mn_{0.33}Ta_{0.67})O_3$	4.027 (2)[b]	$Sr(Mn_{0.33}Ta_{0.67})O_3$[b]	
$Eu(Mn_{0.33}Nb_{0.67})O_3$	4.028 (3)[b]	$Sr(Mn_{0.33}Nb_{0.67})O_3$[b]	
$Eu(Al_{0.5}Ta_{0.5})O_3$	7.794 (2)[a]	$Sr(Al_{0.5}Ta_{0.5})O_3$	
$Eu(Ti_{0.5}Ta_{0.5})O_3$	3.964 (2)	$Sr(Ti_{0.5}Ta_{0.5})O_3$	3.967 (1)[g]
$Eu(Ti_{0.5}Nb_{0.5})O_3$	3.965 (2)	$Sr(Ti_{0.5}Nb_{0.5})O_3$	
$Eu(V_{0.5}Ta_{0.5})O_3$	3.974 (2)	$Sr(V_{0.5}Ta_{0.5})O_3$	3.967[h]
$Eu(V_{0.5}Nb_{0.5})O_3$	3.971 (2)	$Sr(V_{0.5}Nb_{0.5})O_3$	3.965[h]
$Eu(Cr_{0.5}Ta_{0.5})O_3$	3.938 (2)	$Sr(Cr_{0.5}Ta_{0.5})O_3$	3.94[i]
$Eu(Cr_{0.5}Nb_{0.5})O_3$	3.938 (2)	$Sr(Cr_{0.5}Nb_{0.5})O_3$	3.93[j]

[a] These phases had the ordered $(NH_4)_3FeF_6$ structure. [b] Indexed as simple cubic; superlattice lines too weak to permit reliable determination of hexagonal cell parameters. [c] Numbers in parentheses indicate the standard deviation in the last significant figure. [d] Reference 5. [e] Reference 6. [f] Reference 7. [g] This work. [h] Reference 8. [i] Reference 9. [j] Reference 10.

Full assay analyses were not done for any of the compounds of Table III. Therefore the compositions reported are idealized with respect to both metal and oxygen content. $EuTiO_3$ is known to exist in oxygen-deficient form, $EuTiO_{3-x}$, and some of these new phases might exhibit similar behavior[17]. A europium deficiency could also arise given the well-known tendency of the starting material to decompose according to $4EuO(s) \rightarrow Eu(v) + Eu_3O_4(s)$ at the preparation temperatures used here[18]. Any vapor thus produced would react with the ampoule walls to form europium silicates.

Discussion

Since Sr^{2+} analogs exist for all phases shown in Table II, it is reasonable to infer that the nonexistence of the $Eu(M,M')O_3$ perovskite is due to the reducing power of Eu^{2+} in oxides. In part I (preceding paper) guidelines for predicting the existence of $EuMO_3$ perovskite were presented. Here we extend these guidelines to include the ions encountered in the $Eu(M,M')O_3$ phases. In this analysis we compare at the reference temperature, 1500°K, $\Delta G_f(T)$/mol of O_2 for the hypothetical reaction $2Eu_2O_3 \rightarrow 4EuO + O_2$ with those for reactions in which complete reduction to the element occurs

$$2Mg_2O \rightarrow 4M + O_2 \tag{1}$$

$$2MO \rightarrow 2M + O_2 \tag{2}$$

$${}^2/_3M_2O_3 \rightarrow {}^4/_3M + O_2 \tag{3}$$

$$^2/_5M_2O_5 \rightarrow {}^4/_5M + O_2 \tag{4}$$

$$^2/_3MO_3 \rightarrow {}^2/_3M + O_2 \tag{5}$$

and with those for which reduction to a lower oxide occurs

$$2MO_3 \rightarrow 2MO_2 + O_2 \tag{6}$$

$$2M_2O_5 \rightarrow 4MO_2 + O_2 \tag{7}$$

$$2M_2O_3 \rightarrow 4MO + O_2 \tag{8}$$

These data are shown in Tables IV and V and can be compared directly with Table II.

Type ($M^{II}_{0.5}M^{VI}_{0.5}$). Table IV predicts that the 2+ ions Sr^{2+}, Mg^{2+}, and Ca^{2+} should resist reduction by Eu^{2+} while Co^{2+} and Ni^{2+} should not, in agreement with the results of Table II. Fe^{2+} should also be reduced but no experiment was carried out here. Mn^{2+} is a borderline case which is found to be stable. Eu^{2+} should also be stable as a B-site ion but apparently is not. Table IV indicates that no 6+ ions should be compatible with Eu^{2+}, yet W^{6+} exists in four mixed perovskites and the scheelitie $EuWO_4$. These results suggest that the lattice free energy is critical in stabilizing W^{6+} in the presence of Eu^{2+}. Of relevance here are the tolerance factors shown in Table VI for all of the mixed perovskites. Those compounds which are either difficult or impossible to prepare,

Table IV. Free Energy of Reduction of Binary Oxides Per Mole of O_2 to the Element at 1500°K (kcal mol^{-1})[a]

Oxide	ΔG(1500 °K)
CaO	231
$(RE)_2O_3$ (RE = La-Lu)	218-230
SrO	212
MgO	202
Al_2O_3	190
Li_2O	180
Ti_2O_3	178
B_2O_3	142
V_2O_3	137
Ta_2O_5	136
....	
MnO	130
Cr_2O_3	118
Ga_2O_3	95
FeO	82
WO_3	80
ZnO	78
Na_2O	76
In_2O_3	75
MoO_3	66
K_2O	56
NiO	54
CoO	53

[a] Dotted line indicates position of the reaction $2EuO + O_2 \rightarrow 2Eu_2O_3$.

Table V. Free Energy of Reduction of Binary Oxides Per Mole of O_2 to Lower Oxides at 1500°K (kcal mol^{-1})[a]

Reaction	ΔG(1500°K)
....	
$2Nb_2O_5 \rightarrow NbO_2 + O_2$	90
$2Fe_2O_3 \rightarrow 4FeO + O_2$	51
$2MoO_3 \rightarrow 2MoO_2 + O_2$	35
$2Mn_2O_3 \rightarrow 4MnO + O_2$	22
$Sb_2O_5 \rightarrow Sb_2O_3 + O_2$	<0
$2UO_3 \rightarrow 2UO_2 + O_2$	<0

[a] Dotted line indicates position of the reaction $2EuO + O_2 \rightarrow 2Eu_2O_3$.

(Eu,W) and (Sr,W), have the least favorable tolerance factors and presumably the least favorable lattice free energy for perovskite formation. The (M^{II},W^{VI}) systems which do exist also exhibit ordering among the B-site cations which adds a favorable term to the Madelung energy[12].

According to Tables IV and V all other 6+ ions should be even less stable than W^{6+}, with respect either to reduction to the element (Mo^{6+}, Re^{6+}) or to a lower oxidation state (U^{6+}). The failure to form any perovskite phases containing Mo^{6+}, Re^{6+}, or U^{6+} is in good accord with these predictions. The existence of the scheelite $EuMoO_4$ is perhaps surprising. Apparently, the relatively small Mo^{6+} and W^{6+} ions find fourfold coordination in the scheelite to be more favorable energetically than the sixfold site of perovskite.

$Eu(M^{III}_{0.5}M^{V}_{0.5})O_3$. Tables IV and V predict that Eu^{3+} (and the other lanthanides as well), Al^{3+}, Ti^{3+}, and V^{3+} should all be stable to reduction while Mn^{3+}, Fe^{3+}, and In^{3+} should not, in good agreement with Table II. The ability of Eu^{2+} to reduce Fe^{3+} has been noted by McCarthy, *et al.*, in their study of the Eu–Fe–O system.[13] Cr^{3+} and Ga^{3+} are borderline cases with Cr^{3+} being stable and Ga^{3+} being reduced according to experiment. The case of Mn^{3+} merits some comment. Clearly, Mn^{3+} should be easily reduced to Mn^{2+}. In all attempts to prepare $Eu(Mn_{0.5}Ta_{0.5})O_3$ and $Eu(Mn_{0.5}Nb_{0.5})O_3$ a perovskite phase was the major product along with weaker lines of a fcc phase. The cell constant for the perovskite phase was found to be identical with that of $Eu(Mn^{II}_{0.33}Ta^{V}_{0.67})O_3$ indicating Mn^{3+} reduction as predicted. The Eu^{3+} generated probably forms the fcc phase which appears to be Eu_3NbO_7 or Eu_3TaO_7.[14]

Table VI. Tolerance Factors[a] for Mixed Perovskites

M	t	M	t
I. Type $Eu(M^{II}_{0.5}W^{VI}_{0.5})O_3$			
Eu	0.884	Mg	0.980
Sr	0.884	Ni	0.985
Ca	0.918	Co	0.975
Mn	0.957		
II. Type $Eu(M^{III}_{0.5}Ta^{V}_{0.5})O_3$ or $Eu(M^{III}_{0.5}Nb^{V}_{0.5})O_3$			
Al	1.01	Ti	0.976
Cr	0.990	Mn	0.985
Ga	0.990	In	0.950
Fe	0.985	Eu	0.916
V	0.985		
III. Type $Eu(M^{II}_{1/3}Ta^{V}_{2/3})O_3$ or $Eu(M^{II}_{1/3}Nb^{V}_{2/3})O_3$			
Mg	0.972	Ni	0.975
Mn	0.957	Eu	0.907
Co	0.971		
IV. Type $Eu(M^{III}_{2/3}M^{VI}_{1/3})O_3$			
Cr,W	1.00	V,W	0.995
Fe,W	0.995	Ti,W	0.985
Cr,Re	1.01	Cr,U	0.975
V. Type $Eu(M^{I}_{0.25}Ta^{V}_{0.75})O_3$			
Li	0.974	K	0.901
Na	0.941		

[a] The tolerance factor is defined as

$$t = \frac{r(Eu^{2+}) + r(O^{2-})}{\sqrt{2}[r(M,M')_{av} + r(O^{2-})]}$$

where $r(M,M')_{av}$ is the weighted average of the radii of cations occupying the sixfold site. The radii are from ref 11 with careful attention to coordination number.

Among the pentavalent ions, Ta^{5+} should be stable but Nb^{5+} is a borderline case and indeed should be reduced to Nb^{4+} according to Table VI. This reduction may have occurred to a limited extent in our preparations but the cell constants for the corresponding tantalates and niobates are essentially identical indicating that substitution of Eu^{3+}–Nb^{4+} for Eu^{2+}–Nb^{5+} within the perovskite lattice is probably small. However, traces of additional phases were normally found in the niobate products.

$Eu(M^{II}_{0.33}M^{V}_{0.67})O_3$. The same divalent ions which were stable in the (M^{II},M^{VI}) systems are stable here, and similarly for pentavalent ions in the systems (M^{III},M^{V}). The comments made in the two preceding subsections apply here as well. It is worth noting that we did attempt to prepare a phase of the type $Sr(Sr_{0.33}Ta_{0.67})O_3$ without success.

$Eu(M^{III}_{0.67}M^{VI}_{0.33})O_3$. No compounds of this type could be made. This is surprising for $Eu(Cr_{0.67}W_{0.33})O_3$ since Cr^{3+} is stable in the (M^{III},M^{V}) phases and W^{6+} in certain (M^{II},W^{VI}) phases. Furthermore, the tolerance factor for this composition is near the ideal value, and the Sr analog is reported to show some degree of ordering between Cr^{3+} and W^{6+}.[15] Nonetheless, all of our preparations resulted in a multiphase mixture of $EuCrO_3$, $EuWO_4$, Eu_6WO_{12}, and W.

$Eu(M^{I}_{0.25}M^{V}_{0.75})O_3$. Although this system was not investigated experimentally here, we can speculate upon the outcome of attempted preparations. $Sr(Na_{0.25}Ta_{0.75})O_3$ has been reported[16] while $Sr(Li_{0.25}Ta_{0.75})O_3$ has not, though clearly its tolerance factor is favorable. $Sr(K_{0.25}Ta_{0.75})O_3$ may exist but its tolerance factor is least favorable. From the redox point of view only ($Li_{0.25}Ta_{0.75}$) should definitely form. ($Na_{0.25}$-$Ta_{0.75}$) is a marginal case, and $(M_{0.25}Ta_{0.75})5$ seems quite unlikely.

Extension to Crystal Systems Other than Perovskites. Table I of part I lists stable europium(II) oxides of many structure types. There is good agreement between this table and our redox guidelines contained in Tables IV and V of this paper and Tables II and III of part I. This confirms the generality of these guidelines for the prediction of new europium(II) oxide phases, providing the proposed phase has an Sr^{2+} analog and the lattice energy of the phase is favorable. In fact the lattice energy often favors the existence of a complex phase, as in $EuMoO_4$, $EuWO_4$, and various Eu–M–W–O phases, where it is sufficient to overcome unfavorable redox thermodynamics.

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Registry No. $Eu(Mg_{0.5}W_{0.5})O_3$, 53881-32-6; $Eu(Mn_{0.5}W_{0.5})O_3$, 53182-85-7; $Eu(Mg_{0.33}Ta_{0.67})O_3$, 51912-62-0; $Eu(Mg_{0.33}Nb_{0.67})O_3$, 53973-48-1; $Eu(Mn_{0.33}Ta_{0.67})O_3$, 51912-63-1; $Eu(Mn_{0.33}Nb_{0.67})O_3$, 53973-49-2; $Eu(Al_{0.5}Ta_{0.5})O_3$, 51846-03-8; $Eu(Ti_{0.5}Ta_{0.5})O_3$, 53973-50-5; $Eu(Ti_{0.5}Nb_{0.5})O_3$, 53992-02-2; $Eu(V_{0.5}Ta_{0.5})O_3$, 53973-51-6; $Eu(V_{0.5}Nb_{0.5})O_3$, 53973-52-7; $Eu(Cr_{0.5}Ta_{0.5})O_3$, 51912-44-8; $Eu(Cr_{0.5}Nb_{0.5})O_3$, 53973-53-8; $Sr(Ti_{0.5}Ta_{0.5})O_3$, 53992-01-1.

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Contribution from the Department of Chemistry,
University of Michigan, Ann Arbor, Michigan 48104

Preparation and Some Properties of Ytterbium Carbide Hydrides

JOHN M. HASCHKE

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Equilibria in the ytterbium–carbon–hydrogen system have been investigated for various carbon to metal ratios at 900° and 0.5 atm of hydrogen. Samples were prepared by reaction of the dihydride and graphite in molybdenum containers. Two ytterbium carbide hydride phases have been identified by X-ray diffraction and chemical analysis; hexagonal $YbC_{0.5}H$ ($a = 3.575 \pm 0.002$, $c = 5.786 \pm 0.004$ Å) and fcc $YbCH_{0.5}$ ($a = 4.974 \pm 0.001$ Å) are observed. Magnetic, electrical, and hydrolysis data have been obtained and employed in describing these phases on the basis of ionic models. Structures which account for the observed nonstoichiometry and phase equilibria of the carbide hydrides are proposed. In the presence of oxygen, metastable fcc products with lattice parameters in the range 4.85–4.96 Å have been observed between the $YbO_{0.5}C_{0.5}$ and $YbCH_{0.5}$ compositions; this quaternary phase appears to be the metal-rich carbide reported for the composition range $YbC_{0.30}$–$YbC_{0.65}$. Attempts to prepare the analogous carbide hydrides of europium were unsuccessful; however, the previously reported metal-rich europium carbide, EuC_x, has been identified as EuO.

Introduction

Several investigations of the ytterbium–carbon system have been described;[1-4] however, conflicting reports have appeared on the composition and properties of the most metal-rich carbide, the so-called hypocarbide. The existence of a nonstoichiometric fcc phase ($a = 4.993$ Å) near $YbC_{0.33}$ was first reported by Spedding, *et al.*,[1] who prepared their product by direct combination of the elements. By treating ytterbium dihydride with graphite, Lallement[2] also obtained an fcc phase of variable composition ($YbC_{0.3}$ to $YbC_{0.65}$) with lattice parameters which ranged from 4.88 to 4.96 Å at the carbon-rich and metal-rich boundaries, respectively. Haschke and Eick,[3] who investigated the composition range from Yb to YbC_2 by direct reaction of the elements, obtained a dimorphic phase near the $YbC_{0.5}$ composition; an ordered anti-$CdCl_2$-type rhombohedral Yb_2C phase ($a = 6.176$ Å, $\alpha = 33.33°$) was found to coexist with a disordered fcc $YbC_{0.5\pm z}$ phase ($a = 5.001$ Å) of variable composition. Laplace and Lorenzelli[4] repeated the procedures of Lallement and found a similar fcc phase with a between 4.85 and 4.97 Å. Their investigation was also extended to the europium–carbon system for which an analogous fcc phase ($a = 5.141$–5.145 Å) was observed. The noticeable differences between results obtained in the presence and absence of hydrogen led Haschke and Eick[3] to suggest that the phase reported by Lallement is a carbide hydride of variable composition.

In an effort to resolve the differences in the data for the metal-rich carbides and to investigate the possible existence of carbide hydrides of europium and ytterbium, an investigation of the phase equilibria in the metal–carbon–hydrogen systems of these elements was initiated.

Experimental Section

Preparative Procedures. Phase equilibria in the Yb–C–H system were examined at constant temperature and constant hydrogen pressure with various C:Yb ratios, x, according to eq 1. The dihydride

$$YbH_2(s) + xC(s) \rightarrow YbC_xH_y(s) + [(2-y)/2]H_2(g) \qquad (1)$$

was prepared from the elements (Yb, 99.9%, distilled, Rare Earth Research Corp.; H_2, prepurified, Matheson) by procedures similar to that described previously,[5] and oxygen-free samples were prepared by a vapor-transport procedure. Samples of YbH_2 or Yb metal were placed in a Mo tube (6.4-mm o.d. × 150 mm) under 0.5 atm of H_2. The dihydride was transported and single crystals were grown under a temperature gradient of 900–600°. The powdered dihydride was combined with finely divided graphite (spectrographic grade rod, Ultra Carbon) in the desired stoichiometric ratios; the components were mixed throughly and placed in reaction containers fashioned of 6.4-mm o.d. × 40-mm length molybdenum tubing. The capsules were welded at one end and were closed at the other with a snugly fitting plug which