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Phase Equilibria in the Fe–Fe_2O_3–Eu_2O_3 System at 1200 °C

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The standard Gibbs energies of the reaction of $EuFeO_3$ and $Fu_3Fe_5O_{12}$ were determined to be -63300 ± 200 cal and -297800 ± 600 cal respectively at 1200 °C by means of following reactions: $Fe+1/2\ Eu_2O_3+3/4\ O_2=EuFeO_3$ and $5\ Fe+3/2\ Eu_2O_3+15/4\ O_2=Eu_3Fe_5O_{12}$, based on the phase equilibria in the Fe–Fe_2O_3–Eu_2O_3 system.

Many works on the double oxides involving rare earth sesquioxide and iron oxide have been investigated from the standpoint of crystal chemistry and the magnetic properties of perovskite and garnet structures.[1] Recently, Bedford and Catalano[2] have confirmed the existence of EuO, Eu_3O_4, and Eu_2O_3 at 1500 °C; they were first found by Bärnighausen.[3] McCarthy and Fischer[4] have also studied the Eu–Fe–O system at 1200 °C in a flowing argon atmosphere; they have also confirmed these compounds in addition to $EuFeO_3$ and $Eu_3Fe_5O_{12}$. However, very few studies have been done on the Gibbs energy of the reaction of lanthanoid-iron -perovskite or -garnet.

Recently, Kimizuka and Katsura[5] have determined the standard Gibbs energy of the reaction of $LaFeO_3$ from metallic iron, La_2O_3, and oxygen on the basis of the phase equilibria in the Fe–Fe_2O_3–La_2O_3 system at 1204 °C. They[6] have also established the phase equilibria in the Fe–Fe_2O_3–Y_2O_3 system at 1200 °C and determined the Gibbs energy of the reactions of $YFeO_3$, $Y_3Fe_5O_{12}$, and YFe_2O_4.

In the present study, we have determined the standard Gibbs energy of the reaction of $EuFeO_3$ and $Eu_3Fe_5O_{12}$ at 1200 °C on the basis of the phase equilibria in the Fe–Fe_2O_3–Eu_2O_3 system.

Experimental

Materials. High-purity-grade (99.9%) Eu_2O_3 and guaranteed-reagent-grade Fe_2O_3 were employed as the starting substances. Eu_2O_3 was heated at 1200 °C in air for 2 days to obtain B-type Eu_2O_3.[7] Fe_2O_3 was heated at 900 °C in air for 1 day. The subsequent procedures to obtain the sintered mixtures were the same as those described in a previous paper.[5]

Apparatus and Procedures. The quenching and thermogravimetric methods were adopted in the present study; the details of the procedures have been described by Kimizuka and Katsura.[5],[6] The weight of the sample in oxygen was chosen as the reference for thermogravimetry. The equilibrium composition was determined by means of two side reactions. The quenching method employed in the present study is the same as that described in a previous paper,[6] the phases in quenched samples were identified by the powder X-ray diffraction method, with Mn-filtered Fe-$K\alpha$ radiation. The Fe^{2+}/Fe^{3+} ratio in the quenched nonstoichiometric $EuFeO_3$ was determined by the wet chemical method.[8]

Results and Discussion

Phase Equilibria. The equilibrium data at 1200 °C are summarized in Table 1 and are illustrated in Fig. 1. The following phases were stable under the present ex-

TABLE 1. DATA FOR EQUILIBRIA IN THE Fe–Fe_2O_3–Eu_2O_3 SYSTEM AT 1200°C

log P_{O_2} ($\pm$0.02)	Fe	Fe_2O_3 (mole %)	Eu_2O_3	Phases
0.00	0.00	38.00	62.00	E+Pv
	0.00	50.00	50.00	Pv
	0.00	57.00	43.00	Pv+G
	0.00	62.50	37.50	G
	0.00	78.56	21.44	H+G
	0.00	80.00	20.00	H+G
	0.00	90.00	10.00	H+G
3.88	0.00	57.00	43.00	Pv+G
	0.00	62.50	37.50	G
	10.14	70.92	18.94	M+G
	9.36	70.20	20.44	M+G
	15.05	75.70	9.25	M+G
9.14	3.75	53.39	42.91	M+Pv
	6.01	57.61	36.38	M+Pv
	12.50	67.40	20.10	M+Pv
	13.10	68.21	18.69	M+Pv
	16.92	73.93	9.15	M+Pv
9.27	6.42	51.96	41.62	W+Pv
	11.01	53.55	35.44	W+Pv
	23.39	57.68	18.93	W+Pv
	24.26	58.16	17.58	W+Pv
	30.96	60.60	8.44	W+Pv
9.80	25.44	57.10	17.46	W+Pv
10.26	26.68	55.99	17.33	W+Pv
10.82	28.06	54.74	17.20	W+Pv
11.26	29.31	53.62	17.07	W+Pv
11.92	8.45	50.37	41.18	W+Pv
	14.47	50.74	34.79	W+Pv
	29.29	52.42	18.31	W+Pv
	30.65	52.41	16.91	W+Pv
	38.49	53.44	8.07	W+Pv
12.09	23.59	38.48	37.93	Fe+Pv
	40.10	29.92	29.98	Fe+Pv
	72.25	14.05	13.70	Fe+Pv
	75.15	12.36	22.49	Fe+Pv
	88.75	5.69	5.56	Fe+Pv
12.51	0.69	37.53	61.78	E+Pv
	1.58	48.84	49.58	Pv
13.02	76.69	0.19	23.12	Fe+E
	87.61	0.34	12.05	Fe+E
	88.71	0.16	11.13	Fe+E
	94.56	0.17	5.27	Fe+E
15.80	66.66	0.01	33.33	Fe+E
	54.97	0.07	44.96	Fe+E
	72.22	0.31	27.47	Fe+E

Abbreviations have the following meaning: E=Eu_2O_3, Pv=$EuFeO_3$, G=$Eu_3Fe_5O_{12}$, H=Fe_2O_3, M=Fe_3O_4, W=FeO, Fe=metallic iron.

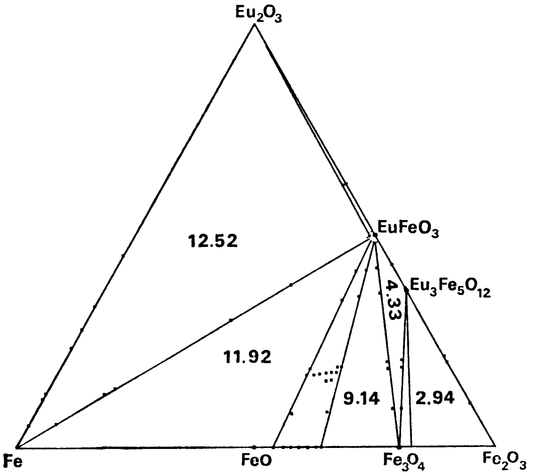

Fig. 1. Phase equilibria in the Fe-Fe$_2$O$_3$-Eu$_2$O$_3$ system at 1200 °C.
Numbers in the Figure mean values of $-\log P_{O_2}$ at which three crystalline phases are in equilibrium state. Small dots show the experimental results given in Table 1.

TABLE 2. LATTICE CONSTANTS OF Eu$_2$O$_3$ AND EuFeO$_3$

a) Eu$_2$O$_3$ (monoclinic B-type)

Lattice constants	Stoichiometric Eu$_2$O$_3$	Non-stoichiometric Eu$_2$O$_3$	Hoekstra[12]
a (Å)	14.102±0.005	14.113±0.004	14.12
b (Å)	3.601±0.001	3.603±0.001	3.600
c (Å)	8.806±0.004	8.808±0.003	8.801
β(deg)	100.02 ±0.3	100.05 ±0.2	99.98
V (Å^3)	440.3 ±0.3	441.0 ±0.2	

b) EuFeO$_3$ (Space group: D_{2h}^{16}-Pbnm, orthorhombic perovskite structure)

Lattice constants	EuFeO$_3$ coexisting with		Non-stoichiometric EuFeO$_3$	Stoichiometric EuFeO$_3$	Geller and Wood[13]
	Eu$_2$O$_3$	Eu$_3$Fe$_5$O$_{12}$			
a (Å)	5.373	5.371	5.373	5.373	5.371
b (Å)	5.607	5.605	5.607	5.604	5.611
c (Å)	7.683	7.684	7.685	7.684	7.686
V (Å^3)	231.4	231.3	231.5	231.3	231.6

Deviations in a, b, and c are ±0.001 by the least squares method, and those of V ±0.1.

perimental conditions: Europium sesquioxide (Eu$_2$O$_3$), hematite (Fe$_2$O$_3$), magnetite (Fe$_3$O$_4$), wüstite (FeO), metallic iron (γ-Fe), europium-iron-perovskite (EuFeO$_3$), and europium-iron-garnet (Eu$_3$Fe$_5$O$_{12}$). The equilibria among the three condensed phases are as follows: (1) EuFeO$_3$, Eu$_2$O$_3$, and metallic iron, (2) EuFeO$_3$, wüstite, and metallic iron, (3) EuFeO$_3$, magnetite, and wüstite, (4) EuFeO$_3$ Eu$_3$Fe$_5$O$_{12}$, and magnetite, and (5) Eu$_3$Fe$_5$O$_{12}$, magnetite, and hematite. The following phases were characterized with respect to the stoichiometry: (a) Pure Eu$_2$O$_3$ was stable down to an oxygen partial pressure of $10^{-15.80}$ atm. However, it showed a small degree of non-stoichiometry at $10^{-15.80}$ atm. McCarthy and White[9] have reported the approximate phase relation of the Eu-Eu$_2$O$_3$ system at elevated temperatures up to 2200 °C; they showed the non-stoichiometry for Eu$_2$O$_3$ at 1200 °C and about 10^{-15} atm P_{O_2}, but they did not ascertain the extent of this non-stoichiometry. In the present study, by means of the thermogravimetric method, we determined the composition of the non-stoichiometric Eu$_2$O$_3$ phase to be Eu$_2$O$_{2.98\pm0.02}$ at $10^{-15.80}$ atm P_{O_2}: The lattice constants of both stoichiometric and non-stoichiometric Eu$_2$O$_3$ are given in Table 2. It is supposed that the non-stoichiometric Eu$_2$O$_3$ has a larger unit cell volume than the stoichiometric Eu$_2$O$_3$; this may be caused by the substitution of Eu^{2+} for Eu^{3+}. (b) The deviation from the stoichiometric composition of Eu$_3$Fe$_5$O$_{12}$ was not observed, and the lattice constants of the respective Eu$_3$Fe$_5$O$_{12}$ compounds equilibrated with Fe$_2$O$_3$, EuFeO$_3$ and with Fe$_3$O$_4$ were identical with each other. The values of stoichiometric Eu$_3$Fe$_5$O$_{12}$ are identical with those obtained by Espinosa.[10] (c) EuFeO$_3$ showed a significant deviation from the stoichiometry at relatively low oxygen partial pressures. The degree of non-stoichiometry was determined by both thermogravimetry and wet chemical analysis. These results were consistent with each other. The maximum deviation was determined to be EuFeO$_{2.976}$ at an oxygen partial pressure of $10^{-12.52}$ atm; at this point the non-stoichiometric EuFeO$_3$ was in equilibrium with both metallic iron and stoichiometric Eu$_2$O$_3$. EuFeO$_3$ shows a small but equivocal solubility of the three components. Since we could not determine the exact boundary of the EuFeO$_3$ field, the EuFeO$_3$ field was approximately bounded by the dotted line shown in Fig. 1. The lattice constants of EuFeO$_3$ in equilibrium with Eu$_2$O$_3$ and Eu$_3$Fe$_5$O$_{12}$, and of non-stoichiometric EuFeO$_3$ with the composition of EuFeO$_{2.976}$, were compared with those of stoichiometric EuFeO$_3$ given in Table 2.

(2) Calculation of the Standard Gibbs Energy of the Reaction of EuFeO$_3$ and Eu$_3$Fe$_5$O$_{12}$. On the basis of the phase equilibria, we may determine the following two standard Gibbs energies of the reaction of EuFeO$_3$ and Eu$_3$Fe$_5$O$_{12}$ from metallic iron, Eu$_2$O$_3$, and oxygen:

$$\mathrm{Fe} + 1/2\,\mathrm{Eu_2O_3} + 3/4\,\mathrm{O_2} = \mathrm{EuFeO_3} \qquad (1)$$

$$5\,\mathrm{Fe} + 3/2\,\mathrm{Eu_2O_3} + 15/4\,\mathrm{O_2} = \mathrm{Eu_3Fe_5O_{12}} \qquad (2)$$

Since the EuFeO$_3$ component in equilibrium with metallic iron and Eu$_2$O$_3$ has the composition of EuFeO$_{2.976}$, it is convenient to choose the reference activity of the EuFeO$_3$ component as unity at this composition. As has been described before, the Eu$_2$O$_3$ component had a small compositional variation at lower oxygen partial pressures. However, the composition of Eu$_2$O$_3$ was nearly stoichiometric at an oxygen partial pressure of $10^{-12.52}$ atm, at which Reaction (1) was in the equilibrium state. Thus, with reference to Eq. (1), we may determine the standard Gibbs energy of the reaction of EuFeO$_3$ as follows

$$\Delta G^0(1) = 3/4\,RT \ln P_{O_2} = -63300\pm200\ \mathrm{cal\cdot mol^{-1}},$$

where R and T indicate the gas constant and the absolute temperature respectively. The experimental error was estimated on the basis of the fluctuations of both temperature and the oxygen partial pressure.

Because the stoichiometric $Eu_3Fe_5O_{12}$ was in equilibrium with both stoichiometric $EuFeO_3$ and Fe_3O_4 at an oxygen partial pressure of $10^{-4.33}$ atm, the standard Gibbs energy change, referred to the following equation (3), may be calculated to be -4900 ± 200 cal:

$$3\,EuFeO_3 + 2/3\,Fe_3O_4 + 1/6\,O_2 = Eu_3Fe_5O_{12} \qquad (3)$$

According to Darken and Gurry,[11] the activity of metallic iron in stoichiometric magnetite in equilibrium with wüstite is $10^{-1.545}$ at 1200 °C, while the oxygen partial pressure related to the wüstite-magnetite equilibrium in $10^{-9.14}$ atm. Thus, the standard Gibbs energy of the formation of Fe_3O_4, $\Delta G^0(4)$, referred to the following equation (4) may be calculated to be -154500 ± 300 cal at 1200 °C:

$$3\,Fe + 2\,O_2 = Fe_3O_4 \qquad (4)$$

By adding $\Delta G^0(3)$, $2/3\Delta G^0(4)$, and $3\Delta G^0(1)$, we obtain the standard Gibbs energy of the reaction of $Eu_3Fe_5O_{12}$, $\Delta G^0(2)$, referred to Equation (2), as -297800 ± 600 cal.

It is interesting to compare the present Gibbs energy data with those of $LaFeO_3$, $YFeO_3$, and $Y_3Fe_5O_{12}$ which have been determined by Kimizuka and Katsura.[5,6] Comparing these data, we may observe that the standard Gibbs energy of the reaction of lanthanoid-iron perovskite from metallic iron, lanthanoid sesquioxide, and oxygen increases with decrease in the ionic radii of lanthanoid ions. The relationship between the ionic radii and the Gibbs energy will be discussed in more detail in the near future.

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