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Phase Equilibria in the Er_2O_3-V_2O_3-V_2O_5 System at 1200 °C

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The phase equilibria in the Er_2O_3–V_2O_3–V_2O_5 system have been established at 1200 °C. In this system, Er_2O_3, $Er_8V_2O_{17}(4Er_2O_3\cdot V_2O_5)$, $ErVO_3$, $ErVO_4$, V_nO_{2n-1}(n: 2 to 7), and VO_2 found to be stable, $Er_8V_2O_{17}$, $ErVO_4$, V_2O_3, and VO_2 of which had non-stoichiometric compositions. On the basis of the phase equilibria, the standard Gibbs energies for the reactions,

$$ErVO_3 + 1/2O_2 = ErVO_4, \qquad (1)$$

$$3Er_2O_3 + 2ErVO_3 + O_2 = Er_8V_2O_{17}, \qquad (2)$$

have been determined to be -121 ± 1 and -256 ± 1 kJ, respectively. It has been shown that the standard Gibbs energy for Sm, Er, and Lu in Eq. 1 decreases linearly with increasing ionic radius of lanthanoid.

In previous papers,[1,2] the phase equilibria in the Sm_2O_3–V_2O_3–V_2O_5 and the Lu_2O_3–V_2O_3–V_2O_5 systems were reported at 1200 °C. In both systems, the existence of the V_nO_{2n-1} (n: 2 to 7) phases were confirmed. In the former system, $Sm_{10}V_2O_{20}(5Sm_2O_3\cdot V_2O_5)$, $SmVO_3$, and $SmVO_4$, and in the latter, $LuVO_3$, $LuVO_4$, $Lu_7V_3O_{16}$, $Lu_2V_2O_7$, and LuV_4O_8 were stable as ternary compounds. On the basis of these phase equilibria, the standard Gibbs energies for the reactions related to the ternary compounds have been determined.

It has been reported that $ErVO_3$ is only the stable ternary compound in the Er_2O_3–V_2O_3 system, and that it belongs to the orthorhombic crystal system.[3,4] Recently, Brusset *et al.*[5,6] have studied the phase equilibria in the Er_2O_3–V_2O_5 system in the temperature range from 600 to 1500 °C, and found the existence of $4Er_2O_3\cdot V_2O_5$ and $5Er_2O_3\cdot V_2O_5$ in addition to the established tetragonal $ErVO_4$ phase, and concluded that $4Er_2O_3\cdot V_2O_5$ is stable at temperatures from 1350 to 1500 °C, and $5Er_2O_3\cdot V_2O_5$ from 1250 to 1500 °C.[5] Brusset *et al.*[7] reported that the $4Er_2O_3\cdot V_2O_5$ phase belongs to the monoclinic system, and determined the relative intensities, spacings and assignments of the index of this phase. The precise phase equilibria in the Er_2O_3–V_2O_3–V_2O_5 system have, however, not been investigated.

The objectives of the present study have been (1) to establish the detailed phase equilibria in the Er_2O_3–V_2O_3–V_2O_5 system at 1200 °C in order to clarify the stable ternary compounds, (2) to calculate the Gibbs energies of the reactions for ternary compounds, and (3) to ascertain, prior to pursuing the complete studies of the Ln–V–O system (Ln: La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y), wether or not there exists a linear relationship between the standard Gibbs energy of reaction and the ionic radius of the lanthanoid, as found in the Ln–Fe–O system.[8] Er_2O_3 has been selected as one of the lanthanoid sesquioxides in this paper.

Experimental

Analytical grades of Er_2O_3 (99.9% purity) and V_2O_5, made by heating guaranteed reagent grade NH_4VO_3 in air for 24 h at 500 °C, have been employed as starting materials. The desired ratios of Er_2O_3/V_2O_5 were obtained by mixing the appropriate quantities thoroughly in an agate mortar under ethyl alcohol. The mixtures thus obtained were treated by procedures previously described.[1]

Apparatus and procedures for controlling the partial pressure of oxygen, for keeping the temperature constant, the method of thermogravimetry, the criterion for establishing equilibrium, the method of identification of solid phases after quenching, of lattice constant determination, the method of measurement of the actual oxygen partial pressure, and the method of wet chemical analysis are the same described in previous papers.[1,9–11] On the basis of the previous results,[1] the weight of sample measured at an oxygen partial pressure of 10^{-12} atm has been chosen as the standard reference weight for thermogravimetry.

Results and Discussion

Phase Equilibria. Seven starting samples with different Er_2O_3/V_2O_5 ratios of 5.67, 4.00, 2.33, 1.50, 1.00, 0.667, and 0.250 were prepared. Figure 1 illustrates, as an example, the relationship between the oxygen partial pressure and the composition change, W_{O_2}/W_T, for samples with Er_2O_3/V_2O_5 ratios of 5.67, 1.50, and 0.250. W_{O_2} represents the weight gain of the samples assuming the reaction, $V_2O_3+O_2=V_2O_5$, were completed. Table 1 gives the results of the phase identification after quenching, and Fig. 2 illustrates the phase diagram. The following phases were found to be stable under the present experimental conditions; Er_2O_3(R), $ErVO_4$(B), $ErVO_3$(C), V_2O_3(D), V_3O_5(E), V_4O_7(F), V_5O_9(G), V_6O_{11}(H), V_7O_{13}(I), VO_2(J), and $Er_8V_2O_{17}$(N) ($4Er_2O_3\cdot V_2O_5$). The letters in parentheses are the abbreviations of compounds. The existence of the $4Er_2O_3\cdot V_2O_5$ phase contradicts the results of Brusset *et al.*[5] The stoichiometric existence of Er_2O_3 has been certified by Kitayama and Katsura.[12] As seen in Fig. 2, the phases $ErVO_4$, V_2O_3, VO_2, and $Er_8V_2O_{17}$ are of non-stoichiometric composition. The relationship between N_O/N_d and $\log P_{O_2}$ values for the solid solutions has been obtained using the results of thermogravimetric analysis and the method of least squares. Here, N_O/N_d indicates the deviation of the oxygen atoms from the stoichiometric composition d.[1,10] The empirical equations for $Er_8V_2O_{17}$ and $ErVO_4$ have been obtained as

$$N_O/N_{Er_8V_2O_{17}} = 0.0443 \log P_{O_2} + 0.108$$

and

$$N_O/N_{ErVO_4} = 0.0236 \log P_{O_2} + 0.180,$$

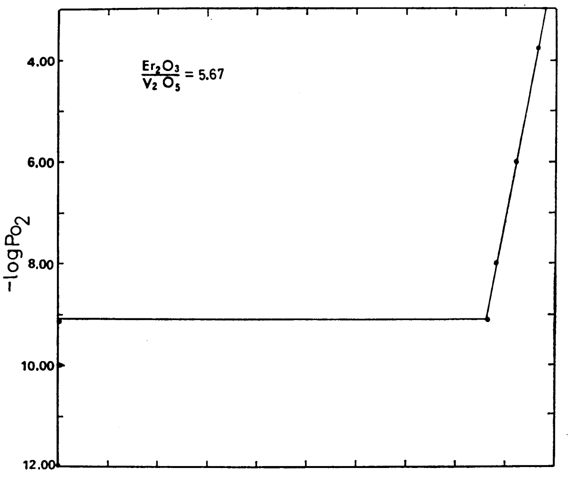

Fig. 1-1. The relationship between $-\log P_{O_2}$ and weight gains of the sample, $Er_2O_3/V_2O_5=5.67$.

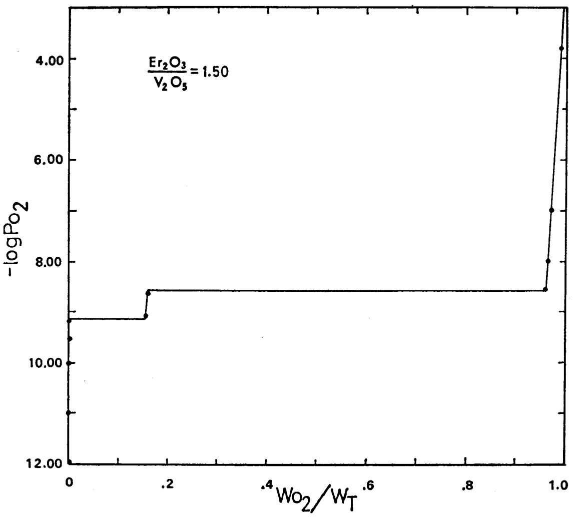

Fig. 1-2. The relationship between $-\log P_{O_2}$ and weight gains of the sample, $Er_2O_3/V_2O_5=1.50$.

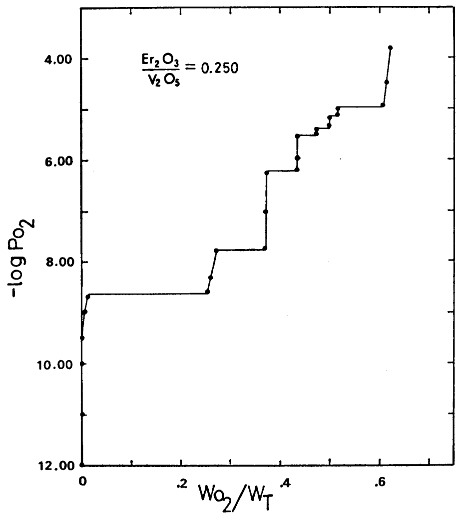

Fig. 1-3. The relationship between $-\log P_{O_2}$ and weight gains of the sample, $Er_2O_3/V_2O_5=0.250$.

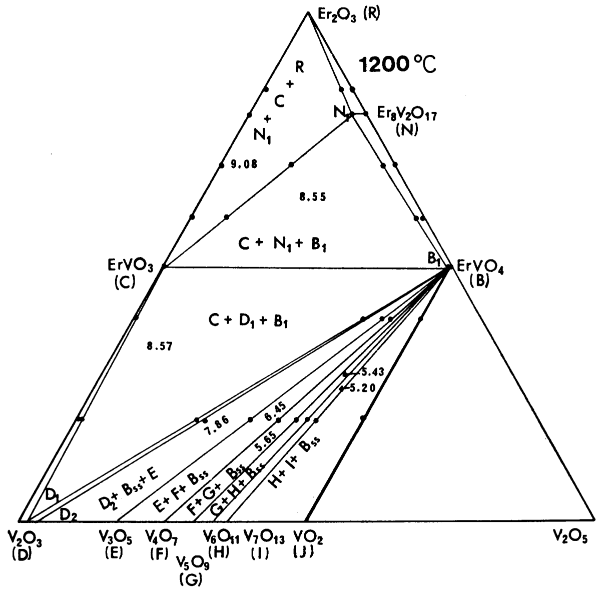

Fig. 2. Phase equilibria in the Er_2O_3–V_2O_3–V_2O_5 system at 1200 °C. Numerical values in three solid phases regions are the oxygen partial pressures in terms of $-\log P_{O_2}$. Abbreviations are the same as those in Table 2.

TABLE 1. IDENTIFICATION OF PHASES

Starting material (mol %)		$-\log P_{O_2}$ (atm)	Time (h)	Phase
Er_2O_3	V_2O_5			
0.85	0.15	12.00	5	$Er_2O_3+ErVO_3$
		9.50	18	$Er_2O_3+ErVO_3$
		9.00	24	$Er_2O_3+Er_8V_2O_{17}$
		8.50	25	$Er_2O_3+Er_8V_2O_{17}$
		0.68	19	$Er_2O_3+Er_8V_2O_{17}$
0.70	0.30	12.00	5	$Er_2O_3+ErVO_3$
		9.50	18	$Er_2O_3+ErVO_3$
		8.50	25	$ErVO_4+Er_8V_2O_{17}$
		0.68	19	$ErVO_4+Er_8V_2O_{17}$
0.40	0.60	12.00	5	$ErVO_3+V_2O_3$
		9.50	18	$ErVO_3+V_2O_3$
		9.00	24	$ErVO_3+V_2O_3$
		8.50	25	$ErVO_4+V_2O_3$
		8.00	27	$ErVO_4+V_2O_3$
		7.00	25	$ErVO_4+V_3O_5$
		5.75	34	$ErVO_4+V_4O_7$
		5.50	34	$ErVO_4+V_5O_9$
		5.30	40	$ErVO_4+V_6O_{11}$
		5.10	44	$ErVO_4+V_7O_{13}$
		4.50	48	$ErVO_4+VO_2$
0.20	0.80	12.00	5	$ErVO_3+V_2O_3$
		9.50	18	$ErVO_3+V_2O_3$
		9.00	24	$ErVO_3+V_2O_3$
		8.50	25	$ErVO_4+V_2O_3$
		8.00	27	$ErVO_4+V_2O_3$
		7.00	25	$ErVO_4+V_3O_5$
		5.75	34	$ErVO_4+V_4O_7$
		5.50	34	$ErVO_4+V_5V_9$
		5.30	40	$ErVO_4+V_6O_{11}$
		5.10	44	$ErVO_4+V_7O_{13}$
		4.50	48	$ErVO_4+VO_2$

TABLE 2. COMPOSITIONS, STABILITY RANGES IN OXYGEN PARTIAL PRESSURES, AND ACTIVITIES IN SOLID SOLUTIONS

Component	Composition	Symbol	$-\log P_{O_2}$	$\log a_i$
$Er_8V_2O_{17}$	$Er_8V_2O_{17.0}$	N	0.68[a]—2.44[b]	0.489
	$Er_8V_2O_{16.8}$	N_1	9.08	0
$ErVO_3$	$ErVO_{3.00}$	C	8.55 —12.00[c]	0
$ErVO_4$	$ErVO_{4.00}$	B	0.68[a]—7.63[b]	5×10^{-3}
	$ErVO_{3.98}$	B_1	8.55	0

a) Stability range in log P_{O_2} may be higher than −0.68. b) These values were obtained by extrapolation using the thermogravimetric values. c) Stability range in log P_{O_2} may be lower than −12.00.

respectively.

In Table 2, the compositions, the stability ranges in oxygen partial pressures, and the abbreviations of the compounds are tabulated. As given in Table 2, $Er_8V_2O_{17}$ has a composition ranging from $Er_8V_2O_{16.8}$ at $\log P_{O_2} = -9.08$ to $Er_8V_2O_{17.0}$ at $\log P_{O_2} = -2.44$. $ErVO_3$ exhibites no deviation from the stoichiometric composition within the limits of experimental error. The deviation from the stoichiometric composition of $ErVO_4$ extends up to $ErVO_{3.98}$ at $\log P_{O_2} = -8.55$.

The lattice constants for $ErVO_4$, $ErVO_3$, and $Er_8V_2O_{17}$ are given in Table 3 together with the previous data.[3–5,7,13] The values obtained in this study are in reasonable agreement with previous results. As seen from Table 3, the non-stoichiometric dependence of the lattice constants for $Er_8V_2O_{17}$ has not been observed, and this may be due to compensation of the V^{4+} ion for the V^{5+} ion and the corresponding oxygen deficiency on the cell volume. The results for the V–O binary system have been reported in a previous paper.[1]

Calculation of Standard Gibbs Energy of Reaction. On the basis of the phase equilibria, the standard Gibbs energy of reaction to form the $ErVO_4$ and $Er_8V_2O_{17}$ compounds can be calculated by referring to the following reactions:

$$ErVO_3 + 1/2O_2 = ErVO_4, \tag{1}$$

$$3Er_2O_3 + 2ErVO_3 + O_2 = Er_8V_2O_{17}. \tag{2}$$

The standard Gibbs energies of these reactions can be directly calculated by adopting the equilibrium oxygen partial pressures corresponding to Eqs. 1 and 2. Here, the activity of each component, $ErVO_4$ and $Er_8V_2O_{17}$ at the composition of B_1 and N_1 in Fig. 2, respectively, was set equal to unity. The standard Gibbs energy of each reaction was calculated from the equation, $\Delta G° = -RT \ln K$, where R is the gas constant, T the absolute temperature, and K the equilibrium constant. The detailed method of obtaining the equilibrium constant K, has been described by Kimizuka and Katsura.[14] In this study, the standard Gibbs energy for Reactions 1 and 2 found to be -121 ± 1 and -256 ± 1 kJ, respectively.

In similar studies,[1,2] Kitayama and Katsura determined the standard Gibbs energies of reaction for $SmVO_4$ and $LuVO_4$ to be -127 ± 1 and -116 ± 1 kJ, respectively. Thus by utilizing this data, the relationship between the standard Gibbs energy of reaction (expressed as $LnVO_3 + 1/2O_2 = LnVO_4$ (Ln; Sm, Er, and Lu)) and the ionic radius of Ln^{3+} ion may be found. The value of each ionic radius has been determined by Shannon and Prewitt[15] to be Sm^{3+} 1.09, Er^{3+} 1.00, and Lu^{3+} 0.97Å with a coordination number of 8. Although the data was limited, the standard Gibbs energy of the reaction was found to decrease linearly with increasing ionic radius. A similar trend in the Fe-lanthanoid-perovskite system has been established.[8,16] It is conceivable that the thermodynamic properties of Ln–V–O compounds are closely related to the structural stability. In order to demonstrate this the study of the phase equilibria in the Ln–V–O system needs further research.

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TABLE 3. UNIT CELL DIMENSIONS OF COMPOUNDS

Compound	$-\log P_{O_2}$	a(Å)	b(Å)	c(Å)	β	V(Å^3)	Reference
$ErVO_4$	0.68	7.094±0.001		6.271±0.001		315.6±0.1	present
		7.101±0.002		6.274±0.003			5
		7.0975		6.2723			4
$ErVO_3$	12.00	5.260±0.001	5.590±0.001	7.566±0.001		222.5±0.1	present
		5.256	5.581	7.559		221.8	3
		5.262	5.604	7.578			4
$Er_8V_2O_{17}$	0.68	10.45±0.02	8.42±0.02	16.05±0.10	98.08±0.23	1397±9	present
	8.50	10.47±0.02	8.39±0.02	16.01±0.07	98.56±0.18	1391±7	
		10.498±0.003	8.399±0.003	16.104±0.011	98.13±0.04		7

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