Phase Equilibria in the Lu_2O_3–V_2O_3–V_2O_5 System at 1200 °C

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The phase equilibria in the Lu_2O_3–V_2O_3–V_2O_5 system were established at 1200 °C. In this system, Lu_2O_3, $LuVO_3$, $LuVO_4$, V_2O_3, V_3O_5, V_4O_7, V_5O_9, V_6O_{11}, V_7O_{13}, and three new compounds $Lu_7V_3O_{16}$, $Lu_2V_2O_7$, and LuV_4O_8 are stable. $LuVO_4$, V_2O_3, VO_2, $Lu_7V_3O_{16}$, $Lu_2V_2O_7$, and LuV_4O_8 have non-stoichiometric compositions. The relationships between the composition and the $-\log P_{O_2}$ values of the solid solutions were obtained from the thermogravimetric results. On the basis of the phase equilibria, the standard Gibbs free energies of several reactions were determined. The spacings, relative intensities, and densities of new compounds were also determined.

In a previous paper,[1] the authors have established the phase equilibria in the Sm_2O_3–V_2O_3–V_2O_5 system at 1200 °C. In this system, we reported the existence of three ternary compounds, $Sm_{10}V_2O_{20}$ ($5Sm_2O_3 \cdot V_2O_5$), $SmVO_3$, and $SmVO_4$, and the homologous series of V_nO_{2n-1} of n=2—7. They also determined the standard Gibb energies of formation referred to reactions, $SmVO_3 + 1/2O_2 = SmVO_4$ and $4Sm_2O_3 + 2SmVO_3 + 2O_2 = Sm_{10}V_2O_{20}$, and the standard Gibbs energies of oxidation of the vanadium oxides found in the system.

In this paper, we choose Lu_2O_3 as one of the rare earth sesquioxides in the Lu_2O_3–V_2O_3–V_2O_5 system because its ionic radius is the smallest of the lanthanoid elements. The precise phase equilibria in the Lu_2O_3–V_2O_3 system have not yet been investigated, but the existence of orthorhombic $LuVO_3$ as a ternary compound in the system is well known, and its crystallographic properties have been reported.[2]

Recently, Brusset *et al.*[3] have studied the Lu_2O_3–V_2O_5 system in the temperature range from 600 to 1500 °C. They showed the existence of $4Lu_2O_3 \cdot V_2O_5$ together with a well-known tetragonal $LuVO_4$ phase, although the stable temperature range was not clear. As for the crystallographic properties of $4Lu_2O_3 \cdot V_2O_5$, they showed a simple X-ray diffraction diagram with only three peaks 2θ by Cu $K\alpha$(about 29.5, 31.9, and 32.3). However, the possibility of the existence of $4Lu_2O_3 \cdot V_2O_5$ was so ambiguous that they said that the diagram was incomplete.

The objectives of the present study are: (1) to establish the detailed phase equilibria in the Lu_2O_3–$V_2O_3 \cdot V_2O_5$ system at 1200 °C by changing the oxygen partial pressure; (2) to calculate the thermochemical properties based on the phase equilibria; and (3) to ascertain, upon the completion of the studies of the Ln–V–O system, whether or not the relationship between related standard Gibbs free energies of reaction and the ionic radii of rare earth ions as in the Ln–Fe–O system.[4]

Experimental

Analytical grades of Lu_2O_3(99.9%) and V_2O_5, which was obtained by heating the guaranteed grade of NH_4VO_3 at 500 °C in air for 24 h, have been employed as the starting materials. The desired ratios of Lu_2O_3/V_2O_5 were obtained by mixing thoroughly in an agate mortar under ethyl alcohol. The mixtures thus obtained were treated by the procedures described previously.[1]

The apparatus and procedures for controlling the oxygen partial pressure, keeping at a constant temperature, the method of thermogravimetry, the criterion for equilibrium establishment, the method of identifying solid phases after quenching, the method of lattice constant determination, the method of measuring the actual oxygen partial pressures, and the method of wet chemical analysis are the same as those discussed in previous papers.[1,5–7]

The oxygen partial pressure of $10^{-12.00}$ atm was chosen as the reference weight standard as was determined in the Sm_2O_3–V_2O_3–V_2O_5 system.

Results and Discussion

Phase Equilibria. Eleven samples with the different Lu_2O_3/V_2O_5 compositions of 0.1111, 0.2500, 0.3333, 0.4286, 0.5385, 1.0000, 1.500, 1.857, 2.333, and 4.000 were prepared. In Fig. 1, the relationships between the oxygen partial pressures and the compositions, W_{O_2}/W_T, of the samples with Lu_2O_3/V_2O_5 compositions of 0.1111, 0.2500, 0.4286, 1.500, 2.333, and 4.000 are shown as representative, where W_{O_2} is the weight gain from the reference weight standard, and W_T the toal weight gain of the samples as if the $V_2O_3 + O_2 = V_2O_5$ reaction were to be completed. In Table 1, the results of the identification of phases are shown; in the first column are the compositions of the starting material; in the second column, the experimental con-

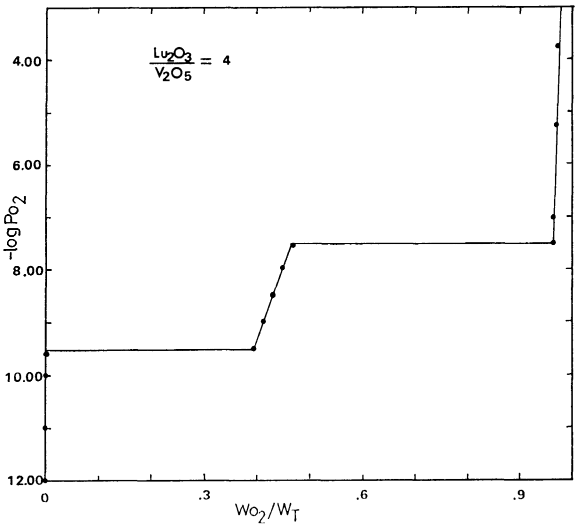

Fig. 1-1. The relationship between $-\log P_{O_2}$ and weight gains of the sample, $Lu_2O_3/V_2O_5 = 4$.

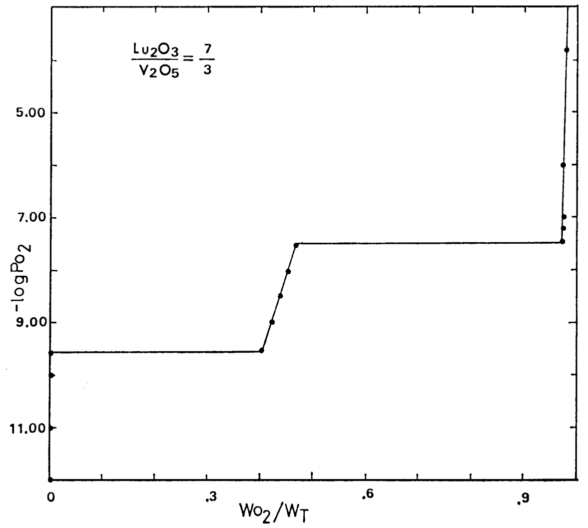

Fig. 1-2. The relationship between $-\log P_{O_2}$ and weight gains of the sample, $Lu_2O_3/V_2O_5=7/3$.

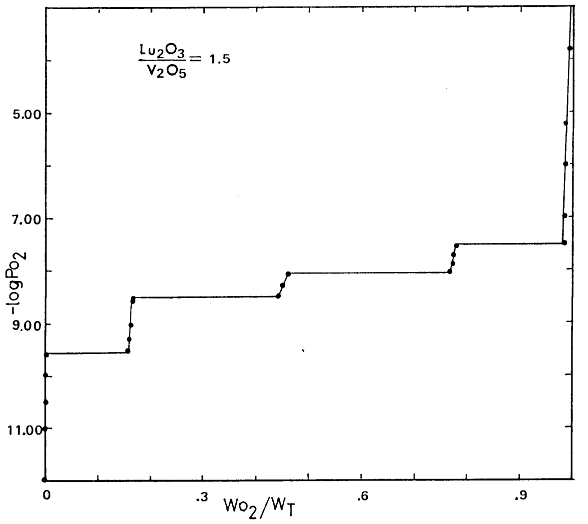

Fig. 1-3. The relationship between $-\log P_{O_2}$ and weight gains of the sample, $Lu_2O_3/V_2O_5=1.5$.

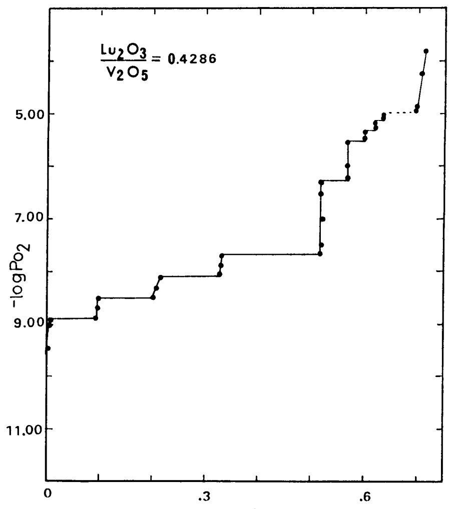

Fig. 1-4. The relationship between $-\log P_{O_2}$ and weight gains of the sample, $Lu_2O_3/V_2O_5=0.4286$.

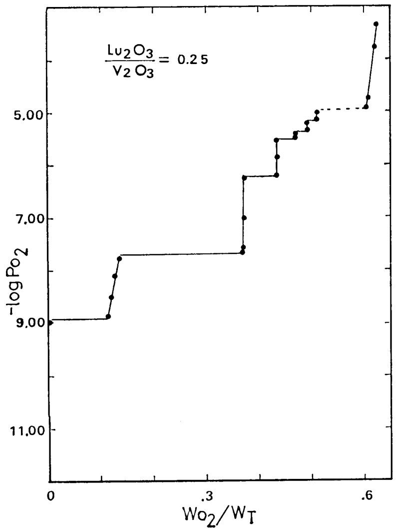

Fig. 1-5. The relationship between $-\log P_{O_2}$ and weight gains of the sample, $Lu_2O_3/V_2O_5=0.25$.

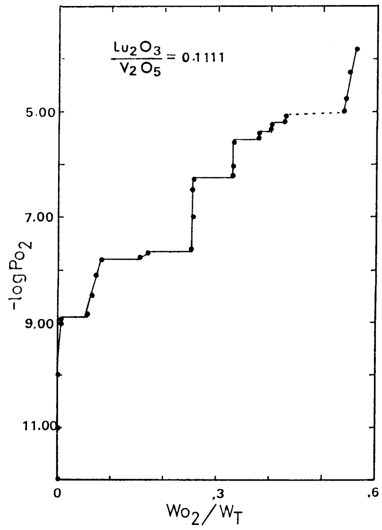

Fig. 1-6. The relationship between $-\log P_{O_2}$ and weight gains of the sample, $Lu_2O_3/V_2O_5=0.1111$.

ditions of log P_{O_2}, and in the third, the experimental time duration. Based on the experimental results of the thermogravimetry and the identification of the phases, the phase diagram shown in Fig. 2 was obtained. Following phases are stable under the present experimental conditions; Lu_2O_3(R), $LuVO_4$(B), $LuVO_3$(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 three new compounds, $Lu_2V_2O_7$(K), $Lu_7V_3O_{16}$(L), and LuV_4O_8(M). The letters in parentheses are the abbreviations of the compounds. $4Lu_2O_3\cdot V_2O_5$, which has been reported by Brusset *et al.*,[3] did not appeared under the present experimental conditions. From the present results and Brusset's, $4Lu_2O_3\cdot V_2O_5$ seems not to be stable, at least below 1500 °C.

Lu_2O_3 was stable under the present experimental conditions, as has already pointed out by Sekine and Katsura[8]. $LuVO_4$, $Lu_2V_2O_7$, $Lu_7V_3O_{16}$, LuV_4O_8, V_2O_3, and VO_2 have apparent deviations from the

TABLE 1. IDENTIFICATION OF PHASES

Starting materials (mol%)		$-\log P_{O_2}$ (atm)	Time (h)	Phase
Lu_2O_3	V_2O_5			
80	20	12.00	7	$Lu_2O_3+LuVO_3$
		9.00	64	$Lu_2O_3+Lu_7V_3O_{16}$
		7.90	71	$Lu_2O_3+Lu_7V_3O_{16}$
		7.00	70	$Lu_2O_3+LuVO_4$
		0.68	120	$Lu_2O_3+LuVO_4$
60	40	12.00	7	$Lu_2O_3+LuVO_3$
		9.00	64	$LuVO_3+Lu_7V_3O_{16}$
		8.30	123	$Lu_2V_2O_7+Lu_7V_3O_{16}$
		7.90	71	$LuVO_4+Lu_7V_3O_{16}$
		7.00	70	$Lu_2O_3+LuVO_4$
		3.80	82	$Lu_2O_3+LuVO_4$
35	65	8.70	52	$LuVO_3+LuV_4O_8$
		8.00	71	$LuVO_4+LuV_4O_8$
30	70	12.00	7	$V_2O_3+LuVO_3$
		9.00	64	$V_2O_3+LuVO_3$
		8.30	49	$Lu_2V_2O_7+LuV_4O_8$
		7.90	71	$LuVO_4+LuV_4O_8$
		7.60	49	$V_3O_5+LuVO_4$
		7.00	70	$V_3O_5+LuVO_4$
		5.80	57	$V_4O_7+LuVO_4$
		5.50	62	$V_5O_9+LuVO_4$
		5.30	62	$V_6O_{11}+LuVO_4$
		5.10	80	$V_7O_{13}+LuVO_4$
		3.79	82	VO_2+LuVO_4
10	90	12.00	7	$V_2O_3+LuVO_3$
		9.00	64	$V_2O_3+LuVO_3$
		8.70	52	$V_2O_3+LuV_4O_8$
		7.90	53	$V_2O_3+LuV_4O_8$
		7.70	50	$V_3O_5+LuV_4O_8$
		7.00	70	$V_3O_5+LuVO_4$
		5.80	57	$V_4O_7+LuVO_4$
		5.50	62	$V_5O_9+LuVO_4$
		5.30	62	$V_6O_{11}+LuVO_4$
		5.10	80	$V_7O_{13}+LuVO_4$
		3.80	82	VO_2+LuVO_4

TABLE 2. THE RELATIONSHIP BETWEEN THE COMPOSITIONS AND OXYGEN PARTIAL PRESSURES OF THE SOLID SOLUTIONS $N_o/N_d = a+b\log P_{O_2}+c(\log P_{O_2})^2$

d	a	b	c
$Lu_7V_3O_{16}$	1.22	0.107	0
$Lu_2V_2O_7$	0.971	0.127	0
$LuVO_4$	4.20×10^{-3}	2.16×10^{-3}	0
LuV_4O_8	0.824	0.101	0
V_2O_3	1.76	0.363	0.0187

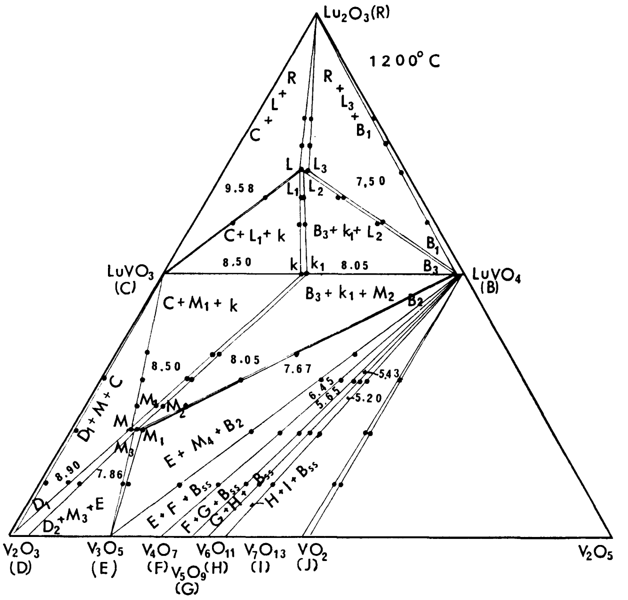

Fig. 2. Phase equilibria in the Lu_2O_3-V_2O_3-V_2O_5 system at 1200 °C. Numerical values in three solid phases regions are the oxygen partial pressures in $-\log P_{O_2}$ in equilibrium. Abbreviations are same as those in Table 3.

TABLE 3. COMPOSITIONS, STABILITY RANGES IN OXYGEN PARTIAL PRESSURES, AND ACTIVITIES IN SOLID SOLUTIONS

Component	Composition	Symbol	$-\log P_{O_2}$	$\log a_i$
$LuVO_4$	$LuVO_{4.00}$	B	0.68a)—1.94b)	0.0201
	$LuVO_{3.99}$	B_1	7.50	0.00346
	$LuVO_{3.99}$	B_2	7.67	0.00243
	$LuVO_{3.99}$	B_3	8.05	0
$LuVO_3$	$LuVO_{3.00}$	C	9.50—12.00c)	0
V_2O_3	$V_2O_{3.00}$	D	9.98—12.00c)	0
	$V_2O_{3.01}$	D_1	8.90	−0.00085
	$V_2O_{3.07}$	D_2	7.86	−0.0180
$Lu_2V_2O_7$	$Lu_2V_2O_{6.89}$	K	8.50	0
	$Lu_2V_2O_{6.95}$	K_1	8.05	0.0180
$Lu_7V_3O_{16}$	$Lu_7V_3O_{16.2}$	L	9.58	0
	$Lu_7V_3O_{16.3}$	L_1	8.50	−0.137
	$Lu_7V_3O_{16.4}$	L_2	8.05	−0.212
	$Lu_7V_3O_{16.4}$	L_3	7.50	−0.319
LuV_4O_8	$LuV_4O_{7.93}$	M	8.90	0
	$LuV_4O_{7.97}$	M_1	8.50	0.0109
	$LuV_4O_{8.01}$	M_2	8.05	0.0136
	$LuV_4O_{8.03}$	M_3	7.86	0.0116
	$LuV_4O_{8.05}$	M_4	7.67	0.00786

a) The stability range in $\log P_{O_2}$ may be higher than −0.68. b) This value was obtained by extrapolation by using the experimental values. c) The stability range in $\log P_{O_2}$ may be lower than −12.00.

stoichiometric composition, judging from the results of thermogravimetry. The relationship between the N_o/N_d and the $\log P_{O_2}$ of the solid solutions is obtained by using the results of the thermogravimetry and by the method of the least squares with the general quadratic equation; $N_o/N_d=a+b\log P_{O_2}+c(\log P_{O_2})^2$. Here, N_o/N_d indicates the deviation of the oxygen atoms from the stoichiometric compound d.6) The factors used to obtain a, b, and c, for each solid solution are given in Table 2. As for the V_2O_3 solid solution, previous data1) were used to obtain a, b, and c. In Table 3, the compositions, the stability ranges in the oxygen partial pressures, and the abbreviations of the compounds are tabulated. The deviations from the

Table 4. Spacing and relative intensities of $Lu_7V_3O_{16}$ and LuV_4O_8

$Lu_7V_3O_{16}$				LuV_4O_8			
d	I/I_0	d	I/I_0	d	I/I_0	d	I/I_0
5.702	20	1.7022	16	5.041	20	2.1656	49
5.106	7	1.6793	21	4.852	59	2.0805	20
4.234	3	1.6094	22	4.570	14	2.0459	20
3.501	3	1.5941	24	4.416	61	2.0412	20
3.397	4	1.5823	6	3.899	28	1.9912	11
3.347	2	1.5667	12	3.581	11	1.9544	10
3.164	100	1.5518	24	3.439	26	1.9418	12
3.021	97	1.5107	12	3.372	18	1.9063	14
2.996	26	1.4817	14	3.010	20	1.8801	11
2.855	46	1.4615	12	2.950	34	1.7913	41
2.669	34	1.4284	13	2.776	29	1.7554	20
2.5978	61	1.3633	8	2.670	24	1.7243	10
2.5534	17	1.3153	5	2.6505	67	1.7066	22
2.1869	20	1.2996	8	2.6208	100	1.6622	17
2.1186	19	1.2899	8	2.5923	22	1.6462	28
2.0737	12	1.2755	5	2.5429	18	1.5257	11
2.0188	7	1.2588	5	2.5068	20	1.5082	17
1.9227	50	1.2520	11	2.4787	12	1.4746	17
1.9014	21	1.2382	6	2.4349	39	1.4398	17
1.8330	7	1.2306	10	2.3650	11	1.4075	11
1.7801	26			2.3264	10	1.3931	14

stoichiometric composition of $LuVO_4$ extended up to $LuVO_{3.99}$ at $\log P_{O_2}=-8.05$. $Lu_2V_2O_7$ has the composition ranges from $Lu_2V_2O_{6.89}$ at $\log P_{O_2}=-8.50$ to $Lu_2V_2O_{6.95}$ at $\log P_{O_2}=-9.58$ to $Lu_7V_3O_{16.4}$ at $\log P_{O_2}=-7.50$, and LuV_4O_8 from $LuV_4O_{7.93}$ at $\log P_{O_2}=-8.90$ to $LuV_4O_{8.05}$ at $\log P_{O_2}=-7.67$.

The relative intensities, spacings, assignments of indices, and density of $Lu_2V_2O_7$ have already been reported.[10] Recently, Bazuev *et al.*[11] reported the existence of $Lu_2V_2O_7$. According to them, $Lu_2V_2O_7$ was prepared from a mixture of Lu_2O_3 and VO_2 using the ceramic technique and had a ferromagnetic property. The lattice constant, 9.932±0.001 Å, is in very good agreement with ours, 9.934±0.001 Å.

In this study, we did not succeed in assigning the indices for new compounds, $Lu_7V_3O_{16}$ and LuV_4O_8. The relative intensities and spacings are given in Table 4. The sample powders of $Lu_7V_3O_{16}$ and LuV_4O_8 which were used in the X-ray diffraction and in the measurement of the density were prepared at an oxygen partial pressure of $\log P_{O_2}=-8.30$ and for 72 h and 92 h heating respectively. The densities of $Lu_7V_3O_{16}$ and LuV_4O_8 were determined to be 8.63 and 6.66 g/cm³ respectively, using the powder picnometric method; they are given in Table 5, together with the powder color. The values in the second column in Table 5 imply the oxygen partial pressures at which the samples were prepared.

Table 5. Densities and colors of new compounds

Compound	$-\log P_{O_2}$ (atm)	Density (g/cm³)	Color
$Lu_7V_3O_{16}$	8.30	8.63	dark brown
$Lu_2V_2O_7$	8.30	7.64	black
LuV_4O_8	8.20	6.66	black

The lattice constants of $LuVO_4$ and $LuVO_3$ are given in Table 6, together with the previous data.[2,3,12] Both data are in good agreement with the previous data, and neither depends on the oxygen partial pressure at which the samples were prepared.

The results and discussion of the V–O system have been presented in a previous paper.[1]

Calculation of Standard Gibbs Engergies of Reactions. On the basis of the phase equilibria, the standard Gibbs energies of reaction, referred to the equations in Table 7, can be calculated from the equation; $\Delta G^\circ = -RT\ln K$, where R is the gas constant; T the absolute temperature, and K the equilibrium constant of each reaction. The activity of each component, $LuVO_4$, V_2O_3, $Lu_2V_2O_7$, $Lu_7V_3O_{16}$, and LuV_4O_8, in each solid solution at the compositions of B_3, D, K, L, and M may be set equal to unity. The activity of each component in the solid solution can readily be calculated by means of the Gibbs-Duhem equation on the basis of the experimental results presented in Table 2. A detailed calculation method has been described in a paper of Kimizuka and Katsura.[13] Activities which are necessary to calculate the standard Gibbs energies of the reaction are listed in the fifth column in Table 3. As an example, we will calculate the standard Gibbs energy of the reaction

$$2Lu_2O_3 + 3LuVO_3 + 1/2O_2 = Lu_7V_3O_{16}. \qquad (1)$$

The equilibrium constant of Reaction 1 is represented as follows:

$$K(1) = a_{Lu_7V_3O_{16}}/(a_{Lu_2O_3}\cdot a^3_{LuVO_3}\cdot P_{O_2}^{-1/2}) = P_{O_2}^{-1/2}.$$

Here, $a_{Lu_2O_3}$ and a_{LuVO_3} are unity and $a_{Lu_7V_3O_{16}}$ may

TABLE 6. UNIT-CELL DIMENSIONS OF $LuVO_4$ AND $LuVO_3$

Sample	$-\log P_{O_2}$	a(Å)	b(Å)	c(Å)	V(Å)$^{3)}$
$LuVO_4$	0.68	7.022±0.001		6.230±0.001	307.2±0.1
	7.00	7.024±0.001		6.230±0.001	307.4±0.1
		7.0243$^{12)}$		6.2316	
		7.025±0.002$^{3)}$		6.233±0.002	
$LuVO_3$	10.00	5.210±0.001	5.568±0.001	7.527±0.001	218.3±0.1
	12.00	5.212±0.001	5.565±0.001	7.526±0.001	218.3±0.1
		5.214±0.002$^{2)}$	5.561±0.002	7.530±0.002	218.3±0.05

TABLE 7. STANDARD GIBBS FREE ENERGIES OF REACTIONS

	Equation	$-\log P_{O_2}$ (atm)	$-\Delta G°$ (kcal)
(1)	$2Lu_2O_3+3LuVO_3+1/2O_2=Lu_7V_3O_{16}$	9.58±0.02	32.3±0.1
(2)	$Lu_7V_3O_{16}+O_2=3LuVO_4+2Lu_2O_3$	7.50±0.10	52.8±0.8
(3)	$2LuVO_3+1/2O_2=Lu_2V_2O_7$	8.50±0.02	28.6±0.1
(4)	$Lu_2V_2O_7+1/2O_2=2LuVO_4$	8.05±0.02	27.0±0.1
(5)	$LuVO_3+1/2O_2=LuVO_4$		27.8±0.2
(6)	$2LuVO_3+3V_2O_3+1/2O_2=2LuV_4O_8$	8.90±0.10	29.8±0.4
(7)	$LuV_4O_8+1/2O_2=V_3O_5+LuVO_4$	7.67±0.02	25.8±0.1

be set as equal to unity, as has been described above. Using the above equation, $\Delta G°=-RT \ln K=1/2\, P_{O_2}$, $\Delta G°(1)=-32.3$ kcal/mol is obtained, where P_{O_2} implies the equilibrium oxygen partial pressure of Reaction 1. The standard Gibbs energies of reaction, referred to Eqs. 1 to 7, are summarized in Table 7. The values of Reaction 5 are obtained by using the values of Reactions 3 and 4.

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