

## Thermogravimetric Study of the *M*-Ni-O System. II. *M* = La at 1200°C

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Phase equilibria in the La-Ni-O system at 1200°C were established at oxygen partial pressures ranging from 1 to  $10^{-12.00}$  atm. In this system,  $\text{La}_2\text{NiO}_4$  and  $\text{La}_6\text{Ni}_5\text{O}_{15}$  are stable as the ternary oxide. The latter is probably a new compound and its spacings and relative intensities are presented.  $\text{La}_3\text{Ni}_2\text{O}_7$  and  $\text{La}_4\text{Ni}_3\text{O}_{10}$  are not stable.  $\text{La}_2\text{NiO}_4$  has nonstoichiometric compositions, as is well known, and the relationship between the composition and the oxygen partial pressure is presented. The standard Gibbs energies of the reactions which appear in the system are obtained. © 1990 Academic Press, Inc.

In the La-Ni-O system there are seven previously reported phases,  $\text{La}_2\text{Ni}_2\text{O}_5$ ,  $\text{LaNiO}_2$ ,  $\text{LaNiO}_3$ ,  $\text{La}_2\text{NiO}_4$ ,  $\text{La}_3\text{Ni}_2\text{O}_7$ ,  $\text{La}_4\text{Ni}_3\text{O}_{10}$ , and  $\text{La}_5\text{Ni}_4\text{O}_{13}$ . Their crystallographic and physical properties have been examined.

Low-temperature reduction of  $\text{LaNiO}_3$  led to compounds such as  $\text{La}_2\text{Ni}_2\text{O}_5$  (monoclinic) and  $\text{LaNiO}_2$  (tetragonal) (1).

$\text{LaNiO}_3$ , which has the perovskite structure (2), has a high catalytic activity for oxygen reduction and is used as an oxygen electrode (3). For  $\text{LaNiO}_3$  the optimum temperature of synthesis is 773 K and the optimum calcination time is 20 hr (4).  $\text{LaNiO}_3$  is stable in the temperature range lower than 900°C (5).

$\text{La}_2\text{NiO}_4$ , which has the tetragonal  $\text{K}_2\text{NiF}_4$ -type structure (6), has a broad range of lattice constants, indicative of variations in composition and of the extent of oxygen nonstoichiometry.  $\text{La}_2\text{NiO}_{4+x}$  has been prepared and chemical analysis revealed the

presence of about 5% of  $\text{Ni}^{3+}$  (7). Rao *et al.* (8) have observed a monoclinic cell in a  $\text{CO}_2$ -annealed crystal of  $\text{La}_2\text{NiO}_4$  at 1470 K. Saéz-Puche *et al.* (7) also found that  $\text{La}_2\text{NiO}_{4+x}$  (tetragonal) changed to  $\text{La}_2\text{NiO}_4$  (monoclinic) in  $\text{H}_2$  at 430°C, in which the weight loss value was higher than 0.7%. On the other hand, the structure of a reduced form of  $\text{La}_2\text{NiO}_4$ , prepared under a  $P_{\text{O}_2}$  between  $10^{-7}$  and  $10^{-6}$  Pa, was determined to be orthorhombic using X-ray and neutron diffraction. The tetragonal form of  $\text{La}_2\text{NiO}_4$  is stabilized by the presence of a small amount of  $\text{Ni}^{3+}$  ions (9).

Magnetic measurements of  $\text{La}_2\text{NiO}_4$  were carried out (7, 8, 10). The electrical conductivity of reduced compositions of  $\text{La}_2\text{NiO}_4$  has been measured between 20 and 1000 K and compared to that of the air-prepared ones (11).

The existence of a homologous series,  $\text{La}_{n+1}\text{Ni}_n\text{O}_{3n+1}$ , was reported (12).  $\text{La}_3\text{Ni}_2\text{O}_7$ , orthorhombic type, was prepared

by heating in air at 1150°C for 5 hours and  $\text{La}_4\text{Ni}_3\text{O}_{10}$  by heating at 1080°C for 12 hr. The powder pattern of  $\text{La}_4\text{Ni}_3\text{O}_{10}$  can be indexed on the orthorhombic cell (13). Samples of nominal composition  $\text{La}_3\text{Ni}_4\text{O}_{13}$  were prepared by heating  $\text{La}_2\text{O}_3$  and  $\text{NiO}$  in a  $\text{K}_2\text{CO}_3$  flux at 1050°C for 24 hr but it was difficult to determine whether or not a new phase existed (12).

The thermodynamic stability of ternary oxides in the La–Ni–O system was investigated by Petrov *et al.* (14) and a simple phase diagram was presented. In the diagram the nonstoichiometry of  $\text{La}_2\text{NiO}_4$  was not shown clearly.

As described above, the principal interest in the system seems to be concentrated in the crystallographic and physical properties of the compounds which are stable in the system. The reliable information on the stability of these compounds is still limited and the range of nonstoichiometry of  $\text{La}_2\text{NiO}_4$  between 1000–1200°C is still ambiguous.

The objectives of the present study were: (1) to establish the detailed phase equilibria in the La–Ni–O system at 1200°C as a function of the oxygen partial pressure, (2) to determine the relationship between the nonstoichiometry of  $\text{La}_2\text{NiO}_4$  and the oxygen partial pressure, and (3) to calculate the thermodynamic properties based upon the established phase diagram.

### Experimental

Analytical-grade  $\text{La}_2\text{O}_3$  and  $\text{NiO}$  of 3N purity were used as starting materials. These oxides were dried at about 1200°C by calcining in the air before use. Mixtures with the desired molar ratios of  $\text{La}_2\text{O}_3/\text{NiO}$  were obtained by mixing the calculated amounts of constituent binary oxides thoroughly in an agate mortar. The mixtures thus obtained were heated to 1200°C several times with intermittent mixing and were used in the

thermogravimetric analysis with the same procedures as described previously (15).

The apparatus and means for controlling the oxygen partial pressure and temperature, as well as the method of equilibration, have been described previously (15, 16). To characterize the phases in the quenched samples in the system, X-ray powder diffractometry was used, employing Ni-filtered  $\text{CuK}\alpha$  radiation. Lattice constants were also determined on the mixed quenched samples by the powder X-ray method with a slow scanning speed of  $0.5^\circ 2\theta/\text{min}$ . A standard specimen of silicon was used as  $2\theta$  calibrant without mixing with the quenched samples.

Mixed gases of  $\text{CO}_2$  and  $\text{H}_2$  and of  $\text{CO}_2$  and  $\text{O}_2$  were used to achieve the required oxygen partial pressure. The actual oxygen partial pressures were measured by means

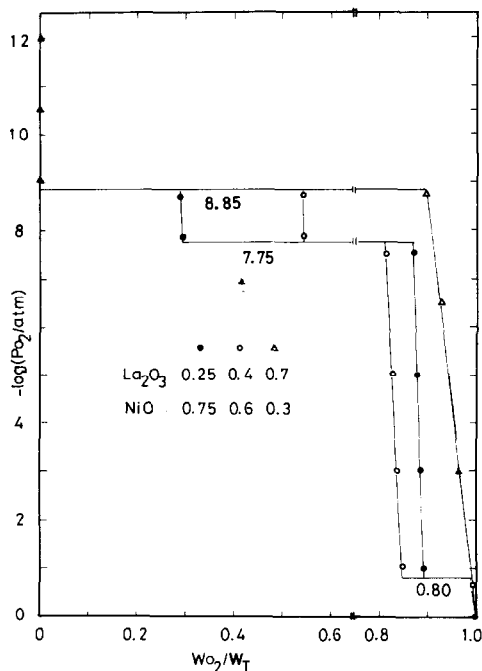


FIG. 1. The relationship between  $-\log(P_{\text{O}_2}/\text{atm})$  and the weight change,  $W_{\text{O}_2}/W_T$ , of the three representative samples. The weight at  $\log P_{\text{O}_2} = -12.00$  was used as the reference.

TABLE I  
THE IDENTIFICATION OF PHASE

La <sub>2</sub> O <sub>3</sub> (mole %)	NiO	-log P <sub>O<sub>2</sub></sub> (atm)	Time (h)	Phase	
20	80	0.68	55	NiO	+ La <sub>6</sub> Ni <sub>5</sub> O <sub>15</sub>
		3.00	21	NiO	+ La <sub>2</sub> NiO <sub>4</sub> <sup>a</sup>
		7.50	24	NiO	+ La <sub>2</sub> NiO <sub>4</sub> <sup>b</sup>
		8.70	24	Ni	+ La <sub>2</sub> NiO <sub>4</sub> <sup>b</sup>
		10.00	8	Ni	+ La <sub>2</sub> O <sub>3</sub>
45	55	0.68	55	La <sub>2</sub> NiO <sub>4</sub>	+ La <sub>6</sub> Ni <sub>5</sub> O <sub>15</sub>
		3.00	21	NiO	+ La <sub>2</sub> NiO <sub>4</sub> <sup>a</sup>
		7.50	24	NiO	+ La <sub>2</sub> NiO <sub>4</sub> <sup>b</sup>
		8.70	24	Ni	+ La <sub>2</sub> NiO <sub>4</sub> <sup>b</sup>
		10.00	8	Ni	+ La <sub>2</sub> O <sub>3</sub>
70	30	0.68	55	La <sub>2</sub> O <sub>3</sub>	+ La <sub>2</sub> NiO <sub>4</sub>
		3.00	21	La <sub>2</sub> O <sub>3</sub>	+ La <sub>2</sub> NiO <sub>4</sub> <sup>a</sup>
		8.70	24	La <sub>2</sub> O <sub>3</sub>	+ La <sub>2</sub> NiO <sub>4</sub> <sup>b</sup>
		10.00	8	Ni	+ La <sub>2</sub> O <sub>3</sub>

<sup>a</sup> Weak additional peaks appear, but these are not so clear. La<sub>2</sub>NiO<sub>4</sub> tetragonal.

<sup>b</sup> Orthorhombic.

of a solid electrolytic cell, (ZrO<sub>2</sub>)<sub>0.85</sub>(CaO)<sub>0.15</sub> (17).

Lanthanum and nickel were precipitated by oxalic acid and dimethylglyoxime, respectively, and determined gravimetrically. Iodometry was adopted for Ni<sup>3+</sup> determination.

## Results and Discussions

### (1) Phase Equilibrium at 1200°C

Eight mixtures with La<sub>2</sub>O<sub>3</sub>/NiO mole ratios of 7/3, 6/4, 45/55, 4/6, 35/65, 3/7, 25/75, and 2/8 were prepared for use in the thermogravimetric experiments. There are detailed discussions of the Ni-O system in the previous report (18).

In Fig. 1 the relationships between the oxygen partial pressure, -log(P<sub>O<sub>2</sub></sub>/atm), and the weight change, W<sub>O<sub>2</sub></sub>/W<sub>T</sub>, were represented for three samples, La<sub>2</sub>O<sub>3</sub>/NiO = 7/3, 4/6, and 25/75. Here, W<sub>O<sub>2</sub></sub> is the weight increase of the samples from a reference weight at log P<sub>O<sub>2</sub></sub> = -12.00, at which La<sub>2</sub>O<sub>3</sub>

and Ni metal are stable. W<sub>T</sub> is the total weight gain from the reference weight to the weight at 1 atm O<sub>2</sub>, at which two phases, La<sub>2</sub>O<sub>3</sub> + La<sub>2</sub>NiO<sub>4</sub> solid solution, La<sub>2</sub>NiO<sub>4</sub> solid solution + La<sub>6</sub>Ni<sub>5</sub>O<sub>15</sub>, and NiO + La<sub>6</sub>Ni<sub>5</sub>O<sub>15</sub>, are stable depending upon the total composition of the samples. Abrupt weight changes are observed at -log P<sub>O<sub>2</sub></sub> = 8.85, 7.75, and 0.80 in Fig. 1. These values correspond to the oxygen partial pressures in equilibrium with three solid phases. One of these values, -log P<sub>O<sub>2</sub></sub> = 7.75, is identical with that of the reaction, Ni + ½ O<sub>2</sub> = NiO at 1200°C (18).

The identification of phases was carried out on samples which were quenched under different conditions of oxygen partial pressure. The results tabulated in Table I are for the two-phase combinations. In Table I, La<sub>2</sub>NiO<sub>4</sub><sup>b</sup> and La<sub>2</sub>NiO<sub>4</sub><sup>a</sup> denote samples which were quenched in an oxygen partial pressure lower than that of air. These samples have additional X-ray diffraction peaks, 2θ = 32.3, 43.9, 56.5,

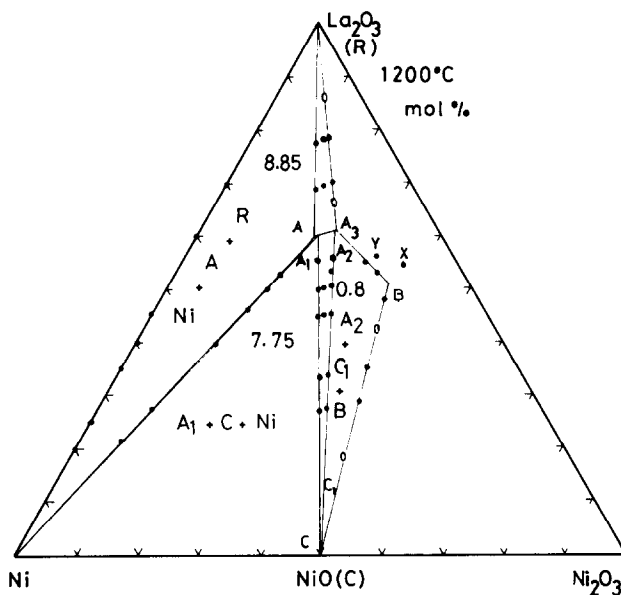


FIG. 2. Phase equilibria in the  $\text{La}_2\text{O}_3$ -Ni- $\text{Ni}_2\text{O}_3$  system at  $1200^\circ\text{C}$ . Numerical values in the three solid-phase regions are the equilibrium oxygen partial pressure in  $-\log P_{\text{O}_2}$ . Abbreviations are the same as those in Table V.

and 57.1, in comparison to air-quenched  $\text{La}_2\text{NiO}_4$ . This fact might indicate the transformation from a tetragonal to a monoclinic system as suggested by Rao *et al.* (8) and Sáez-Puche *et al.* (7). But the X-ray powder pattern is very similar to that of orthorhombic  $\text{La}_2\text{CoO}_4$  as noted by Odier *et al.* (9).

On the basis of the results of the thermogravimetry and the identification of phases, a phase diagram at  $1200^\circ\text{C}$  was depicted with apices of  $\text{La}_2\text{O}_3$ , Ni, and  $\text{Ni}_2\text{O}_3$ .  $\text{Ni}_2\text{O}_3$  is not stable under the present experimental conditions. The diagram is shown in Fig. 2. Numerical values in Fig. 2 are the oxygen partial pressure  $-\log P_{\text{O}_2}$  in equilibrium with three solid phases. Five phases,  $\text{La}_2\text{O}_3(\text{R})$ ,  $\text{NiO}(\text{C})$ , Ni,  $\text{La}_2\text{NiO}_4$  (A), and a new phase  $\text{La}_6\text{Ni}_5\text{O}_{15}$  are stable in the diagram.  $\text{La}_2\text{Ni}_2\text{O}_5$ ,  $\text{LaNiO}_2$ ,  $\text{LaNiO}_3$ ,  $\text{La}_4\text{Ni}_3\text{O}_{10}$ ,  $\text{La}_3\text{Ni}_2\text{O}_7$ , and  $\text{La}_5\text{Ni}_4\text{O}_{13}$  are not found. X and Y in Fig. 2 indicate  $\text{La}_4\text{Ni}_3\text{O}_{10}$  and  $\text{La}_3\text{Ni}_2\text{O}_7$ , respectively.  $\text{LaNiO}_3$  is not

stable even in 1 atm of  $\text{O}_2$  as shown in Fig. 2. This fact supports the results of Petrov *et al.* (14) and Odier *et al.* (9), and suggests that to prepare  $\text{LaNiO}_3$  it might be necessary to use oxygen pressures higher than 1 atm. Demazeau *et al.* (19) have prepared  $\text{LaNiO}_3$  at 60 Kbar and  $950^\circ\text{C}$ .  $\text{La}_2\text{NiO}_4$  has an oxygen-rich nonstoichiometry as is well known and its relation between the oxygen partial pressure and the composition is represented by the equation,  $N_{\text{O}}/N_{\text{La}_2\text{NiO}_4} = 9.65 \times 10^{-3} \log P_{\text{O}_2} + 0.0790$ . Here,  $N_{\text{O}}$  and  $N_{\text{La}_2\text{NiO}_4}$  are the mole fraction of the substance denoted by the subscript in the solid solution. From this equation the oxygen partial pressure of the  $\text{La}_2\text{NiO}_{4.00}$ ,  $N_{\text{O}}/N_{\text{La}_2\text{NiO}_4} = 0$ , is calculated as  $-8.20$  in  $\log P_{\text{O}_2}$ . This value is comparable to  $-8.50$  (10).

Recently, Buttrey *et al.* (20) have reported that the oxygen nonstoichiometry arises from the presence of excess lattice oxygen, most likely in the form of peroxide species. This conclusion is based upon XPS

TABLE II  
THE SPACINGS AND RELATIVE INTENSITIES OF  $\text{La}_6\text{Ni}_5\text{O}_{15}$  TOGETHER WITH THOSE  
OF  $\text{La}_3\text{Ni}_2\text{O}_7$  AND  $\text{La}_4\text{Ni}_3\text{O}_{10}$

$\text{La}_6\text{Ni}_5\text{O}_{15}$		$\text{La}_3\text{Ni}_2\text{O}_7^a$					$\text{La}_4\text{Ni}_3\text{O}_{10}^b$				
$d(\text{\AA})$	$I/I_0$	$d(\text{\AA})$	$h$	$k$	$l$	$I/I_0$	$d(\text{\AA})$	$h$	$k$	$l$	$I/I_0$
3.825	18	3.773	1	1	1	16	3.817	1	1	1	14
3.571	9	3.423	0	0	6	8	3.558	1	1	3	4
3.497	11	3.348	1	1	3	4	3.500	0	0	8	8
2.806	35	2.804	1	1	5	100	3.170	1	1	5	3
2.778	100	2.727	0	2	0	47	2.774	1	1	7	100
2.744	47	2.701	2	0	0	51	2.736	0	2	0	31
2.711	51	2.408	0	2	4	1	2.711	2	0	0	30
2.162	15	2.331	1	1	7	8	2.419	1	1	9	6
2.138	15	2.133	0	2	6	26	2.153	0	2	8	15
2.003	11	2.120	2	0	6	23	2.1415	2	0	8	9
1.9297	38	1.961	1	1	9	18	2.1210	1	1	11	3
1.6846	11	1.919	2	2	0	30	1.9975	2	0	10	5
1.6183	11	1.7114	0	2	12	5	1.9242	2	2	0	35
1.5916	22	1.6708	3	1	3	3	1.8770	1	1	13	1
1.5823	18	1.5888	1	3	5	30	1.7482	0	0	16	2
		1.5785	3	1	5	15	1.7245	1	3	1	2
		1.4772	3	1	7	6	1.7120	3	1	1	2
		1.3683	3	1	9	10	1.6856	2	2	8	6
							1.6781	1	1	15	7
							1.6120	0	2	14	5
							1.6090	2	0	14	6
							1.5856	1	3	7	18
							1.5752	3	1	7	13

<sup>a</sup> Ref. (12).

<sup>b</sup> Ref. (13).

TABLE III  
LATTICE CONSTANTS OF  $\text{La}_2\text{NiO}_4$

Sample	$-\log P_{\text{O}_2}$ (atm)	Other phases	$a$ ( $\text{\AA}$ )	$b$ ( $\text{\AA}$ )	$c$ ( $\text{\AA}$ )	$V$ ( $\text{\AA}^3$ )	$\gamma$	Ref.
$\text{La}_2\text{NiO}_4$	8.70	Ni	5.536(2)	5.465(2)	12.535(4)	379.2(3)		This study
	8.70	$\text{La}_2\text{O}_3$	5.536(2)	5.463(2)	12.528(4)	378.9(3)		This study
	0.68	$\text{La}_6\text{Ni}_5\text{O}_{15}$	3.860(2)	—	12.67(1)	188.8(2)		This study
	0.68	$\text{La}_2\text{O}_3$	3.864(3)	—	12.66(2)	189.0(4)		This study
				3.855(1)		12.652(3)		6
				5.535(2)	5.468(2)	12.547(3)		9
				3.871(1)	3.871(1)	12.570(6)		90
				3.886(5)	3.87(1)	12.55(3)		90°27'

TABLE IV  
THE STANDARD GIBBS ENERGY OF REACTION AT 1200°C

Reaction	$-\log P_{O_2}$ (atm)	$-\Delta G^\circ$ (kJ)	$-\Delta G^{\circ a}$ (kJ)
(1) $Ni + La_2O_3 + \frac{1}{2} O_2 = La_2NiO_4$	$8.85 \pm 0.05$	$124.8 \pm 1.0$	$124.5 \pm 0.3$
(2) $2 NiO + 3 La_2NiO_4 + \frac{1}{2} O_2 = La_6Ni_5O_{15}$	$0.8 \pm 0.05$	$22.1 \pm 0.8$	

<sup>a</sup> Value calculated with an equation from Ref. (14).

results and the absence of evidence for the presence of  $Ni^{3+}$  ion under the conditions of the experiments. According to the present phase diagram, the chemical formula  $La_2NiO_{4+\alpha}$  should be used, as already described in the other reports, because the nonstoichiometric compositions of  $La_2NiO_4$  lie in the triangle  $La_2O_3$ - $NiO$ - $Ni_2O_3$ . The results of a chemical analysis on a sample prepared in air using the quenching technique confirmed the presence of  $Ni^{3+}$  as 4.75 wt%  $Ni_2O_3$  assuming that the species to oxidize  $I^-$  ion was only  $Ni^{3+}$ . This result contrasts with 3.56% calculated with the composition  $La_2NiO_{4.08}$  in the phase diagram. However, iodometry does not distinguish between  $Ni^{3+}$  and  $O_2^{2-}$ . When prepared in air,  $La_2NiO_4$  is black and is not completely dissolved during the analysis to determine the  $Ni^{3+}$  contents. So this difference might result from the failure to quench in the correct nickel valence state, the presence of peroxide species (20), and the difficulty of the chemical analysis. When prepared in the at-

mosphere  $-\log P_{O_2} = 8.20$ ,  $La_2NiO_{4.00}$  is brown and is easily soluble.

In Fig. 2, B is an intersecting point of the isooxygen pressure line of 1 atm  $O_2$  and its composition corresponds to  $La_6Ni_5O_{15.3}$ . As shown in Fig. 1, a weight change was observed in the oxygen partial pressure range from  $-\log P_{O_2} = 0$  to 0.80. So the compound might be regarded as the solid solution of two components, oxygen and  $La_6Ni_5O_{15}$ .

Even in the  $O_2$  atmosphere the weight change was very sluggish. In the thermogravimetry, the equilibrium among condensed and gaseous phases was certified by both oxidation and reduction reactions. As in this case 1 atm  $O_2$  was the highest oxygen atmosphere, the reverse reaction was impossible. So the equilibrium was determined when the weight change became within 1 mg per  $\sim 15$  hr for a  $\sim 4.5$ -g sample weight of  $La_2O_3/NiO = 25/75$ , for example.

In Table II  $d$ -spacings and relative intensities of  $La_6Ni_5O_{15}$  are presented together with

TABLE V  
COMPOSITIONS, SYMBOLS, AND STABILITY RANGES IN OXYGEN PARTIAL PRESSURES, AND ACTIVITIES IN SOLID SOLUTIONS

Component	Composition	Symbol	$-\log P_{O_2}$ (atm)	$\log a_i$
$La_2NiO_4$	$La_2NiO_{3.994}$	A	8.85	0
	$La_2NiO_{4.004}$	A <sub>1</sub>	7.75	$6.02 \times 10^{-4}$
	$La_2NiO_{4.071}$	A <sub>2</sub>	0.80	-0.131
	$La_2NiO_{4.079}$	A <sub>3</sub>	0	-0.161

those of  $\text{La}_3\text{Ni}_2\text{O}_7$  (12) and  $\text{La}_4\text{Ni}_3\text{O}_{10}$  (13). The X-ray powder pattern is very similar to that of  $\text{La}_4\text{Ni}_3\text{O}_{10}$ . Therefore, the possibility that  $\text{La}_6\text{Ni}_5\text{O}_{15}$  might be a solid solution of  $\text{La}_4\text{Ni}_3\text{O}_{10}$  should still be considered.

As described above, there are three types of  $\text{La}_2\text{NiO}_4$ , tetragonal, orthorhombic, and monoclinic. Lattice constants of  $\text{La}_2\text{NiO}_4$  made in air were determined with the aid of the data of Rabenau and Eckerlin (6). Those of  $\text{La}_2\text{NiO}_4$ , which was made under the condition of an oxygen partial pressure of  $\log P_{\text{O}_2} = -8.70$ , were determined with the aid of orthorhombic  $\text{La}_2\text{CoO}_4$  (10). Values obtained are tabulated in Table III together with previous values. Lattice constants are not affected by the coexistence of other phases and are in good agreement with previous values.

### (2) The Standard Gibbs Energy of Reaction

Two chemical reactions, except for the reaction  $\text{Ni} + \frac{1}{2}\text{O}_2 = \text{NiO}$ , are revealed in the present phase diagram. These reactions are shown in Table IV together with the oxygen partial pressures in equilibrium with three solids, a previous  $\Delta G^\circ$  value, and present  $\Delta G^\circ$  values, which were calculated from the equation,  $\Delta G^\circ = -RT \ln K$ . Here,  $R$  is the gas constant,  $T$  the absolute temperature, and  $K$  the equilibrium constant. The necessary activities of the  $\text{La}_2\text{NiO}_4$  component in the solid solution are tabulated in Table V. The  $\Delta G^\circ$  value obtained is in good agreement with the previous value (14).

### (3) Other Lanthanide Systems

Attempts were made to establish the phase diagrams of other Ln-Ni-O systems (Ln = Ce, Pr, Nd, Sm, and Gd) using the same procedures and conditions, but no ternary compound was found. Buttrey *et al.*

(21), Petrov *et al.* (14), and Nakamura *et al.* (22) reported stable phases,  $\text{Pr}_2\text{NiO}_4$ ,  $\text{Nd}_2\text{NiO}_4$ , and  $\text{LaNiO}_3$  at temperatures lower than  $1200^\circ\text{C}$ , respectively. This suggests that further experiments are desirable in the lower temperature ranges.

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