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Phase Equilibria of the System La_2O_3–NiO–Li_2O at 700, 800, and 900°C

Guobao Li,[1] Jianqing Yang, Yongxin Fan, Shujian Tian, and Chaogui Zheng

Department of Chemistry, Peking University, Beijing 100871, China

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Phase relations in the system La_2O_3–NiO–Li_2O at 700, 800, and 900°C have been investigated by solid synthesis, X-ray diffraction analysis, and chemical analysis. Only the ternary compound La_4NiLiO_8 was found in the system. X-ray diffraction data of La_4NiLiO_8 are presented. © 1998 Academic Press

Key Words: **phase relations; La_3O_3–NiO–Li_2O system; La_4NiLiO_8.**

I. INTRODUCTION

The system La_2O_3–NiO–Li_2O has been studied extensively. There are several different functional materials in this system. $LiNiO_2$ is a promising cathode material for the lithium ion battery (1), which now is the focus of study and development of the chemical battery. La_4NiLiO_8 is a useful catalyst for CH_4 oxidation (2), whereas the mixed oxides $LaNiO_3$ and La_2NiO_4 were studied as catalysts for direct decomposition of NO (3). Much published work has been focused on the above-mentioned functional materials. Are there any new functional materials in this system? Is there any new compound in this system? We are very interested in finding out the answers to these two questions. Here, we present our work on the phase relations in the system La_2O_3–NiO–Li_2O.

II. PRIOR STUDIES

The System Li_2O–NiO

Several phase relation studies of the system Li_2O–NiO have been reported (4–7). It had been reported that there existed two solid solutions: $Li_xNi_{2-x}O_2$ ($0.56 \geq x \geq 0$) and $Li_xNi_{2-x}O_2$ ($1 \geq x \geq 0.6$), at 600–850°C. Their crystal systems are cubic and hexagonal, respectively. Between the two solid solutions there is narrow two-phase area. A monoclinic phase Li_2NiO_{3-y} was found by Bronger (6). It is a classic β-Li_2SnO_3-type compound and is stable at relatively low temperature (below 450°C under normal conditions or below 670°C under a 150-MPa oxygen atmosphere). A CdI_2-type compound Li_2NiO_2 can be formed by intercalating lithium into hexagonal $LiNiO_2$ at room temperature (8). When this compound is heated to 400°C, orthogonal Li_2NiO_2 is obtained (9). At 150–300°C, hexagonal $Li_{0.5}NiO_2$, formed by deintercalating lithium from hexagonal $LiNiO_2$ at room temperature, can be transformed to cubic spinel $LiNi_2O_4$ (10, 11).

The System Li_2O–La_2O_3

The system Li_2O–La_2O_3 has been reported (12–14). Sevostyanova *et al.* (12) reported the existence of the phase $LiLaO_2$ with an orthogonal form which had been synthesized under an H_2 atmosphere. However, Gondrand (13) and Abbattista and Vallino reported the existence of the phase $LiLaO_2$ with a monoclinic form at 800°C in air. Moreover, Attfield and Ferey synthesized a compound $La_4Li_2O_7$ with a defect K_2NiF_4-type structure at 950°C in air by solid synthesis.

The System NiO–La_2O_3

In the system NiO–La_2O_3, a stable orthogonal $LaNiO_3$ is formed below 800°C, which decomposes and forms members of the Ruddlesden–Popper series $La_{n+1}Ni_nO_{3n+1-\delta}$ above 825°C (16–18). It was reported that heating orthogonal $LaNiO_3$ at 1100°C for 30 min produced orthogonal $La_4Ni_3O_{10}$ (18), whereas heating for 24 h gave orthogonal $La_3Ni_2O_7$ (18). At 1166°C, orthogonal $LaNiO_3$ decomposes into tetragonal La_2NiO_4 (19).

There are many arguments about the structures and the phase transition of $La_2NiO_{4+\delta}$. Five phases were reported at room temperature: orthorhombic *Bmab* ($0 \leq \delta \leq 0.02$ (20, 21), $\delta \leq 0.003$ (22)), pseudotetragonal ($\delta \approx 0.02$ (22–24)), orthorhombic ($0.055 \leq \delta < 0.09$ (22), $0.07 < \delta < 0.10$ (24)), tetragonal $P4_2/ncm$ ($\delta \approx 0.10$ (24)), tetragonal $I4/mmm$ ($0.10 \leq \delta < 0.15$ (22), $0.14 < \delta$ (25), and orthorhombic *Fmmm* ($0.15 < \delta < 0.18$ (22), $0.13 < \delta$ (20, 21)). Furthermore, several different phase transitions were reported. Rodrigues-Carvajal *et al.* (25) reported two structural phase transitions for stoichiometric $La_2NiO_{4.00}$:

[1]To whom correspondence should be addressed.

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from tetragonal $I4/mmm$ to orthorhombic $Bmab$ around 497°C and from orthorhombic $Bmab$ to tetragonal $P4_2/ncm$ around −193°C. Kajitani *et al.* (23, 24) reported a phase transition around −203°C for $\delta = 0$ from orthorhombic to orthorhombic and a phase transition from tetragonal $P4_2/ncm$ to tetragonal $I4/mmm$ around 287°C at $\delta \approx 0.10$. Tranquada *et al.* (26) reported a phase separation around −3°C at $\delta = 0.15$. Tamura *et al.* (22) showed a phase transition from orthorhombic $Fmmm$ to tetragonal $I4/mmm$ with increasing transition temperature from 47°C for $\delta = 0.15$ to 157°C for $\delta = 0.18$. Finally, Kulichenko *et al.* [27] reported that $La_{2-x}NiO_{4+\delta}$ $(0 \le x \le 0.5)$ could be synthesized after several hours at 950°C and that $La_{2-x}NiO_{4+\delta}$ $(0 \le x \le 0.4)$ is of K_2NiF_4-type structure ($I4/mmm$) and $La_{2-x}NiO_{4+\delta}$ $(0.4 < x \le 0.5)$ is of $La_3Ni_2O_7$-type structure.

The System La_2O_3–NiO–Li_2O

One compound, La_4NiLiO_8, was synthesized at 950°C under an oxygen atmosphere (28). It was of K_2NiF_4-type structure, and has been extensively studied as a catalyst for oxidation of CH_4. However, indexed X-ray diffraction data are absent.

TABLE 1
Results of Determination in the System La_2O_3–NiO–Li_2O at 700°C

Run	Composition (mol %) Li_2O	La_2O_3	NiO	t (h)	Results of X-ray analysis
A1	14.2		85.8	80	NiOss
A2	28.0		72.0	80	$LiNiO_2$ss
A3	33.1		66.9	80	$LiNiO_2$
A4	40.7		59.3	80	$LiNiO_2 + Li_2O$
A5		30.0	70.0	200	$NiO + LaNiO_3$
A6		33.33	66.67	240	$LaNiO_3$
A7		38.0	62.0	220	$LaNiO_3 + La_2O_3$
A8		95.0	5.0	220	$LaNiO_3 + La_2O_3$
A9	5.0	95.0		200	$La_2O_3 + LiLaO_2$
A10	45.0	55.0		200	$La_2O_3 + LiLaO_2$
A11	50.0	50.0		200	$LiLaO_2$
A12	27.0	28.0	45.0	180	$La_4NiLiO_8 + LiNiO_2 + Li_2O$
A13	13.0	41.9	45.1	180	La_4NiLiO_8 + NiOss
A14	44.0	46.6	9.4	180	$La_4NiLiO_8 + LiLaO_2 + Li_2O$
A15	14.3	57.1	28.6	180	La_4NiLiO_8
A16	16.4	73.7	10.0	180	$La_4NiLiO_8 + LiLaO_2 + La_2O_3$
A17	3.0	75.0	22.0	180	$La_4NiLiO_8 + LaNiO_3 + La_2O_3$
A18	19.7	4.3	76.0	180	$La_4NiLiO_8 + LiNiO_2$ss
A19	2.2	27.0	70.8	200	$La_4NiLiO_8 + NiO + LaNiO_3$

Note: NiOss, solid solution of cubic $Li_{1-x}Ni_xO$; $LiNiO_2$ss, solid solution of hexagonal $Li_{1-x}Ni_xO_2$.

TABLE 2
Results of Determination in the System La_2O_3–NiO–Li_2O at 800°C

Run	Composition (mol %) Li_2O	La_2O_3	NiO	t (h)	Results of X-ray analysis
B1	14.2		85.8	80	NiOss
B2	28		72	80	$LiNiO_2$ss
B3	21.3		78.7	80	$LiNiO_2$ss
B4	33.1		66.9	80	$LiNiO_2$
B5	40.7		59.3	80	$LiNiO_2 + Li_2O$
B6		30.0	70.0	126	$NiO + LaNi_3O_3$
B7		5.0	95.0	108	$NiO + LaNiO_3$
B8		38.0	62.0	86	$LaNiO_3 + La_2O_3$
B9		95.0	5.0	126	$LaNiO_2 + La_2O_3$
B10	5.0	95.0		126	$La_2O_3 + LiLaO_2$
B11	45.0	55.0		126	$La_2O_3 + LiLaO_2$
B12	50.0	50.0		126	$LiLaO_2$
B13	60.0	13.5	26.5	86	$La_4NiLiO_8 + LiNiO_2 + Li_2O$
B14	2.0	4.8	93.2	86	La_4NiLiO_8 + NiOss
B15	44.0	50.6	5.4	112	$La_4NiLiO_8 + LiLaO_2 + Li_2O$
B16	14.3	57.1	28.6	90	La_4NiLiO_8
B17	55.0	35.0	10.0	90	$La_4NiLiO_8 + LiLaO_2 + La_2O_3$
B18	3.1	75.0	11.9	90	$La_4NiLiO_8 + LaNiO_3 + La_2O_3$
B19	17.0	28.0	55.0	90	$La_4NiLiO_8 + LiNiO_2$ss
B20	2.5	32.5	65.0	90	$La_4NiLiO_8 + NiO + LaNiO_3$
B21	32.2	3.0	64.8	90	$La_4NiLiO_8 + LiNiO_2$
B22	15	65	20	90	$La_4NiLiO_8 + LiLaO_2 + La_2O_3$

Note: NiOss, solid solution of cubic $Li_{1-x}Ni_xO$; $LiNiO_2$ss, solid solution of hexagonal $Li_{1-x}Ni_xO_2$.

III. EXPERIMENTAL

La_2O_3 (99.99%), NiO (A.R.), and Li_2CO_3 (A.R.) were used as starting materials. Previously, Li_2CO_3 and NiO were dried at 300°C for 2 days, and La_2O_3 was dried in an electric muffle furnace at 900°C for 12 h to drive off H_2O and CO_2.

Mixtures totaling 2–3 g were weighed out precisely and then mixed into a paste with acetone using an agate mortar and pestle, dried, and prefired at 700°C for 4 h. Finally, the samples were pressed into pellets and fired in Al_2O_3 crucibles in an electric muffle furnace at a definite temperature. The mixtures were heated for different lengths of time to find out the conditions required for attaining equilibrium. After 1 day, the pellets were removed from the furnace, crushed to a fine powder, repelletted, and reheated for another 2–4 days. At the end of the heating period, samples were removed from the furnace and air-quenched.

Phase analysis was carried out by X-ray powder diffraction using a D/max-2000 type diffractometer, Cu$K\alpha$

TABLE 3
Results of Determination in the System La_2O_3–NiO–Li_2O at 900°C

Run	Composition (mol %) Li_2O	La_2O_3	NiO	*t*, (h)	Results of X-ray analysis
C1	15.2		84.8	48	NiOss
C2		11.9	88.1	72	NiO + $La_4Ni_3O_{10}$
C3		66.7	33.3	72	$La_4Ni_3O_{10}$ + La_2O_3
C4	13.0	40.0	47.0	60	La_4NiLiO_8 + NiOss
C5	9.0	62.0	29.0	60	La_2O_3 + La_4NiLiO_8 + $La_4Ni_3O_{10}$
C6	14.3	57.1	28.6	60	La_4NiLiO_8
C7	8.0	43.0	49.0	60	La_4NiLiO_8 + $La_4Ni_3O_{10}$ + NiO
C8	58.0	13.0	29.0	60	La_4NiLiO_8 + Li_2O + NiOss
C9	44.5		55.5	48	Li_2O + NiOss
C10	52.4	47.6		60	Li_2O + La_2O_3
C11	20.0	58.6	21.4	60	La_4NiLiO_8 + Li_2O + La_2O_3

Note: NiOss, solid solution of cubic $Li_{1-x}Ni_xO$.

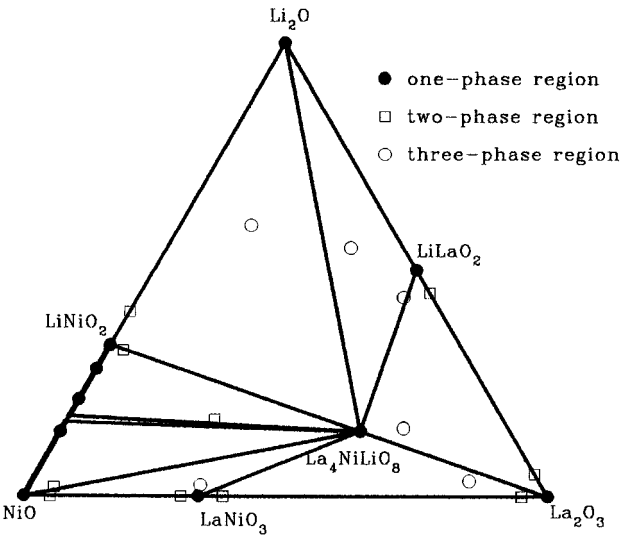

FIG 2. Phase diagram of the system La_2O_3–NiO–Li_2O at 800°C.

radiation, a Ni filter, 40 kV, and 100 mA. Si was used as an internal standard.

The final composition of the samples was determined by ICP-AES for lithium (determination error was 5%) and chemical analysis for nickel and lanthanum (determination error of EDTA titration was 1–2%).

IV. RESULTS

Subsolidus relations in the system La_2O_3–NiO–Li_2O were determined at 700, 800, and 900°C, respectively. The preparation conditions and results of analysis are given in Tables 1–3; the corresponding phase relations are shown in Figs. 1–3.

The stable phases at the apices of the ternary phase diagram are Li_2O, NiO, and La_2O_3. No intermediate phase is present in the binary Li_2O–NiO at 900°C; however, stable hexagonal $LiNiO_2$ is formed at 800 and 700°C. Two solid solutions, cubic $Li_xNi_{2-x}O_2$ $(0.56 > x \geq 0)$ and hexagonal $Li_xNi_{2-x}O_2$ $(1 \geq x > 0.6)$, were found in the binary Li_2O–NiO at 800 and 700°C, and only one solid solution, cubic $Li_xNi_{2-x}O_2$ $(0.56 > x \geq 0)$, was found at 900°C. These results agree with those reported in the literature (4–11). Hexagonal $LiNiO_2$ decomposes at 900°C; therefore solid solution hexagonal $Li_xNi_{2-x}O_2$ $(1 \geq x > 0.6)$ disappears at this temperature.

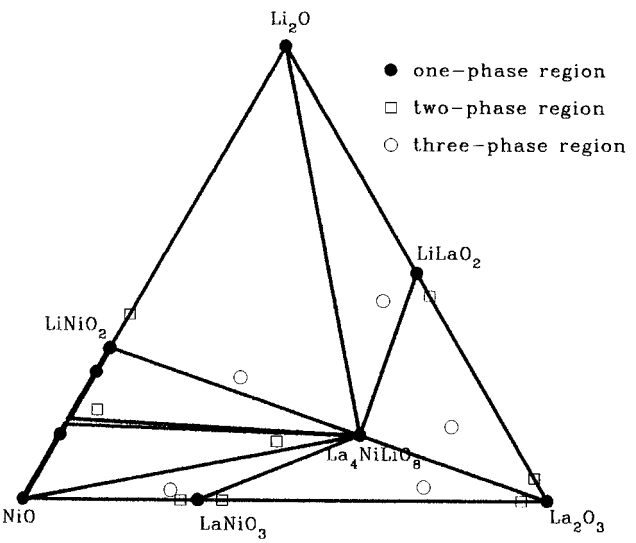

FIG 1. Phase diagram of the system La_2O_3–NiO–Li_2O at 700°C.

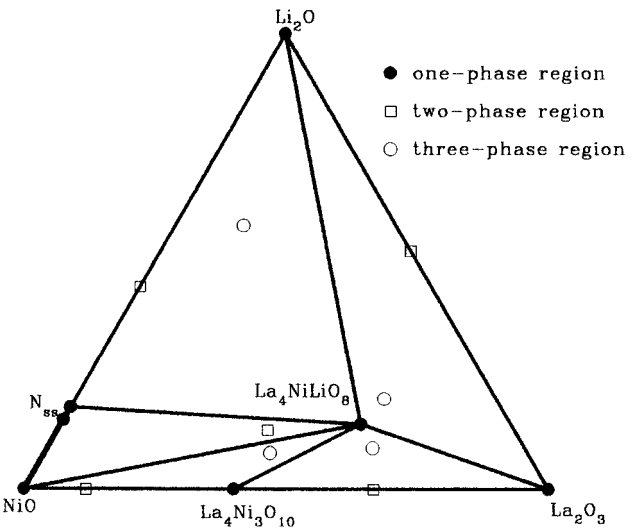

FIG 3. Phase diagram of the system La_2O_3–NiO–Li_2O at 900°C.

TABLE 4
Indexed Diffraction Data for La_4NiLiO_8[a]

h	k	l	d_{obs} (nm)	d_{cal} (nm)	I/I_0
1	0	1	0.36056	0.36050	60
0	0	4	0.32222	0.32214	30
1	0	3	0.28271	0.28271	100
1	1	0	0.26557	0.26552	72
1	1	2	0.24557	0.24549	6
0	0	6	0.21474	0.21477	11
1	0	5	0.21247	0.21249	28
1	1	4	0.20491	0.20489	61
2	0	0	0.18776	0.18775	44
1	1	6	0.16698	0.16698	11
2	1	1	0.16650	0.16652	17
1	0	7	0.16529	0.16529	24
2	0	4	0.16221	0.16221	20
0	0	8	0.16106	0.16107	7
2	1	3	0.15640	0.15640	7
2	0	6	0.14135	0.14135	37
2	1	5	0.14069	0.14070	10
1	1	8	0.13771	0.13771	13
2	2	0	0.13275	0.13276	10
0	0	10	0.12887	0.12886	1
3	0	1	0.12458	0.12458	4
2	1	7	0.12406	0.12406	18
2	2	4	0.12275	0.12275	18
2	0	8	0.12225	0.12225	8
3	0	3	0.12017	0.12017	11
3	1	0	0.11875	0.11874	8
1	1	10	0.11592	0.11593	4
2	2	6	0.11292	0.11293	4
2	0	5	0.11260	0.11259	3
1	0	11	0.11184	0.11183	12
3	1	4	0.11142	0.11142	16

[a]Unit cell: $a = 0.37553(2)$ nm; $c = 1.28872(8)$ nm; $V = 0.18174$ nm^3; $d_{obs} = 7.120$ g/cm^3, $d_{cal} = 7.202$ g/cm^3 for $Z = 1$.

Monoclinic $LiLaO_2$ is the only intermediate phase found in this study in the system La_2O_3–Li_2O at 800 and 700°C; it decomposed at 900°C, and no intermediate phase was found in this system at 900°C. These results also agree well with those in the literature (12–15).

Orthogonal $LaNiO_3$ was the only intermediate phase found in the binary system La_2O_3–NiO at 800 and 700°C, and orthogonal $La_4Ni_3O_{10}$ was the only intermediate phase at 900°C. A phase transition between 800 and 900°C was observed. The X-ray diffraction data for $La_4Ni_3O_{10}$ found at 900°C were very similar to the reported data (18). $La_2NiO_{4+\delta}$ and $La_{2-x}NiO_{4+\delta}$ were not found, although several researchers (20–27) have reported their existence around 900°C. The main difference between the present work and the reported work (20–27) is the difference of synthesizing time of the samples. Our prolonged synthesizing time ensures that the samples reach the equilibrium state, and maybe the samples in Refs. (20–27) did not reach the equilibrium state because the synthesizing times for those samples were too short.

TABLE 5
Structure Refinement Parameters for La_4NiLiO_8
[*I4/mmm*: $a = 0.37553(2)$ nm, $c = 1.28872(8)$ nm]

Atom	Site	x/a	y/b	c/z	Occupancy
Li	2*a*	0	0	0	1.00
Ni	2*a*	0	0	0	1.00
La	4*e*	0	0	0.363648	1.00
O(1)	4*e*	0	0	0.178681	1.00
O(2)	4*c*	0	0.5	0	1.00
	$R_p = 5.76$	$R_{wp} = 8.87$	$R_i = 0.85$	$R_{exp} = 4.66$	

La_4NiLiO_8 was the only ternary compound found in the system La_2O_3–NiO–Li_2O. It was reported to be a K_2NiF_4-type compound (28), and our results confirm that. The indexed diffraction data are in Table 4. The crystal structure was refined by the Rietveld method using the program Rietan-94 (29). In the final stages, all positional parameters, isotropic temperature factors for Li/Ni and La, and anisotropic temperature factors for O were refined. The overall site occupancies were constrained to be unity and the overall Li and Ni contents were constrained to be consistent with the formula La_4NiLiO_8. The final parameters are listed in Table 5.

V. CONCLUDING REMARKS

1. The phase diagram of the systems La_2O_3–NiO–Li_2O at 700–900°C has been determined for the first time.
2. It has been found that only one ternary compound, La_4NiLiO_8, is formed in this system, and the indexed diffraction data were given.
3. The solid solutions, cubic $Li_xNi_{2-x}O_2$ ($0.56 \geq x \geq 0$) and hexagonal $Li_xNi_{2-x}O_2$ ($1 \geq x \geq 0.6$), were found at 700–800°C, and only one solid solution, cubic $Li_xNi_{2-x}O_2$ ($0.56 > x \geq 0$), was found at 900°C.
4. Monoclinic $LiLaO_2$ and hexagonal $LiNiO_2$ are found between 700 and 800°C, but both of them decompose above 900°C.
5. Orthogonal $LaNiO_3$ is stable between 700 and 800°C and changes to orthogonal $La_4Ni_3O_{10}$ at 900°C.

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